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WATER, A FUNDAMENTAL ELEMENT

INTRODUCTION

Throughout the universe there is one molecule which man seeks above all others for its discovery in the atmosphere of some distant planet would immediately unleash mankind's wildest dreams.

This molecule may be easily depicted as a simple triangle distinguished by an interatomic angle of 105° owing to the electronegativity of two of its poles. If its bonds were exclusively covalent, this angle would be 90°. The water molecule has an electric moment that is reflected in its physical and electric properties.

The formula for water can thus be very simply written as H_2O.

Water - the very word brings to mind an image born of recent space voyages the picture of a blue planet: Earth.

Water is the most common mineral on the earth's surface. It makes up the hydrosphere. Its volume is estimated at 1370 million cubic kilometers; the volume of fresh water distributed between rivers, lakes and ground water is considered to be between 500,000 and one million cubic kilometers. The volume of polar ice caps represents 25 million cubic kilometers of fresh water. Finally, there are 50,000 cubic kilometers of water in the atmosphere in the form of vapour and clouds. Annual evaporation is estimated at 500,000 cubic kilometers and precipitation on the continents is calculated at 120,000 cubic kilometers yearly.

Above all, however, water is a synonym for biological life.

It is the major component of living matter. On the average, it accounts for 80% of its composition. In higher animals, the percentage of water is between 60 and 70%. In marine organisms, such as jellyfish and certain algae, the proportions reach extremes of 98%. On the other hand, bacteria in a state of sporulation or suspended animation, which makes them resistant, experience a drop in water content to 50%.

A principal element in the mineral and biological worlds, water is also the preeminent vector of life and human activity. At present, the world's use of water, counting domestic, industrial and agricultural, totals an impressive 250 m^3 per person per year. Moreover, disparities are enormous: from 100 m^3 for developing countries to 1500 m^3 for the United States. Man's need for water is, thus, certain to grow.

This makes it imperative that water be protected. It must be treated, whether to produce water for general consumption, or for specific industrial uses or to limit the discharge of pollution into the environment.

1. THE PHYSICAL STRUCTURE OF WATER

1.1

THE THREE STATES

The structure of water depends on its physical state.

The gaseous state (vapour) corresponds exactly to the formula H_20 and in particular to the triangular diagram shown in Figure 1.

The condensed states (water and ice) are, however, more complicated and this accounts for their abnormal properties.

In the solid state, the elementary arrangement consists of a central water molecule and four peripheral mole

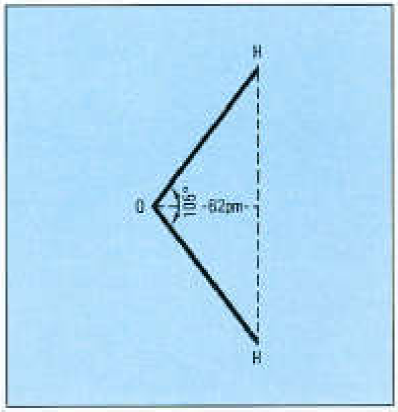

Figure 1. Structure of water as vapour.

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cules forming the shape of a tetrahedron (figure 2). The study of the crystallographic variations, especially with the aid of the Raman spectrum, enables us to understand the transition to the liquid state from the open crystalline structure of ice.

In water in the liquid state, several molecules are associated by special bonds called hydrogen bonds, each hydrogen atom of a water molecule being linked to the oxygen atom of the neighbouring molecule. The structure is tetrahedral in space.

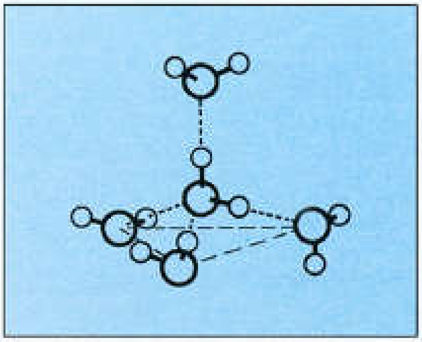


Figure 2. Tetrahedral structure of water in a solid state.

1.2.
PHYSICAL PROPERTIES

The following are the most important physical properties with regard to water treatment:

1.2.1. Density

Through the compacting of the molecular structure, the density varies with temperature and pressure. Pure water varies as follows:

C	*Density kg. dm*$^{-1}$	*T°C*	*Density kg. dm*$^{-1}$
0	0.99987	20	0.99828
4	1.00000	25	0.99707
10	0.99973	30	0.99567
15	0.99913	100	0.95838

At pressures encountered in hydraulic processes, water is considered a non compressible fluid. In fact, however, it is elastic: its volume decreases about 0.048% each time the pressure rises one atmosphere.

Sea water, with a salinity of 35 $g.l^{-1}$, has an average density of 1.0281 $kg.l^{-1}$ at 0°C. A variation in salinity of 1 $g.l^{-1}$ causes the density to change by 0.0008 $kg.l^{-1}$.

1.2.2. Thermal properties

* **Specific heat:** 4.18 kJ/kg.°C (1 kcal/kg.°C) at 0°C. This varies with temperature and reaches a minimum at +35°C.

e **The latent heat** of transformation is for fusion: 330 $kJ.kg^{-1}$ (or 79 $kcal.kg^{-1}$) and for vaporization: 2250 $kJ.kg^{-1}$ (or 539 $kcal.kg^{-1}$) at normal pressure and at 100°C.

Owing to the substantial amount of specific heat and latent heat of vaporization, the large expanses of water on the earth's surface constitute veritable heat stores. This is also the reason for the use of water as a heat transfer fluid.

1.2.3. Viscosity

This is the ability of a liquid to resist various movements, both internal and overall, such as flow. It is the basic cause of head loss and therefore plays an important part in water treatment. Viscosity diminishes when temperature increases.

T°C	Absolute viscosity ? mPa.s	T°C	Absolute viscosity ? mPa.s
0	1.797	20	1.007
5	1.523	25	0.895
10	1.301	30	0.800
15	1.138	35	0.723

On the other hand, it increases with the higher content of dissolved salts; sea water is therefore much more viscous than river water.

Salinity in Cl- ion in g.l^{-1}	Absolute viscosity ? at 20°C in mPa.s
0	1.007
4	1.021
8	1.035
12	1.052
16	1.068
20	1.085

Pressure has a very special effect on the absolute viscosity of water. Contrary to what happens with other liquids, a moderate pressure makes water less viscous at low temperatures; it crushes its molecular structure, as it were. When the pressure continues to increase, the water resumes the structure of a liquid free from any internal stresses, and again complies with the general rule that viscosity increases with pressure.

1.2.4. Surface tension

This is a property peculiar to interfaces (boundary surfaces of two phases). It is defined as a tensile force which is exerted at the surface of the liquid and which tends to reduce the area of this surface to the greatest possible extent.

It is such as to cause a capillary rise of 15 cm at 18°C in a tube with a diameter of 0.1 mm.

Surface tension diminishes with a rise in temperature.

T°C	Surface tension 10-3 N.m^{-1} (dyn.cm^{-1})	T°C	Surface tension 10 3 N.m^{-1} (dyn.cm^{-1})
0	75.60	50	67.91
10	74.22	60	66.18
20	72.75	70	64.4
30	71.18	80	62.60
40	69.56	100	58.9

The addition of dissolved salts generally increases surface tension (γ = 74.6 x 10^{-3} N.m^{-1} for an aqueous solution of NaCI at 1 mol.l^{-1} at 18°C).

Other substances reduce surface tension: these are said to be surface-active.

1.2.5. Osmotic pressure

Osmotic pressure describes a phenomenon which occurs between liquids with different concentrations that are separated by a semi-permeable membrane.

A simple equation relates osmotic pressure to concentration:

$$? = \Delta CRT$$

ΔC: The difference in concentration in mol.m^{-3}
R : The constant of ideal gases: 8.314 J/mol.K
T : The temperature in K
Π : The osmotic pressure in Pa

Thus, sea water at 35 $g.l^{-1}$ in NaCl at 15°C creates an osmotic pressure equal to 14.38×10^5 Pa

This parameter is essential in the sizing of reverse osmosis systems.

1.2.6. Electrical properties

. **Dielectric constant:** the dielectric constant of water, of the order of 80 Farad Steradian per metre, is one of the highest known; this is why the ionizing power of water is so great.

. **Electrical conductivity of water:**
water is slightly conducting. The conductivity of the purest water ever obtained is 4.2 microsiemens per metre at 20°C (this corresponds to a resistivity of 23.8 megohms-centimetre). The presence of dissolved salts in water increases its conductivity (see page 487) which varies according to the temperature.

1.2.7. Optical properties

The transparency of water depends on the wavelength of the light passing through it. While ultraviolet light passes through it well, infrared rays, so useful from the physical and biological viewpoints, hardly penetrate it. Water absorbs a large proportion of the orange and red components of visible light; this explains the blue colour of light which has passed through a thick section of water.

This transparency is often used to measure certain forms of pollution and, consequently, the efficiency of purification treatments.

1.3.

PHYSICAL STATE OF WATER IMPURITIES

Water found in nature and, by extension, that which is treated, is never pure.

The impurities that water contains in its three states: solid, liquid or gaseous, may be described by their size in solution (figure 3). They may be the size of an isolated particle or that of a structured mass. The degree of hydrophobicity of the impurities plays an important role in these structures.

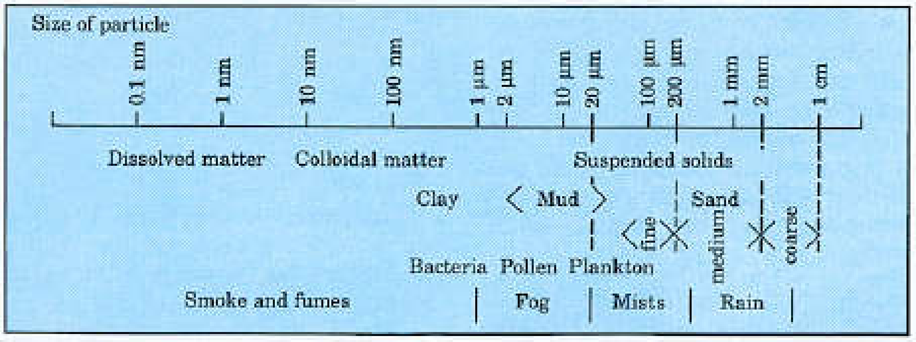


Figure 3. Sizes of various particles.

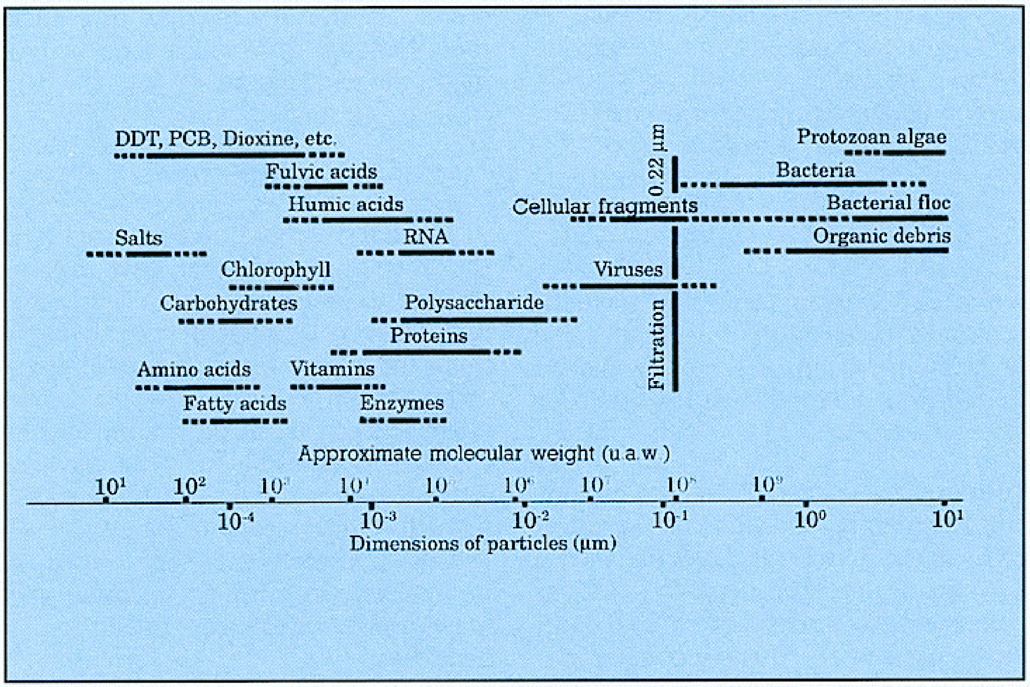


Figure 4. Example of organic substances in municipal wastewater (MWW).

Figure 4 gives the dimensions of particles and molecular weights of the main organic substances in municipal wastewater.

These can be classified according to the following solutions types.

. **True or molecular solutions:** these are homogeneous (single phase) systems:
- crystalloid solutions: the dissolved particles are small molecules (less than one nanometre), both ionized (acids, bases, salts) and non-ionized (sugars, etc.);
- macromolecular solutions: formed from particles that are much bigger than a nanometre. They may include ionized groups.

. **Colloidal suspensions:** also called micellar or pseudo-solutions, these are two-phase, distinctly heterogeneous systems, in which the dispersed particles' molecular weights measure generally between 0.5 and 500 nm (or 100 nm). They may appear as a cloudiness to the naked eye when viewed perpendicular to a light beam but they add little to the turbidity of the water. The term "colloid" then, is used to describe finely divided suspended solids with a specific surface area carrying an electrostatic charge that is generally negative.

. **Suspensions - Emulsions:** when the particles are visible under an optical microscope, they constitute suspensions (solids) or emulsions (liquids).

These suspended particles cause the turbidity or opacity of water.

2. THE CHEMISTRY OF WATER

The formation energy of the . water molecule, 242 $kJ.mol^{-1}$ (58 $kcal.mol^{-1}$), is. high. Water is, therefore, extremely stable. This stability, linked with its characteristic electrical properties and molecular composition, makes water particularly suitable for dissolving many substances Most mineral substances are, in fact, soluble in water as are also a large number of gases and organic substances

2.1.
WATER AS A SOLVENT

To dissolve a substance is to destroy its cohesion, which it owes to electrostatic or Coulomb forces which may be:

. **Interatomic**
Strong chemical bonds: covalency bonds (between atoms), electrovalency or ionic bonds (atom-electrons).

. **Intermolecular**
Bonds of cohesion between molecules (hydrogen bonds).

. **Weak forces of attraction** (London, Van der Waals), which hold the whole substance together.

The hydrating attraction of water (bipolar molecule) has the effect of completely or partially destroying (beginning with the weakest) the various electrostatic links between the atoms and molecules of the substance to be dissolved, which are replaced by new links with its own molecules, and creating new structures; a genuine chemical reaction (solvation) takes place. Complete solvation is dissolution.

2.1.1. Solubility of the various phases

. **Gases**
The solubility of gases obeys Henry's laws (see page 276 and page 509).

For example, at 10°C, the solubility of principal gases under a pressure of pure gas equal to 102 kPa (1 bar), is:

Gas	Solubility $mg.l^{-1}$
N_2	23.2
O_2	54.3
CO_2	2,318
H_2S	5,112
CH_4	32.5
H_2	1.6

Anhydrides (CO_2, SO_2) and various volatile acids (HCl) dissolve and then combine. Their solubility coefficient is much higher than that of other gases.

Oxygen is more soluble than nitrogen; the dissolved gases extracted from a water will be richer in oxygen than the initial atmosphere from which they came.

. Liquids

As the water molecule is polar, the solubility of a liquid in water depends on the polarity of the molecules of the liquid in question. For instance, molecules containing the groups OH^- (e.g., alcohol, sugars), SH^- and $NH2^-$, being very polar, are very soluble in water, whereas other liquids (hydrocarbons, carbon tetrachloride, oils and fats, etc.). which are non-polar, are very sparingly soluble.

There may be partial miscibility; for instance, two substances are miscible only above a critical temperature (a temperature above 63.5°C for a mixture of water and phenol) or below a minimum temperature (trimethylamine is only soluble in all proportions below 18.5°C), or between two critical temperatures, one upper and one lower (the water-nicotine system).

2.1.2. Hydrophilization

The solubility of a substance may differ in various solvents: for example, sodium chloride is much more soluble in water than in alcohol, whereas paraffin is soluble in benzene but not in water.

Solubility in water depends on the nature of the substance or at least on certain of its constituent groups; the characteristic groups are therefore classified as hydrophilic (OH-CO-NH_2 etc.) or hydrophobic (CH_3-CH_2-C_6H_5).

In some cases, solvation or simple wetting take place with the aid of a third constituent called a solubilizer for true solutions, a peptizer for colloidal suspensions, a **stabilizer or emulsifier** for emulsions and suspensions, and a wetting agent for surface effects.

These intermediary agents create genuine links between the solvent and substance to be dissolved, to be held in dispersion or to be wetted (they lower the surface tension).

The link on the solvent side is due to a hydrophilic group, while the link on the side of the substance to be transformed can be a chemical link (action of bases and strong acids) or a cohesion link. The latter are formed from dissymetrical (semi-hydrophilic) molecules. One of the ends is similar to water and hydrophilic, while the other tends to associate (the action of detergents, trisodium phosphate, wetting agents) with the molecules of the substance to be stabilized or to be adsorbed on its surface. More hydrophilic aggregation or adsorption complexes are then formed.

. Loss of hydrophilic properties

The intermediary agent can break the link between the solvent and the substance which is dissolved, dispersed or wetted. Depending on the case in question, this agent will be called a **precipitant, coagulant, flocculant, thickener** or wetting depressant. This break can be the result of chemical action, for instance the loss of OH- ions or of ionized groups. The intermediary agent may destroy the semi-hydrophilic cohesion link by neutralizing the hydrophilic part or by attracting the hydrophobic part on the surface either of air bubbles (flotation) or of a more or less hydrophilic insoluble adsorbent.

The break may be the result of neutralization of the electrostatic forces (by the action of polyvalent cations and ionic polyelectrolytes).

2.1.3. Activity and concentration

The relationship between solute and solvent may be expressed in several ways:

- mole fraction: ratio of number of moles of solute to total number of moles (solvent + solute),
- molarity: number of moles dissolved in one litre of solution.

The molecules of a solute behave in the same way as a gas would in another gas, and indeed it has been observed that when the solute is greatly diluted, the law of ideal gases holds good. When the concentration becomes sizable, the dissolved molecules are less active than the same number of molecules of ideal gas. Concentration (c) is replaced by activity [a]:

$$[a] = f(c)$$

f is called the activity coefficient and tends towards 1 when the solution is very dilute.

2.2.
IONIZATION

An inorganic compound dissolved in water dissociates to a greater or lesser extent, with the formation of negatively charged ions (anions) and positively charged ions (canons). The dissolved substance is called an electrolyte and facilitates the flow of electric current:

$$AB \rightleftharpoons A^+ + B^-$$

Where a single solution contains a number of electrolytes, each is dissociated to a certain extent and ions formed may combine with one another to form new compounds. For example, if two compounds AB and CD are dissolved, the solution will be found to contain molecules AB, CD, AD and CB in equilibrium with the ions A^+, B^-, C^+ and D^-. This equilibrium may change if insoluble compounds, complexes or gases form (Le Chatelier's principle). For example, if the compound AD is insoluble, the equilibrium is almost entirely displaced to the right, in accordance with the reaction:

$$AB + CD \rightleftharpoons AD + CB$$

$$CB \rightleftharpoons C^+ + B^-$$

Some acids or bases are entirely dissociated even in relatively concentrated solutions. They are **called strong electrolytes.**

Exemple: $NaCl \rightleftharpoons Na^+ + Cl^-$

Other substances, such as acetic acid CH3COOH, are only partially dissociated in solution. These are **weak electrolytes.** In this case we. must distinguish between total acidity wich comprises all possible H^+ ions and free acidity which comprises dissociated H^+ ions.

Water, itself, is partially dissociated into ions according to the reversible reaction:

$$H_2O \rightleftharpoons H^+ + OH^-$$

This means that in water there are both H_2O. molecules and OH^- (hydroxide ion) and H^+ ions (in the hydrated H_3O^+ form called hydronium ion).

. **Law of mass action**

In the case of a chemical reaction at equilibrium:

$$mA + nB \underset{2}{\overset{1}{\rightleftharpoons}} m'C + n'D$$

the reaction velocity in direction 1 is given by the relationship:

$$V_1 = k_1[A]^m\ [B]^n$$

The velocity in direction 2 is:

$$V_2 = k_2[C]^{m'}\ [D]^{n'}$$

where [A], [B], [C] and [D] represent the activity of compounds in solution. At equilibrium V1 = V2, therefore:

$$k_1[A]^m\ [B]^n = k_2[C]^{m'}\ [D]^{n'}$$

$$\frac{[A]^m\ [B]^n}{[C]^{m'}\ [D]^{n'}} = \frac{k_2}{k_1} = K$$

This is the law of mass action. K is called the constant of thermodynamic dissociation. To make it easier, we use the designation pK = colog K. Tables list the values of pK (see page 505).

Application of the law of mass action to water: pH concept

Assuming that the coefficients of ionic activity are equal to 1, we obtain:

$$\frac{(H^+)\ (OH^-)}{H_2O} = K$$

Since the dissociation is always weak, the concentration of the water molecules is practically constant and we may write:

$(H^+)\ [OH^-] = K_e$.

The value of the dissociation (or ionization) constant of water is of the order of 10^{-14} (mol.l^{-1})2 at 23°C. This value varies with the temperature:

Temperature C	Ionization constant $K_e\ 10^{14}$	pK_e
0	0.12	14.93
18	0.59	14.23
25	1.04	13.98
50	5.66	13.25
100	58.5	12.54

In pure water, we have:

$(H^+) = (OH^-) = 10^{-7}$ mol.l^{-}.

By convention, the exponent of the concentration of H+ ions or pH (hydrogen potential) is used:

pH = colog (H^+)

The pH is measured by means of coloured indicators or, preferably, by an electrometric method (glass-electrode pH meter).

An acid medium is a solution in which (H^+) is greater than 10^{-7} mol.l^{-1} (pH < 7), an alkaline medium is one in which (H^+) is less than 10^{-7}mol.l^{-1} (pH > 7).

. Strength of acids and bases in aqueous solution

An acid is a substance capable of losing protons, that is, H+ ions. A base is a substance capable of accepting these protons. There is, thus, in an aqueous solution, an acid-base equilibrium defined by the following equation:

$$\text{Acide} + H_2O \rightleftharpoons \text{Base} + H^+$$

Applying the law of mass action and taking the concentration of H_2O molecules as a constant, we obtain:

$$\frac{[\text{Base}]\ [H^+]}{[\text{Acid}]} = K_A, \text{ and } pK_A = \text{colog } K_A$$

K_A, thus defined, is called the affinity constant of the acid-base couple.

The strength of an acid is determined by the extent to which it gives off H+ ions, that is, the larger the value of K_A or the smaller the value of pK_A the stronger the acid. The smaller the value of K_A, the stronger a base.

Thus, the ammonium ion NH_4^+ is a weak acid with pK_A = 9.2. The corresponding base NH40H is a fairly strong base.

The concept of pK_A makes it possible to calculate the pH of mixtures of corresponding solutions of acids, bases and salts:

- the pH of a solution of an acid with a total concentration c is:

$$pH = 1/2\ pK_A - 1/2 \log c$$

- the pH of a solution of a base is:

$$pH = 7 + 1/2\ pK_A + 1/2 \log c$$

- the pH of a solution of a salt is:

$$pH = 1/2\ pK_1 + 1/2\ pK_2$$

K_1 and K_2 being the affinity constants of the corresponding acid and base.

. Buffer solutions

In the case of a mixture of an acid of concentration (A) and the corresponding base, of concentration (B), if (A) = (B), this solution is called a buffer solution.

Example: acetic acid - acetate.

A buffer solution is a solution the pH of which varies little with the addition or removal of H+ ions. These solutions are useful when it is desired that a reaction should take place with a constant pH.

Acetates, acid phthalates and monopotassium phosphates serve as the basis for the preparation of a whole range of buffer solutions.

Solubility of sparingly-soluble compounds. Solubility product

The ionic equilibrium state of a sparingly soluble or insoluble substance is:

$$AC \rightleftharpoons A^- + C^+$$

$$[A^-]\,[C^+] = K_s$$

The magnitude of K_S, or solubility product, is constant for a given temperature and ionic strength of the solution. The less soluble the substance, the smaller the value of K_S. For calcium carbonate, the solubility of which is 12 $mg.l^{-1}$, the solubility product KS is 10"z ($mol.l^{-1}$). By analogy with the pH, we write: pKs = colog $10^{-8.32}$ = 8.32.

2.3. OXIDATION-REDUCTION

Water can take part, under certain experimental conditions, in oxidation-reduction with the following possible reactions:

$$2H_2O - 4\,e^- \rightleftharpoons 4H^+ + O_2$$

$$2H_2O + 2\,e^- \rightleftharpoons 2OH^- + H_2$$

In the first case, the water is a donor of electrons; it is a reducing agent: the acceptor of electrons is an oxidant. In the presence of water an oxidant releases oxygen. In the second case, water is an electron acceptor; it is an oxidant: the electron donor is a reducing agent. In the presence of water a reducing agent releases hydrogen.

But reactions are very slow without catalysts and in general the action of water with respect to oxidation-reduction reactions may be ignored.

However, very strong oxidants and reducing agents react remarkably quickly on water: for example, chlorine easily changes into the Clanion state according to the following reaction:

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Thus with water:

$$2Cl_2 + 2H_2O \rightarrow 4H^+ + 4Cl^- + O_2$$

oxygen is released and the medium becomes acid.

Water can be broken down into oxygen and hydrogen according to the following reaction:

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

The oxidation-reduction neutrality corresponds to the equal pressures of oxygen and hydrogen, that is a pressure of pH_2 equal to 10^{-22} Pa.

The concept of oxidation-reduction potential enables us to classify the various oxidants and reducing agents in relation to hydrogen and thus to each other (see page 249).

3. THE BIOLOGY OF WATER

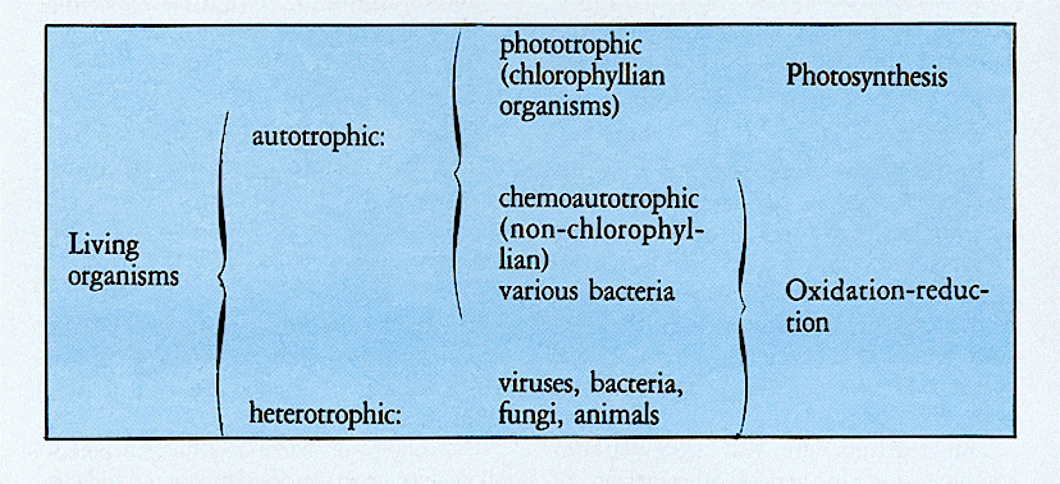
3.1.
WATER AND CELL METABOLISM

It is in the external environment in which it lives that the cell seeks the essential substances, also called essential metabolites, which it needs to maintain the rhythm of its activities.

Some cells are capable of synthesizing these from mineral components; they transform water, carbon dioxide and mineral salts into their own substance the molecular structure of which is extremely complex. These are the autotrophic cells which obtain the necessary energy from the external environment (light energy or chemical energy produced by the transformation of certain mineral radicals), and synthesize reserves which are usable at any time, thus constituting potential energy.

Heterotrophic cells, on the contrary, are incapable of synthesizing all their growth factors and use nutritive substances which they split up and "oxidize" exothermically into simpler substances: the energy released (kinetic energy) during these chemical reactions will supply the cell's needs (growth, locomotion, reproduction).

The term **metabolism** is used to cover all the energy reactions, the term **anabolism** being employed when there is a gain of potential energy (endothermic reaction), and therefore synthesis of living matter, and **catabolism** when there is a gain in kinetic energy (exothermic reaction) and therefore degradation of nutritive substances.



The study of energy sources therefore consists essentially of the analysis of photosynthesis and of oxidation-reduction phenomena in fermentation processes

. Anabolism

(a) Photosynthesis

The typical case is the production of glucides by plants from the CO_2 in the atmosphere and the water in the raw sap with the aid of solar energy and in the presence of chlorophyll which can be summarized by the overall equation:

$$6\,CO_2 + 6\,H_2O \rightleftharpoons C_6H_{12}O_6 + 6\,O_2$$
$$- 2{,}72\ kJ.mol^{-1}\ (- 650\ cal.mol^{-1})$$

This biological process is quantitatively the most important in nature.

(b) Mineral oxidation-reduction

Other autotrophic organisms are incapable of utilizing solar energy because they have no fixing pigments; they obtain the energy necessary for their existence from the oxidation-reduction phenomena of mineral substances. Worthy of mention here are the bacteria of the genus Nitrosomonas which oxidize ammonia to nitrites, those of the genus Nitrobacter which transform nitrites to nitrates, the iron and manganese bacteria which oxidize ferrous and manganous bicarbonates to ferric and manganic hydroxides, sulphur bacteria which transform hydrogen sulphide to colloidal sulphur, sulphate-reducing bacteria which reduce sulphates to H2S, and thiobacilli which oxidize the latter to sulphuric acid.

. Catabolism - Fermentation process

The process of decomposition of cellular alimentary substances, or catabolism, involves the formation of water or the participation of water molecules in organic oxidation and reduction reactions making use of the chemical energy contained in all nutritive substances.

The terms aerobic and anaerobic are used to characterize the type of decomposition which is in fact dehydrogenation taking place within the heterotrophic cell. If hydrogen combines with the molecular oxygen the process is called aerobic. If, on the contrary, the process involves the transfer of hydrogen from the dehydrogenated compound to a hydrogen acceptor other than molecular oxygen, it is **called anaerobic.** Hence the concept of obligate aerobic bacteria, obligate anaerobic bacteria and facultative anaerobic bacteria.

Decomposition (aerobic or anaerobic) of organic substances is assured by enzymes secreted by the organisms. These are complex proteins with a characteristic three-dimensional conformation and to which the organic molecules or substrate can become fixed. The specificity of enzymes is linked to their threedimensional structure.

The process of biological breakdown leads, depending on whether it takes place under aerobic or anaerobic conditions, to different final breakdown products (see page 286).

3.2.

WATER, THE MEDIUM FOR MICROBIAL LIFE

Medical and biological science has recognized the role played by water in the appearance and transmission of certain diseases. This has led to the discovery and identification of a number of unicellular organisms present in water. The ones that cause **pathogenic illnesses are very** few in number relative to the total microbial population. Others are used by man for their synthesis (metabolites, etc.). **Bacteria** play an especially important role in

Like all living cells, the bacterial cell contains a nucleus mainly composed of chromosomes massed together in the chromatin and consisting of deoxyribonucleic acid (DNA). The nucleus controls reproduction, preserves cell lineage in a genetic code and conducts by means of messenger RNA (ribonucleic acid) the synthesis of proteins and especially enzymes (this takes place in the cytoplasm, a jelly containing RNA particles, ribosomes, as well as various organoids such as mitochondria, lysosomes, etc. which play a very definite role). The cell is surrounded by a rigid membrane giving the bacterium its shape. The motile type of microorganisms has cilia or flagella (figure 5).

The ratio of surface area to volume is higher than in the case of other organisms. Since the metabolic rate rises with this ratio, a bacterium is more active than more advanced organisms. The rate of reproduction depends on the concentration of nutritive substance in the medium. In the most favorable cases a cellular division has been observed to take place in 15 to 30 minutes; sometimes it takes several days. The speed depends on the temperature.

Bacteria can only live in a medium possessing certain characteristics: water content, pH, salinity, oxidation-reduction potential and temperature. The favourable oxidation-reduction potential can vary considerably depending on whether the bacteria are operating under aerobic or anaerobic conditions. These conditions are closely linked with the composition of the enzymatic complex secreted by the bacteria.Major variations in the characteristics of the medium may result in a species selection

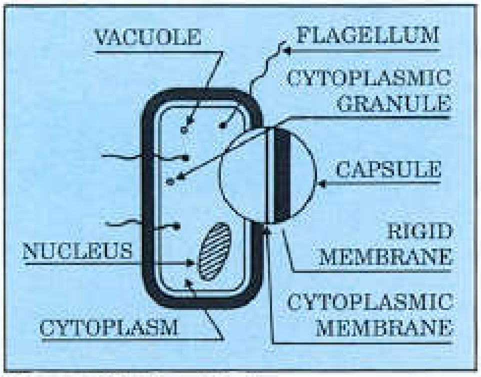


Figure 5. The bacterial cell.

Bacteria may be classified, according to the optimum temperature for their enzymes, as **thermophilic** (temperature over 40°C), **mesophilic** (temperature around 30°C), **psychrophilic** (0 to 15°C) and **cryophilic** (-5 to 0°C).

Some bacterial species may have a special shape owing to sporulation: the spores which they produce are cells in suspended animation with a structure which makes them much more resistant, for instance, to heat and dryness. When conditions return to normal the spores germinate and recreate active bacteria.

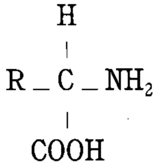
A complex bacterial culture may therefore adapt itself through selection and mutation to slow changes in the composition of the substrate on which it feeds.

3.3.
NUTRITIVE SUBSTANCES

3.3.1. Carbonaceous substrates

The principal nutritive substrates for heterotrophic organisms are protides, glucides and lipids.

Protides, the most important components of living matter, form the basis of protoplasmic and cytoplasmic matter. They consist of an assembly of simple substances, the **amino acids.** An amino acid is a substance whose molecule contains one or more acid groups COOH and one or more amino groups NH_2- linked to the same C atom:



$$\begin{array}{c} H \\ | \\ R - C - NH_2 \\ | \\ COOH \end{array}$$

Protides behave like acids or bases depending on the pH of the medium in which they are located. The acid and amino functions can become fixed to each other and can form long-chain macromolecules the molecular weight of which can be very high (50 000 and above). A distinction is drawn between peptides, simple proteins and conjugated proteins.

Glucides used to be called sugars, owing to the flavour of the simplest among them, or carbohydrates, because they correspond to the general formula: $C_m(H_2O)_n$. Owing to their abundance in vegetable tissue, these are the usual foods of heterotrophic organisms.

They exist in a non-hydrolyzable form (the oses, such as glucose) or a hydrolyzable form (osides, such as starch, cellulose and glycogen).

Simple or complex **lipids** are esters of more or less complex fatty acids and alcohols. They are generally insoluble and can emulsify in water. They constitute, both in plants and in animals, an important reserve material for meeting their energy requirements.

Under certain conditions, heterotrophic organisms may adapt themselves so that they can feed on other organic substrates such as alcohols, phenols, aldehydes, hydrocarbons, etc.

Autotrophic organisms may synthesize their own substance from a carbon source such as carbon dioxide, methane, etc.

3.3.2. Nitrogen, Phosphorus and Trace elements

Besides the nutritive substances already mentioned, bacterial organisms (autotrophic and heterotrophic) need mineral elements, some in the form of trace elements, which are indispensable for their growth.

The percentage of nitrogen and phosphorus in the bacterial mass is appreciable. The average values are as follows:

N: 7 to 10%   P: 2 to 3%

They play various roles in the cell (structure, metabolism) but phosphorus is chiefly involved in the storage mechanism and in the release of energy. This energy reserve is located in the P-P bonds which are found in certain molecules: the adenosine-mono-, di- and triphosphate (AMP, ADP and ATP).

A release of energy occurs with a break in the P-P bond, thus transforming ATP to ADP to AMP. The energy potential per molecule is as follows:

$$\text{ATP} + H_2O \rightleftharpoons \text{ADP} + \text{phosphates} + 30{,}5\ \text{kJ.mol}^{-1}\ (7{,}3\ \text{kcal.mol}^{-1})$$

Strictly speaking, trace elements are generally cations or anions. In the growth environment, concentrations of a microgramme per litre are ample to respond to cellular requirements. These elements quickly become toxic at high levels. They control numerous conditions inside the cell such as the ionic transmembrane gradient (Na^+). They are also involved in the formation of certain macromolecules associated with enzymatic complexes.

All bacterial groups have in common the requirement for these elements but certain ones, depending on the bacterial family, have very specific requirements. For instance, nickel is specifically tied to enzymes which control the methylation of acetate in methane-producing bacteria and is therefore indispensable to proper methane fermentation.

4. THE LANGUAGE OF WATER CHEMISTRY

In order to treat water, we must understand it and be able to describe it in as much detail as possible. Certain expressions used in water treatment are far removed from usual scientific terminology. The most common of these are listed below.

. **Turbidity**

Together with the measurement of suspended solids, this gives an initial indication of the level of colloidal matter of inorganic or organic origin. Turbidity is judged either by comparing the specimen with reference opalescent solutions (formazin, mastic, etc.) or by measuring the limit of visibility using a well-defined object (a platinum wire or a Secchi disc).

. **The Fouling index**

It is a measure of the fouling potential of water. It is also linked with suspended solids and is involved in water treatment by membranes.

. **Suspended solids (SS)**

This includes all matter suspended in water that is large enough to be retained on a filter with a given porosity.

. **Colour**

True colour after filtration is due most often to the presence of dissolved or colloidal organic matter. There is no relationship between the colour and the quantity of organic matter. Colour is measured by comparing the specimen with a reference solution (Platinum-Cobalt method).

. **Concentration (by volume)**

This is a measure of the quantity of matter dissolved or dispersed in a given volume of water. As an example, it is indicated as $mg.l^{-1}$, $g.m^{-3}$, $g.l^{-1}$ etc.

. **Gramme-equivalent**

The gramme-equivalent is equal to the molar weight of a substance divided by the number of charges of the same sign carried by the ions released by a molecule of that substance in an aqueous solution.

For instance, a molecule of orthophosphoric acid, H_3PO_4, releases three positive charges and three negative charges. One gramme-equivalent of H_3PO_4 is therefore equal to one third of the weight of one mole of H_3PO_4.

. **Normality**

A normal solution is one containing one gramme-equivalent of the relevant substance per litre. Multiples and submultiples of the normal solution are also used (2N, N/10, N/25, N/50, N/100, etc. solutions).

In general, when a volume V_1 of an electrolyte of normality N_1 is acted upon by another electrolyte of normality N_2, the volume V_2 is determined from the relation:

$$N_1V_1 = N_2V_2$$

. Milliequivalent per litre

The unit often used in practice is the milliequivalent per litre ($meq.l^{-1}$) which is obtained by dissolving a quantity of the electrolyte equal to one thousandth of its gramme-equivalent in one litre of water. This is the concentration of an N/1000 solution.

. The French degree

The unit used in practical water treatment is the French degree which corresponds to the concentration of an N/5000 solution.

$1\ (meq.l^{-1}) = 5$ French degrees

Example: A solution of a calcium salt at 25 French degrees contains in calcium Ca (of molar weight 40 g and valency 2):

$$\frac{40 \times 5}{2 \times 1\,000} = 0.1 \text{ g per litre}$$

. The equivalence of various degrees

1 French degree = 0.56 German degree = 0.7 English degree = 10 ppm $CaCO_3$

1 German degree = 1.786 French degrees = 1.25 English degrees = 17.86 ppm $CaCO_3$

1 English degree = 1.438 French degrees = 0.8 German degree = 14.38 ppm $CaCO_3$

1 ppm $CaCO_3$ = 0.1 French degree = 0.056 German degree = 0.07 English degree.

. Titration for hardness (TH)

The titration for hardness indicates the concentration of alkaline-earth ions in water.

The various types:

(A) Total TH: content of Ca and Mg.
(B) Calcium TH: content of Ca.
(C) Carbonate hardness: content of bicarbonates and carbonates of Ca and Mg. It is equal to the M alk. (see below) if the TH exceeds the M alk., or to the TH if the M alk. exceeds the TH.
(D) Noncarbonate hardness (permanent hardness): indicates the content of Ca and Mg corresponding to strong anions. It is equal to the difference between A and C.

. Phenolphthalein alkalinity (P alk.) and methyl orange alkalinity (M alk.)

The relative values of P alk. and M alk. indicate the quantities of alkaline or alkaline-earth hydroxides, carbonates or bicarbonates in the water (see table page 18).

The P alk. value therefore includes all the hydroxide content but only half the carbonate content.

The M alk. therefore indicates the bicarbonate content.

In some very polluted waters (wastewaters) the M alk. also covers organic acids (acetic, etc.).

. Measurement of salts of strong acids (SSA)

Natural waters contain no free strong acids (free mineral acidity, or FMA) but only their salts, in particular the sulphates and chlorides of calcium, magnesium and sodium. The SSA expresses the total content of these salts of strong acids.

. Salinity

The overall salinity of water corresponds to the total number of cations and anions as expressed in $mg.l^{-1}$.

. Permanganate value

Grouped under this heading are all substances susceptible to oxidation by potassium permanganate ($KMnO_4$).

Various methods of analysis are used depending on the temperature, the type of environment and the procedure.

Dissolved salts	Value of degree in mg.l^{-1}	Respective values of P alk. and M alk.				
		if P alk. = 0	if P alk. $< \frac{\text{M alk.}}{2}$	if P alk. $= \frac{\text{M alk.}}{2}$	if P alk. $> \frac{\text{M alk.}}{2}$	if P alk. = M alk.
OH^-	3.4	0	0	0	2 P alk. -M alk.	M alk.
CaO	5.6					
$Ca(OH)_2$	7.4					
MgO	4.0					
$Mg(OH)_2$	5.8					
NaOH	8					
CO_3^{2-}	6	0	2 P alk.	M alk,	2(M alk. -P alk.)	0
$CaCO_3$	10					
$MgCO_3$	8.4					
Na_2CO_3	10.6					
HCO_3	12.2	M alk.	M alk.-2 P alk.	0	0	0
$Ca(HCO_3)_2$	16.2					
$Mg(HCO_3)_2$	14.6					
$NaHCO_3$	16.8					

Chemical oxygen demand (COD)

The COD indicates the total hot oxidation by potassium dichromate and covers the majority of organic compounds as well as oxidizable mineral salts.
France sometimes uses the CODAD which corresponds to chemical oxygen demand after a sample has been allowed to settle for two hours.

.**Biochemical oxygen demand (BOD)**

This is the quantity of oxygen consumed at 20°C and in darkness during given period to produce by biological means oxidation of the biodegradable organic matter present in water. By convention, BOD5 is used, which is the quantity of oxygen consumed after five days incubation. BOD5 normally represents only the biodegradable carbonaceous organic pollution.

. **Total organic carbon (TOC)**

This indicates the content of carbon linked to organic material by measuring the CO_2 after complete oxidation.
Although this means is quick and- requires only a small specimen, it is difficult to correlate it with the preceding

measures. On the other hand, in most often mistakenly called total nitrogen. cases, the suspended solids must be removed prior to measurement.

. Kjeldahl nitrogen (TKN)

TKN groups organic nitrogen with ammonia nitrogen. This procedure is

. Total nitrogen (TN)

This applies to all forms of nitrogen in water, such as organic nitrogen, ammonia nitrogen, nitrites and nitrates. It is an extension of TKN with the addition of oxidized forms of nitrogen.

2

TREATMENT.WHAT TYPE OF WATER AND WHY?

Figure 6. The Iguacu Falls (Argentina/Brazil).

1. NATURAL WATER

Available stores of natural water are made up of groundwater (from infiltration, aquifers), impounded or flowing surface water (reservoirs, lakes, rivers), and sea water

1.1.
GROUNDWATERS

1.1.1. Origin

The porosity and structure of the ground determine the type of aquifer and underground circulation.

Groundwater may be free. In this case it is directly fed through seepage from run-off. The level of groundwater fluctuates with the amount of water held.

Groundwater may be **confined.** In this case it is separated from the soil surface by an impervious stratum. In general, the water is deeper-lying.

Alluvial groundwater presents a special case: this groundwater is located in alluvial soil close to a river. Thus, the quality of the river water directly influences the quality of the groundwater.

Groundwater may **circulate and be stored** in the entire geological stratum under study; this is the case in porous soils such as sand, sandstone and alluvium. It may circulate and be stored in fissures or faults in compact rocks. Most volcanic or metamorphic rocks are compact rocks with narrow cracks. These rocks are not, in themselves, permeable. Water trickles through the rocks and circulates because of localized and dispersed fissures.

Compact rocks with large fissures or caverns are typical of limestone: the original fissures grow progressively larger as the limestone dissolves into the circulating water which contains carbon dioxide. This process leads to large caverns with, at times, true underground waterways; this is **karst** terrain. Marl can sometimes be found here and very occasionally sandstone.

1.1.2. General characteristics

The geological nature of the terrain determines the **chemical composition** of the held water. Water is constantly in contact with the ground in which it stagnates or circulates; an equilibium develops between the composition of the soil and that of the water. Water that circulates in a sandy or granitic substratum is acidic and has few minerals. Water which circulates in limestone contains bicarbonate alkalinity.

Table 1 shows the characteristics of groundwater based on main analysis parameters.

Among the characteristics of this water, weak turbidity, a constant temperature and chemical composition, and an almost overall absence of oxygen, are noteworthy. In the case of a confined groundwater, principally one circulating in karst terrain, one can find extreme variations in the composition of the water with the appearance of turbidity and various pollutants. Such variations are connected to those in the aquifer flow which are due to precipitation. Furthermore, groundwater is often very pure microbiologically.

1.1.3. Potability

Groundwater has for a long time been synonymous with "clean water" and natually meets the standards for potabil ity. This water is, in fact, less susceptible to accidental pollution.

A free aquifer, fed by the entire ground surface lying above it, is more susceptible than a confined aquifer. Alluvial aquifers are also threatened over their entire surface by the tributary network of the river.

Once an aquifer has been polluted, it is very difficult to bring it back to its original purity; the pollutants which contaminated the aquifer are not only present in the water but are attached to and adsorbed on the rocks and minerals in the substratum.

Groundwater may also contain elements in concentrations that greatly exceed the standards for drinking water.
This is due to the composition of the ground where the water is stored. Notable are Fe, Mn, H_2S, F, etc.

Groundwater must be treated before distribution whenever the concentration of one or several elements exceeds the limits authorized by regulations.

1.1.4. Mineral water and spring water

French law defines the terms **"mineral water" and "spring water".**

Mineral water is deep-lying water which may contain some elements in higher concentration than that authorized for drinking water and is known for its therapeutic properties. It is distributed in bottles and sometimes undergoes certain well-defined treatments such as natural settling, iron removal by simple aeration and removal and/or reintroduction of the original CO_2.

Spring water is water which, unlike mineral water, must meet the criteria for potability at its source; it may not run dergo any treatment.

In contrast to these two types of water, the term **"table water"** refers to bottled water which need only meet the criteria for potability, and for which preliminary treatment of any kind is authorized.

1.2. SURFACE WATER

This term encompasses all water on the surface of the continents, both flowing and stored.

1.2.1. Origin

It originates either from deep-lying groundwater which feeds streams and rivers or from run-off. Water from various sources flows together; it is characterized by a moving surface that is constantly in contact with the atmosphere and by an impressively swift flow. It can be found stored naturally (lakes) or artificially (storage reservoirs); in this case, it has a virtually immobile water/atmosphere exchange surface, a depth that can be considerable and a long retention time.

Table 1. Main differences between surface and groundwater.

Characteristics	Surface water	Groundwater
Temperature	Varies with season	Relatively constant
Turbidity, SS(true or colloidal)	Level variable, sometimes high	Low or nil (except in karst soil)
Colour	Due mainly to SS (clays, algae) except in very soft or acidic waters (humic acids)	Due above all to dissolved solids (humic acids for example)
Mineral content	Varies with soil, rainfall, effluents, etc.	Largely constant, generally appreciably higher than in surface water from the same area
Divalent Fe and Mn (in solution)	Usually none, except at the bottom of lakes or ponds in the process of eutrophication	Usually present
Aggressive CO_2	Usually none	Often present in quantities
Dissolved 0_2	Often near saturation level. Absent in very polluted waters	Usually none at all
H_2S	Usually none	Often present
NH_4	Found only in polluted water	Often found, without being; a systematic index of bacterial pollution
Nitrates	Level generally low	Level sometimes high
Silica	Usually moderate proportions	Level often high
Mineral and organic micropollutants	Present in the water of developed countries but liable to disappear rapidly once the source is removed	Usually none but any accidental pollution lasts a very long time
Living organisms	Bacteria (some pathogenic), viruses, plankton (animal and vegetable)	Iron bacteria frequently found
Chlorinated solvents	Rarely present	Often present
Eutrophic nature	Often. Increased by high temperatures	No

1.2.2. General characteristics

The **chemical composition** of surface water depends on the type of terrain the water has passed through before flowing into the drainage area. Along its course, water dissolves various components of the soil. The exchange between water and air at the surface causes gases (oxygen, nitrogen, carbon dioxide) to dissolve in the water.

Table 1 compares those substances found in surface water with those found in groundwater. Worthy of note:

- nearly universal presence of dissolved gases, especially oxygen,

- heavy concentration of **suspended solids** (SS), at least in flowing water. These suspended solids are extremely varied, from colloidal particles to structured elements carried by rivers whenever there is a considerable increase in flow. For reservoir water, the largest solids tend to settle naturally while the water is contained; the remaining turbidity is, therefore, colloidal,

- presence of natural **organic matter** resulting from the decomposition of vegetable or animal organisms living at the surface of the drainage area or in the river. These organisms (vegetable, animal, etc.) decompose after death,

- presence of plankton: surface water houses a large phytoplankton (algae, etc.) and zooplankton growth. Under some conditions, an intense water life develops vegetable, macrophyte and fish populations,

- daily fluctuations (temperature, amount of sunshine) or seasonal **fluctuations:** climate changes (temperature, snow melt), vegetation changes (fall of leaves). These fluctuations can be hazardous: sudden inundations, storms, accidental pollution. In confined surface water, the quality at the surface is different from that at the bottom of the body of water (O_2, Fe, Mn, permanganate value, plankton). Each of these elements varies according to the time of year,

- organic pollution often leading to eutrophication of the water (see page 30).

1.2.3. Potability of surface water

Untreated surface water is rarely potable. Besides the substances mentioned in 1.2.2, surface water is usually polluted with bacteria. Moreover, there may be several types of pollution:

- municipal: discharge from municipal wastewater (human and domestic wastes) after water purification treatment,

- industrial: organic pollutants and micropollutants (hydrocarbons, solvents, synthetic products, phenols), or inorganic (heavy metals, ammonia, toxic products),

- agricultural: fertilizers and pesticides or herbicides carried by rainwater and run off. Also, organic wastes from large livestock rearing facilities.

1.3. SEA WATER AND BRINE

Table 2 shows the composition of "standard" sea water (ASTM type). This water is characterized by a strong **salinity** that may vary depending on the source.

Source	**Salinity** g.l
Baltic Sea	17
Atlantic and Pacific	32 to 35
Mediterranean Sea	38 to 40
Red Sea	43 to 45
Dead Sea	270

Some **physical characteristics** of sea water are especially important: turbidity, suspended solids, number of particles (in excess of 2 or 5 µm per ml or 100 ml) and clogging index. They vary depending on the location:

- offshore, the suspended solids consist mainly of zooplankton and phytoplankton, the value of which is some $mg.l^{-1}$;
- near the shores, the salt level may be high depending upon agitation (winds, tides) and depth (presence of a continental shelf). Furthermore, near densely populated regions, pollution from municipal and industrial wastewater can become excessive: the SS level can vary from several tens of $mg.l^{-1}$ to one or two hundred;

Table 2. Standard analysis of sea water - pH = 8.2-8.3.

	French deg.		French deg.
Titration for hardness (TH)	650	Free alkalinity……………………………	0
Carbonate hardness	15	Phenolphthalein alkalinity (P alk.)…….	0
Permanent hardness	635	Methyl orange alkalinity (M alk.)…….	15
Calcium hardness (CaH)	110	Salts of strong acids (SSA)………..	3,085
Magnesium hardness (MgH)	540	Total salinity………………………	3,100

Anions	$mg.l^{-1}$	$meq.l^{-1}$	**Cations**	mg.l-'	meq.l-'
chloride Cl^-	19 880	560	calcium Ca^{2+}	440	22
sulphate $S0_4^{2-}$	2 740	57	magnesium Mg^{2+}	1 315	108
nitrate $N0_3$	-	-	sodium Na^+	11 040	480
bicarbonate $HC0_3$	183	3	potassium K^+	390	10
bromide Br^-	68	0.9	strontium Sr^{2+}	1.3	0.3
	22 871	620.9		13 186.3	620.3
Total salinity: 36.4 $g.l^{-1}$					

- in estuaries, the mixing of rivers with the sea as well as the influence of the tides (with an intrusion of sea water into the river bed and tidal bores) cause substantial variations in the salinity and SS level of water samples taken from a given area. Agitation caused by changing of currents replaces sediment back into suspension and forms a "plug" the SS level of which can reach several $g.l^{-1}$;
- the plankton level may also vary greatly depending on geographical conditions (shallow and motionless sea) and climate (proliferation of algae in the North Sea, for instance).

1.4.

THE NITROGEN CYCLE

The nitrogen cycle is shown diagrammatically in figure 7.

In an aerobic environment, organic nitrogenous matter and ammonium salts are converted to nitrites and then to nitrates, with the consumption of oxygen. This is the process known as **nitrification** which covers two successive reactions:

- **nitrite production** is the action of nitrite-forming bacteria such as Nitrosomonas, Nitrosocystis, Nitrosospira, Nitrosoglea, etc.,
- **nitrate production (nitration)** is the work of bacteria of the genera: Nitrobacter, Nitrocystis, Bactoderma, Microderma, etc.

All these bacteria are autotrophic and strictly aerobic. They use the energy produced by the oxidation of ammonia and of nitrites to reduce inorganic carbon originating from carbon dioxide or carbonates.

4.6 mg of oxygen is necessary per mg of nitrogen if the oxidation is to be complete according to the simplified reaction:

$$NH_3 + 20_2 \rightarrow HN0_3 + H_20$$

Actually, no oxidation of ammonia nitrogen reaches the nitrate stage (intermediate compounds make up the bacterial mass) and in practice, 4.2 mg of oxygen is sufficient to oxidize a mg of nitrogen.

The process of nitrification tends to reduce the oxygen content in waterways as does assimilation of organic pollution.

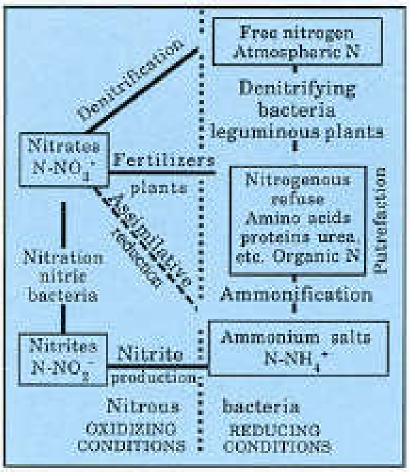


Figure 7. Nitrogen cycle.

These nitrates make up an oxygen reserve which can be given back through denitrification when conditions become reducing and anaerobic again, but little hope can be placed on such conditions in a river.

1.5.
BACTERIA INVOLVED IN THE SULPHUR CYCLE

The sulphur cycle is shown in the diagram in figure 8. Anaerobic sulphur fermentation converts sulphur-containing organic compounds to H_2S.

Other aerobic bacteria can oxidize H_2S to sulphur (which they are sometimes capable of storing in the form of light-refracting granules, dispersed in their cytoplasm) and possibly to sulphuric acid:

- simple **oxidation-reduction** reactions in:

- the **Leucothiobacteriales** (or colour-less sulphur bacteria), such as Beggiatoa or Thiothrix:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

- some **Protobacteriaceae**, such as Thiobacillus thiooxidans which then oxidizes the sulphur to sulphuric acid:

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

The final end-point in an anaerobic environment may thus be the appearance of sulphates; on the other hand, in an anaerobic environment these may be reduced by other bacteria (Desulfovibrio or Sporovibrio desulfuricans, some Clostridium, etc.) which secrete sulphatoreductases, capable of catalysing the global reaction:

$$H_2SO_4 + 4H_2 \rightarrow H_2S + 4H_20$$

Sulphite-reducing bacteria also exist (certain species of Clostridium and Welchia).

Some of these bacteria take part in the process of corrosion of cast iron, steel or concrete pipework (see page 419).

- **photosynthetic** reactions in the **Rhodothiobacteriales** (or purple sulphur bacteria such as Chromatium, Thiospirillum (see figure 9) or Thiopedia, in the same way as in the case of the **Chlorothiobacteriales** (or green sulphur

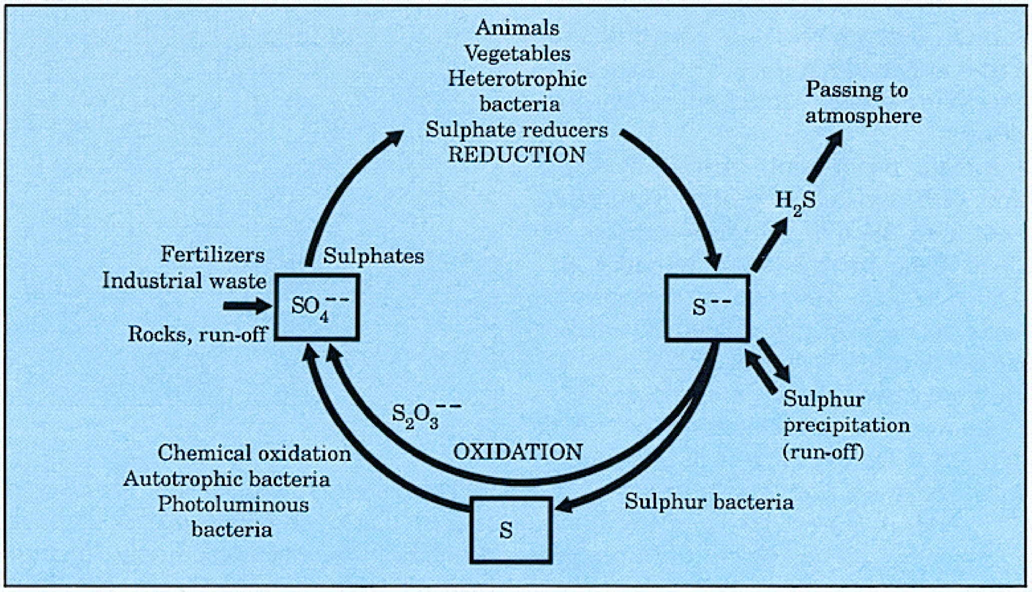


Figure 8. Sulphur cycle

bacteria) such as Chlorobium or Chloro bacterium; elemental sulphur is formed first:

$$2H_2S + CO_2 \xrightarrow[\text{energy}]{\text{light}} (CH_2O)^* + H_2O + 2S$$

The sulphur produced is, depending on. the species, either stored in the bacterial cell or excreted. It may later be converted to sulphuric acid:

$$2S + 3CO_2 + 5H_2O \xrightarrow[\text{energy}]{\text{light}} 3(CH_2O) + 2H_2SO_4$$

The global reaction may then be written:

$$H_2S + 2CO_2 + 2H_2O \xrightarrow[\text{energy}]{\text{light}} 2(CH_2O) + H_2SO_4$$

In these reactions (CH_2O) represents synthesized organic matter

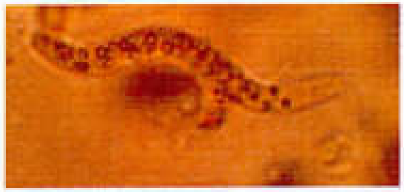


Figure 9. Thiospirillum x 1000.

1.6.
BACTERIAL OXIDATION-REDUCTION OF IRON AND MANGANESE

- **Iron**

The exothermic oxidation of iron can be catalyzed by some bacteria due to the oxidation-reduction enzymes which they excrete (flavins): trivalent iron, rendered insoluble in hydroxide form, is then stored in the mucilaginous secretions (sheaths, stalks, capsules, etc.) of these bacteria. The organisms responsible for these phenomena are mainly the Siderobacteriales, particularly:

- Chlamydobacteriaceae: Leptothrix (L. ochracea, L. crassa, L, discophora),
- Crenotrichaceae: Crenothrix (Cr. polyspora), Clonothrix (Cl. ferruginea, Cl. fusca),
- Siderocapsaceae: Siderocapsa, Ferrobacillus, Sideromonas,
- Gallionellaceae: Gallionella (G. ferruginea, G. major).

This property is also shared by Protobacteriaceae (Thiobacillus ferrooxidans).

- **Manganese**

All the above organisms can also cause the oxidation of manganese if it is distinctly more abundant than iron; in addition, there are other bacteria which show a specific activity in this respect, for example:

- true bacteria: Pseudomonas (Ps. manganoxidans), Metallogenium (M. personatum, M. symbioticum),
- Siderobacteriales: Leptothrix (L. echinata, L. lopholes),
- Hyphomicrobiales: Hyphomicrobium (H. vulgare).

The action of all these microorganisms can be very important in the processes of iron and manganese removal.

Some of these bacteria, when placed in a reducing medium, can use the Mn that they have stored in their sheath for their metabolism. It is then dissolved and released in the form of Mn^{++}.

- **Bacterial corrosion**

Although the processes described in the preceding paragraph are beneficial in a deep-water treatment installation, they can, on the other hand, be very damaging in a cast iron or steel pipe.

Traces of iron in water are sufficient to induce the development of the iron bacteria mentioned above. Three main genera can easily be recognized under the microscope:

- **Leptothrix:** a filament (or trichome) containing a single line of cylindrical cells and surrounded by a sheath; this is at first thin and colourless but becomes thicker and develops a brown colour which becomes increasingly darker as it is impregnated with iron oxide (figure 10),

Figure 10. Leptothrix ochracea x 680.

- **Crenothrix:** the trichomes have an open end through which cells escape, in several rows, to form new trichomes. The development of the sheath is similar to that of Leptothrix,
- **Gallionella:** isolated cells usually growing on twisted stalks (with or without ramifications) which they have secreted. The linkage is, in fact, fragile and frequently only the stalk is found (figure 11).

Figure 11. Gallionella ferruginea x 680.

The activity of these bacteria results in the formation of tubercles which can block a pipe (the presence of these tubercles can be shown by partial dissolution in a concentrated acid and examination of the residue under the microscope). Areas coated with these tubercles become anaerobic, allowing the development of sulphate-reducing bacteria (a typical example being Desulfovibrio desulfuricans). This bacterial growth promotes corrosion.

1.7.
EUTROPHICATION

This term is used to describe an evolutionary process in the quality of lake water or other artificially impounded water. It is sometimes extended to include river water.

1.7.1. Lake eutrophication

The evolution of lake may be summed up in the following manner:

- a lake which is young and deep is **oligotrophic:** its water is blue and transparent; dissolved oxygen is present down to the bottom; the biomass is sparse,

- as ageing proceeds, the lake becomes enriched in organic matter, due to its primary photosynthetic production (algae) and possibly due to contributions from external sources; it then becomes successively **mesotrophic, then eutrophic;** the following phenomena are then found: decrease in depth by progressive silting; colouring of the water (green to brown); reduced transparency; oxygen depletion in the deeper levels; greater biomass, with the appearance of species indicative of eutrophication (especially of Cyanophyceae, or blue algae, of which the best known is Oscillatoria rubescens). The final stage is the pond, swamp, etc.

The transition from one type to the next takes a very long time, which can be measured in thousands of years. But this natural process has in some cases been accelerated to such an extent as to become apparent during a human lifespan. This situation is the result of human waterside activities which carry organic matter and fertilizing elements (nitrogen and phosphorus, in particular) to the stagnant waters: agriculture, municipal and industrial wastewater.

The consequences of this artificial eutrophication can be disastrous for the tourist trade and for fishing; furthermore, the cost of water treatment is considerably increased as the result of the equipment and reagents necessary for the removal of the organisms themselves or of their metabolic products.

It is possible to combat eutrophication with:

- curative measures (oxygenation, destratification, chemical or biological methods),
- preventative measures: diversion of the effluents by use of an intercepting sewer (e.g., Lake of Annecy) or by a change in course; tertiary treatment in purification plants (reduction in SS, phosphorus, nitrogen).

1.7.2. In the case of rivers: biotic indices

The same problems do not arise in running water, to which the full definition of eutrophication cannot be applied. For a long time now **saprobic** degrees have been used to describe the extent of pollution of a river; these are linked to the chemical properties of the water and to biological zones, which are defined by the presence of members of the various animal and vegetable communities (Kolkwitz and Marsson's system, 1909).

France prefers to use the method of Verneaux and **Tuffery biotic indices** (1967) which was adapted from the method developed in Great Britain by the Trent River Authority: analysis of the benthic macroinvertebrate population (molluscs, crustaceans, worms, insect larvae), from which an index of the river quality can be deduced, expressed on an increasing scale from 0 to 10.

Changes in biocoenose are particularly distinct downstream of a pollutant discharge (change in the type of dominant zoological group, reduction in the number of species, increase in the number of individuals in each species); using the method quoted above, punctual organic pollution is immediately reflected by a massive drop in the biotic indices downstream, which increase again, further down, as a result of self-purification. Such methods give valuable information for the study of pollution or in the assessment of the efficacy of effluent treatment, etc.

1.8. RADIOACTIVITY

1.8.1. Natural radioactivity

Natural sources of radioactivity are made up of radionuclides emitted by cosmic and earth radiations as well as radio elements present in living organisms. In water, this radioactivity is due to dissolved elements from these natural sources as well as isolated elements such as potassium-40.

- **Groundwater**

Radioactivity in groundwater is essentially due to the emission of radium which is present in all rocks. Radium is barely soluble but its daughter product radon-222 is very soluble

Other radioactive elements such as uranium, thorium, lead and polonium are associated with granite and deposits of uranium, lignite and phosphate. The chief types are uranium-238, present in more than 99% of the deposits, and its daughter product uranium-234 (highest uranium content in mineral water: 79 µg.l^{-1}).

- **Surface water**

Radioactive elements emitted in the atmosphere bind to aerosols and are carried to earth by rain: ^{3}H and ^{222}Ra for the most part, argon, beryllium, phosphorus.

Radon, uranium, etc. account for the solubilization of radioactive elements from the soil. In general, natural radioactivity of surface waters is very low; the presence of radioactivity in these waters is due to human activities.

- **Uranium mines**

Downstream of sites, the ratio of radioactivity is high, whether or not the mine is being worked. In the areas involved, water consumption from individual wells is very frequent while it should obligatorily pass through a water treatment plant. Contamination of surface water is seen in an increase in minerals and SS; radioactivity is often raised by 4 or even 5. In the case of drinking water, the essential problem is radon which is easily carried to the faucet due to the fact that it is soluble in cold water under pressure.

1.8.2. Artificial radioactivity

Most ß-ray emitters (except radon-228) are linked to human activities.

- **Radioactive elements in the environment**

- PWR power stations: ^{58}CO, ^{60}Co, ^{54}Mn ^{3}H
- Atomic power plants and bursts: ^{137}Cs ^{90}Sr, ^{3}H to ^{106}Ru ^{131}I
- Hospitals: ^{131}I
- The working of uranium mines:

$^{230\mathrm{Th}}$, ^{226}Ra (a-ray emitters)

^{228}Ra ^{210}Pb (ß-ray emitters)

Surface water can therefore be contaminated in various ways: dilution of atmospheric fallout, leaching of soil by industrial effluents and nuisance. No liquid discharge from industry is allowed into the water table and goes, instead, into rivers and the sea.

Soluble elements can first go through natural adsorption onto the suspended clay in turbid water.

Legal discharge from nuclear power plants varies according to rated powers and refers solely to the minimum and maximum flows of the receiving river. The fixed amounts are daily averages and in France the maximum volume added can, when authorized, reach, inside of 30 days, a maximum of 10 times the authorized annual average.

- **Tritium $^{3}H^{+}$** (T)

This is one of the radioactive elements that merit special attention even though the rays emitted by tritium $^{3}H^{+}$ at the same level as the other elements mentioned above, pose less of a danger.

Tritium is a naturally occurring element in the atmosphere but it is also the radioactive element discharged into the environment (nuclear power plants explosion sites) in the largest amount.

Origin: water on ocean surface	3 $nCi.m^{-3}$
Rain	4 $nCi.m^{-3}$
land water	6 to 24 $nCi.m^{-3}$

Discharge: 4 MCi per year in the world

Forecast for the year 2000: 30 MG per year.

99% of tritium is found as tritiated water ("HTO"): oxidation converts $^{3}H^{+}$ into liquid or vapour. Tritiated water dispersed into the soil (vapour), becomes easily part of the biological fluids and the entire organism, and, unlike other radioactive elements, does not bind with the sediment or the SS.

2. WATER FOR CONSUMPTION

2.1.

QUANTITIES REQUIRED

We know that, on the average, man consumes 2 litres of water per day for drinking and cooking. The quantity depends on the climate and increases to 3 or 4 litres in hot countries but is low in comparison to domestic use of water. This can vary from several litres per day in countries without public supply and with low household usage to several hundreds of litres in very developed countries.

Location	**Distribution**	**Quantity of water distributed***	
		Min. - Max.	Average
City	in houses fire hydrants	70 - 250 25 - 70	140 40
Countryside	in houses, or fire hydrants	25 - 70	40

* in litres per day per consumer

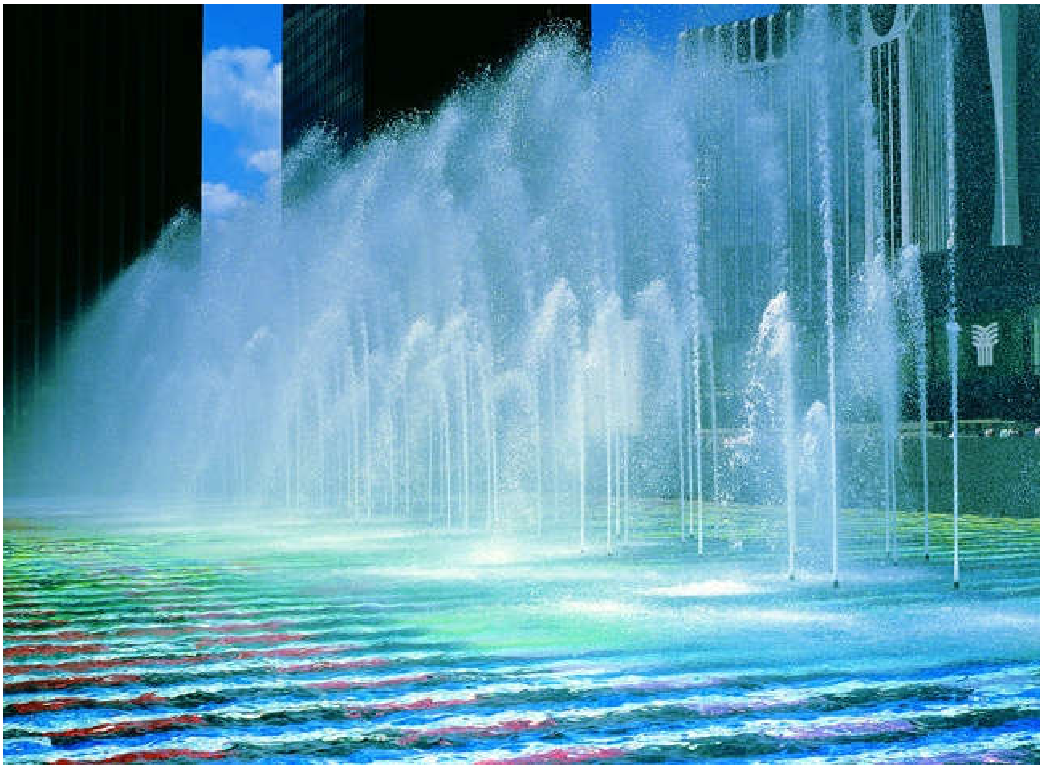


Figure 12. La Defense fountains (Paris).

A third group of consumers must be added to these. This group consists of offices and companies and various public services (schools, hospitals, swimming pools, street cleaning operations) and uses a large amount of the water supplied. Furthermore, some industries also use the public water supply.

Lastly, the condition of the supply system and the water lost through leaks in the system must also be taken into account in the water demand. The yield of a system is defined as the relation between the volume of water received by consumers and the volume leaving the pumping plant. A good system should be able to attain a yield of 80%. In France, 50% of the systems yield less than 70%; in 25% of the systems, the yield is less than 60% (taken from Lyonnaise des Eaux Handbook).

The following table shows the variations in demand for different lifestyles.

Location	**Quantity in m^3 per person per year**
Rural population	12 to 50
Detached house	110
Apartment buildings:	
- Low rent	60
- Luxury	200
Offices	25
Paris	150
Lyon	1/40
New York	500

(Taken from Lyonnaise des Eaux Handbook)

2.2. WHY TREAT WATER?

All water made available to consumers through a supply system must be treated even if only a small fraction of it is directly consumed by the individual. It would be hazardous to public health and economically prohibitive to set up a double supply system with one distributing water for consumption and the other supplying water for other uses.

Water coming out of the consumer's faucet must be "potable", that is, it must conform to standards in force (see page 575), regardless of how the consumer chooses to use it.

Water must be treated every time one of the analytical measurements rises above the current legal standard in the country in question. WHO (World Health Organization) sets recommendations for each measurement that must be followed by each country depending upon health conditions in that country and the state of its economy; the goal is to establish national standards.

2.3. CRITERIA FOR CHOICE

A number of factors determines which water should be treated before it is distributed. For each available water source (groundwater, flowing or stored surface water) we must assess:

- the **quantity:** the "source" must be able to furnish the required quantity of water at all times. In countries where the amount of rainfall varies greatly, it may be necessary to set up a reservoir and fill it during the rainy season with enough water to meet the needs of the dry season,

- the **quality:** in some countries the quality of available raw water must meet current legal standards. A determination must be made as to which treatment process would be best to make the water drinkable. This process would have to be weighed against previous years' fluctuations in the quality of water (daily, seasonal, climate variations) and against potential fluctuations that may occur in the future (with the construction of a dam, for example).

In addition, it must be remembered that groundwater is not synonymous with pure water: actually, many aquifers are polluted with bacteria, nitrates, phytosanitary products, chlorinated solvents or hydrocarbons,

- the **cost:** for each available source, the capital and operating costs must be compared so as to assure both quantity and quality of water for distribution: storage and transport of raw water, water treatment, storage and transport of treated water.

2.4. BIOLOGICAL IMPURITIES

All water is vulnerable to pollution by microorganisms.

2.4.1. Bacteria and viruses

The **bacteria** which are **indicators** of fecal contamination are brought into the environment by the discharge of municipal wastewater, which may or may not have been treated. These bacteria indicate possible contamination by bacteria or viruses which are pathogenic for man (see page 396).

The growth of **common germs** may create major problems in the distribution system: consumption of dissolved oxygen corrosion, bad taste of water

2.4.2. Various microorganisms: phytoplankron and zooplankton

Surface water contains many organisms that make up phytoplankton and zooplankton. Many of these organisms, such as Actinomycetes and Cyanophyceae, secrete compounds (such as geosmin) which give water a bad taste and smell. Others are pathogenic for man (amoebae).

The presence of algae and macroorganisms in the water system (Asellus, Copepoda, Nematoda) is unpleasant for the consumer and their growth can lead to major disturbances (proliferation, sediments, appearance of anaerobic conditions).

Moreover, while they grow or at their death, some microorganisms (Cyanophyceae, for instance), excrete metabolites that are toxic to higher animals.

2.5.
MINERAL IMPURITIES

Some of these impurities influence the organoleptic qualities of water, its aesthetic appearance or its behaviour in the distribution system but do not have any appreciable effect on the health of the consumer, whereas others have a known effect.

2.5.1. Impurities which do not have any appreciable effect on health

- **Turbidity**

Together with colour, this is the first quality the consumer notices. All water is turbid but if the turbidity is too noticeable, the consumer rejects the water. There are other reasons, also, why turbidity must be removed:

- to permit proper disinfection of water,
- to remove any pollutant adsorbed on suspended solids (heavy metals, etc.),
- to guard against sedimentation in the distribution system.

- **Colour**

Colour may be due to some mineral impurities (iron, etc.), but it may equally be due to some organic matter (humic and fulvic acids). It must be removed in order to make the water pleasant to drink.

The removal of colour goes hand in hand with the removal of some undesirable organic substances (precursors of haloforms, etc.).

- **Mineralization**

Alkalinity and hardness contribute to the carbonate balance of water together with the pH and the dissolved carbonic acid (see page 262). An attempt is made to attain such a balance in water in order to avoid scale formation in, or corrosion of, the system. If the amount of sulphates in water is too high, it affects the taste and gives it the quality of a laxative. If the amount of chlorides is too high, it also affects the taste and the water becomes corrosive.

- **Certain metals**

Iron and manganese can colour the water and initiate sedimentation in the system. This can result in corrosion. In addition, they affect the organoleptic quality of water as do other metals: copper, aluminium, zinc.

- **Dissolved gases**

H_2S indicates an anaerobic condition and an oxidation-reduction potential that is too low; it causes a bad smell and may initiate corrosion. It must be removed.

- **Ammonium NH_4^+**

This has no appreciable effect on the health of the consumer but its presence in water indicates pollution. In deep-lying water, NH_4 may be equally due to reducing conditions in an aquifer. Ammonium must be removed from water for consumption as it is a nutritive element that may allow some bacteria to grow in distribution systems.

2.5.2. Impurities affecting health

2.5.2.1. Study methods

It is difficult to study the effect of a given product directly on man. We can guard against accidents from acute toxicity by certain products which lead to death (poisoning). In the same measure, we can carry out epidemiological studies which correlate the ingestion of certain products with death, cancer risk or a given illness.

However, given the number of factors that can enter into the environment of each person along with the mobility of populations in the modern world, epidemiological studies are long, costly and the results are questionable. It is therefore preferable to employ experimental methods. To gain a better understanding of the effects of various pollutants on the health of consumers, studies and experiments are not performed directly on man but rather on those animals whose reactions are known to be similar to man's. The results obtained are then extrapolated to conform to man by means of models which best reproduce the transfer from animal to man.

The effects observed on different animals can be described in various ways:

- **acute toxicity:** the product quickly leads to death of the animal. The LD 50 value indicates the lethal dose leading to death in 50% of individuals in a given time (24 hours, for example),

- **chronic toxicity:** this is a dose, which when ingested on a daily basis, leads to premature death of individuals. ADI (Acceptable Daily Intake) indicates a maximum dose ingested daily over a lifetime that the metabolism of an individual is able to withstand without risk,

- **cytotoxicity:** toxicity may be studied by using cell cultures in the place of living organisms: the product under study leads to the death of a certain percentage of cells: this defines, then, cytotoxicity,

- **mutagenicity:** ingesting a product causes mutations in individuals. The risk of mutagenicity exists regardless of the dose ingested. The risk is low if the ingested dose is low and the risk increases if the ingested dose is increased,

- **carcinogenic effect:** exposing an individual to the product under study or having him ingest it causes a malignant tumor to appear. As for mutagenicity, the carcinogenic effect exists whatever the dose ingested.

2.5.2.2. Chief impurities

- **Metals**

In particular, cadmium, chromium, lead, mercury, selenium and arsenic must be removed from water. Generally, they are adsorbed on suspended solids in raw water and the removal of these suspended solids is therefore sufficient to ensure their removal. In some cases, the metals may be complexes either of natural organic substances (mercury, for example), or of chemical compounds discharged by industry or homes. The treatment must be able to destroy these complexes to ensure their removal.

- **Nitrates**

There has been a general increase in the concentration of nitrates in raw water and these must be removed because they are known to have a harmful effect when present in high concentrations in drinking water. They cause methaemoglobinaemia in infants.

- **Asbestos fibres**

Although asbestos has been recognized as carcinogenic when inhaled from the air, the carcinogenic effect of asbestos fibres in drinking water has not been clearly demonstrated. It is, however, desirable to remove them as completely as possible. Asbestos fibres can be carried in steam (boiling water, showers, etc.). By reducing turbidity, a reasonable amount of asbestos fibres can be removed.

- **Hardness**

It has no tangible effect on health. However, softening water by ion exchange in the sodium cycle leads to a higher content of sodium in the water; a high sodium content seems to promote hypertension.

- **Fluorine**

Too much fluorine leads to the fluorosis of bones. In such a case, the fluorine concentration must be reduced.

2.6.
ORGANIC IMPURITIES

Many natural organic substances are found in ground- and surface water. These are classified in six main groups: humic substances, hydrophilic acids, carboxylic acids, peptides and amino acids, carbohydrates and hydrocarbons.

Figure 13 shows the composition of fractions of organic carbon found in natural water, classified according to their molecular weight (MW).

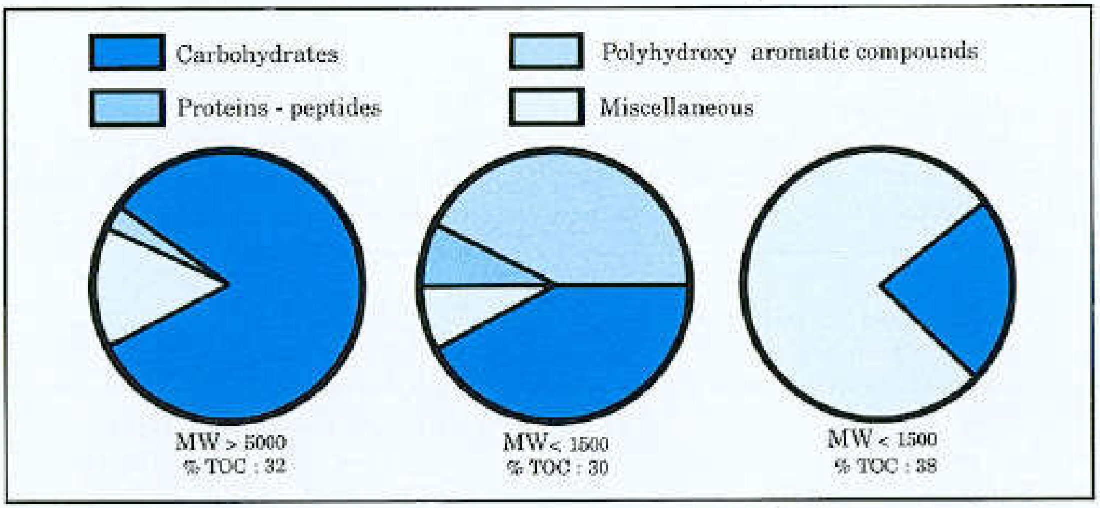


Figure 13. Distribution of fractions of organic carbon in water from the Seine River (From Bruchet – 1985).

Organic substances resulting from urban activities are also found.

Organic substances are defined analytically by measuring them against overall indices, reagent groups, or well-defined substances.

2.6.1. Overall parameters

These are measurements which do not show the concentration of a well-defined organic substance, but rather indicate a characteristic common to several substances.

Permanganate Value and Total Organic Carbon (TOC) indicate the concentration of organic substances that may be natural (fulvic acid, humic acid) or that come from municipal or industrial effluents. The concentration of these parameters should be reduced as much as possible in treated water to avoid the growth of microorganisms in the distribution system.

Absorbance measured in ultraviolet rays at 254 nm indicates the concentration of double bonds (aliphatic, carboxylic, benzenoid).

The **TOCL (or TOX)** indicates the concentration of chlorinated (or halogenated) organic substances. It increases following chlorination of water and should be as low as possible by the time it reaches the consumer's faucet.

- **The usefulness of overall parameters** It is impossible to relate an overall parameter to a measurement of toxicity and/or cytotoxiciry or carcinogenic and/or mutagenic effect; and thus it is impossible to determine concentration limits based on some effect or other on the health of the consumer. However, being aware of the overall parameters during the whole treatment procedure allows us to make optimum use of a treatment plant and compare procedures.

2.6.2. Pesticides and plant growth regulators

These products are used in agriculture to combat organisms that attack vegetables. Some become hydrolysed rather quickly but others are especially resistant and accumulate in the food chain. Some of these products are toxic while others are mutagenous or carcinogenic. The WHO issued (1985) the ADI for some products.

Simazin and atrazine are now seen more and more frequently.

These dangerous products must be removed as completely as possible to protect the health of the consumer.

Compound or group of isomers	**Recommendations** µg.l^{-1}	**ADI** mg per kg of the person
DDT (all isomers)	1	0.005
Aldrin and dialdrin	0.03	0.0001
Chlordan (all isomers)	0.3	0.001
Heptachlor and hexachloro-epoxy	0.1	0.0005
Gamma HCH (hexachlorohexane-lindane)	3	0.01
Methoxychlor	30	0.1
2,4-dichlorophenoxyacetic acid	100	0.3

2.6 3. Haloforms

(cf. para 2.8)

2.6 4. Chlorinated solvents

These substances have contaminated many deep-lying waters, through industrial discharges, dumping into disused wells and leachates. These substances are carcinogenic or mutagenic and it is important to remove them. Notable are: carbon tetrachloride, 1,2-dichloroethane, 1,1-dichloroethene and 1,1,1-trichloroethane.

2.6 5. Phenols and derivatives

Phenols and their derivatives are the mark of industrial pollution. Their worst effect is that, in the presence of chlorine, very small quantities of these products leave a taste of chlorophenol. Normally there is no taste if the pure phenol content is kept down to 1 µg.l^{-1} but there is sometimes a slight taste of chlorophenol with a content of 0.1 to 0.01 µg^{-1}

When chlorophenols are first detected organoleptically, they are still far below the threshold where they pose a danger to the health of the consumer; these substances must be removed until they can no longer be tasted.

2.6 6. Hydrocarbons

The hydrocarbons likely to pollute surface or groundwater supplies come mainly from oil refinery wastes, industrial effluents of various kinds, gasworks effluents, fumes, etc. Aromatic hydrocarbons are especially soluble.

Such wastes may contain petroleum, kerosene, petrol, fuel oil, other oils or lubricants.

Biodegradability is slow. Accidental pollution is short-lived at the intake of a river purification plant but can last a long time in the case of groundwater (up to several years because of the soil's power of retention). This is why groundwater supplies have to be strictly protected against the risk of hydrocarbon contamination.

- **Harmful and toxic effects**

- formation of a film which interferes with the re-oxygenation and self-purification of surface water,
- interference with the operation of drinking water treatment plants; flocculation and settling are affected and the hydrocarbon is likely to remain in the filter material for a long time,
- the taste and smell threshold varies very widely according to the product involved (from 0.5 $\mu g.l^{-1}$ for petrol to 1 $mg.l^{-1}$ for oils and lubricants),
- toxicity: there is a danger of toxicity in drinking water at concentrations above those at which taste and smell appear. Skin troubles have been caused by fuel oil additives.

2.6.7. Polycyclic aromatic hydrocarbons (PAH)

Some of these substances are very carcinogenic and it is important to remove them completely before the water is distributed. Noteworthy are benzo(3,4)pyrene, benzo (11,12) fluoranthene, benzo (1,12) perylene, benzo (3,4) fluoranthene and indeno (1,2,3Cd) pyrene.

2.6.8. Polychlorobiphenyls (PCB)

These products have been developed over the past few years for various uses: plasticizers, solvents, lubricants, hydraulic heat transfer fluids. They are mainly used in the manufacture of transformers and capacitors. In France they are known by their brand name, Pyralene.

Through combustion or pyrolysis, they can give off products suspected to be very toxic: polychlorodibenzofurans ("furans") and polychlorodibenzodioxins ("dioxins°). These products are especially stable, and as such, are dispersed in the environment. They are assimilated by living organisms and may be carried in the food chain. Although it has not yet been formally demonstrated, their toxicity is strongly suspected.

2.6.9. Detergents

Detergents are synthetic surface-active compounds which enter the water with municipal and industrial effluents.

Commercial products contain active compounds in the form of surfactants and aids.

- **Surfactants:** their structure modifies the physical properties of surfaces by lowering surface tension and gives them cleaning power. There are various types:

- anionic surfactants: for a long time the most commonly used substances were "hard," slightly biodegradable, branchedchain products, such as the alkylbenzene sulphonates (ABS), which have been mainly responsible for the problems created by the presence of detergents in water. They have usually been replaced by at least 80% biodegradable, linear-chain detergents.

The concentration of anionic surfactants can be measured easily by methylene blue analysis; their biodegradability over a period can then be followed without difficulty,

- non-ionic surfactants (those now used have an alkylphenol or even polyethoxyl alcohol base). These are being used on an increasing scale, but problems have still to be solved as regards dosing,
- cationic surfactants, consisting of quaternary ammonium salts, are little used and are reserved for special uses linked with their biostatic properties.

- **Aids**

These include:

- aids proper such as polyphosphates, carbonates, silicates,
- chelating and complexing agents (polyphosphates),
- reinforcing agents to improve the action of the active constituents (amino oxides, carboxymethylcellulose, alkanolamides),
- additives: bleaching agents, perborates, optical bleaches, dyes, perfumes,
- mineral salt fillers to improve the appearance of products,
- enzymes which should be regarded as pre-adjuvants and help to hydrolyse certain types of fouling.

- **Concentrations found in water**

Before the introduction of biodegradable products, the concentration of anionic detergents in river water varied from 0.05 to 6 $mg.l^{-1}$. The figure has dropped since.

Concentrations of non-ionic detergents are difficult to express because of the many methods of analysis, their accuracy and limits of detection.

- **Harmful effects**

The harmful effects caused by the presence of detergents in water are:

- formation of foam, which hinders natural or artificial purification, concentrates impurities and is liable to spread bacteria and viruses; anionic detergent concentrations of 0.3 $mg.l^{-1}$ and over are sufficient to produce a stable foam,
- formation of a barrier film on the surface, which slows down the transfer and dissolution of oxygen in the water, even when there is no foam,
- a soapy taste, at concentrations well above the foam point,
- higher phosphate content due to the combination of polyphosphates with surfactants, leading to the eutrophication of lakes and the growth of plankton in rivers; in some countries, a large proportion of polyphosphates is replaced by NTA (nitrilotriacetic acid),
- a gradual increase in the boron content of surface and groundwater supplies, due to the large quantities of sodium perborate used in detergents.

Detergents do not kill bacteria, algae, fish and other forms of river life, so long as the concentration does not exceed 3 $mg.l^{-1}$.

Lastly, the enzymes recently added to detergents have no ill effects either on the receiving water or at purification plants.

The introduction of detergents which are at least 80% biodegradable has led to a very marked improvement, at least in the case of anionic detergents, which can be successfully checked.

Non-ionic detergents raise problems because they stimulate the formation of foam by anionic detergents and then stabilize it. The non-ionic products now used are resistant to biodegradation, particularly in cold weather.

2.7. RADIOACTIVITY

The ingestion of radioactive products can have a somatic effect on man, causing malignant tumors, or mutations that might appear in future generations.

The water produced must meet regulations in each country. Treatment of water includes precipitation by lime, ion exchange or reverse osmosis.

2.8. INDUCED POLLUTION

Introducing a reagent into water can lead to two types of pollution: impurities from the reagent itself, and products produced by a reaction of the reagent with organic matter in the water.

2.8.1. Impurities due to the reagent

In many countries, the use of a reagent must be approved by the health authorities. Regulations may determine, for each reagent, the maximum concentration of impurities allowed. A precise analysis of the products must be undertaken. In the event that the presence of impurities is established, it is important to make sure that the planned chain of treatment will remove them.

- **Inorganic coagulants**

Some coagulants are made from minerals in which the level of impurities is noteworthy: acid attack on bauxite, making aluminium sulphate; attack on metal structures, making ferric chloride. This attack also dissolves impurities (tungsten, manganese, arsenic).

Other coagulants are made from byproducts coming from another industry. Chlorinated copperas made from ferrous sulphate which comes from the manufacture of titanium, may contain a substantial amount of manganese.

- **Polyelectrolytes, coagulant aids**

Synthetic polyelectrolytes are made by polymerization of monomers (polyacrylamides, polyamines, etc.). In drinking water treatment, each country's regulations may establish the type of monomer that may be used, the maximum monomer content in the polymer and the maximum treatment rate allowable (0.5% of acrylamide monomer in the case of polyacrylamides, for example).

- **pH correction**

The impurities in the lime and caustic soda must be analysed to make sure no mercury is present (caustic soda from a membrane procedure).

- **Disinfection using chlorine**

Since disinfection by chlorine is the last stage in the treatment process, it is important to verify the purity of the product before disinfection.

- **Stripping air**

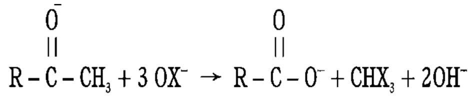
The air used in certain stages of the treatment may introduce undesirable elements: impurities in the atmosphere, exhaust gas, fumes, bacteria, etc.

2.8.2. Impurities due to a reaction between the reagent and organic matter in water

During the oxidation phases which occur all along the treatment line, oxidants (ozone, chlorine dioxide, chlorine) can react on organic matter present in the water. Chlorine, especially, reacts with certain of these (precursors) leading to the appearance of haloforms.

This reaction can occur directly by means of the chlorine in the water which is in the form of $C1O^-$, or by means of another halogen (bromine or iodine) which could have been replaced by chlorine (resulting in XO^-, which would then react with the organic matter to form organohalogen compounds).

The basic reaction to form the trihalomethane compounds is the following:



$$R-\overset{\overset{O}{\|}}{C}-CH_3+3\,OX^- \rightarrow R-\overset{\overset{O}{\|}}{C}-O^-+CHX_3+2OH^-$$

Carbonaceous organic substances capable of causing this reaction are, for the most part, methyl ketones, or, to put it more generally, all organic products which by means of oxidation can be oxidized into methyl ketones.

The chlorination of organic compounds also leads to the formation of other compounds, some of which, until today, remain unidentified (see figure 14).

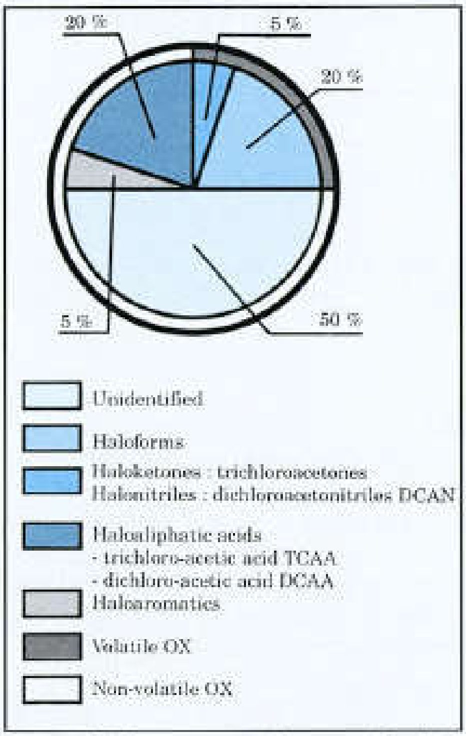


Figure 14. Halogen compounds present after chlorination of water.

- **Hazards**

All these products are suspected of being carcinogenic. It is important that the plant and its operation be such as to produce water that contains as few trihalomethanes and organochlorinated compounds as possible.

It must be remembered that the attempt to reduce the level of organochlorinated compounds must not compromise the thorough disinfection of water for distribution.

2.9.
POLLUTION FROM EXTERNAL SOURCES

Substances which make up several of the products used for water treatment can be a source of pollution. As an example of this, take the case of ion exchange resins or that of membranes. Certain regulations have established a list of products authorized for use in the manufacture of these resins (or membranes); tests have been worked out to ascertain that there is no release while the product is being used in the treatment line (removal of nitrates by ion exchange resins, for example).

Materials making up the supply system may also be a source of pollution: solvents used for the painting and coating of structures, monomers and additives used in plastic pipe and tube manufacture, metals used in valves and fittings or even lead used in the manufacture of pipes and tubes (which might cause lead poisoning), especially in home plumbing systems. Some of these materials may release organic carbon which may serve as food for common bacteria, thus aiding their proliferation in the supply system; they may also cause the water to taste bad.

3. INDUSTRIAL WATER

Figure 15. Cooling towers in a nuclear power station.

3.1.

THE USES OF WATER AND THE QUALITY REQUIRED

The quality of water required by industry is variable and corresponds to unequal valorization degrees. If the needs of small and medium size companies can often be met with drinking water or well water, the size and the situation of large factories may force them to turn to less expensive sources of water, possibly even including sea water.

Moreover, the growing need for water justifies water recirculation and the variety of functions that water serves often gives rise to the imposition of specific quality standards.

3.1.1. Basic functions of water in industry

Use	Chief applications
Steam	Boilers, air humidifiers.
Heat exchange	Condensation of steam, cooling of fluids and solids, heating, aqueous cutting fluids.
Gas scrubbing	Steel industry, incineration of household refuse, desulphurization of smoke.
Washing of solids	Coal, ore, agricultural products,
Transport of solids	Paper pulp, coal, pulp, agrifood industry, electrophoresis pigments,
Surface rinsing	Surface treatment, semiconductors, microelectronics, dye works, agrifood industry,
Transport of ions	Surface treatment baths.
Quenching	Coke, slag, granulation of cast iron.
Maintaining pressure	Secondary recovery of oil.
Kinetic energy.	Descaling steel, granulation (slag, scarfing).
Manufacture	Beer and carbonated drinks.

Water can be used (figure 16):

- for a single purpose:

- in **open system** or as direct make-up,

- in **recirculation,** with or without water deterioration;

- for two different successive purposes:

- **reuse.**

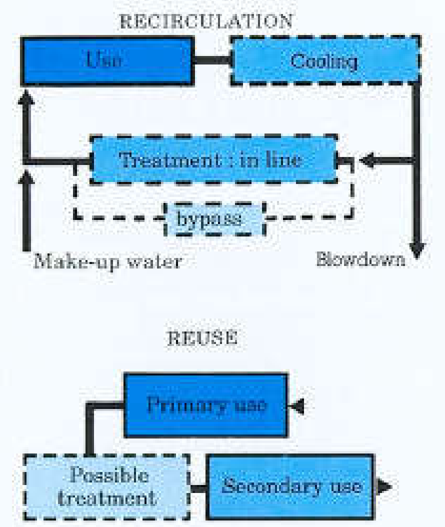


Figure 16. Recirculation and reuse of water.

3.1.2. Recirculation without water deterioration

Recirculation means the indefinite reuse of the same water for the same nonpolluting purpose. Make-up water replaces various losses in the form of liquid (leaks, drift loss) or steam in the case of evaporation, a frequent occurrence. Normally the water is not altered with the introduction of foreign ions, dissolved gases or the diffusion of organic or inorganic solids during the process. Only the initial salts condense and accumulate through evaporation.

Two typical examples of recirculation are the cooling by means of a cooling tower, called an "open recirculating system", and use in a boiler with the return of condensates (see pages 49 and 59).

The recirculation rate may be high and the increased concentration of various dissolved salts through evaporation requires preliminary purification of the less soluble salts in the make-up water and a blowdown of the water in the system.

Determining the concentration ratio C in recirculation is basic and rests on the ratio between the amount of water supplied, or make-up water A, and the amount of water lost as a liquid or through blowdown

$$C = \frac{A}{D}$$

Where E represents evaporation, as an initial approximation, the concentration ratio can be expressed as a ratio of the salt content in the circulating water S to that in the make-up water s:

$$C = \frac{S}{s} = \frac{A}{D} = \frac{E + D}{D}$$

The **recirculation rate** R is also used or the Q/A ratio of the circulating flow of water to the flow of make-up water.

In an open recirculating cooling system, C may vary between 1 and 6 or even 10. This ratio may be measured, in practice, by comparing the chloride concentration in such a system to that of the make-up water since no chlorides are being introduced. In a boiler, C is much higher (100, for example, in a PWR).

3.1.3. Recirculation with water deterioration

This means the reuse of water in a polluting operation where foreign compounds are introduced into the make-up water. This operation may be:

- **done in conjunction with a cooling process:**

gas scrubbing with the presence of HCl (incineration of household refuse),

- gas scrubbing with the presence of SO_2 (boiler fluegas),
- gas scrubbing with the presence of HF, HCN (gas from blast furnaces, etc.),
- descaling of steel and spraying of rolling mills with the entrainment of oils and scales,
- prilling of nitrogen fertilizer with solubilization of ammonia nitrogen,
- transport of slag and quenching of coke with solubilization of sulphur compounds.

- **done without a cooling process:**

- rinsing in the electroplating process with a more substantial addition of soluble salts,
- gas scrubbing in the phosphate industry,
- transport of raw materials with the introduction of suspended solids as well as salts (various washing plants, hydrometallurgy).

The salt concentration ratio is no longer due solely to evaporation and, in practice, often becomes difficult to measure if chlorides are introduced from outside. Moreover, because of moisture condensation, the input of make-up water (scrubbing of wet gas) can be difficult to assess.

The recirculation rate R is the single measure of the degree to which make-up water is utilized.

Depending on the amount of pollution introduced into a system, it may be blown down by a purification unit placed on the system or on a by-pass (see figure 16).

If the amount of pollution is considerable (such as in the case of gas scrubbing), the salinity and impurities in the make-up water become a secondary factor and as such do not require primary purification any longer. The problem to be resolved is far more closely related to that of recirculated industrial effluents (see sub-chapter 5).

If the amount of pollution is low (an extreme case is in ultrapure water) loops), the impurities in the make-up water justify a thorough treatment of the latter; the in-line treatment becomes quantitatively, but not qualitatively, less important.

3.1.4. The reuse of water

Recirculation may not be a sufficiently economical use of water in view of decreasing availability. The reuse of water is another means which consists in using water for two successive but different purposes, which may be separated by an intermediate lifting or treatment stage.

The second purpose is usually not as "noble" as the first, and therefore, an intermediate treatment may not be necessary. For example, the draining of an open recirculating system of gas from steel production using oxygen may be used to directly feed a gas scrubbing system from blast furnaces:

Table 3. Main industrial uses of water and possible water sources.

Use		**Sources of acceptable water** (often after adequate treatment)
Noble manufacturing water	- Beers, carbonated drinks - Agrifood industry - Pharmaceuticals - White paper - Textiles - Dye works - Chemicals	Water with average mineral content Drinking water or Well water or only slightly polluted surface water
Demineralised water	- Pharmaceuticals - MP and HP boilers - Preparation of various baths - Electroplating rinses - Ultrapure water - Desalination by reverse osmosis	Well water or only slightly polluted surface water
Cooling water in an open recirculating system	- Cooling towers	- Surface water with a low Cl- content - Wastewater after tertiary treatment
Cooling water in a once-through system	- Condensers and exchangers	- Surface water - Sea water - Effluents after treatment
Gas scrubbing or product wash water Transport water	- Scrubbing of metallurgical gas and incineration - Coal scrubbing	- Strained and settled surface water - Wastewater after secondary treatment

3.1.5. Choice of water sources

Independent of the economic aspect, the criteria determining the choice of water, whenever possible, are the following:

- compatibility of water with its uses: carbonate balance, hardness, temperature, and, as regards concentration, levels of SO_2, $Si0_2$, Ca^{2+}, Cl^-,
- compatibility of water with the types of treatment that are planned (membranes, ion exchangers).

Table 3 suggests the choice of an available water source depending on its use. Attention must be paid to those factors difficult to correct by means of a simple intermediate purification process (colour, OM, PAH, SO_4, etc.).

Sea water may be used without reducing its salinity in the following two applications:

- condenser cooling,
- secondary offshore recovery.

In most cases, desalination is necessary.

3.2. BOILER WATER

3.2.1. Boiler water circuit

For all types of boilers, the water circuit can be very simply summarized as follows (figure 17):

The boiler receives feedwater, which consists of varying proportions of recovered condensed water (known as "return water") and fresh water which has been purified in varying degrees and is known as "make-up water."

The steam, which escapes from the boiler, frequently contains liquid droplets (drift) and gases (in particular, carbon dioxide). At high pressures, it carries salts volatilized by genuine "steam carryover" such as silica, and at very high temperatures, chlorides.

The water remaining in liquid form at the bottom of the boiler picks up all the foreign matter from the water that was converted to steam (except the substances carried over in the steam). The impurities must be "blown down" by the discharge of some of the water from the boiler to the drains.

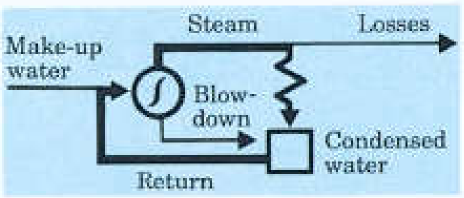


Figure 17. Boiler water circuit.

Assuming that the boiler operates at a continuous rating and, for simplicity, that the salinity carried over by the steam is negligible, the mineral content will be in stable equilibrium when the weight of salts discharged to the drains is equal to the weight of salts brought in by the make-up water (because the condensed water is considered to be pure). This gives the equilibrium state:

$$A \times s = D \times S$$

A: flow of make-up water, concentration, s
D: blowdown rate,
S: concentration in the boiler.

$$S = s \times \frac{A}{D}$$

If all the steam is lost and if the purification problem is stated not in production of make-up water but in tonnes of steam (T), it must be remembered that A = T + D and that the concentration factor will then be expressed by:

$$\frac{S}{s} = \frac{T + D}{D}$$

In practice, the permissible percentage of blowdown at a plant is strictly limited by running costs and initial outlay. The tendency is to reduce this percentage to an ever smaller figure.

3.2.2. Nuclear generators and forced circulation boilers

Certain generators used in nuclear power plants have no chamber, nor any provision for blowing down water, so that all impurities dissolved in the feedwater are found on the steam generating surfaces or in the steam. Therefore, the above method of calculation does not apply, and it is generally essential to limit the extraneous matter contained in the water to levels that can be tolerated in the steam.

The above also applies to all conventional boilers of the forced circulation type and to those boilers used in the chemical industry known as "recovery boilers" which have no chamber or provision for blowing down water.

3.2.3. Difficulties caused by impurities in the water

The principal difficulties caused by water in boiler or turbine operation are as follows:

- **Scaling,** due to the deposition of crystalline precipitates on the walls of the boiler. This interferes with heat transfer and may cause hot spots, leading to local overheating. The less heat they conduct, the more dangerous they are. The values corresponding to their thermal conductivity are as follows:

- steel	15	kcal/m^2.h per degree C
- $CaS0_4$	1-2	kcal/m^2.h per degree C
- $CaC0_3$	0.5-1	kcal/m^2.h per degree C
- SiO_2	0.2-0.5	kcal/m^2.h per degree C

Scaling is mainly due to the presence in the water of calcium salts (carbonates or sulphates), which are less soluble hot than cold, or to too high a concentration of silica in relation to the alkalinity of the water in the boiler. In boilers giving off a lot of steam there can be an oversaturation of salts in the superheated outer film or hide out with a lesser salinity in the blowdown.

- **Priming,** which is the carryover of varying amounts of droplets of water in the steam (foam and mist) which lowers the energy efficiency of the steam and leads to the deposit of salt crystals on the superheaters and in the turbines. Priming is related to the viscosity of the water and its tendency to foam. These properties are governed by alkalinity, the presence of certain organic substances and by total salinity or TDS (total dissolved solids). The degree of priming also depends on the design of the boiler and its steaming rate.

- **Carryover in the steam** of volatile minerals at boiling point, the most harmful of which is silica which is produced at above 250°C. These salts are deposited on turbine vanes and cause serious operating problems. Carryover increases with pressure and, therefore, with temperature. The quantity, of course, depends on the amount of harmful substances such as silica in the chamber.

- **Corrosion** of widely varying origin and nature due to the action of dissolved oxygen, to corrosion currents set up as a result of heterogeneities on metal surfaces, or to the iron being directly attacked by the water. Before turning to corrective measures, it is first necessary to consider the quantity of the various harmful substances which can be allowed in the boiler water without risk of damage to the boiler or turbine. Starting from these figures, and allowing for the amount which can be blown down, the permitted concentration in the make-up water is thus defined.

3.2.4. Standards for water for use in a conventional steam generating plant

Because of the growing tendency to increase the rate of heat transfer through the heated surfaces of modern boilers, only relatively wide ranges can be given as to maximum levels of alkalis, salts, silica, phosphates, etc., in relation to working pressure. The actual maximum levels must be obtained from the boiler manufacturer, who will base them on the characteristics of the boiler in question.

A point constantly debated is the maximum level of NaOH, which decreases as the steaming rate per m2 of tube increases, but which in low-and mediumpressure boilers can be raised if antipriming conditioning is applied.

The following are extracts of recommended levels from APAVE (Association of electrical and steam unit owners) (tables 4a, 46, 4c) up to pressures of 100 bar for medium steaming rates and for volumes of water in the chambers sufficient to properly control the blowdown rates.

Table 4a. Characteristics of water for firetube boilers (up to 25 bar)

Working pressure	= 10 bar	10-15 bar	15-25 bar
Conditioned feedwater (purified make-up water + return water) PH	= 8.5	= 8.5	= 8.5
TH (French deg.)	< 0.5	< 0.5	< 0.2
O_2	Physical removal of dissolved oxygen by thermal Deaeration and/or use of reducing reagents or corrosion inhibitors		
Oily substances		absence	
Boiler water M alk. (French deg.) P alk. (French deg.)	= 120 P alk ≃ - 0.7 M alk.	= 100 P alk. ≃ 0.7 M alk.	= 80 P alk. ≃ 0.7 M alk.
$Si0_2$ (mg.l^{-1}) $Si0_2$/M alk.*	< 200 = 2.5	< 200 = 2.5	< 150 = 2
TDS (mg.1^{-1}) Cl^-	= 5,000 = 1,000	= 4,000 = 800	= 3,000 = 600
Phosphates $P0_4^{3-}$ (mg.1^{-1})	30 to 100	30 to 100	30 to 100
p**H**	10.5to12	10.5to12	10.5to12

* This ratio must equal that of the feedwater.

Table 4b. Characteristics of water for watertube boilers. Natural circulation. Softened or softened, carbonate-free make-up water.

Working pressure	= 15 bar	15-25 bar	25-35 bar	35-45 bar
Conditioned feed-water (purified make-up water + return water) pH	= 8.5	= 8.5	= 8.5	= 8.5
TH (French deg.)	< 0.5	< 0.2	< 0.2	< 0.1
O_2	Physical removal of dissolved oxygen by thermal deaeration - and/or use of reducing reagents or corrosion inhibitors		Physical removal of dissolved oxygen by thermal deaeration and use of reducing reagents or corrosion inhibitors	
Oily substances	absence			
Boiler water M alk. (French) deg.) P alk. (French deg.)	= 100 P alk. $\simeq$ 0.7 M alk.	= 80 P alk. $\simeq$ 0.7 M alk.	= 60 P alk. $\simeq$ 0.7 M alk.	= 40 P alk. $\simeq$ 0.7 M alk.
$Si0_2$ ($mg.l^{-1}$) $Si0_2$/M alk.*	= 200 = 2.5	= 150 = 2	= 90 = 1.5	= 40 = 1
TDS ($mg.1^{-1}$) Cl^-	< 4,000 = 800	< 3,000 = 600	< 2,000 = 400	< 1,500 = 300
Phosphates $P0_4^{3-}$ ($mg.l^{-1}$)	30 to 100	30 to 100	20 to 80	20 to 80
pH	10.5 to 12	10.5 to 12	10.5 to 12	10.5 to 12

* This ratio must equal that of the feedwater.

Table 4c. Characteristics of water for watertube boilers. Natural circulation. Demineralized make-up water.

Working pressure	40-60 bar	60-75 bar	75-100 bar
Conditioned feedwater (demineralized + return water) PH	= 8.5	= 8.5	= 8.5
TH (French deg.)	< 0.05	< 0.05	< 0.05
O_2	Physical removal of dissolved oxygen by efficient thermal deaeration ($O_2 < 0.02$ mg.l^{-1}) and use of reducing reagents or corrosion inhibitors.		
Oily substances (mg-l^{-1})		< 0.05	
Total max. Fe (mg.l^{-1})	< 0.05	< 0.05	< 0.03
Total max. Cu (mg.l^{-1})	< 0.03	< 0.03	< 0.01
Boiler water M alk. (French deg.) P alk.	< 15 < 10 < 5 P alk. = 0.5 M alk. imperatively		
$Si0_2$ (Mg.l^{-1}) $Si0_2$/M alk.*	= 15 < 1	= 10 < 1	= 5 < 1
Free NaOH (mg.l^{-1})	< 20	< 10	< 5
pH	10 to 11	10 to 11	9.5 to 10.5
TDS (mg.l^{-1})	< 500	< 300	< 100
Phosphates $P0_4^{3-}$ (mg.l^{-1})	10 to 60	10 to 40	5 to 20

* This ratio must equal that of the feedwater.

Other recommendations for feedwater quality

Experience has shown that it is advisable to also limit other pollutants liable to enter the boiler:

Characteristics in mg.l^{-1}	Working pressure	
	< 40 bar	40 to 70 bar
Total iron	< 0.2	< 0.1
Copper	< 0.020	< 0.010
Organic matter (expressed as $KMn0_4$)	< 5	< 5
TOC	< 5-7	< 5-7
Oils and hydrocarbons	< 0.2	< 0.2
SS	< 1	< 1

Supervision of LP and MP boiler water

With the development of automatic control of boilers, a manual check of the following items may be cut back (once a day for LP and once per shift for MP):

	Purified water	Boiler feedwater	Boiler
PH	X	X	X
TH	X	X	
P alk. - M alk.	X	X	X
$Si0_2$	X	X	X
$P0_4$			X
N_2H_4/ $S0_3^{2-}$			X

3.2.5. High pressure or high heat flow boilers

For very heavy-duty boilers, dissolved salts must be reduced as much as possible and thus, phosphate conditioning must be eliminated.

Limits for TDS and alkalinity in the boiler cannot, therefore, be defined because the thorough silica removal from the make-up water simultaneously reduces the TDS to that of a trace product. Under these conditions, the alkalinity and TDS of the boiler water are determined essentially by the conditioning method.

The manufacturers of boilers must be consulted for they, themselves, may set very restrictive conditions concerning feedwater or boiler water.

Return condensates can introduce impurities into the feedwater, such as:

- dissolved salts (from condenser leaks or boiler priming);
- corrosion products from the introduction of oxygen.

Thus, condensate treatment is, at times, justified.

3.2.6. Plants with a pressurized water reactor (PWR)

3.2.6.1. Organization

These pressurized water reactor plants have two separate systems (see figure 18):

- a primary system that handles the extraction of heat from the core of the reactor; this system is called "active",
- a secondary system, where steam is produced, comprising the turbine, the condenser, the reheaters, the feed pump and possibly the treatment of condensates; except in the case of generator leaks, this system is not active.

In the primary system, water is maintained in a liquid state under a pressure of about 150 bar, at a temperature leaving the reactor in the neighborhood of 320°C (return temperature of 280°C).

The primary system is conditioned with two reagents:

- lithium hydroxide to maintain a basic pH and prevent corrosion;
- boric acid which acts as a moderator in the neutron flow and allows the power furnished by the reactor to be controlled.

E.D.F. (Electricité de France) system terminology

A.P.G.: Steam generator blowdown system.

G.V.: Steam generator.

P.T.R.: Reactor cavity and spent fuel pit cooling and treatment system.

R.C.V.: Chemical and volume control system.

T.E.P.: Boron recycle system.
T.E.U.: Liquid waste treatment system.

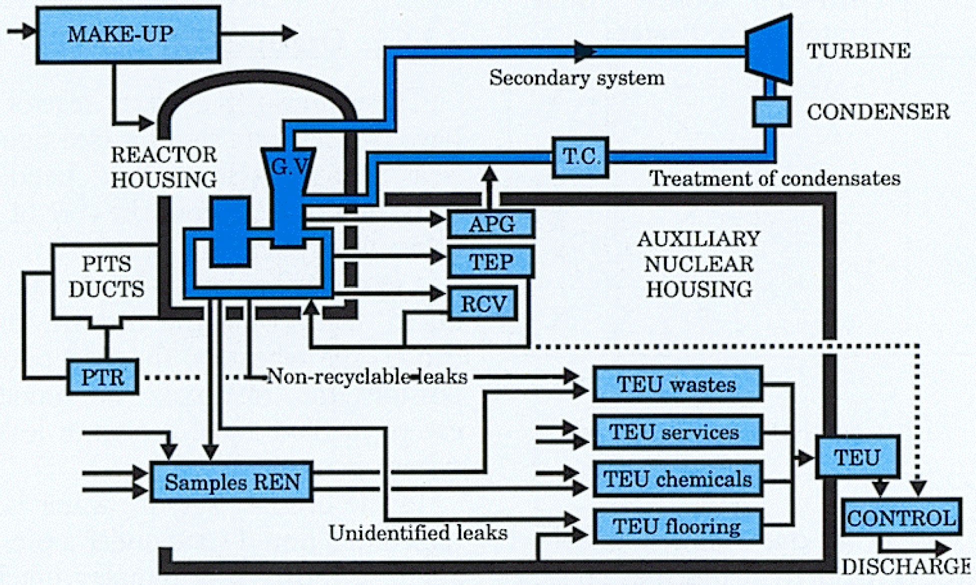
3.2.6.2. System control

Corrosion must be brought under control completely in the two systems as the water must satisfy strict standards. The principal parameters for EDF chemical standards are shown in tables 5a and 5b.

- **Primary system**

Table 5a. Make-up water in a primary system.

Parameter	Unit	Expected value	Limit value
Oxygen	mg.kg^{-1}		< 0.10
Chloride + Fluoride	mg.kg^{-1}		< 0.10
Sodium	mg.kg^{-1}		< 0.015
Total conductivity at 25°C	µS.cm^{-1}		< 1.0
		25	
Total or ionized silica	mg.kg^{-1}		< 0.1



PWR plant systems

Figure 18. PWR plant systems.

The circulation cycle takes about 1 minute. Various radioactive impurities coming from micro-leaks in the fuel ducts or resulting from the activation of corrosion products may accumulate in the pressurized water. For this reason, several purification systems are installed in parallel on the loop of the primary system.

Table 5b. Main primary system (normal operating power).

Parameter	**Unit**	**Expected value**	**Limit value**
Boron	mg.kg^{-1}	0 to 2,500	
Lithium	mg.kg^{-1}	decrease curve	
Oxygen	mg-4^{-1}	< 0.010	< 0.10
Chloride	mg.kg^{-1}	< 0.05	< 0.15
Fluoride	mg.kg^{-1}	< 0.05	< 0.15
Hydrogen	mg.kg^{-1}	25 to 35	25 to 50
Sodium	mg.kg^{-1}	< 0.1	< 0.2
Ionized silica	mg.kg^{-1}		< 0.2

- **Secondary system** Tables 6a, 6b and 6c all show the principal parameters of chemical standards as established by EDF.

Table 6a. Secondary system make-up water (conditioned, demineralized water).

Parameter	**Unit**	**Expected value**	**Limit value**
pH at 25°C			< 9.2
Sodium	µg.kg^{-1}	< 2	< 5
Cationic conductivity at 25°C	µS,cm^{-1}	< 1	
Total silica	µg.kg^{-1}	< 50	
Ionized silica	µg.kg^{-1}		< 20
SS	µg.kg^{-1}	< 50	

Table 6b. Steam generator feedwater (normal operating power P > 25% rated P).

Volatile conditioning		**Morpholine**		**Ammonia**		
Parameter	**Unit**	**Expected value**	**Limit value**	**Expected value**	**Limit value**	**Parameter**
pH at 25°C			9.1 to 9.3		9.0 to 9.2	presence of copper
			9.1 to 9.7		9.6 to 9.8	absence of copper
Total conductivity at 25°C	µS.cm^{-1}	3 to 5		2.7 to 4.2		presence of copper
		3 to 13		10 to 17		absence of copper
Oxygen	µg.kg^{-1}		< 5		< 5	

Table 6c. APG - Steam generator blowdown system (operating at **P** > 25% rated P).

Parameter	Unit	Expected value	Limit value	Observations	
Cationic conductivity at 25°C	µS.cm^{-1}	< 0.6	< 1.0		
Sodium	µg.kg^{-1}	< 5	< 20	sea water	condenser feedwater
			< 10	river water	
pH at 25°C		9.0 to 9.2	8.9 to 9.3	presence of copper	morpholine
		9.0 to 9.6	8.9 to 9.7	absence of copper	
		8.8 to 9.0	8.7 to 9.1	presence of copper	ammonia
		9.4 to 9.7	9.3 to 9.8	absence of copper	
Total conductivity 25°C at	µS.cm-1	2.5 to 5.0		presence of copper	morpholine
		2.5 to 14		absence of copper	
		1.8 to 2.6		presence of copper	ammonia
		6.7 to 12		absence of copper	
Ionized silica	mg.kg^{-1}	< 1			
SS	mg.kg^{-1}	< 1			

3.3. COOLING SYSTEMS

3.3.1. Types of cooling systems

Appliances that have to be cooled vary extensively:

- condensers and heat exchangers,
- oil, air, gas and liquid refrigeration systems,
- motors and compressors,
- blast furnaces, steel furnaces, rolling mills, continuous casters, converters, etc.,
- chemical reactors.

The operation of these appliances depends on:

- type of construction (shell-and-tube, plate, etc.),
- type of water circulation (internal, external, velocity, etc.),
- type of metals in contact with water (steel, stainless steel, copper and alloys, aluminium, etc.).

The materials used in the auxiliary equipment of the system (concrete, wood) that come in contact with water must also be considered.

There are three possible conditions (figure 19):

- the hot water is discharged into a river or drain; this is a once-through system,
- it is cooled by contact with a secondary fluid (air or water) and is returned to the appliance which has to be cooled without

coming into contact with the atmosphere; this is a **closed recirculating** system,

- it is cooled by partial evaporation in a cooling tower and then returned to the appliances; this is an **open recirculating system**.

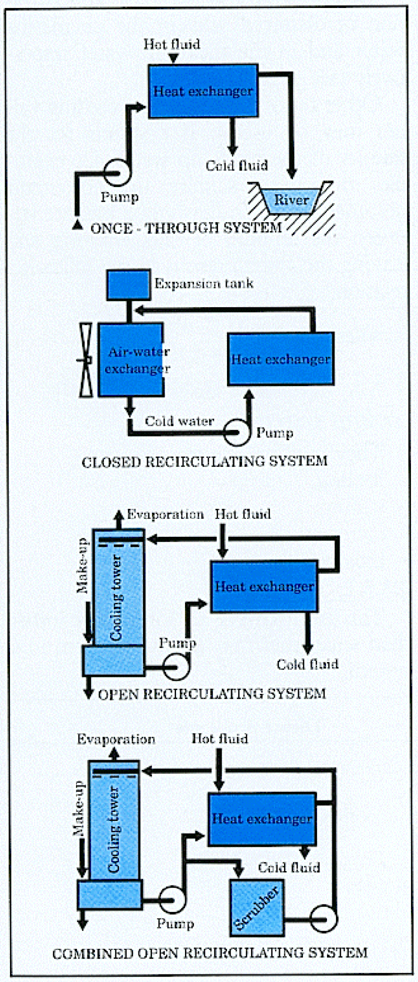


Figure 19. Different cooling systems.

In other combined open recirculating systems, the water can also come into direct contact with pollutants given off by various processes (for example, gas scrubbing), thus, this makes the conditioning of the water more difficult.

In closed recirculating systems, that is, without evaporation, very little make-up water is required and it may have to meet conductivity levels related to this process. Complete and virtually permanent protection can be obtained with corrosion inhibitors. Open recirculating systems are, however, the most commonly used type.

3.3.2. Open recirculating systems

The main operating parameters of the system are:

V(m^3): total volume of water in the system, i.e., in:

- the hot water tank,
- the cold water tank,
- the heat exchangers,
- the connecting pipes, etc.

Q(m3.h^{-1}): the *flow* of hot water delivered to the cooler.

?T(°C): difference in temperature between the water entering and leaving the cooler.

T max.(°C): temperature of the film of water ("skin" temperature) in contact with the hottest wall of the system.

W(kcal.h^{-1}): power of the cooling tower; this is the product of the two preceding figures, I.e.:

W = 1,000 Q. ?T

E(m^3.h^{-1}): evaporation *flow,* i.e., the quantity of water evaporated to cool the flow Q.

This evaporation flow consists of pure water which does not entrain any dissolved salts. Assuming a latent heat of evaporation of 560 th per m^3, the following equation results:

$$E = \frac{Q.\,\Delta T}{(560)}$$

Ev($m^3.h^{-1}$): Drift flow. This is the water carried over in the flow of air in the form of liquid droplets. Drift therefore consists of water with the same composition as the water circulating in the system. Manufacturers are progressively reducing the amount of drift loss. The figure is now about 0.05% Q with the possibility of being reduced to 0.01 %; in practice, the following equation can be used:

$$Ev = 0.1\ \%\ Q$$

D($m^3.h^{-1}$): total blowdown flow, calculated in order to maintain a maximum admissible concentration of dissolved salts. To prevent deposits from forming, some of the water in circulation (P) must be blown down in addition to the amount of water lost Ev, such that:

$$P+Ev=D$$

A($m^3.h^{-1}$): make-up flow.

This must make up all water lost from the system, chiefly by evaporation and total blowdown:

$$A = E + D$$

t(h): residence time t at the end of which the concentration of an injected reagent reduces by one half, because of the blowdown:

$$t = \frac{V}{D} L_n 2 \simeq 0{,}7\ \frac{V}{D}$$

C: concentration ratio.

This is the ratio between the concentration of dissolved salts in the circulating water and in the make-up water respectively (see page 47).

Other ratios between the preceding values may be useful. If s stands for the salinity of the make-up water, for example, this same salinity in the circuit becomes s x C. Establishing a balance between the amount of salts entering and leaving the system results in the following relation:

whence:

$$s \times A = D \times s \times C$$

$$D = E/(C-1)$$

3.3.3. Problems connected with cooling systems

They may be due to:
- fouling,
- scaling,
- corrosion,
- biological growths.

3.3.3.1. Fouling

This term covers all substances (other than scale) that may deposit or form in a system.

Types	Direct problems
• Suspended solids and colloids	Deposits, erosion, overconsumption of an inhibitor
- dust from the air	
- oxides, silts and clays ~	Blockage of orifices
- vegetable refuse _	
- algae and bacteria	Formation of mucilage
- mushrooms and yeasts }	Attack on wood
• Dissolved substances	
- organic matter *j*	Growth of algae and acidification
- nitrogen and phosphorus	
• Hydrocarbons (leaks)	Films

Fouling can come from a number of sources:

- make-up water,
- air from the atmosphere,
- manufacturing processes.

- **Make-up water**

It may contain:

- grainy materials which can be removed by suitable treatment to prevent their being deposited at points in the system where the flow is lowest,
- unstable colloidal matter: this may be transformed into an adhesive and adsorbent gel by a slight rise in temperature or by concentration, the colour of which varies according to the matter contained. Only in concentrated open recirculating systems is it usually possible to remove most of this matter.

- **Air from the atmosphere**

A cooling tower is an excellent air scrubber; all matter entrained by the cooling air is transferred to the circulating water:

- air-borne sand (desert regions, ore storage areas),
- NaCI-rich spindrift from coastal regions,
- dust from oxides and lime used in steel and cement manufacture,
- FIG and SO_2 downwind from incinerators or combustion machines,
- NH_3 and NH_4NO_3 from fertilizer factories.

Soluble gases or salts can permanently alter the chemical make-up of circulating water, often in ways that vary according to the direction of the wind. Therefore, these sources of pollution and their location should be known when planning the conditioning of a system if only to provide the necessary equipment for stricter control (pH, for example).

- **Manufacturing processes**

There are two different cases:

- simple open recirculating system: the pollution is usually accidental and comes from leakages of oil, fluids (solvents) and cooled gases (NH_3); their accumulation in the system is noxious and must be avoided (prevention, control, etc.),
- combined open recirculating system: the permanent pollution comes during the second usage of water (scrubbing or transport).

3.3.3.2. Scale formation

Scale formation is the precipitation of sparingly soluble salts of calcium and possibly, silica, on metal surfaces. The chief conditions that control scale formation are:

- temperature, a rise in which usually reduces the solubility of these salts,
- ion concentrations,
- mixing.

- **Calcium salts**

The main sparingly soluble salts encountered are:

- carbonates, the principal cause of scale formation (see page 273) which can be redissolved by chemical means,
- sulphates, which reach maximal solubility at 40°C and can precipitate in the cold to form gypsum $CaSO_4.2H_2O$ or in heated conditions to form anhydrate or hemihydrate (see page 497). In an open recirculating system the concentrations of mineralized water and sea water must be limited particularly when there is high heat transfer.

Once formed, calcium sulphate redissolves only very slowly in circulating water.

- orthophosphates $Ca_3(PO_4)_2$ in which scale, powdery and non-adherent in its pure state, can crystallize with calcium carbonate to form a hard scale.

(crust)

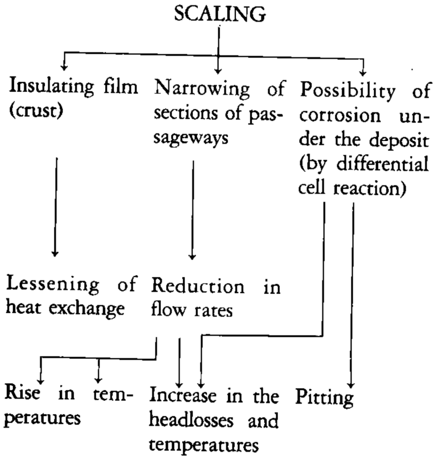
. **Silica**

It must be remembered that silica is found in various forms in water:

- ionized Si02,
- colloidal Si02,
- calcium or magnesium aluminosilicates (clay).

The solubility of silica depends on the pH and on the temperature (see page 497). Silicated scale is hard, very adherent and insulating.

- **Damage caused by scaling**



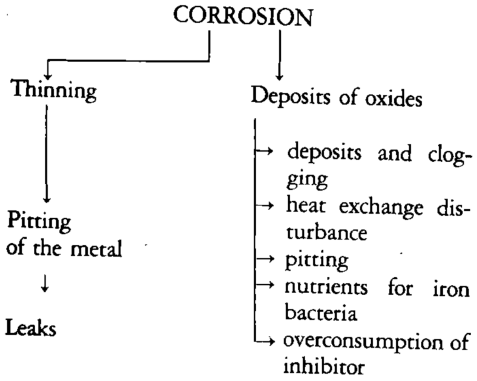
3.3.3.3. Corrosion

Corrosion is the alteration of various metals which carry water. The processes are described in Chapter 7. Thinning by means of so-called acid, uniform corrosion, is rarely seen. More frequently seen are formations of deposits or 'surface penetration' (heterogeneous corrosion or that caused by differential cell mechanism) which may lead to pitting.

Due to various anodic and cathodic reactions, these deposits may contain a substantial amount of $CaC0_3$.

Deposits due to bacterial growth are called tubercles and lead to both rapid narrowing of passageways and pitting.

- **Damage caused by corrosion**



3.3.3.4. Biological growth

A cooling system is an ideal medium for the growth of living organisms. It provides air, heat and light. Either care must be taken not to supply any nutrients that are rapidly assimilated or organic compounds that are easily biodegradable, or a bacteriostatic treatment must be envisaged.

Over and above the problem of obstruction, the progressive formation of an insulating film caused by fouling reduces the exchange coefficients and raises the head losses. In the long term this leads to the proliferation of corrosion under the deposits which can produce leaks.

3.3.4. Amount of water involved

3.3.4.1. Cooling electric power station condensers

(a) Circulation flow

- Conventional thermal power stations running at maximum level (600 MW):

- full speed circulation

(?T = 8.7°C): 20-21 $m^3.s^{-1}$

- low speed circulation

(?T = 12°C): 14-15 $m^3.S^{-1}$

- Nuclear power plants running at maximum level (1,200 MW):

(?T = 12°C): 47-48 m3.s'

(b) Supply in open recirculating systems

With a concentration ratio of 3 to 4 and depending on the relative humidity of the air:

- thermal power plant: 1.2 to 2 m3.h^{-1} per MW,

- nuclear power plant: 2.2 to 3 m3.h^{-1} per MW.

3.3.4.2. Various cooling operations in industry

The orders of magnitude of the volumes in circulation can be listed for several processes (other than gas scrubbing):

fertilizer factories	
NH_3	250 to 350 m^3 per t
Urea	65 to 100 m^3 per t
NH_4N0_3	80 to 100 m^3 per t
methanol (from petroleum products)	
	100 to 250 m^3 per t
coking plants	30 to 40 m^3 per t of coke
blast furnaces	20 to 30 m^3 per t of cast iron
converters	2-3 to 10 m^3 per t of steel, according to the production, or not, of steam
continuous casting	10 to 25 m^3 per t of steel
hot strip mills	30 to 50 m^3 per t of steel
wire mills	5 to 10 m^3 per t of steel

As long as the temperature does not drop excessively, cooling by an air-cooled heat exchanger can be used instead of atmospheric cooling, thus reducing the amount of make-up water.

3.4.

WATER FOR MANUFACTURING PROCESSES

The need for boiler water and cooling water is common for most industries and it has been seen that this need can be determined quite accurately by professional studies. In the case of water for manufacturing purposes, the need has been determined for only a few industries.

3.4.1. Water for breweries and carbonated drink plants

3.4.1.1. Breweries

- **Uses**

- the brewing of beer,

- washing of vats, equipment and brewing floors,

- cooling, -possible washing of bottles.

- **Quality of make-up water**

The professional standards for the

Make-up water are closely tied to the quality of beer produced. Thus, in brewing beer, it is important to prevent the precipitation of bicarbonates when malt, which is rich in calcium phosphate, is added.

To start with, the following rules should be kept in mind:

- systematically remove bicarbonates,
- keep the Mg concentration as low as: possible (< 10 mg.l^{-1}),
- maintain an SO_4/Cl ratio higher than 1 (mellowness of beer),
- maintain an Na concentration lower than 100 mg.l^{-1} to minimize bitterness,
- keep NO_3 < 50 mg.l^{-1} and NO_2 < 1 mg.l^{-1} (limits of toxicity during fermentation and of potability).

Examples of mineral analyses of beer may be noted:

Concentration Mg.l^{-1}	**Pale Ale Burton**	**Lager**		**Stout**
		Light	Strong	Munich
		Pilsen	Dortmund	
Na + K	15-30	0	20	10
Mg	80	1	24	20
Ca	370	7	260	70
Cl	34	3	107	2
SO_4	895	3	290	18
Dry residue	1,800	51	1,100	270

- **Amounts required**

5 to 6 hl per hl of beer, which can be reduced to 4 to 5 by recirculation:

- brewing of beer: 1.5,
- various washings: 3 to 4,
- cooling: 1 to 2.

3.4.1.2. Carbonated drinks

Water used to manufacture drinks must systematically conform to the standards for drinking water.

Although manufacturers often determine their own water treatment processes themselves, especially the holding time, there has been a tendency recently to look for specific qualities in water. Among these is an alkalinity below 5 French degrees and a TDS content below 500 mg.l^{-1}. For water used for washing, on the other hand, an excess in residual chlorine of several mg.l^{-1} is in order.

Requirements are 3 l of water for 1 l of drink.

3.4.2. Dairy industries

Water is used for:

- disinfecting the equipment and tanks,
- cleaning the ground,
- washing the products,
- reconstituting milk,
- cooling.

The various uses of water correspond to 4.5 to 8 l per litre of milk.

3.4.3. Sugar mills and refineries

3.4.3.1. Beet sugar mills

The treatment of industrial water is involved in the purification of make-up water and of the juice itself.

- **washing of beets:** polluted water is recirculated through scraper type settling tanks to recover the water,
- **diffusion of cossettes** (preparation of raw juice): treatment of condensed ammonia liquor recirculated to the head of the diffusion battery,
- **treatment of thin juice:**

- purification of second carbonation juice (protecting evaporation units against scale),

- demineralization of the juice (to reduce the level of molasses),

- decolourizing of syrups through activated carbon or adsorbent resins.

- **.evaporation of juice, crystallization of sugar:** conditioning of juice in evaporators,
- **treatment of by-products** (mother liquor or molasses) in order to reduce the level of molasses:

- treatment of mother liquors through cationic resin regenerated with magnesium chloride (Quentin process). Replacing the Na and K ions by Mg ions reduces sugar remaining in the molasses;

- deionization of mother liquor or molasses by ion exchange, with possible complementary treatment to obtain liquid sugar.

- **Make-up water:**

- boiler make-up at the beginning of the campaign or where condensate return is insufficient,

- permanent make-up to the cooling system of the turboalternators and when the 65 beets are received (5 to 101 per tonne of beets).

The sugar mill has an extra cycle: water is brought in with the beet and blown down with the waste wash water or sludge (figure 20).

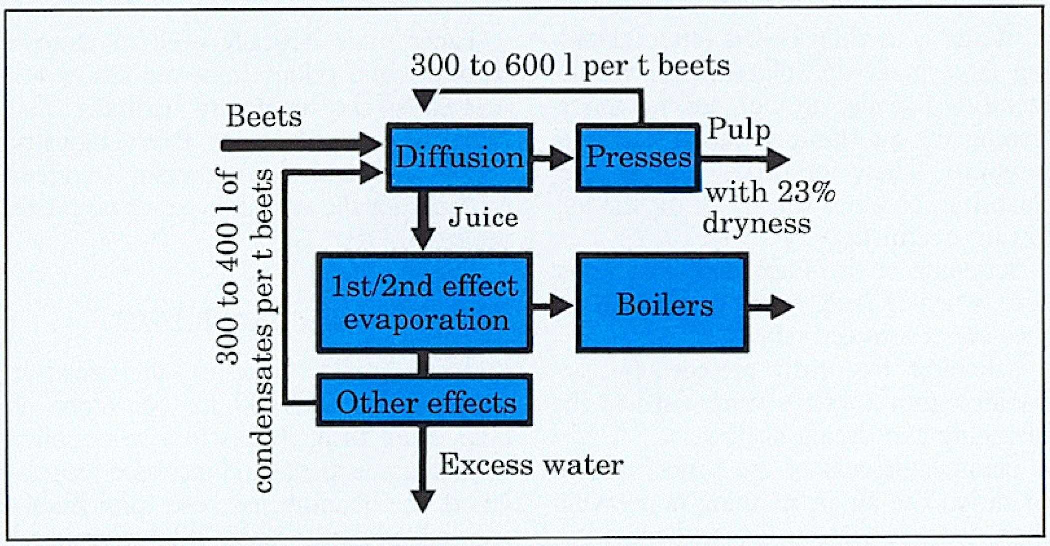


Figure 20. Water cycle in beet sugar mills.

3.4.3.2. Cane sugar mills

in the purification of raw juice, clarification methods similar to those used for water are required:

- accelerated clarification of the lime defecated juice
- flotation of the purified juice in order to separate the bagasse
- disinfection of the circuits (essential).

3.4.3.3. Sugar refineries (beet or cane)

Remelts and liquid sugars must undergo more or less thorough decolourizing treatments.

3.4.4. Vegetable and fruit canneries

Partial softening of process water is generally essential (for fruit, hardness of 10 to 20 French degrees). A reduction in TDS may also be helpful.

3.4.5. The textile industry

Water is used for boilers (often involving large make-up volumes), for manufacturing (dyeing, rinsing), and for conditioning the air (humidification and dust removal). These industries require large quantities of water which call for the following treatments:

- softening or demineralization of water used when making yarn, particularly in the case of artificial fabrics,
- softening, frequently preceded by carbonate removal, of the water used in the bleaching and dyeing of fibers,
- demineralization of the water used to condition the air in spinning or weaving shops (reverse osmosis, ion exchange).

The quantity of water needed, for manufacturing processes alone, may represent 80% of the total required and be divided as follows:

	m^3 per t finished product
degreasing of wool	20 to 40
Finishing and dyeing of wool	70 to200
finishing of cotton and synthetic fabrics	100
dyeing and printing of knits	70

3.4.6. Pulp and paper industries

These industries (see page 98) use large quantities of water for the following:

- steam production,
- pulp preparation,
- making of paper and transport of fibres

3.4.6.1. Water quality

Paper mills basically need to remove turbidity and colour from the raw water as well as the temporary hardness. The National Council of the Paper Industry (USA) has laid down certain standard qualities for the various types of pulp (see table 7).

3.4.6.2. Use of make-up water

Around 1975, make-up water stood at between 100 and 300 m^3 per tonne of pulp. Since then, thanks to a strict policy controlling discharge and increased recirculation, the quantity has been considerably reduced, while the water volume required by each product has remained high:

Table 7 - NCPI standards for water in the paper industry.

Characteristics	Maximum concentration in process water			
	fine quality paper	kraft paper bleached	kraft paper unbleached	mechanical pulp paper
Turbidity ($Mg.l^{-1}$ SiO_2)	10	40	100	50
Colour ($mg.1^{-1}$ platinum/cobalt)	5	25	100	30
TH (French deg.)	10	10	20	20
CaH (French deg.)	5	-	-	-
M alk. (French deg.)	7.5	7.5	15	15
Fe ($mg.l^{-1}$)	0.1	0.2	1.0	0.3
Mn ($mg.l^{-1}$)	0.05	0.1	0.5	0.1
Chlorine residual ($mg.l^{-1}$)	2.0	-	-	-
Soluble silica ($mg.l^{-1}$)	20	50	100	50
Dissolved matter ($mg.1^{-1}$)	200	300	500	500
Free $C0_2$ ($mg.1^{-1}$)	10	10	10	10
Chlorides ($mg.l^{-1}$)	-	-	-	75

Pulp and paper mills	m^3 per t
Pulp production	
- unbleached kraft	25 to 60
- bleached kraft	40 to 80
- bleached sulphite	80 to 150
- semichemical	12 to 20
- CTMP	12 to 25
Deinking	50 to 80
Paper production	
- kraft paper	20 to 40
- newsprint	40 to 60
- fine quality	40 to 100
- cardboard/packaging	3 to 40

3.4.7. Secondary oil recovery

The following requirements must be met:

- non-clogging of the reservoir rock,
- non-corrosion of the tubing,
- no bacterial proliferation,
- chemical compatibility with the water in the reservoir.

Depending upon the permeability of the reservoir, the temperature and the amount of SS in the water, the following treatment criteria are often desirable:

S.S	94 to 97% removal of particles with dia. > 2 μm or final levels of 0.5 to 1 $mg.l^{-1}$
O_2 content:	- cold water: 80 $\mu g.l^{-1}$ to 10 $\mu g.l^{-1}$
	- lukewarm water (30°C): < 10 9$\mu .l^{-1}$

3.4.8. Steel industry

Using vast quantities of water, this industry has for many years installed open recirculating systems adapted to specific working conditions (see page 63).

There are two important ways in which water is used in this industry:

- indirect cooling by exchangers which are extremely varied and often subjected to water heated to high temperatures, sometimes necessitating closed systems.

Make-up water may undergo carbonate removal or demineralization, depending on the case,

- direct cooling, whether it be from the scrubbing of gases or from the granulation of products or descaling, during which the water becomes dirty and must be constantly treated in the system. The quality of make-up water is, therefore, much less important.

- **Coking plant**

- Indirect primary condensation of gases or direct final condensation.
- Wet dust removal system for gases in the charging of preheated coal.
- Wet dust removal system for smoke in the discharging of coke.

- **Blast furnaces**

- Cooling of blast furnace components such as the tuyeres, tymps and wind boxes.
- Quenching of slag, in gutters, in pots, in spools or filter beds with circulating water in the order of 10 to 4 m^3 per tonne.
- Scrubbing of blast furnace gases.

- **Direct reduction**

This new process uses large quantities of water:

- In scrubbing and cooling gases released by the reduction process or in cooling iron sponge The volumes of water used (12 to 30 m per tonne of sponge) are higher than in blast furnaces and, because of the high temperature of the gases, the water is very hot when it leaves the scrubbers (50 to 70°C).
- In the cooling of machinery (compressors and oil coolers) and the cooling of gases. A considerable amount of demineralized water is required to produce steam in the reforming of the reducing gas.

- **Converters**

The predominant use of LD, LWS, LD-AC or BOS processes requires large-scale water systems:

- cooling of the hood and the lance (sometimes by spraying),
- scrubbing of gases: heat is recovered by partial combustion and vaporization of gases in the L.P. boiler making it necessary to add demineralized water.

- **Electric furnaces and ladle metallurgy**

High quality steel is produced in electric arc furnaces (UHP, i.e., ultra high power and other methods) or in ladles (STEP), heated by induction or by arc; it can be completed by vacuum degassing of the steel. Water is used in three ways:

- normal cooling of furnaces and ladles,
- production of steam for the vacuum injectors,
- cooling of the ingot mould and electrodes with demineralized water.

- **Continuous casting of blooms and billets**

There are normally three types of systems:

- for cooling the ingot mould in a closed recirculating system with demineralized water make-up,
- for cooling the machine in an open recirculating system with careful inhibitor conditioning,
- for spraying the machine and the bloom or billets (the wastewater contains scale and flame cutting slag).

- **Hot rolling mills**

Two types of systems must be fed:

- for the indirect cooling of furnaces, compressors, motors, etc.,
- for the direct cooling which is threefold: cooling of the metal, cooling of the rolling mill housings and descaling of steel.

Descaling systems are designed for the prior removal of various oxides (wurtzite, haematite) by washing with water. The water collects fine flakes or scale, in varying quantity and fineness according to the kind of mill and the hardness of the steel.

Rolling mills are of widely varying types:

<u>(a) Strip mills</u>

The chief ones treat between 200 and 500 $t.h^{-1}$ of steel as blooms.

Circulation flows involved:

- direct cooling: 10 to 20,000 $m^3.h^{-1}$,
- indirect cooling: 20 to 30,000 $m^3.h^{-1}$.

Separate cooling systems supply the motors, the oil tanks and the heating furnaces.

In addition to these processes, others used include:

- automatic scarfing which produces large quantities of granular slag,
- cooling of the blooms in pools, in tunnels or by sprays, using large quantities of water without heavy pollution.

<u>(b) Other hot mills</u>

- plate or four-high mills,
- blooming/dabbing mills,
- section, rail and merchant mills,
- rod or wire mills,
- tube rolling mills.

- **Cold rolling mills**

The manufacture of thin rolled and galvanized steel products involves metal pretreatment processes such as degreasing and pickling. The latter process uses sulphuric acid and, with increasing frequency, hydrochloric acid, regenerated on site.

Demineralization plant either in a once-through or a closed recirculating system is needed for the supply of final rinsing water to galvanizing and tinning works. Water of a very pure and soft quality is also required for the preparation of soluble oil baths.

3.4.9. Copper production

The metal can be obtained by either dry or wet processes, according to the nature of the ores. Hydrometallurgical processes, which usually involve leaching with sulphuric acid and electrolysis, are used on an increasing scale, because they allow the treatment of low-grade ores and flotation residues.

Copper wire bar is rolled to make sections, cables and wires.

Roughing involves descaling the surface of the metal with water; valuable copper oxides are left in suspension in the water and these are usually worth recovering. The processes used in making descaling and cooling systems are similar to those used in steel manufacture.

3.4.10. Automobile and aeronautical industries

The automobile industry includes plants that build motors, engines and gear boxes, those that build bodies and do the assembling, and numerous workshops, often independent, that are subcontracted. The demand for make-up water varies greatly depending on the procedure. However, three general areas for its use may be noted:

- in cooling, particularly of compressors and air conditioners,
- in the preparation of various electroplating baths and paint baths that usually require demineralized water,
- as feedwater that is soft or low in minerals for machining and truing.

A description of the various workshops involved is given on page 110.

The needs of the aeronautical industry are much the same.

3.4.11. Manufacturing using ultra pure water

This refers to the manufacture of semi conductors. Make-up water for this use must be made ultrapure and further refined in the distribution loops.

Quality of the make-up water

The recent increases in the amount of memory from several k-bytes to 256 k-bytes, if not 1 M-bytes, have led to the need for even stricter standards for the quality of ultra pure water for rinsing components. Of particular importance is the physical and biological purity.

Worthy of note are the recommendations of ASPEC 86/17 (Association for the control and study of contamination), shown on table 8.

A plastic loop, usually with a storage reservoir, ensures a supply of water while maintaining a relatively constant circulation rate.

3.4.12. Manufacture of chlorine

This is based on the electrolysis of NaCI-saturated brine, the quality of which depends on the procedures used (diaphragm and mercury cells). The purification of brine takes place either in the make-up water system or in a closed recirculating system. The first elements to be removed are Ca^{2+}, Mg^{2+}, Fe^{2+}, possibly followed by $S0_4^{2-}$, and, when recirculation takes place, Hg^{2+}.

In using diaphragm cells, $Ca^{2+} + Mg^{2+} < 5$ $mg.l^{-1}$ should be maintained. For the development of membrane cells and an increase in current density to 7000 Am^{-2}, calcium and organic matter must be completely removed. An extra polishing following purification may have to satisfy the following requirements:

- $Ca^{2+} < 50 \mu g.l^{-1}$
- $SS < 1 \mu g.l^{-1}$

and possibly: - $Sr^{2+} < 50 \mu g.1^{-1}$

The stripping out of excess chlorine and the reduction of possible iodates pres-

Table 8. Ultrapure water for the electronics industry
(Integrated circuits and sensitive surfaces).

		Level of Procedure 1	Level of Procedure 2	Level of Procedure 3
Resistivity		greater than 18 MO.cm at 25°C		
pH		6.5 to 7.5		
Temperature		20°C ± 1°C		
Evaporation residue (max., mg.l^{-1})		1	0.5	0.25
Silicon (Si) (max., mg.l^{-1})		0.02	0.02	0.01
Sodium (Na) (max., mg.l^{-1})		0.01	0.01	0.005
Metallic and metalloidal impurities, each impurit, (max., mg.l^{-1})		0.05	0.05	0.01
Organic matters (TOC) (max., mg.l^{-1})		1	0.25	0.05
Particulate contamination, max.	membrane	class 0 (NAS 1638)	_	-
	optical counter	10,000 per 1 dia. = 0.5 µm	1,000 per 1 dia. = 0.5 µm	100 par 1 dia. = 0.5 µm
Microorganisms(number of colonies per100 ml)	370C/24 h	40	10	1
	220C/72 h	300	30	3

ent may also be necessary in the system after the electrolysers.

3.4.13. Hydrometallurgy

This industry focuses on the extraction of uranium, gold and aluminium by means of the following basic procedures:

- extraction of the metal using acids or alkalis (leaching),
- solids/liquid separation: filtration or settling,
- concentration of metals: solvent extraction or ion exchange,
- various precipitations.

These procedures have the advantage of being done cold and of overcoming corrosion. The processes used are often similar to those used in the treatment of water and may thus benefit from the knowledge gained in that field. The most important parameters, in particular for the clarification of liquors, are:

- **Suspended solids:** after settling, the liquors still frequently contain 100 to 200 mg. l^1 of SS, sometimes several g.l^{-1}. This residual matter is just as trouble some in the direct extraction of the metal as in purification by organic solvent or resins. Many users want to reduce it to less than 10 to 20 mg.l^{-1}.

- **Colloidal silica:** silica is present in water in an ionized form (silicic acid or fluosilicic acid) in concentrations that may be as high as 200 to 500 mg.l^{-1}, or in a gel form as sparingly ionized polysilicic acid. This colloidal dispersion is electropositive and thus does not coagulate but is relatively adsorbable. Silica may precipitate on resins or with solvents.

- **Calcium sulphate:** limestone and dolomite ores treated with sulphuric acid give rise to liquors supersaturated with $CaS0_4$, causing formation of scale and precipitation. Supersaturation must be reduced by neutralization with lime or it must be prevented.

- **Organic compounds:** these are troublesome in two ways:

- in liquid-liquid extraction: the residual solvent inhibits precipitation of the metal, particularly during electrolysis,
- in carbon adsorption: certain organic compounds bound to the carbon may not be eluted during chemical regeneration. Others react with metals to form complexes that do not adsorb onto carbon

4. MUNICIPAL WASTEWATER

4.1.

SOURCE AND COLLECTION METHOD

Municipal wastewater is made up of:

-domestic **wastewater** or **sewage**,

- **rainwater**.

Municipal wastewater is mainly domestic (sewage, etc.); the industrial portion generally keeps pace with population growth.

Factories which discharge an unproportionally large amount of pollution, or pollution requiring special treatment, usually have their own purification system. Depending upon the level of this treatment, the industrial effluent will join the receiving medium or the collection system and treatment system.

The daily volume and pollution of the industrial effluents are frequently expressed in **population equivalents** and correspond to the per capita amounts of domestic wastewater (see pages 74 and 76).

Sewerage comprises collection, transport and treatment of urban effluents.

Figure 21. Lyon (France).

The main two collection systems used in sewerage are of the continuous operation type:

- the **combined** system conveys domestic wastewater and rainwater in the same line;
- the **separate** system is made up of two different pipe networks: one for rainwater, which is about the same size as the combined system, and the other, smaller in size, for the wastewater per se.

The first sewerage systems were combined; the separate system is a more recent development. The collection systems found in densely populated areas are seldom all of one type.

The **partially-separate** system refers to a separate system in which water from roofs and backyards is conveyed to the wastewater network.

The combined systems are equipped with storm overflows that discharge some of the flow directly into a river during rainy periods. In this case, only part of the pollution flow reaches the purification plant. This discharge of pollution into a river during rainy periods constitutes, along with poor self-cleansing of the lines during dry periods, two of the main disadvantages of combined systems. However, their construction is easier to control. An essential property of a network is that it is watertight and keeps out parasites from groundwater or from surface runoff.

Effluents are conveyed, as far as possible, by gravity, however, the topography of a terrain often means that intermediate pumping stations must be installed. These can then be followed by mains of considerable length under pressure. In special cases, the effluents may be collected at the point of emission under pressure or even under vacuum; these methods, developed for small installations, allow pipes to be laid at a higher level.

There are two types of sewerage that do not involve the collective network of sewers:

- **individual or grouped** sewerage serving one residence or several residences situated very close together, often called self-directing sewerage. The domestic wastewater is conveyed directly to a water purification facility, "flowing" normally into the ground (usually a septic tank and subsurface disposal - figure 22),

- the treatment of **night soil** in a centralized plant. This method of sewerage consists of storing the most concentrated effluents from each house in watertight pits which are regulary emptied into tank trucks and conveyed to a central treatment plant. This method is still used in some areas where the houses are very old and/or the ground relief such that a wastewater collection network is not feasible. It is sometimes used to drain off septic tanks. In Asia, this type of collection and treatment of night soil is still in use. The delay in constructing sewage systems is often due to the great density of the population.

It must be mentioned, also, that some countries in Asia follow the ancestral custom of spreading fecal matter directly on crops. Thus, wastewater collected in a sewerage system would have a relatively weak concentration in spite of a low water demand.

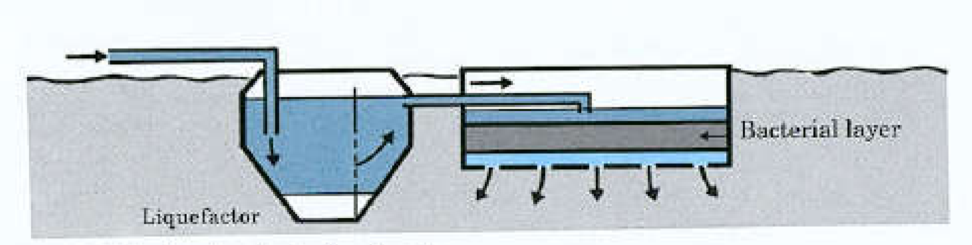


Figure 22. Septic tank and subsurface disposal

4.2. WATER QUANTITIES TO BE TREATED

4.2.1. Wastewater

The per capita volume of wastewater discharged per day usually increases with the population as a result of changes in life style and a larger participation by secondary and tertiary sectors. The volume also varies according to the area of the world and its level of development. The method of determining the consumption rate of drinking water may also have a bearing on it.

Although it accounts for less than 1501/person per day in many rural areas, the amount of municipal wastewater produced during dry periods today in France is about 200 1/person per day in towns with populations in the several tens of thousands. The volume is over 300 1/ person per day in Paris where large amounts of water are used to wash the streets. In many American or Swiss cities, the volume rises well above 400 l/person per day. Frequent catchment in combined sewerage systems of rainwater collected in small streams inflates these ratios. Infiltration water, which very often enters the system unchecked, has the same effect.

These variations can be costly, for the sizing of a purification facility depends very much on its hydraulic capacity

The amount of municipal wastewater varies throughout the day. In less densely populated towns there are two flow peaks; in more heavily populated towns there is only one. Sociological development is causing the latter type to become more generalized (see figure 23). The shorter the sewerage system and the smaller the population served, the greater the size of the peak. The presence of numerous pumping stations on a system may have a comparable effect.

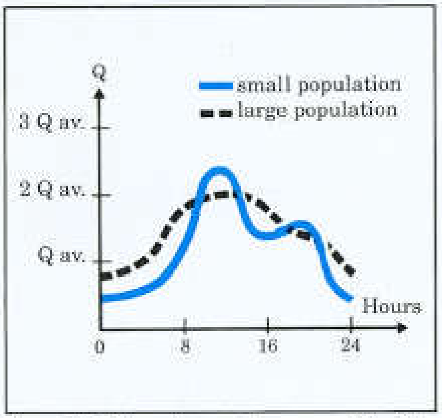


Figure 23. Daily variations of wastewater flow Q in a municipal sewerage system.

In many countries, an average diurnal flow during dry weather may be represented by Qd. If Qj is the daily flow, Qd lies most often between:

Qj/14 and Qj/18

The peak dry weather flow Qp in a separate system can be calculated by the formula:

$$Qp = Qm\ (1.5 + \frac{2.5}{\sqrt{Qm}})\ \text{in } l/s^{-1}$$

with Qm = daily average =

$$\frac{Qj\ (\text{in } l)}{86{,}400}$$

and up to a peak coefficient

$$Qp/Qm \leq 3$$

Besides the daily variations, substantial seasonal variations in wastewater flow are becoming more frequent, even in large cities. These variations are closely tied to vacation periods during which there is a large exodus of city dwellers heading for vacation spots. In very developed countries, many city dwellers leave their principal residence during the winter sports season as well as in summer; in this case, they use three different sewerage systems each year. This is not without consequence on the demand for collective facilities.

4.2.2. Rainwater

The rainwater flow depends:

- on the incline and on the surface of the drainage area,
- on its degree of imperviousness,
- on the rainfall.

Various formulas have been put forth, one of which is Caquot's.

For European urban areas of several hundred hectares, the maximum amount of run-off water over a five-year period is about 2001/s.ha.

4.3
ASSESSMENT OF POLLUTION

4.3.1. SS

Suspended solids loading contributed by raw sewage, per head per day, is generally estimated as follows:

- separate system: 60 to 80 g, including 70% volatile solids,

- combined system: 70 to 90 g, including 65% volatile solids.

The per capita quantity of pollution increases as the standard of living rises and usually as the population grows. However the sewage flow increases faster than the loading, so that the sewage tends to become less concentrated. If the sewerage system is badly constructed, infiltration water can get in and aggravate this tendency. The figures cited above are for SS after Screening grit removal and do not include material collected during preliminary treatment, which is roughly as follows:

screening:

- 2 to 5 dm^3 of screenings per person per year in the case of screens with bars approximately 40 mm apart,

- 5 to 10 dm^3 for screens with bars approximately 20 mm apart,

- 10 to 15 dm^3 for screens with bars approximately 6 mm apart.

The water content of these screenings is about 70 to 80% after natural drainage and pressing.

grit removal:

In a combined system, the volume of grit per head per year is about 12 dm^3 for an area of detached houses, and 5 dm^3 for areas with high-rise apartment buildings

- **Rainwater**

It is interesting to make an assessment of the pollution conveyed by rainwater alone. It is difficult to establish an overall rule since there have not been many in-depth investigations into the matter and on site conditions play a large role. The pollution varies considerably during the course of the precipitation; it is usually more concentrated at the beginning of a storm. The matter entrained in the rain than that found in sewage, does, however, contain hydrocarbons; lead, from motor fuel, is also frequently present.

A study made in France by the Service technique de l'Urbanisme (S.T.U.), assesses the yearly pollution flow at 300 to 1100 kg SS per hectare of drainage area and from 800 to 2650 kg SS per hectare of watertight drainage area.

4.3.2. Carbonaceous organic pollution

the BOD loadings contributed by sewage, per head per day, can be estimated, after preliminary treatment, as follows:

- separate system: 50 to 70 g,

- combined system: 60 to 80 g.

Roughly one third of this pollution is dissolved; the remaining two thirds are tied to particles (settleable or not). In combined systems the percentage of organic pollution that is settleable is usually higher than that found in separate systems.

The COD/BOD_5 ratio in sewage is usually between 2 and 2.5.

The TOC, due to the nature of the analytical method, cannot identify particulate components.

- **Rainwater**

The aforementioned S.T.U. study proposes the following assessment of annual pollutant flow in rainwater:

	Drainage area	**Watertight drainage area**
BOD kg per head	30-85	80-210
COD kg per head	160-460	470-1,100

4.3.3. Other components

- **Nitrogen**

The total nitrogen content (TKN) amounts to about 15 to 20% of the BOD5 in domestic effluents. The daily contribution of TKN is between 10 and 15 g per head.

- **Phosphorus**

The daily contribution of phosphorus is about 4 g per head. It is essentially due to human metabolism and the use of detergents. Moreover, the amount varies according to the day of the week.

- **Surfactants**

Widespread use of biodegradable detergents has lessened the operating problems plants have had with foam; but their use continues to grow.

- **Micro-elements**

The most harmful elements are heavy metals. Their main source is industry. Copper, zinc, cadmium, chromium, lead, mercury and nickel are the pollutants most frequently encountered. The level of these elements is usually less than 1 mg.l^{-1}. Discharging toxic products into sewers and especially into natural receiving waters is prohibited by law (e.g., cyanides, cyclic hydroxyl compounds).

Table 9 gives the value ranges for average characteristics of MWW in France:

Table 9. Characteristics of **French MWW.**

Parameters	**Variation range**	**Settleable fraction**
pH	1.5 to 8.5	
Dry solids mg.l^{-1}	1,000 to 2,000	10%
Total SS mg.l^{-1}	150 to 500	50 to 60%
BOD$_5$ mg.l^{-1}	100 to 400	20 to 30%
COD mg.l^{-1}	300 to 1,000	20 to 3096
TOC mg.1^{-1}	100 to 300	
TKN mg.l^{-1}	30 to 100	10%
N-NH$_4^+$ mg.l^{-1}	20 to 80	0170
N-NO$_2^-$ mg.l^{-1}	< 1	0%
N-N0$_3^-$mg.1^{-1}	< 1	0170
Detergents mg.l^{-1}	6 to 13	0%
P mg.l^{-1}	10 to 25	10%

4.3.4. Pathogenic agents

MWW conveys many microorganisms, some of which are pathogenic: bacteria, viruses, protozoa, helminths (see chapter 6). The pathogenic bacteria most often encountered are salmonella, the level of which is somewhere between 10^2 and 10^3 per 100 ml.

The process of identifying pathogenic organisms in water is a lengthy one; indicator germs are used for routine counting. The most common indicator germs used are the total coliforms and the fecal coliforms (primarily Escherichia *coil)* and sometimes also the fecal streptococci. In 100 ml of domestic sewage, between 10^7 and 10^8 total coliforms and between 10^6 and 10^7 fecal coliforms have been counted most often.

The fact that coliforms are not found in an effluent does not mean that it does not contain any pathogenic germs. In MWW, indicator germs are used, above all, to estimate the level of decontamination (or of partial disinfection); this is expressed by the number of logarithmic units (power of 10) which a treatment has been able to reduce from the initial count in the raw water.

4.3.5. Oxidation-reduction potential-Septicity

Domestic wastewater that is sufficiently fresh has an oxidation-reduction potential of about 100 mV, corresponding, for a pH of about 7, to an rH of about 17 to 21 (see page 249). A potential of +40 mV (let rH = 15 at pH 7) or a negative potential indicates a reducing medium (septic wastewater, putrid fermentation, presence of chemical reducing agents). A potential exceeding 300 mV (rH = 24 at pH 7) reflects an abnormal oxidizing medium.

The septicity of the effluent leads to the formation of sulphur (S^{2-}) and causes release of H_2S.

Figure 24 diagrams the evolution of water depending on its pH and its rH.

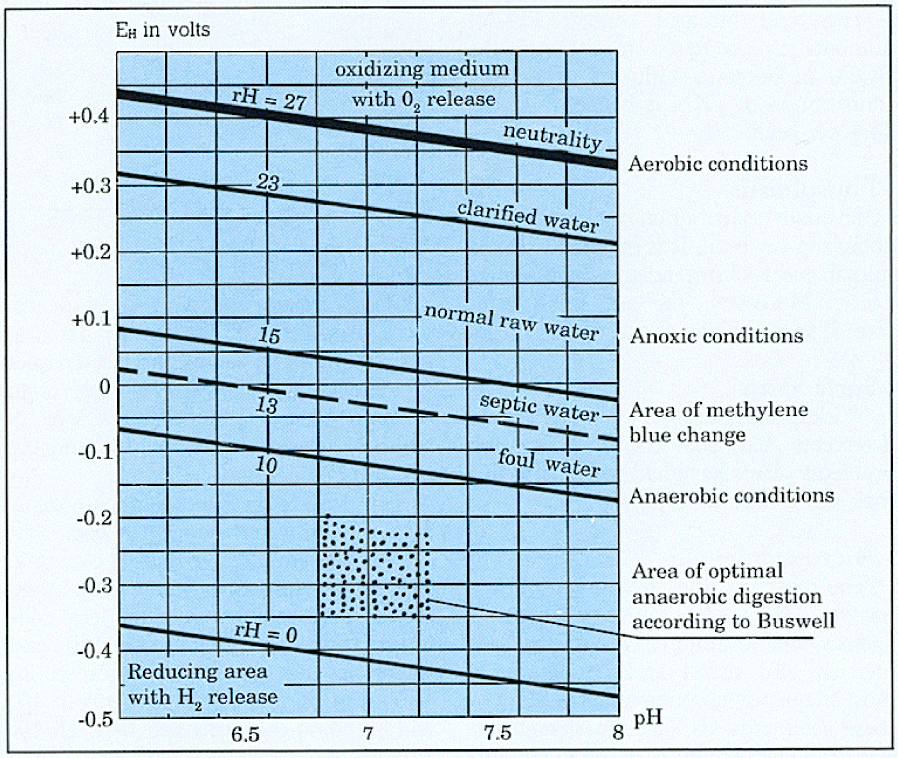


Figure 24. Diagram of redox potential – pH of wastewater

4.3.6. Night soil

The characteristics of night soil may vary greatly, depending on its origin; it comes primarily from two types of watertight pits:

- those with a "water effect" (very small volume of water mixed in with fecal matter), usually emptied once a year; night soil is very concentrated (COD comprised between 12 and 30 g.l^{-1}),
- those equipped with a water flushing unit; they are emptied more frequently and night soil is much more diluted (COD about 2 g.l^{-1}).

The available volume of the cesspool space determines the frequency of emptying and does or does not ensure preliminary digestion of the effluents. Table 10 gives the characteristics of these products in several countries.

4.3.7. Pollution peaks

Usually the pollution level varies at the same time as the flow, so that variations in the pollution flow are greater than those of the flow alone. This phenomenon is particularly noticeable with SS in combined systems.

Table 10. Composition of night soil.

Parameters (concentration in g.l^{-1})	**Usual variations**		**Special cases**
	in France	in Japan	Saudi Arabia (Taif)
pH	7.7 to 8.5	6.4 to 7.9	6.2
COD	2 to 30	8 to 15	1.75
BOD	1.5 to 10	5 to 9	0.42
SS	2 to 10	20 to 35	0.66
Total Kjeldhal nitrogen	0.5 to 2.5	3.5 to 6	0.17
of which ammonia nitrogen	0.4 to 2	3 to 4	0.12

4.4.
THE PURPOSE OF TREATMENT - QUALITY OBJECTIVE

The purpose of the treatment of effluents before discharge is to protect the natural receiving waters. Regulations have progressively diversified the tolerable discharge levels to bring them into line with the objectives of river water quality set down by the authorities in charge of water management. The quality objectives take into account the primary uses of river water in the reaches downstream (fishing, swimming, drinking water). They correspond to the classification of rivers in the example in table 11.

Keeping in mind the hazards of hydrological variations in rivers, these quality objectives must be respected in the case of every flow that is less than the flow of a given frequency (French method), or during a minimum number of days in the year (English method).

In the case of discharge into estuaries and into the sea, the conditions of discharge that have been adopted take into account the particular activities that take place in that coastal area (bathing, shellfish farming).

Table 11. Overall criteria for appraising the quality of river water. (Grid used by the Agence de Bassin Adour-Garonne, France)

		1A	**1B**	**2**	**3**
	Conductivity µS/cm at 20°C	= 400	400 to 750	750 to 1 500	1 500 to 3 000
	Temperature	= 20	20 to 22	22 to 25	25 to 30
	pH	6.5 to 8.5	6.5 to 8.5	6 to 9	5.5 to 9.5
	SS (mg.l^{-1})	= 30	= 30	= 30	30 to 70
	Dissolved 0_2 (Mg.l^{-1})	> 7	5 to 7	3 to 5	aerobic medium
	Dissolved 0_2 in saturation %	> 90%	70 to 90	50 to 70	to be permanently maintained
	BOD_5 (m.l^{-1})	= 3	3 to 5	5 to 10	10 to 25
	PV (mg.l^{-1})	= 3	3 to 5	5 to 8	
	COD (mg.l^{-1})	= 20	20 to 25	25 to 40	40 to 80
	NH_4 (Mg.l^{-1})	= 0.1	0.1 to 0.5	0.5 to 2	2 to 8
	$N0_3$ (Mg.l^{-1})			< 44	44 to 100
	Total N (Kjeldahl)	= 1	1 to 2	2 to 3	
	Fe (mg.l^{-1})	= 0.5	0.5 to 1	1 to 1.5	
	Mn (mg .l^{-1})	= 0.1	0.1 to 0.25	0.25 to 0.5	
	F(mg.l^{-1})	= 0.7	0.7 to 1.7	0.7 to 1.7	> 1.7
	Cu (mg.l^{-1})	= 0.02	0.02 to 0.05	0.05 to 1	> 1
	Zn (mg.l^{-1})	= 0.5	0.5 to 1	1 to 5	> 5
	As (mg.l^{-1})	= 0.01	= 0.01	0.01 to 0.05	> 0.05
	Cd (mg.l^{-1})	= 0.001	= 0.001	= 0.001	> 0.001
	Cr (mg.l^{-1})	= 0.05	= 0.05	= 0.05	> 0.05
	CN (mg.l^{-1})	= 0.05	= 0.05	= 0.05	> 0.05
	Pb (mg.l^{-1})	= 0.05	= 0.05	= 0.05	> 0.05
	Se (mg.l^{-1})	= 0.01	= 0.01	= 0.01	> 0.01
	Hg (mg.l^{-1})	= 0.0005	= 0.0005	= 0.0005	> 0.0005
	Phenols (mg.l^{-1})		= 0.001	0.001 to 0.05	0.05 to 0.5
	Detergents (mg.l^{-1})	= 0.2	= 0.2	0.2 to 0.5	> 0.5
	S.E.C.* (mg.l^{-1})	< 0.2	0.2 to 0.5	0.5 to 1	> 1
	Coliforms (count 100 ml)	= 50	50 to 5 000	5 000 to 50 000	
	Esch. Coli (count 100 ml)	= 20	20 to 2 000	2 000 to 20 000	
	Fec. strep. (count 100 ml)	< 20	20 to 1 000	1 000 to 10 000	
	Diver Divergence of biotic Index** from the normal index	1	2 or 3	4 or 5	6 or 7

Notes : (*) Substances extractible with chloroform.

(**) See page 31.

Note on the use of table 11.

The quality of water depends on many parameters (temperature, ammonium (NH4), mercury (Hg), etc.).

- It is usual to judge water quality on the basis of its least favourable parameter.

- This quality is that which, according to the limits in the table, is achieved by at least 10% of the worst samples in this parameter.

Class 1A: This characterises water that is considered free from pollution and is of a quality to meet the most exacting requirements.

Class 1B: Slightly lower in quality, this water may, nonetheless, meet all needs.

Class 2: "Acceptable" quality: suitable for use in irrigation and industry, it may be used for drinking after extensive treatment. It is generally tolerable for the watering of livestock. Fish may live in it with no ill effects but their reproduction may be impaired. It may be used for water sports as long as there is not excessive contact with the water.

Class 3: "Mediocre" quality: barely suitable for irrigation, cooling and leisure boating use. This water may support fish culture but it may be hazardous to fish life in periods of low flow or high temperatures, for example.

Unclassifiable: Water which exceeds the maximum tolerable limit in class 3 for one or more values. It is considered unsuitable to most uses and may constitute a danger to public health and the environment.

4.5.
THE REUSE OF SEWAGE

4.5.1. Agricultural use

The use of sewage in agriculture is very old and land disposal was the first purification system. The ground is an efficient filter and one hectare contains up to one or two tonnes of microorganisms. Today the main reason for reusing sewage in cultivation is, more often, to supply water so necessary to arid areas, rather than to purify it in the ground or to contribute nutrients.

Measures must be taken in order to avoid deposits and corrosion in the distribution system; it is advisable, in any case, to have raw sewage undergo preliminary settling. Preliminary biological treatment is also often recommendable. In particular, it substantially reduces the risk of bad odours.

Two categories of risks ate associated with the reuse of sewage:

- **Health risks** for close-lying neighbourhoods and for consumers of the produce.

The risks vary greatly depending on the local state of sanitation in the area, farming methods, customs and climate. However, generally speaking, sewage should not be used on or near vegetables that are eaten raw. The risk is reduced with proper management determining when and when not to spread sewage and the drying of the crop. The use of sewage on hay meadows does not seem to pose any great problem, which is not the case for grazed pasture.

Arboriculture, cereals, beets and oleaginous crops are the types of cultivation most suited. Surface irrigation is preferred to spray irrigation

- **Risks to the soil and crops:** clogging the soil, increased salinity, introduction of toxins.

Land disposal can alter the physical properties of the soil. In particular, the introduction of an excessive amount of sodium and the absence of leaching (especially in areas of low rainfall) can destroy the soil structure. Knowing the SAR (sodium absorption ratio) of the effluent is, therefore, important:

$$\mathrm{RAS} = \frac{(\mathrm{Na}^+)}{\sqrt{\dfrac{(\mathrm{Ca}^{2+}) + (\mathrm{Mg}^{2+})}{2}}}$$

If the SAR nears 10, it signals danger; usually this only happens in certain concentrated effluents (distilleries, sugar mills, cheese factories).

An effluent that has an excessive salinity level (> 2 g.l^{-1}) also causes trouble and leads to a stricter control on the quantity of water that is spread and the level of salinity as it develops in the crop soil. The C/N ratio remains essential for crop requirements. The N/P/K usually shows a very excessive amount of nitrogen in domestic sewage. One of the drawbacks to using sewage in agriculture is that it may raise the nitrate level of the groundwater.

Tables 12 and 13 present an example of guidelines for irrigation water adopted in California.

Table 12. Table of guidelines for the main characteristics of irrigation water.

	Limits to use		
Characteristic	None	Moderate	Strict
Salinity mg.l^{-1}	< 450	450-2 000	> 2 000
Specific conductivity µS.cm^{-1} (EC)	< 700	700-3 000	> 3 000
SAR = 0 - 3	> 700	700-200	< 300
= 3 - 6	> 1 200	1 200-300	< 300
= 6 - 12 EC	> 1 900	1 900-500	< 500
= 12 – 20	> 2 900	2 900-1 300	< 1 300
= 20 – 40	> 5 000	5 000-2 900	< 2 900
Na			
Surface irrigation SAR	< 3	3 - 9	> 9
Spray irrigation mg.l^{-1}	< 70	> 70	
C1			
Surface irrigation mg.l^{-1}	< 140	140 - 350	> 350
Spray irrigation mg.l^{-1}	< 100	> 100	-
pH	6.5 to 8.4		

Table 13. Table of guidelines for trace elements in irrigation water (1).

Characteristic	Limit value $mg.l^{-1}$
Al	5
As	0.10
B	0.75
Be	0.10
Cd	0.010
CZ	0.10
Co	0.05
Cu	0.2
F	1
Fe	5
Li	2.5
Mn	0.2
Mo	0.01
Ni	0.2
Pb	5
Se	0.02
Va	0.10
Zn	2.0

(1) These values pertain to land under continuous cultivation with a yearly amount of water of about 1.20 m. For shorter cultivation periods, these values may be raised.

Wastewater may also be used to irrigate leisure areas such as golf courses and parks, etc. This irrigation is often done by spraying. The treatment required is therefore extensive and must end in disinfection after the removal of suspended solids and organic pollution.

4.5.2. Use in industry

Following treatment, urban wastewater may be a source of water that is completely suitable for industrial needs, especially for cooling and washing. Such reuse has nowadays a large number of applications.

Very often, exhaustive removal of organic pollution is necessary and biological treatment is then followed by a finishing treatment.

After very thorough tertiary treatment involving, among others, a demineralization phase, wastewater can be used as feedwater for low-pressure boilers. Prolonged studies have shown that this solution is also workable for medium-pressure boilers.

4.5.3. Domestic and municipal use

The reuse of treated wastewater in the home or at the city level is possible for various levels of quality and in accordance with a number of working plans:

- partial recycling inside buildings. This use, which has been undertaken in the Far East, involves supplying flushing water for toilets from recirculated wastewater that has been treated,
- supplying municipal systems with wash water (streets, trucks, etc), and water for fire-fighting. Its usage must not cause impairments to the system (deposits, bacterial proliferation, corrosion, etc.) or cause unacceptable health hazards,

- partial aquifer recharge (filtering beds, etc.),
- setting up underground hydraulic barriers to prevent the intrusion of sea water into coastal aquifers,
- reinjection into the drinking water system. This usage requires a very complete chain of treatment but does not arrive at a technical impasse. It is being used in deserts and has been under study for use in spaceships. Because of the salinity level in the reused water, it is often necessary to mix it with fresh water to meet drinking water standards. If this is not possible, it must undergo desalination. Great care must be taken to remove organic pollution, ammonium and bacteriological pollution.

5. INDUSTRIAL EFFLUENTS

Figure 25. Industrial effluents.

5.1.
TYPES OF EFFLUENTS

Whereas the nature of domestic wastewater is relatively constant, the extreme diversity of industrial effluents calls for an individual investigation for each type of industry and often entails the use of specific treatment processes.

Therefore, a thorough understanding of the production processes and of the system organization is fundamental.

5.1.1. Origin of the effluents

There are four types of industrial effluents to be considered:

5.1.1.1. General manufacturing effluents

Most processes give rise to polluting effluents resulting from the contact of water with gases, liquids or solids.

The effluents are either continuous or intermittent. They even might only be produced several months a year (campaigns in the agrifood industry, two months for beet sugar production, for example).

Usually if production is regular, pollution flows are known. However, for industries working in specific campaigns (synthetic chemistry, pharmaceutical and parachemical industries), it is more difficult to analyse the effluents as they are always changing.

5.1.1.2. Specific effluents

Some effluents are likely to be separated either for specific treatment after which they are recovered, or to be kept in a storage tank ready to be reinjected at a weighted flow rate into the treatment line.

Such is the case in:

- pickling and electroplating baths; spent caustic soda; ammonia liquor from coking plants,
- condensates from paper production, mother liquors from the agrifood industry,
- toxic and concentrated effluents.

5.1.1.3. General service effluents

- Wastewater (canteens, etc.).
- Water used for heating (boiler blowdown; spent resin regenerants).
- Sludge from the treatment of make-up water.
- Refrigerating water blowdown.

5.1.1.4. Intermittent effluents

These must not be forgotten; they may occur:

- from accidental leaks of products during handling or storage,
- from floor wash water,
- from polluted water, of which storm water may also give rise to a hydraulic overload.

5.1.2. Characterization of effluents

For the correct design of an industrial effluent treatment plant, the following parameters must be carefully established:

- types of production, capacities and cycles, raw materials used,
- composition of the make-up water used by the industrial plant,
- possibility of separating effluents and/or recyling them,
- daily volume of effluents per type,
- average and maximum hourly flows (duration and frequency by type),
- average and maximum pollution flow (frequency and duration) per type of waste and for the specific type of pollution coming from the industry under consideration.

It is often helpful to be informed about secondary pollution, even if is rare, since it can seriously disturb the working of certain parts of the treatment facilities (glues, tars, fibres, oils, sands, etc.).

When a new factory is being designed, these parameters will be ascertained after analysis of the manufacturing processes and compared with data from existing factories.

Knowing the composition of the make-up water is often necessary.

5.1.3. Specific pollution factors

The principal types of pollutants are set out below, classified in accordance with the types of treatment to which they may be subjected:

Insoluble substances which can be separated physically with or without flocculation

- Floating greasy matter (greases, aliphatic hydrocarbons, tars, organic oils, resins, etc.).
- Solids in suspension (sands, oxides, hydroxides, pigments, colloidal sulphur, latexes, fibres, filtration aids, etc .).

Organic substances separable by adsorption

- Dyes, detergents, miscellaneous macro-molecular compounds, phenolated compounds, nitrated derivatives, chlorinated derivatives.

Substances separable by precipitation

- Toxic and nontoxic metals, Fe, Cu, Zn, Ni, Al, Hg, Pb, Cr, Cd, Ti, Be, which can be precipitated within a certain pH range, and sul hides.
- $P0_4^{2-}$, SO_4^{2-}, $S0_3^{2-}$, F^-.

Substances separable by deaeration or stripping

- H_2S, NH_3, SO_2, phenols, light or aromatic hydrocarbons, chlorinated derivatives.

Substances which may require a redox reaction

- CN^-, Cr_{VI} , S^{2-}, Cl_2, NO^{2-}.

Mineral acids and bases

- Hydrochloric, nitric, sulphuric and hydrofluoric acids.
- Miscellaneous bases.

Substances which can be concentrated by ion exchange or reverse osmosis

- Radionuclides such as **I*, Mo*, Cs***.
- Salts of strong acids and bases, ionized organic compounds (ion exchange) or non-ionised organic compounds (reverse osmosis).

Biodegradable substances

- For example, sugars, proteins, phenols. After acclimatization, some organic compounds such as formaldehyde, aniline, detergents and even aromatic hydrocarbons as well as some mineral compounds ($S_20_3^{2-}$, $S0_3^{2-}$), may be oxidized.

Colour

Industrial effluents may be heavily coloured. This colouration is due to colloids (pigments, sulphides) or to dissolved substances (organic matter, nitrated derivatives).

From an analytical viewpoint, the following should be pointed out:

(1) The ratio of COD to BOD_5 in industrial effluents often differs very substantially from that of MWW. It changes during the stages of treatment, the final COD sometimes reaching a value more than ten times that of the corresponding BOD_5.

(2) The presence of very active toxic substances may conceal that of biodegradable substances and thus seriously falsify the measurement of BOD_5.

Basic information on the biological treatabiliry of wastewaters is given in Chapter 4, page 287.

5.2.
DISCHARGE STANDARDS

Discharge standards vary greatly:

- pollution factors are more numerous than in MWW and must be determined industry by industry,
- regulations concerning specific factors (hydrocarbons, heavy metals, F^-, CN^-, phenols in particular) rely on different methods of measurement and are enforced to different degrees depending on the country.

Effluents may be discharged directly into the natural receiving waters or into city sewers which convey them to biological facilities where they should not impair normal operation.

If it is now common practice to set limitations on the concentration of effluent, then regulations concerning maximum quantity of effluent produced per day or per unit manufactured are becoming more common. Monthly averages and daily maxima should also be considered.

Sometimes a certain amount of leeway is foreseen in the application of standards in the case where strict compliance would lead to an economic "impossibility°. In any case, the standards must take into account the sensitivity of measuring methods and the technical possibilities of treatment.

Tables 14 and 15 demonstrate the complexity of this problem.

Table 14. Measuring methods and the range of standards possible for some organic compounds.

Compounds encountered	**Methods**	**Range of standards** (mg.l^{-1})
Free cyanides (Epstein)	- T 90.108 (F) - ASTM D 203682 C	0.2 - 1
Total cyanides (except SCN)	- T 90.107 (F) - ASTM D 203682 A	2 - 6
Phenols transportable in steam (DAAP)	- T 90.204 - API 71657	0.5 - 5
Total phenols		5 - 10
Insoluble hydrocarbons (precipitation on floc, extraction, gravimetry)	- T 90.202 (F) - HMSO 1972 (UK) - API 73253	2 - 10
Total hydrocarbons in refinery (spectrophotometry, IR, 2 peaks)	- T 90.203 (F) - CONCAWE I/72 - S.M. AWWA 502 B	15 - 30
Anionic surfactants	- ASTM D 2330	2 - 10

Table 15. Examples of standards relating to metals (mg.l-1).

These norms often apply to total metal, sometimes to ionized metal.

Total metals	**FRANCE Electroplating surface treatment**	**NETHERLANDS Garbage incineration (GSE)**	**F.R.G. Sulphur removal from smoke (GSE)**	**SWITZERLAND Discharge into lakes**
Ag	-	0.1	-	0.1
Al	5	-	-	10
Cd	0.2	0.05	0.05	0.1
Cr_{III}	3	0.2	0.5	2
Cr_{vI}	0.1	-	-	0.1
Cu	2	-	0.5	0.5
Fe	5	-	-	2
Hg	-	0.01	0.05	0.01
Ni	5	0.5	0.5	-
Pb	1	1	0.1	0.5
Se	-	-	-	2
Zn	5	0.5	1	2
Vd	-	-	-	-

5.3.

EFFECT OF WATER RECIRCULATION AND CLEAN TECHNIQUES

Their development in two successive stages has, in many cases, led to a reduction in the volume of effluents and in the pollution flow.

5.3.1. Recirculation

Recirculation, first used in cooling units to reduce the amount of water used, was subsequently used to control effluents. It has been used very extensively in the iron and steel industry (whose previous consumption of 200 m^3 per tonne of steel has now been reduced to 5 m^3 per tonne, if not 3), in paper production (reduction from more than 50 - 100 m^3 per tonne to less than 5), and in the manufacture of fibreboard. This is feasible as long as the main pollution is insoluble and can be removed by a simple physical - chemical procedure either in the system or on a by - pass.

5.3.2. Clean techniques

Pollute less by producing more efficiently is the environmentalist's challenge to industry which must be taken up in order to optimize manufacturing processes.

The many measures undertaken and their successes are known; only the most significant examples involving just liquid effluents are mentioned.

The replacement of a gaseous emission by a liquid effluent thanks to scrubbing must not entail a transfer of pollution and should result in a simpler way of puri fying the effluent or in a direct recirculation of the wash waters into the process line (ammonium nitrate factories for example).

This may be carried out by several means:

- **Eliminating the effluents** by developing new "dry" procedures such as may be the case in surface treatment:

- replacing chromium baths by hot ionic nitriding,
- replacing cadmium baths by the application of aluminium in ionized steam form,
- replacing galvanization by Rilsanising (plastic).

- **Separation and possible recovery** of dissolved raw materials which are toxic or costly. For example:

- solvents separated by distillation: the manufacture of paint (HC), of sulphonated resins (dichloroethane), pharmaceuticals (ethanol), tawing of hides (petroleum),
- chromium bound to resins: stabilisation of chromium baths by fixing of Cr^{3+} ions on resins, double ion exchange on rinse water after passivation with recycling of the eluates in the baths.

- **Separation of suspended compounds** from manufacturing processes, and reintegration, whenever possible, into the process:

- sludge after settling in cardboard production,
- oils from foodstuffs and margarine refineries,
- greases and proteins from slaughterhouses.

- **Separation of dissolved compounds** synthesised during processes:

- phenol from spent soda with liquidliquid extraction by a recycled oil cut,
- -ammonium from formation water in coking plants or from amino acid production, separated through steam stripping and later recovered through condensation or sulphation.

5.4.
AGRIFOOD INDUSTRIES (A.F.I.)

The characteristics common to all effluents from foodstuff industries are essentially organic and biodegradable pollution, and a general tendency to rapid acidification and fermentation. All these effluents are treated primarily by biological methods, but the medium often becomes deficient in nitrogen and phosphorus.

5.4.1. Piggeries

The amount and degree of pollution depend on the methods of stock breeding, the method of cleaning the sties, the time spent in the sties and the type of feed used.

Discharge per pig per day	**Cleaned hydraulically**	**Cleaned dry**
Water	17 - 25 1	11 - 13 1
BOD_5	100 - 200 g	80 - 120 g
TKN	18-35g	
COD	300 - 500 g	

In hot countries, spraying of the pigs raises the above volume of water.

Manure analysis in g.l^{-1}	
SS	30 to 80
COD	25 to 60
BOD_5	10 to 30
TKN	2 to 5
Total NH_4	3 to 4
Cl	0.8
$S0_4$	1.5 to 2
M alk.	1400 to 1500 Fr. deg.
PH	7 to 8

5.4.2. Slaughterhouses and associated industries

5.4.2.1. Livestock slaughtering plants

Included here, besides the slaughter of livestock, are tripe and offal processing shops and the evacuation of stercoral matter which makes up over 50% of the pollution. This depends on:

- the blood recovery rate (BODS: 150 to 200 $g.l^{-1}$, COD: 300 to 400 $g.l^{-1}$, TKN: 25 $g.l^{-1}$) which can reach 90% in the large slaughterhouses,
- the method of evacuation of stercoral matter, given that hydraulic means are not used,
- the size of the tripe and offal operation,
- associated shops (salting-canning).

As a result, there is less discharge in modern slaughterhouses. In Europe, these amounts may be estimated at:

- 6 to 9 l per kg of cattle carcasses (320 to 350 kg),
- 5 to 11 l per kg of pig carcasses (80 to 90 kg).

According to a study by CEMAGREF, the volume of water consumed is distributed in the following manner:

Shop or facility	Volume in litres per **kg** of **carcass**
Slaughter chain:	
- cattle	4.8 incl. paunch washing
- slaughter of pigs	4.1
- pig paunch washing	2.0
Cattle tripe processing	2.4
Cattle offal processing	0.4 to 0.7
Truck washing	0.2 to 0.6

According to the same study, the average pollution loads were the following:

g per kg of carcass	Cattle slaughterhouses and various	pig slaughterhouses
COD	32.3 ± 5.2	27.3 ± 9
BOD_5	13.2 ± 2.2	13.2 ± 4.3
Fat (SEC)	5.2 ± 1.5	
Total N	1.6 ± 0.3	1.6 ± 0.5
SS	11.8 ± 2.5	9.3 ± 3.4

It is noteworthy that:

- the tripe and offal processing shop contributes more than 50% of the COD pollution from the entire slaughtering plant,
- the high SS levels sometimes found relate to non-biodegradable fibrous cellulosic matter,
- the BOD_5 loads of associated industries (salting and canning) range from 10 to 20 g per kg of finished product.

5.4.2.2. Poultry slaughterhouses

The polluting operations are, for the most part, the following:

- bleeding,
- scalding and plucking with wet or dry (pneumatic) transport,
- evisceration and transport, hydraulically or by dry means, and washing.

Whether the transport water is recycled or not can have a bearing on the water concentration. The shop in which the by products are cooked and dewatered (animal feed) contributes a pollution load of about one tenth that coming from the slaughterhouse itself.

Even with a separate collection system for process water which allows for the recovery of proteins, measurement is often dispersed due to the complexity of the shops and the inertia of the sewage. The separation of hot effluents may permit a cooling process that is less expensive and an easier way of isolating an effluent with a high fat content with a specific pretreatment.

The **CEMAGREF** studies carried out in five plants show the following average values per kg of carcass (average weight 1.4 to 1.5 kg):

Poultry	Measurements
Volume of wastewater in 1	8.1 ± 0.9
COD in g	21 ± 6
BOD_5 in g	9.3 ± 2.5
SS in g	4.5 ± 1

5.4.2.3. Hides, glue and gelatin industries

- **Tanneries and taweries**

These workshops perform a usual preliminary treatment of hides which consists of soaking and hair removal in a bath of lime with sulphides, followed by rinsing; the effluents from this process can contain up to 3/4 of the pollution load (workshop on a river).

The last phase of the treatment is the tanning which can take place:

- in tanneries using vegetable tannins or especially chromium salts that are found in the corresponding wastes,
- in taweries using a brine of NaCI and alums (mainly mineral pollutants).

Evaluation of the wastes: the volumes vary:

- from 20 to 120 m^3 per tonne if tanning is done with chromium (2 to 3 kg Cr^{3+} per tonne of hides),
- from 20 to 90 m^3 per tonne if vegetable tanning is done,
- from 200 to 250 kg COD and 75 to 150 kg SS per tonne of hides (about 30 kg for a cow).

An attempt is made in large plants to collect separately:

- the preliminary treatment effluents,
- the tanning baths (3 to 6 $g.l^{-1}$ Cr^{3+} pH 3.5),
- sulphurized alkaline water.

The wastes contain protein colloids, greases, hairs, colouring matter, chlorine and sulphur compounds from hair removal shops.

- **Glues and gelatins**

In this industry, the raw material is the hides provided by the tanneries and the bones from the slaughterhouses which are subjected to acid solubilization followed by alkaline hydrolysis in a lime slurry. Pig skins undergo a single acid washing of the hide before grease flotation.

The volume of wastewater can measure between 60 and 70 m^3 per tonne of bones and correspond to 50 kg BODS per tonne of glue produced.

5.4.2.4. Reuse of proteins in effluents from slaughterhouses

For 1,000 tonnes of cattle, the amount of proteins lost in the effluents may be in the range of 2 tonnes which are recoverable in the form of protein-rich sludge by primary purification after screening and grit removal.

The physical-chemical treatment with inorganic or organic flocculants results in a reduction of BOD_5 and SS in the effluents of 80 to 85% and 85 to 90% respectively.

Sanitary wastes and water from shop and truck washing must, of course, be separate from that coming from the slaughterhouse.

5.4.3. Dairy products industries

- **Origin of the wastes**

- Pasteurization and packaging: milk losses, dilute wash waters with a pH that varies widely.

- Cheese dairies and casein factories: deproteinized serum which is rich in lactose.

-Butter dairies: buttermilk which is rich in lactose and proteins but poor in fats.

Overall pollution depends greatly on the recovery of whey (minimum losses of 7%).

- **Evaluation of the wastes**

The volume depends upon recirculation (cooling and recovery of condensates).

The concentration also depends upon the type of dairy product discharged.

Table 16. Dairy industry wastes.

Shop or facility	**Volume of water 1 per 1 milk**	**BOD mg.l^{-1}**	**SS-1 mg.l^{-1}**
Liquid milk and yogurt	1-25	120-300	50
Powdered milk and butter dairies	1-3	80-300	30
Casein factories	2-4	400-500	100
Cheese dairies	2-3	400-900	100
Multiproduct dairies	3-6	300-750	120

Table 17. Analysis of dairy products (in g.l^{-1}).

Component	**Full cream milk**		**Skim milk**	**Whey**	**Buttermilk**
	Cow	**Goat**			
BOD_5	90-120		50-73	34-55	60-70
Ca	1.25	1.3	1.2		1.2
K	1.5	2.0			
P	0.95	0.9	0.9	0.8	0.95
Cl	1.1	1.3	1		1
SS	130	114		60-45	
F.O.G.	39	33	0.8	0.5-2	3
SNM*	33	29	35	7.9	30
Lactose	47	43	50	47-50	44
Lactic acid				2-6	1
Ash (g.kg^{-1})	8-9	8		5-7	

(*) SNM= Soluble nitrogenous matter + proteins.

Notes on the characteristics of the effluents:

- The COD/BOD5 ratio is about 1.4 in milk and 1.9 in serum.
- The discharge of TKN varies between 1 and *20* g per 1001 of milk.
- The BOD5 in the effluents in general may vary between 700 and 1,600 mg.l^{-1}.
- The pH, after homogenization, is usually between 7.5 and 8.8.

5.4.4. Breweries

- **Origin of the wastes**

- Filling of bottles.
- Cleaning (returned bottles, fermentation and storage vats, floors).
- Filtration of wort and separation of suspended substances or yeast.

- **Pollution:** caused by the beer, the yeast, and various particles of draff, kieselguhr, diatoms).
- **Evaluation of the wastes**

- *200* to 7001 per hl of beer, with 500 as average, coming chiefly from bottling and from pouring the beer into casks,
- 400 to 800g BOD$_5$ per hl of beer after internal recovery of yeast and draff,
- pH usually alkaline.

Shop or facility	**BOD$_5$ mg.l^{-1}**	**SS mg.l^{-1}**
Bottle washing	200 to 400	100
Washing of fermentation vats and Filters	1,000 to 3,000	500
Washing of storage vats	5,000 to 15,000	< 50

Note: COD/BOD5 ratio after settling is about 1.8. Nutritional deficiency as BOD/N/P is about 1000/10/1.

5.4.5. Potato processing industries and starch factories

The potato contains from *12* to *20%* starch, 70 to 80% water and much protein. Therefore, BOD5 discharge is high in starch whereas the common pretreatments by washing lead to a more mineral pollution.

- **Origin of the pollution**

It is related to the following shops:

- common: washing and transport of tubers (earth and vegetable debris), peeling by soda or steam (strong concentrations of recoverable pulp and starch and proteins),
- specific : production of French fries and crisps (heavy quantity of grease), bleaching (strong BOD).

- **Evaluation of the wastes**

Table 18 shows the characteristics of the wastes.

5.4.6. Starch factories

Starch works extract starch from the tubers of manioc and potatoes; a wet process is used to extract it from the richest cereals (wheat, rice, corn).

The nature of the effluents depends on the specific treatments used on the raw materials after common washing.

Raw Material	**Volume of water** m^3 per t	**BOD$_5$ kg per t**
Corn starch	2-4	5-12
Wheat starch (gravity separation)	10-12	40-60
Rice starch	8-12	5-10

The effluents are rather acidic which is due either to lactic fermentation or to sulphitation (pH 4 to 5). When a wet technique is used to extract starch, the pollution comes from the evaporation of water and is made up of volatile organic acids.

A notably soluble protein-rich pollution may, on the other hand, come from the glucose shop.

Table 18. Potato processing wastes.

Shop or facility	**Volume of water** m^3 per t	**SS** kg per t	**BOD$_5$** kg per t
Preparation			
- Transport and washing	2.5-6 recyclable	20-200	-
- Peeling and cutting	2-3		5-10
Flakes			
- Bleaching and cooking	2-4		10-15
Crisps			
- Bleaching	2.2-5	5-10	5-15
Starch extraction			
- Washing, grating,	2-6	Recyclable	
Grinding	(red water)		20-60*
- Pressing - refining	1	pulp	

(*) Including preparation water.

5.4.7. Effluents from other AFI (agrifood industries).

Industry	**Origin**	**Wastes and pollution**	
		m^3 per tonne	kg COD per tonne
Edible oil production	Extraction of olive oil	0.8-7	50-80
	Palm nut pressing	5	80
Edible oil refining	Condensers and deodorizers	0.2***	0.5-1
	Oil washing by centrifugation	0.15 (pH 10, 50-80°C)	3-5
	Pulp washing	0.6 (PH 1-2)	2-6 (2.5 g.l^{-1} P04)
	Margarine production	0.1 (30°C)	0.2-0.5
Fruit and vegetable canning and freezing	Washing, peeling,	15-30	8-38
	Blanching	5-10	-
Fruit juice	Pressing	0.15-0.25	0.3-1 pH 3-4
Beet sugar mills	Washing and transport	0.4-1.2***	2-3 (200-600 kg SS)
	Water from pressing	0.2	
	Excess condensates	0.1	(NH_4)
	Regeneration eluates	-	(salts)
Cane sugar mills	Washing of cane	5-10	14-25
	Barometric condensers - Excess	0.5-1.5	
	Excess condensates	0.1	
Distilleries **	Grape marc - Phlegmas	3-6	6-12
	Wine lees	2-3	60-200
	Wine	0.6-1.2	25-35
	Cane or beet sugar molasses	1.2-1.8	80-100
	Cane or beet sugar juice	0.8-1.6	25-40
	Grains	0.1-0.2	2-8
Fish, flour and canning	Washing, cooking	15-30	40-60
	Preparation	1-5	15-25
Sauerkraut production	Washing		20-40
Ready-to-eat meals	Preparation, cooking		15-45

(*) Values per hl juice.

(**) Values per hl pure alcohol.

(***)With closed recirculating system.

5.5.

TEXTILE INDUSTRIES

These industries are very diverse; it is easier to characterize the chief polluting activities than the effluents themselves.

5.5.1. The scouring and combing of wool

Raw wool contains many impurities (250 to 600 kg total SS per tonne) which are divided into:

- 25 to 30% grease (suint and fatty acids),
- 10 to 15% soil and sand,
- 40 to 60% organic salts and suint.

A substantial amount of pollution which comes from the scouting process (non-ionic detergent) is discharged. The COD can reach 60 g.l^{-1}.

Parameters	**Pollution contributed kg per t raw wool**
COD after	100-200
BODS grease removal	24-40
Grease	100-150
SS	20-30

The water is hot (40 to 50°C) and has a pH of between 8.2 and 8.4. Its specific volume per tonne of raw wool should be reduced from 7 to 3 m^3.

5.5.2. Preliminary treatments before textile finishing

These essentially involve natural fibres.

Preliminary textile treatment	**Volume m /t**	**BOD$_5$ kg/t**	**Remarks**
Cotton mercerizing	60	20-60	pH 12-14
Hot scouring and rinsing Bleaching of cotton and flax	5-6	60-150	pH 11-13 (grease)
Desizing of cloth (starch removal)	10-20	20-50	COD/BOD = 1.5

5.5.3. Textile finishing

This activity, which is usually very polluting, is made up of the following processes: bleaching, dyeing, printing and final finishing.

The amount of wastes varies widely depending on the combination of finishing treatments, and a comparison of amounts can be given:

-acrylic fibres:	35 m3.t^{-}1
-wool:	70 m3.t^{-1}
- cotton:	100 m3.t^{-1}
- sponge cloth:	200 m3.t^{-1}

A waste of 100 m^3 per tonne from the various manufacturing activities is the goal of the profession as regards environmental protection.

The pollution load depends upon:
- the type of fibres: natural or synthetic,
- the dyeing processes (jiggers, continuous dyeing, kiers), and printing process,
- the products used according to their solubility in water (see table 19).

With the pretreatment effluents, the wastes are more diluted and are typically characterized by the following values:
- pH: 4 to 12, most often basic; 4.5 for woolen knits; 11 for cotton,
- COD: 250 to 1,500 mg.l^{-1} (50 to 150 kg.t^{-1}),
- BOD_5: 80 to 500 mg.l^{-1}; COD/BOD_5 ratio usually between 3 and 5,
- colour: 500 to 2,000 Pt-Co units,
- SS: 30 to 400 mg.l^{-1} (sparse, fibre, flock, down), but may sometimes reach 1,000 mg.l^{-1} (in the case of cotton),
- Crvj: 1 to 4 mg.l^{-1} and S^{2-}: 0 to 50 mg.l^{-1},
- a rise in temperature with a planned reduction in volume.

5.5.4. Industrial laundries

Depending on their size, laundries can discharge high pollution loads which are composed mainly of washing products (sodium carbonate, tripolyphosphate, various soaps, biodegradable detergents, bleaches, chlorine derivatives).

The amount of wastewater in modern countercurrent washing units is 2m^3 per 100 kg of washing and corresponds to 1.5kg to 2kg of BOD_5.

The washing of jeans with pumice stone (1kg per kg) can entrain substantial discharge of SS.

Table 19. **Dyes and wastes in textile finishing.**

Products	Water-soluble	Water-insoluble
Minerals	Mineral acids Organic acids (acetic, citric, formic, tartric) Oxidants (NaC10, H_20_2, borates) Reducing agents	
Dyes	Acid (wools) Basic Leuco vat esters (indigosols) Direct* (cotton) Metal-bearing dyes (Ni, Co, Cr) Chrome dyes Reactive dyes*	Pigments and disperse dyes With sulphur* (pH < 8.5) Azoic dyes* + Naphthols Aniline black
Auxiliary textile products	Alginates (printing) C.M.C. (printing) Retarding agents Detergents	Gums Starch

(*) These dyes cause substantial water leaks that can exceed 20%. Direct dyes and reactive dyes are prepared in NaCI or Na_2S0_4 brines.

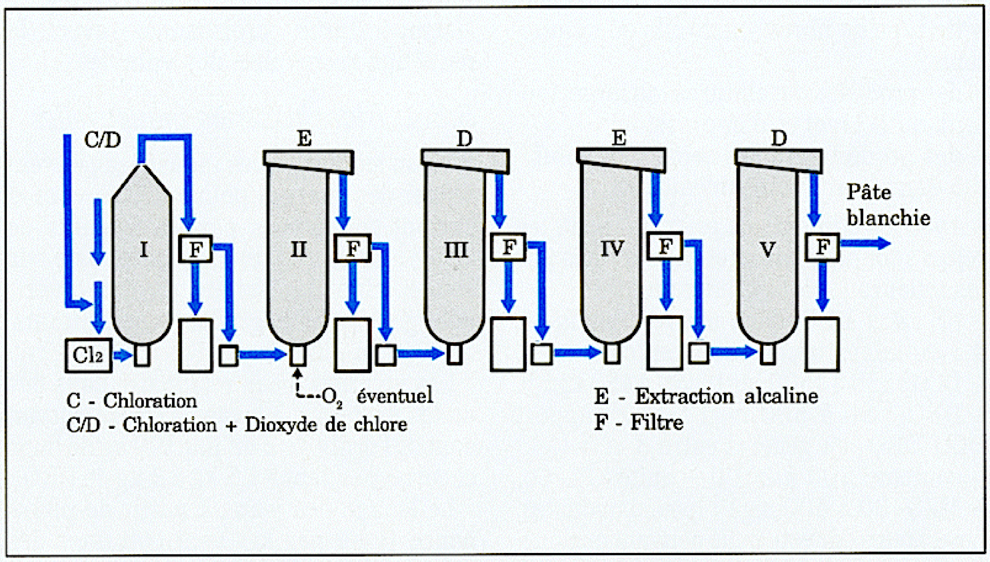


Figure 24. Séquences types de blanchiment.

Figure 24. Typical bleaching sequences

5.6.
PULP AND PAPER INDUSTRIES

These industries cover two types of manufacturing, that of paper pulp and that of paper. The effluents contain very different pollutants. Some companies can integrate the manufacture of both products.

5.6.1. Paper pulp factories

5.6.1.1. Production processes

The composition of wastewater depends on the manufacturing process and on the nature of the vegetable fibres used (wood, bagasse, straw). There are five broad process classes, each of which produces unbleached or, more frequently, bleached pulps. Bleaching (figure 24), which allows a more intensive attack on the lignin residues (mainly by alkaline dissolving of chlorolignin), makes a substantial contribution to pollution, as table 20 shows.

- **Chemical processes** are used to make pulp for fine paper (printing, writing).

The kraft process, based on alkaline cooking (NaOH, Na_2S) of wood dissolves 40 to 50% of the dry solids in the wood: this organic matter reappears in the form of cooking liquors (black liquors) and then of pulp wash waters. When a pulp of this kind is bleached, overall efficiency is reduced by about 10% and the bleaching process contributes considerably to the colour discharged by the effluents.

- **The bisulphite process** is based on acid cooking of wood (solubilization of lignin by Ca, Mg and NH4 bisulphites); these pulps are almost always bleached, overall efficiency reaching 50%.
- **Semichemical processes** combine chemical and mechanical action: the best known is the NSSC (Neutral Sulphite Semichemical) process, which has an efficiency of 75%.

Table 20. Pollution values per tonne of pulp.

Process	**Water consumption m^3 per t**	**BOD$_5$* kg per t**	**SS kg per t**	**Colour Pt-Co kg per t**
Mechanical	30-50	15-30	10-30	-
Bisulphite				
- unbleached	40-60	25-50	10-110	10
- bleached	50-100	40-80	20-50	75
Kraft				
- unbleached	40-60	8-20	10-20	20-50
- normally bleached	80-90	20-40**	10-40	100-240
- bleached with pure 02		10-20		
CTMP				
- bleached	10-30	30-60	10-20	-

Notes:

(*) The COD/BOD$_5$ ratio varies between 6 and 2.5 depending on the type of wood.

(**) Values based on a complete recovery of the black liquor. The alkaline extraction phase of bleaching contributes an excessive amount of COD and colour.

The mechanical and thermo-mechanical processes (TMP) of wood have a 90 to 95% efficiency and are used in the manufacture of pulp for newsprint.

The new CTMP process is used to manufacture pulp for writing and printing paper and has a high extraction efficiency (90%). This process uses less water but more energy and does not emit malodorous gases.

5.6.1.2. Wastewaters

Black liquors are usually treated separately (evaporation, incineration or recovery).

In a modern mill there are three sources of effluents:

- bleaching,
- washing and emptying,
- evaporation condensates.

The effluents from these mills are characterized by the following:

- high flow: from 30m^3 per tonne (mechanical pulp) and 150 m^3 per tonne (chemical pulp),
- high insoluble pollution (fibres and fibrils, CaC0^3, clays) characterized by a noteworthy content of non-settleable solids (about 10 to 30% SS),
- variable soluble pollution according to the processes:

- BOD$_5$: between 100 and 1,000 mg.l^{-1}.
- COD: between 300 and 4,000 mg.l^{-1} (biodegradability depends heavily on the type of wood: pines, deciduous trees).
- Colour: prominent and resistant to biological processes.

Table 20 shows normal values of pollution per tonne of finished product in a modern mill.

- **Black liquor evaporation condensates**

Black liquor evaporation condensates

which are sources of concentrated pollution, may be treated separately from the preceding effluents. They may make-up less than 10% of the volume of wastes while contributing 30 to 50% of BOD$_5$ These condensates may have the following characteristics

Characteristics		Bisulphite pulp	Kraft pulp
PH		1.8-2.2	8-9
COD	g.l^{-1}	4-10	4-7
BOD	g.l^{-1}	2-5	1-2
SO$_2$	g.1^{-1}	0.2-2	0.4-1
Acetate	g.l^{-1}	2.5-4	
Methanol	g.l^{-1}	0.2-1.2	
Formic acid	g.l^{-1}	0.15-0.5	

- **Discharge conditions**

In the pulp industry, purification standards are often expressed in relation

to the mass of material produced (see table 21).

It is also common to find standards relating to colour in which the efficiency of decolouration is most often cited.

In general, the removal of COD and of colour is interrelated and it is difficult to attain a high efficiency rate that is economically feasible.

Table 21. Paper and cardboard: French discharge standards for new mills (in kg per tonne). Technical instructions of January 3, 1989.

Composition of paper or cardboard	Without filler		With filler or coating mix	With filler and coating mix
	Criteria	Monthly	Monthly	Monthly
		Class 1	Class 2	Class 3
Over 90% new fibres	**SS** **BOD$_{5rw}$,** **COD$_{rw}$**	0.7 0.7 2.5	0.7 1 3	0.7 1.4 3
		Class 4	Class 5	Class 6
Over 90176 of recovered fibres	**SS** **BOD5$_{rw}$** **COD$_{rw}$**	0.7 1 3	0.7 1.4 4	0.7 1.8 4

Note: rw (raw water): measured in unclarified water sample. The maximum allowed daily discharge is twice the maximum monthly discharge.

5.6.2. Paper and cardboard mills

Manufacture: Paper is made from new pulp, waste papers from which the ink has or has not been removed, or rags.

These raw materials, whether separated or combined, are used to manufacture products ranging from fine paper to packaging paper and corrugated cardboard.

Depending on the quality desired, various additives and coatings may be introduced:

- mineral fillers: kaolin, $CaC0_3$, talc, TiO_2,
- organic fillers (starch, latex),
- dyes, aluminium sulphate, retention agents.

Deinking may be carried out by two means:

- by backwashing with a high flow of water,
- by mechanical flotation with a lower flow of water but with more reagents (caustic soda, sodium silicate, fatty acids, non-ionic detergents) and with the discharge of a very great amount of suspended solids.

When using waste papers, certain refuse such as staples, plastic, strings, also appears in the water to be treated.

These effluents are therefore characterized by varying amounts of pollution in the form of fibres and additives which are usually sparingly soluble.

Modern machines are generally equipped with two internal systems (see figure 25):

- a **primary system** (called "short") which allows for immediate reuse of fibrerich water drained from the table,
- a **secondary system**, which receives water from suction boxes, press rolls and rinsing sections, and is usually fitted with a device to recover fibres.

The **system** on the outside of the machine **(tertiary)** receives excess water from the secondary system as well as auxiliary water.

Water treatment, which takes place on this system, may be structured to recycle water or sludge, depending on the quality of the paper being produced. Recirculation may involve up to 100% of sludge and between 50 and 100% of water used in a mill using waste papers. The rate of recirculation achieved depends on the competence of the mill in producing paper and in treating water.

The COD of these effluents is usually two or three times higher than the BOD_5.

The concentration of dissolved organic pollution is especially high where waste papers are used in manufacturing.

Figure 25. Industrial effluents.

Table 22 shows the characteristics of pollution from "tertiary" systems.

Table 22. Pollution values per tonne of paper and cardboard.

Manufactured product	Water consumption m^3 per t	SS kg per t	BOD kg per t
Newsprint	20-30	8-20	2-4
Magazine paper	20-30	10-20	2-5
Printing/writing paper	30-50	12-25	3-6
Kraft packing paper	10-20	8-15	1-3
Flat cardboard (from new pulp)	20-30	2-8	2-5
Paper for corrugated cardboard	3-15	10-25	5-12
Fine and special papers	Very dependent on the type produced		

5.7.
PETROLEUM INDUSTRY

There are four groups of activities likely to produce specific effluents:

5.7.1. Petroleum production

Discharge from production is made up of produced water and drilling sludge. Offshore drilling imposes narrow location contingencies.

5.7.2. Transport of crude oil and refined products

At terminals, tanker ballast water must be treated as must sometimes tanker cleaning water.

5.7.3. Refineries

There are simple refineries and complex refineries which often have a fluid cracking unit which increases the volume of wastes and pollution. A small discharge of spent caustic soda translates into a substantial polluting flow (caustic soda, S^{2-}, RSH, phenols).

In these three groups, pollution comes chiefly from hydrocarbons (see table 23).

The proportion of dissolved organic pollution (oxygen compounds, phenols, aldehydes) increases with cracking whereas the increasing refining of heavy and sulphurous crude raises the discharge of sulphides.

5.7.4. Petrochemical industry

Three types of petrochemical complexes exist (see figure 26):

- **synthesis gas complexes**, based on steam reforming; this is at the development stage (includes the synthesis of NH_3 and methanol);

Table 23. Production and refining. The nature of the chief effluents.

Origin	**Volume of water** as % of processed petroleum	Hydrocarbons in mg.l^{-1}	Other pollutants
Production: oil-field produced water	0 - 600	200-1,000 following three-phase separator	NaCl, sands, clays
Drilling: residues and sludge			Salts, bentonite, lignosulphonates
Transport:			
- Ballast water	(25 to 30% of tanker capacity)	After storage average 50 - 80 paraffins-waxes	NaCl, sands
- Tanker cleaning water		500 - 1,000 Emulsions	Detergents Alkalinity
Refining:			
Desalter	5 - 6	50-150 light HC	NaCl, phenols, possibly S^{2-}
Fluid catalytic cracking (FCC)	6 - 10	100-150	S^{2-}, RSH, NH$_4^+$, phenols
Rainwater		Variable	Sands
Condensates from atmospheric distillation	2 - 2.5	50	Phenols, NH$_4^+$
Condensates from vacuum distillation	1 - 1.5	150	Phenols, NH$_4^+$
Other sources		Pollutants in g.l^{-1}	
Spent caustic soda from desulphurization			
FCC: phenolic caustic soda		Phenols: 10 – 60 RSH, S^{2-}: 0.3 - 10	
Merox steam cracking units: sulphurous caustic soda		S^{2-}: 10 - 40 RSH: 0.3 - 20 Phenols: 0.2 - 2	
Lubricating oils: Aromatic and non-paraffin extraction		Furfural Methyl ethyl ketone	

- **olefin complexes,** the best known, are based on the steam cracking of naphtha, gas oil or petroleum,
- **aromatic complexes,** based on catalytic reforming with BTX synthesis and their derivatives.

Polymers are usually produced in plants separate from those where the preceding complexes are processed except in the case of polyethylene and, on occasion, polypropylene.

The effluents are polluted by raw materials, solvents, catalysts and the polymers themselves in suspension or emulsified.

Large amounts of inorganic salts are discharged with:

- NaCI when chlorine compounds are synthesized (PVC and solvents),
- $CaCl_2$, in the case of propylene oxide as well as ethylene oxide,
- $(NH_4)_2SO_4$, in the case of caprolactam and acrylates.

Discharges of $AIC1_3$ corresponding to alkylation reactions occurring during refining (petrols) and during the production of ethylbenzene and cumene (with H_3P0_4 acidity).

Table 24 shows the nature of the chief organic pollutants from various processes.

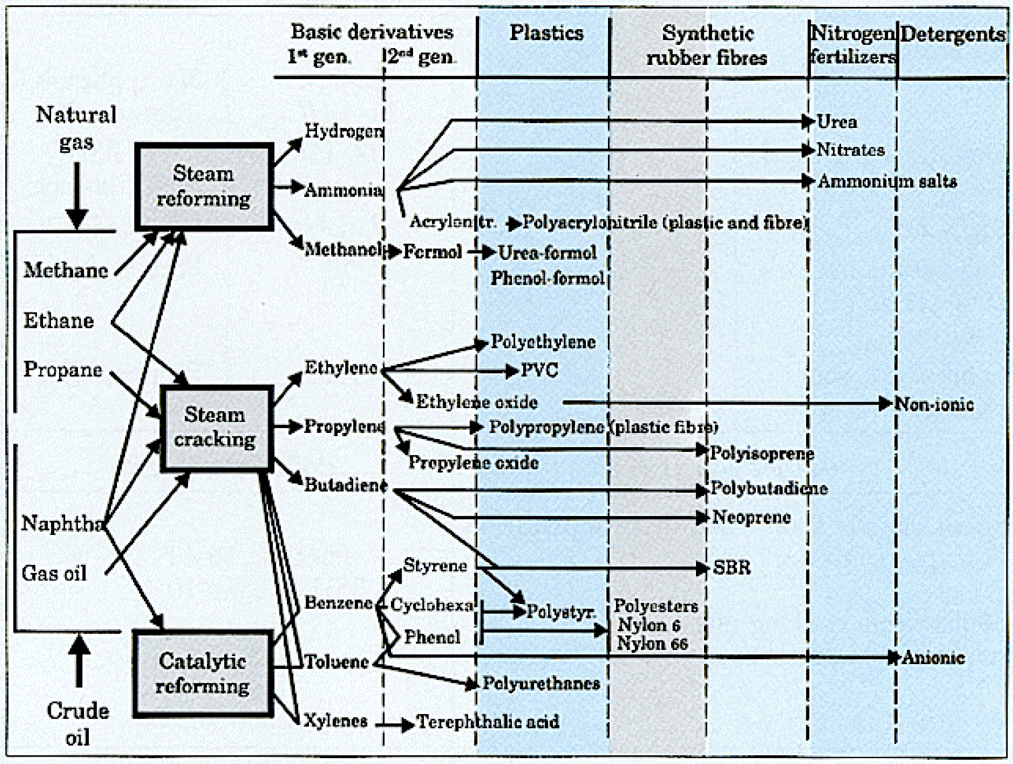


Figure 26. Classification of petrochemical production (document from Institut Français du Pétrole).

Figure 26. Classification of petrochemical production (document from Institut Français du Pétrole).

Table 24. Chief petrochemical products and corresponding pollutants.

	Product/process	Dissolved organic pollution	Other pollution
Steam cracking	Ethylene, propylene, butadiene	Phenols, organic acids	S^{2-}, RSH, hydrocarbons
Chemistry of synthesis gas	Methanol (steam reforming of naphtha and partial oxidation)	Methanol, heavy alcohols	
	Urea	$CO(NH_2)_2(CONH_2)_2NH$	Urea 1 to 10 $g.l^{-1}$ NH_4OH 0.1 to 0.5 $g.l^{-1}$
	Treatment of olefin cuts C4 and C5		
	MTBE (isobutene etherification)	Methanol, isobutene	
	MEC (butene 1 hydration)	Butanol	Sulphuric acid, catalysts
Oxidized or chlorinated by-products	Ethylene oxide (direct oxidation of ethylene)	Ethylene glycol, acetaldehyde, CO_2, hydrocarbons	Hydrocarbons
	Propylene oxide (chlorohydrin)	Dichloropropane, di-isopropylic ether	Alkaline water, $CaCl_2$, $CaCO_3$ sludge
	Tertiary butanol TBA	Propylene oxide, isobutane, acetone	
	Acetaldehyde (ethylene oxidation)	Acetaldehyde, acetic acid, oxalate	Acidic water
	Acetic acid (oxidation of acetaldehyde, methanol, Co)	Formic acid, acetates, acetone	Acidic water, iodides, rhodium
	Phenol (cumene oxidation)	Benzene, cumene	Bentonites, $AlCl_3$, hydrocarbons
Vinyl monomers	Vinyl acetate (from acetylene)	Acetaldehyde, acetone, acrolein, $FeCl_3$	
	Vinyl chloride (ethylene chlorination)	Dichloroethane	HCl, NaCl, hydrocarbons
	Acrylic acid, acrylates, metacrylates (propylene oxidation)	Acetic acid, acrolein	Catalysts, $(NH_4)_2SO_4$
	Acrylonitrile (propylene ammoxidation)	CN^-, acetonitrile	Catalysts, $(NH_4)_2SO_4$

Table 24. (Cont.)

	Product	Main organic pollutants	Other pollution
Vinyl monomers	Caprolactam (nylon 6) via hydroxylamine	Cyclohexane, lactam amine, hydroxylamine	$(NH_4)_2SO_4$, mainly acidic
	Adipic acid	Cyclohexane, benzene	Nitrates, NaOH
	Terephthalic acid (propylene oxidation)	Acetic acid, aromatic acids, xylene	Catalysts
	Polyethers Polyols	Polyethylene glycol Polypropylene glycol	
Monomers Elastomers	Butadiene (butane dehydrogenation)	Olefinic hydrocarbons	
	Neoprene, polychloroprene	Chlorinated derivatives	
	Styrene (ethylbenzene dehydrogenation)	Benzene, ethylbenzene	$AlCl_3$, oils, diatoms
Polymers and resins	Polyesters: – Fibres – Resins	Terephthalic acid, ethylene glycol, Adipic and maleic acids, ethylene glycol	Mainly acidic
	Polyethylene: – LDPE – HDPE		Oils, parasites, PE dust, catalysts
	Polypropylene (dry method)	Hexane, non-ionic detergents	Slight acidity, Al^{3+}, Ti^{4+}, dust/pigments
	Polystyrene	Styrene	Strong acidity, NaCl, H_2PO_4, PS dust, detergents
	PVC	Methanol, PV acetate	Strong acidity, polyvinylic acid, very fine PVC particles
	Rubbers: – SBR – Polybutadiene	Styrene and butadiene Acrylonitrile butadiene, oxygenated compounds	Soaps, catalysts, Al^{3+}, coagulated latex, catalysts, Ti^{4+}, NH_4^+, latex
	Epoxy resins	Epichlorohydrin, aromatic phenols	
	Acrylic resins	Dimethyl metacrylates	CN^-
	Polyurethane resins	Di-isocyanates and etherpolyols, polyesters-polyols	
	Phenolic resins	Acetaldehyde, formaldehyde, phenols	H_2SO_4, non-ionic detergents

5.8.
IRON AND STEEL INDUSTRY

There are four groups of activities: some (coking, pickling) produce effluents with a high level of dissolved pollution and are thus not recylable after treatment (table 25); others (rolling and gas scrubbing) produce effluents with a high level of suspended pollution (oxides, SS, insoluble hydrocarbons) and are almost entirely recylable (table 26).

5.8.1. Coking

This generates ammonia liquors which come from coal moisture (8%) and from formation water (4%). These are weak ammonia liquors that are rich in phenols. Gas scrubbing, itself, generates strong ammonia liquors which are rich in free NH4.

5.8.2. Pickling

Pickling produces rinse water with a high content of Fe^{2+} and H_2S0_4 if it is sulphuric. If it is hydrochloric, thermal regeneration of HCI can eliminate a large part of the acid and dissolved iron wastes. The lubrication of high reduction rate stands produces alkaline wastewater that is rich in animal or vegetable fats. The same holds true for electrolytic degreasing before tinning. The spraying of low reduction rate stands is accomplished with aqueous fluids (usually, conventional soluble oils) in which a small fraction will be treated in the blowdown.

5.8.3. Gas scrubbing

This is used in balling, agglomeration, blast furnaces, direct reduction and steel works. The pollution consists mainly of suspended solids except in the case of some direct reduction procedures and of slag granulation. In almost all mills, the systems are of the open recirculating type and small amounts of blowdown remain to be treated.

5.8.4. Rolling

From the continuous casting of steel and the scarfing of blooms to product finishing (hot strip mills, section mills, fourhigh mills, tube rolling mills), water plays a role in a whole series of mechanical operations (descaling, granulation, spraying). It entrains oxides (scale) or slag which can be joined by small quantities of hydrocarbons from the lubrication of mill housings or the steel.

The presence of dissolved pollution is unusual (hydraulic fluid leaks from continuous casting). All the systems may therefore be of the open recirculating type with a small blowdown to be treated.

In an iron and steel complex well equipped with a recirculation system, make-up water may equal 3 to 6 m^3 of water per tonne of steel, based on an overall concentration factor of 3 to 4, and the total volume of effluents from open recirculating systems is then 1 to 1.5 m^3 per tonne of steel.

Table 25. Effluents from iron and steel mills

(not recylable by simple and economical means).

	Workshop	Volume l per t coke	Main pollutants
Coking	Weak ammonia liquors* (WAL)	110 to 160	Tars Phenol 1-4 g.l^{-1} Free NH_4^+ 2-6 g.l^{-1} Bound NH_4^+ 0.5-4 g.l^{-1} H_2S, CN^-, SCN
	Strong ammonia liquors (SAL)	30 to 60	Free NH_4^+ 8-14 g.l^{-1} HCO_3^- 1-4 g.l^{-1} S^{2-}
	By-products and final condensation blowdown workshops	10 to 100	Phenol 0-50 mg.l^{-1} CN^- 100-400 mg.l^{-1}
	Dust removal blowdown from coal charging	50 to 300	SS
Cold rolling**		m^3 per t steel	
	H_2SO_4 pickling HCl pickling	2 0.1	Fe^{2+} 50-300 mg.l^{-1}
	High reduction rate rolling	1	SS 0.2 g.l^{-1} Oils 0.4-0.6 g.l^{-1} COD 0.7-1.2 g.l^{-1}
	Electrolytic degreasing before tinning	1.5 to 2	SS 0.5-1 g.l^{-1} Oils 0.1-0.2 g.l^{-1} COD 0.3-1 g.l^{-1} Silicates

(*) The WAL salinity depends on how rich they are in Cl^-: nearly non-existent in South African coal and concentrated in Saar-Lorraine coal.

(**) In the first case, the water is recylable.

As a reminder, electrogalvanizing, chromium-plating, tinning (see page 110).

Table 26. Blowdown of systems in iron and steel mills where the effluents are recirculated.

Workshop	**Origin**	**Specific volume** (1 per t)	**Pollutants** (mg-1-1)
1. Gas scrubbing			
Blast furnaces	Blowdown of the gas scrubbing system or sludge filtrate	50 - 300	Dust 200-1,000 NH_4^+ 0-500 CN- 0-20 Zn^{2+}, Pb^{2+} 5-20
	Slag granulation	200 - 500	S^{2-} 0-600 S_203^{2-} 100-400 SiO_2 - slag dust
Direct reduction	Gas scrubbing and cooling	500	NH_4HC0_3 $KHC0_3$ $S0_2^{2-}/S0_3^{2}$- 500-5,000 SS, oxides
Steel production with oxygen	System blowdown or sludge filtrate	20 - 100	$CaC0_3$ $Ca(OH)_2$ or K_2C0_3 Oxides 1,000-5,000
2. Rolling and granulation			
Continuous casting	System blowdown or filter wash water	50 - 100	Scales - HC - Hydraulic fluid, F^-
Bloom scarfing		20 - 50	Scales - slag
Wire mills		100 - 200	Scales - HC
Tube rolling mills		50 - 100	Scales

5.9.
AUTOMOBILE AND AERO NAUTICAL INDUSTRY

Depending upon the finished manufactured product, the wastewater is from:

- blowdown of the aqueous cutting fluids,
- pickling and degreasing effluents,
- demineralization eluates,
- blowdown from washing machines,
- blowdown from paint spray booths,
- blowdown from cooling systems,
- effluents in general (sanitary and shop floor washing)

Moreover, machining centres, painting workshops and washing equipment have closed recirculating systems which can convey up to 500 to 1,000 $m^3.h^{-1}$ of a liquid the quality of which must be kept constant throughout the whole or a part of the flow. The figure (opposite) describes the various stages concerned.

5.10.
SURFACE TREATMENT INDUSTRIES

- **Origin and nature of the wastes**

Surface treatment is applied mainly to metal parts, but also to certain synthetic materials. It involves the following

- a preliminary preparation of the surface (degreasing, pickling),
- a coating by means of electroplating,
- a coating by chemical means.

These procedures must be followed by rinsing.

The effluents must be separated into three categories (figure 28):

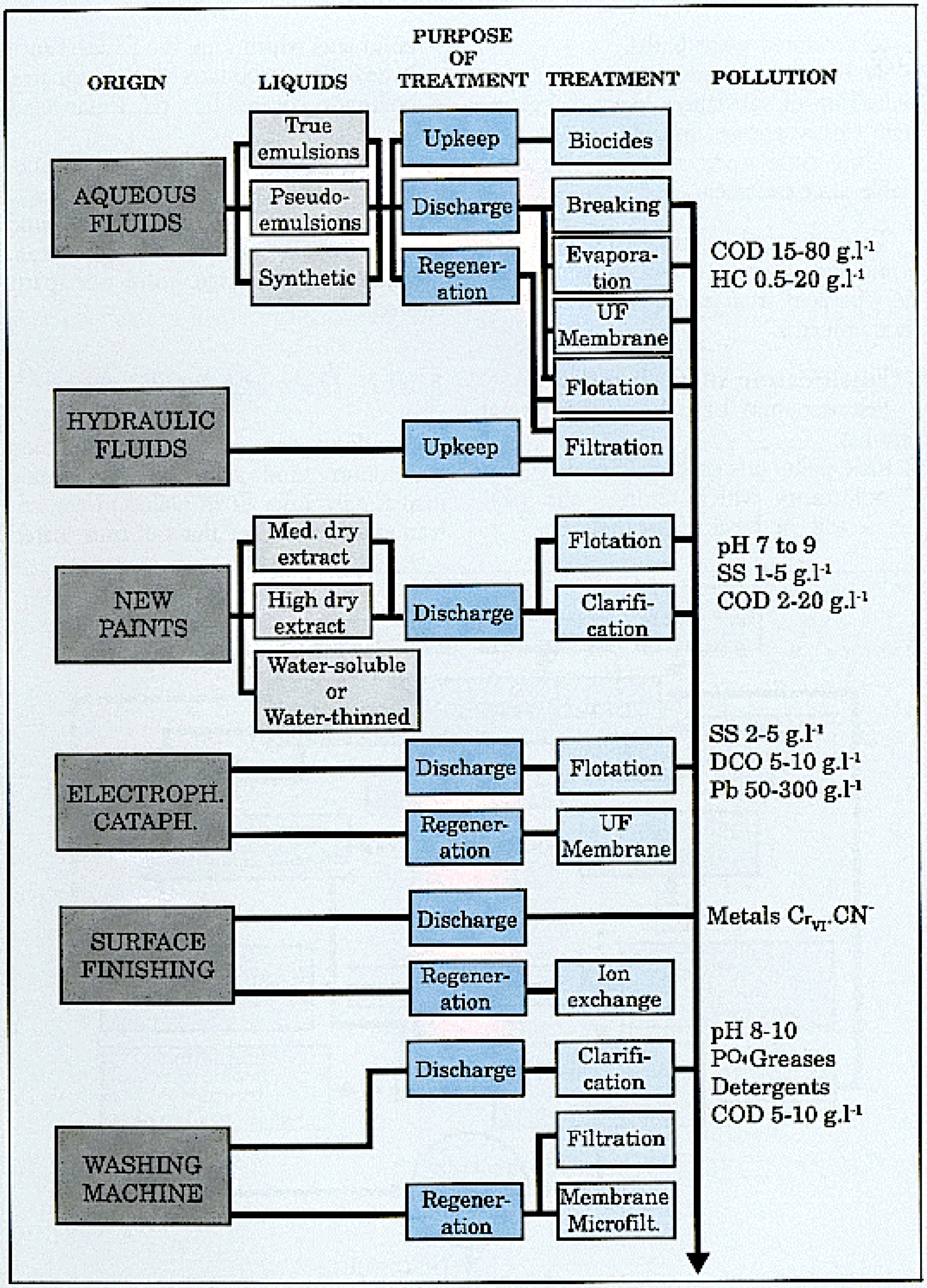


Figure 27. Organization of baths and wastewaters in the automobile industry.

Figure 27. Organization of baths and wastewaters in the automobile industry.

- concentrated spent baths,
- wash waters containing an average concentration of substances likely to precipitate (soaps, greases, metallic salts),
- dilute rinse water that may be recyclable after treatment.

To secure and facilitate treatment, the acidic and chromate-laden effluents must be separated from the alkaline and cyanide effluents.

- **Classification of pollutants**

Pollution may be divided into several families:

- toxic pollutants such as CN^-, Cr_{VI}, F^-, - pollutants which change the pH, i.e., acidic or basic substances,
- pollutants which raise the SS level such as hydroxides, carbonates and phosphates,
-pollutants covered by a particular regulation, S^{2-}, Fe^{2+},
- organic pollutants (EDTA, etc.), especially from degreasing.

All the constituents of baths are found in the rinse water which may also contain metallic ions dissolved from the parts treated.

5.10.1. Discharge conditions

Standards vary greatly depending on the country and are rapidly becoming increasingly strict as to pollution concentration as well as the flows of rinse water.

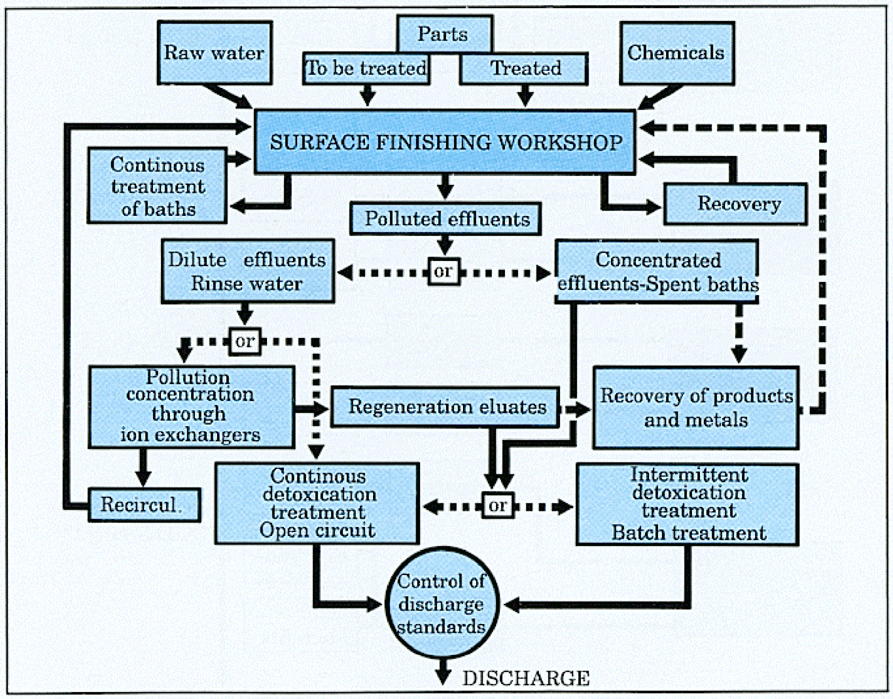


Figure 28. Effluents circuit in surface treatment.

In France, for example (decree of November 8, 1985):

- Effluent volume limited to 81 per mz of treated surface for each fraction of rinsing. - Metals: Zn + Cu + Ni + Al + Fe + Cr + Cd + Pb + Sn < 15 mg.l^{-1}. In particular, the following thresholds should not be exceeded (mg.l^{-1}):

CR_{VI}	0.1	Zn	5.0
Cr_{III}	3.0	Fe	5.0
Cd	0.2	Al	5.0
Ni	5.0	Pb	1.0
Cu	2.0	Sn	2.0

Other metals and metalloids, likely to be used in workshops (zirconium, vanadium, molybdene, silver, cobalt, magnesium, manganese, titanium, beryllium, silicon, etc.) may be subject to special limits.

Notes

(1) In the case of workshops where more than five metals are used (among which iron and aluminium), the 15 mg.l^{-1} limit may, in certain cases, be raised to 20 mg.l^{-1}.

(2) Cadmium presents a special case. Regulations limit not only the concentration in cadmium wastes but also the mass flow: less than 0.3 g of Cd discharged per kg of Cd used.

(3) Thresholds for other pollutants in mg.$^{-l}$

SS	30	P	10
CN	0.1	COD	150
F	15	Total Hydrocarbons : 5	
Nitrites	1		

(4) Certain arrangements can be made to meet the standards relating to F, PO_4^{2-} and COD. Each case is taken individually to determine which method is the best one available and the most economically feasible.

Pollution prevention and product recycling is essential if detoxication standards are to be met economically.

5.10.2. Prevention

The aim is to reduce the emission of pollutants at the workshop level by:

- reducing the bath-to-bath carryover (assembly line set-up, workpiece mountings, optimizing drip times),
- modifying the characteristics of baths used.

5.10.3. Reclamation

- **Water**

Usually, an effort is made to recover and reuse, if possible, a certain amount of water that is commonly lost.

The first aim is the rationalization of water use in the workshops. It can be shown that for a given operation with equal rinsing and manufacturing quality, there are rinsing structures which allow substantial savings of water by:

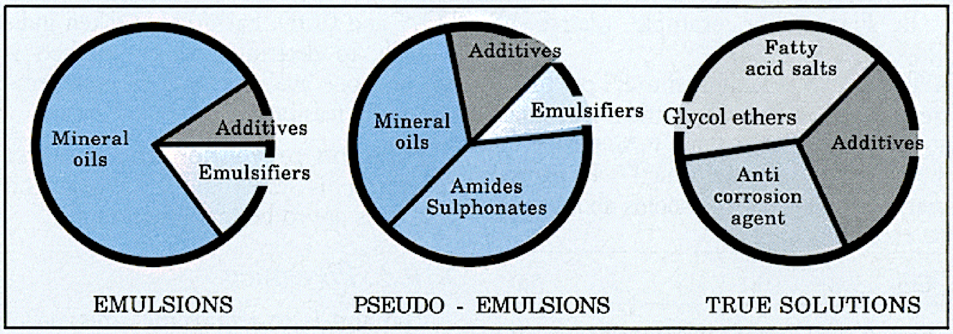
- static or recycling rinsing facilities,
- cascade rinsing facilities, possibly recirculated on ion exchangers.

- **Raw materials**

It may be possible to recover them "in situ" by:

- membrane treatment (salts of Ni, Cu or other metals),
- ion exchange (chromium salts, acid from pickling baths),
- electrolysis (Cu, Zn, Cd, Ag).

This system, which is under development, is the best from the point of view, of cost and the environment



The three families of aqueous cutting fluids.

The three families of aqueous cutting fluids.

5.11.

AQUEOUS CUTTING FLUIDS

They are involved in the mechanical, automobile and aeronautical industries and in rolling mills.

The discharge of these fluids which are sometimes called "soluble oils" or "cutting oils" and contain 90 to 97% water and a high COD level, presents a problem for treatment because they may contain various organic compounds that are neither biodegradable nor can be flocculated. Therefore, it is important to distinguish three product groups (see above and table 27).

These fluids are circulated by power units with capacities of 10 to 500 m .h^{-1}. The following types of pollution cause their deterioration:

- metallic dust and oxides,
- foreign oils or parasites,
- oxidized or polymerized organic matter,
- biological sludge and organic acid from fermentation.

They must be regenerated (SS and foreign oil reduction) and stabilized in a closed system: the volume discharged for treatment can vary from some in 3.h^{-1} to some m3.d^{-1}.

Table 27. Characteristics of aqueous cutting fluids.

Type	Composition	Solute content	Optical density	COD g.l^{-1}
True emulsions	Dispersed mineral oils + emulsifiers (15-20% of oils)	5-15%	20-150	20-100
Semisynthetic fluids or semi-emulsions	Mineral oils, emulsifiers, non-ionic detergents, sulphonates, fatty acid amides	3-6%	1-20	40-50
Synthetic fluids or true solutions	Salts of short chain fatty acids and acrylsulphamido-carboxyl, glycol polyethers	3%	< 1	40-50
Possible common additives: . Anti-corrosion and anti-foam agents . Bactericides and fungicides, dyes				

5.12.
ENERGY

Table 28. Main effluents connected to energy production.

Energy	Origin of wastes	Pollution
Thermal power stations	Fuel storage	Hydrocarbons, SS
	Cleaning of air heaters Cleaning of boilers	Oxidizing alkaline baths, Fe, Vd, Ni, Cu Citric acid, NaF or H_2SO^{4-} NH_4F
	Ash removal - Transport of fly-ash and slag	SS, Ca(OH)z or KOH alkalinity, rare S02 acidity, Ca(OH)2
Flue gas scrubbing	Desulphurization: GSE NOx NOx removal	HCI + H_2S0_4 acidity - heavy metals, H_2S0_3, gypsum, HCOOH, NH_4^+ , strong salinity
Coal gasification	Formation water and GSE: 1st gasifier generation 2nd generation	Phenols, NH_4^+, CN^-, SCN, acids, tars NH_4^+, CN^-, SCN, HCOOH, hydantoins
Coal mines	Washing plants	SS 10 - 100 g.l-1
Incineration of household refuse	GSE	HCI, CI^-, $S0_2^{2-}$ - heavy metals
PWR nuclear power plants	Wash-houses, floor washing, laboratories Sampling Steam generator blowdown (APG)	Radioactivity < 10^{-3} am^{-3} to be reduced to 2.10^{-5} $Ci.m^{-3}$ Salts, SS APG: very accidental radioactivity
Reprocessing of irradiated fuels	Effluents that may be treated by chemical precipitation or adsorption: Hazardous effluents or with little actrvrry Moderately active effluents Fuel storage pools	Colloids, activity < 10^{-5} $Ci.m^{-3}$ 10^{-5} to I $Cr.m^{-3}$: ^{90}Sr, ^{137}Cs, Salts 10^{-3} $Ci.m^{-3}$: few salts

5.13

METALLURGY AND HYDROMETALLURGY

Table 29. Principal effluents from metallurgy and hydrometallurgy.

Industry	Origin of wastes	Pollution
Aluminium	GSE from cryolithe electrolysis Crushing of lining Manufacture of prebaked anodes Cooling of castings in ingot moulds	$S0_2$ acidity, HF, C dust and cryolithe F^- and CN^-, C dust Acidity, Al^{3+}, F^-, tars Kaolin and grease
Gold (hydro-metallurgy)	Cyanide process Thiourea process	NaOH, CN- H_2S0_4, Fe^{2+}, thiourea
Uranium (hydrometallurgy)	Water pumped out from mines	Water is usually acidic, rich in sulphates and dissolved metals (Fe, Ur). Sometimes radioactive: 50 to 100 picocuries (Radium-226)
	Extraction by ion exchange or solvents	Refined product slightly acidic (SO_4^{2-}) and radioactive (radium), solvents
	Sterile sludge facility	SS
Zinc (metallurgy)	Roasting and reduction: GSE	Water is slightly acidic - Zn, Pb, Cd, sometimes Hg and Se.

In these types of industry, presence of pumped out water which has been acidified and sulphated by biological oxidation of the sulphides present.

5.14.
GENERAL CHEMISTRY

Table 30. General chemistry effluents.

Industry	Origin of wastes	Pollution
Chlorine industry (Hg cells)	Gas scrubbing and floor washing Brine losses	Essentially Hg pollution (metal and ions); possible Hg recirculation
NH_3	Condensates 1 m^3 per tonne	1-4 $g.l^{-1}$ NH_4HC0_3, 0.2-1 $g.l^{-1}$ methanol
NH_4N0_3 synthesis	Basic condensates 0.5 m^3 per tonne Workshop washing	2-3 $g.l^{-1}$ NH_4N0_3, 0.2-0.8 $g.l^{-1}$ NH_40H NH_4N0_3, SS
Urea	Condensates 0.6 m^3 per tonne Floor washing	Without hydrolyser, concentration of from 0.1 to 0.5 $g.l^{-1}$ NH_4, 0.5-2 $g.l^{-1}$ urea
Super-phosphates	GSE	Very acidic water: H_2S0_4, SiF_6H_2, HF, H_3P0_4, gypsum of High quantity sludge SiO_2, CaF_2 and $Ca_3(PO_4)_2$
H_3P0_4	GSE	
Pharmaceutical industry	Wash water	Often high dissolved organic pollution. Possible antibiotics and biocides
Dyes	Manufacture	D.N.T., D.N.B., chlorinated solvents, nitrophenol, nitro-aniline
Detergents Washing powders	Manufacture	ABS - LAS - tripolyphosphates, borates, sulphated or etoxylated fatty alcohols, SO_4^{2-}

5.15.
OTHER INDUSTRIES

Table 31. Effluents from various other industries.

Industry	Origin of wastes	Pollution
Glass- and mirrormaking	Glass frosting, decoration and shape Sawing, polishing, finishing	High acidity: HF, ammonium bifluoride Corundum, pumice and emery powders, cerium oxide, garnet
Glass fibres	Fibre manufacture, oiling	High SS, BOD and COD due to dextrin, gelatin, silicones, miscellaneous acetates, phenolic resins
Cosmetics	Packaging	High levels of grease, anionic and non-ionic detergents. Dissolved, readily biodegradable COD
Abrasives on supports	Preparation of adhesive mixtures	Phenol-formaldehyde and urea-formaldehyde resins, gelatins, starch, epoxy resins and solvents High COD, average BOD and SS
Ceramics	Drying of ware Floor washing	High SS level Possible crystallization reactions
Fibreboard		Wood fibres High dissolved COD
Glues and adhesives		Vinyl copolymers Glues and gums, high COD, emulsifiers Possible compaction
Tyres	Body manufacturing	Iron and copper Lubricating oils, soluble oils Pickling effluents
	Rubber synthesis Tyre manufacture	Soaps and metallic salts, solvents Hydraulic fluids, greases

Table 31 (cont.). Effluents from various other industries.

Industry	Origin of wastes	Pollution
Powders and explosives	Manufacture of nitro compounds	High sulphuric and nitric acidity; colouration and non-biodegradable COD
	Prilling and impregnation of simple-base powders	Ethyl acetate, nitrocellulose, nitroglycerin, Na_2S0_4, glues, plasticizers. Relatively biodegradable effluents
Aircraft and airport washing	Cleaning of painted surfaces	High concentrations of COD and detergents, silicates, phosphates, chromic acid, fatty oils, phenols. Kerosene

6. SLUDGE

The great majority of solid pollutants, and the converted substances they produce, removed during the liquid phase of all types of water treatment, finally collect as suspensions which can vary in concentration and are known as "sludge."

The characteristic common to all these sludges is that they are still very liquid and are of little or no commercial value. Some sludge is chemically inert, but that originating from biological treatment processes is fermentable and often has an offensive smell.

All organic sludges require a special form of treatment, whether they are recycled, reused or discharged into the natural environment. This is more and more frequently the same case for sludges which are essentially mineralized.

Urbanization and the protection of the environment are making it more and more difficult to return sludge as is, without a previous conditioning treatment, back to the natural environment. Sludge treatment has inevitably become a corrolary of water treatment, and, as such, calls for technical and financial input that sometimes exceeds that needed for water treatment.

6.1. CLASSIFICATION

Table 32 endeavours to classify the various types of sludges according to their origin and to their composition.

It is essential to classify a sludge in order to select the treatment method applicable to it, and to forecast the performance of the equipment to be used.

Loading sludge on a truck

The composition of a sludge depends both on the nature of the initial pollution of the water and the treatment processes to which that water has been submitted, whether physical, physical-chemical or biological.

- **Hydrophilic organic sludge:** this is one of the largest categories. The difficulties encountered in dewatering this sludge are due to the presence of a large proportion of hydrophilic colloids. All types of sludge resulting from the biological treatment of wastewater and whose volatile solids content may be as much as 90% of the total dry solids content (wastewater from the agrifood industry, organic chemical industry, for example) are included in this category.

Hydrophilic inorganic sludge: this sludge contains metal hydroxides formed during the physical-chemical treatment process as a result of the precipitation of metallic ions present in the raw water (Al, Fe, Zn, Cr) or due to the use of inorganic flocculants (ferrous or ferric salts, aluminium salts).

- **Oily sludge:** this is characterized by the presence in the effluents of small quantities of mineral (or animal) oils or fats. These oils are in emulsion form or adsorbed onto the hydrophilic or hydrophobic sludge particles. A proportion of biological sludge may also be present in cases of final activated sludge treatment (e.g., treatment of refinery effluents).
- **Hydrophobic inorganic sludge:** this sludge is characterized by a preponderant amount of particulate matter with a low amount of bound water (sand, silt, slag, rolling mill scale, crystallized salts, etc.).
- **Hydrophilic-hydrophobic inorganic sludge:** this sludge comprises mainly hydrophobic substances, but contains a sufficient amount of hydrophilic substances so that when sludge is dewatered they exert a preponderantly negative influence. These hydrophilic substances are often metallic hydroxides (coagulants).
- **Fibrous sludge:** this sludge is generally easy to dewater, except when the intensive recovery of fibres makes it hydrophilic because of the presence of hydroxides or biological sludge.

Table 32. Classification of sludge.

Main characteristic of sludge	Origin-Industry	Water treatment	Constituents
Hydrophilic organic	1. MWW	1. All biological or physical-chemical treatments	Predominant organic matter: OM/DS: 40 to 90% - Protein substances often very fermentable - Vegetable or animal waste - Animal and sometimes mineral oils and greases - Hydrophilic hydroxides (Al, Fe) in physical-chemical treatment - Hydrocarbons (petrochemical industry)
	2. WW from agrifood industry: . Breweries . Slaughterhouses . Potato processing . Dairies . Canneries . Stock rearing (piggery manure)	2. Settling and/or biological purification among which: extended aeration, aerobic stabilization or anaerobic digestion	
	3. WW from textile industry, organic chemical industry	3. Physical-chemical (flocculation-settling) and possibly biological	
	4. Any polishing biological treatment	4. Biological	
Hydrophilic oily	1. WW from refineries	- Oil removal	- Mineral oils and greases
	2. WW from engineering works (soluble oils)	- Flocculation-settling-flotation	- Hydrocarbons - Hydroxides (Al, Fe)
	3. WW from cold rolling mills	- Biological treatment (refineries)	- Biological OM (possibly)
Hydrophobic oily	WW from steel rolling mills	- Settling	- Dense and readily settleable DS (scale, Fe oxides) - Considerable amounts of mineral oil and grease
Hydrophilic inorganic	1. Rivers with few SS (dams and wells)	1. Clarification (flocculation-settling) Chemical iron removal	1. Predominantly hydrophilic sludge with metal hydroxides (Fe, Al) reaching 60% over DS. OM content varies with algae and plankton content and can surpass 30% over stagnant water

Table 32. Classification of sludge (cont.).

Main characteristic of sludge	Origin-Industry	Water treatment	Constituents
Hydrophilic inorganic	2. Rivers with average SS (30-70 mg.l^{-1})	2. Clarification (flocculation-settling)	2. Hydroxide level of 20 to 30% + possibly activated carbon powder (10-15%)
	3. Rivers in spate and rivers with input of clays or silt with hydrophobic tendency	3. Clarification	3. Hydroxides (15-20%) Clays or silt (25-60%)
	4. Rivers and well water	4. Partial carbonate removal	4. $CaCO_3$ (50-55%) Fe and Al hydroxides (20-30%) OM (10-20%)
	5. WW from surface treatment: . pickling . anodizing . electroplating . painting	5. Neutralization + flocculation-settling Detoxication (CN^-, Cr_{VI}) + flocculation-settling	
	6. WW from inorganic chemical industry	6. Clarification - Neutralization (flocculation-settling) + possible biological treatment	
	7. WW from colouring agents, dyeworks	7. id. 6	7. Mineral + organic
	8. WW from tanneries	8. id. 6	8. Mineral + organic + animal fats and OM
	9. Final treatment of WW for recirculation	9. id. 6	
Hydrophobic inorganic	1. Well water	1. Biological removal of iron and manganese	1. Fe_2O_3 and MnO_2
	2. Rivers and well water	2. Carbonate removal	2. $CaCO_3$ (60-90%) Fe and Al hydroxides (5-15%) OM < 10%
	3. Iron and steel industry (steelworks, foundries)	3. Settling	3.4.5. Low content of metallic hydroxides. Low OM content
	4. Coal washing	4. Settling	
	5. Flue gas scrubbing (refuse incineration)	5. Neutralization Settling	

Table 32. Classification of sludge (cont.).

Main characteristic of sludge	Origin-Industry	Water treatment	Constituents
Fibrous	1. WW from paper mills	1. Flocculation 1.a) Settling (or flotation) alone	1.a) Fibre content variable from 20 to 80% over DS + (Al) hydroxides. Concentration: 3-5% if fibre rate > 60% DS, 10-12% if fibre rate < 30% DS.
		1.b) With biological treatment	1.b) Physical-chemical sludge/biological sludge: 75%/25% to 85%/15%
	2. WW from paper pulp mills	2.a) Flocculation Settling	2.a) Primary sludge with high fibre content (and sometimes lime or $CaCO_3$). DS level of 4 to 6%
		2.b) With biological treatment	2.b) If excess sludge is returned to the primary settling tank. Concentration of thickened sludge: 3-5% DS. Phys.chem/biol. # 50%/50%
		2.c) Sludge from deinking Flotation	2.c) 40-60% fibres Various types of fillers
	3. WW from cardboard mills	If no biological treatment	Total recirculation, often in factory

Notes:

It should be noted that in the treatment of MWW, fresh sludge has a 90% concentration of pathogenic germs and contains:

- enterobacteria 10^7 to 10^{10} per ml
- salmonella 10 to 10^7 per ml
- parasite eggs 10 to 10^7 per ml as well as amoebae and viruses.

6.2.

THE NATURE OF SLUDGE

6 2.1. Factors characterizing the nature of sludge

(A) Dry solids content (DS):

This is generally expressed in grammes per litre or as a percentage by weight and is determined by drying at 105°C to a constant weight. In the case of liquid sludge, it generally approximates the suspended solids content (SS), determined by filtration or centrifugation.

(B) Volatile solids content (VS):

This is expressed as a percentage by weight of the dry solids content and is determined by gasification in a furnace at 550-600°C.

In the case of hydrophilic organic sludge in particular, this is often close to the organic matter content and is characteristic of the nitrogenous matter content.

(C) Weight of element contents

(especially in the case of organic sludge):

- C and H to assess the degree of stabilization or to deduce the net calorific value,
- N and P to evaluate the agricultural value of the sludge,
- other contents (e.g., heavy metals). In the case of inorganic sludge, the Fe, Mg,

Al, Cr, calcium salts (carbonates and sulphates), and silica contents are often useful.

(D) Composition of the interstitial

water:

- dissolved substances,
- M alk., P alk.,
- COD, BOD_5, pH, etc.

6 2.2. Factors characterizing the structure of sludge

(A) Apparent viscosity in relation to the rheological behaviour:

Sludge suspensions are non-Newtonian fluids: the value found for viscosity is quite relative and depends on the shearing stress applied.

In the case of some sludges, and with certain precautions, a viscosity known as the Bingham viscosity may be deduced for a characteristic stress TB (see figure 29).

Viscosity may be considered as a measurement of the intensity of the interparticulate forces. It also permits evaluation of the thixotropic nature of a sludge (the capacity of a sludge to compact when motionless and to return to the fluid state when only lightly stirred). This property is very useful for assessing the possibility of collecting, transporting and pumping sludge.

Figure 29. Determination of the Bingham viscosity.

(B) Particle size distribution.

(C) Nature of the water contained in the sludge:

This water is the sum of:

- free water which can be fairly easily removed,
- bound water comprising: colloidal hydration water, cellular and chemically bound water.

The release of bound water requires considerable energy; for instance, cellular water, in particular, is only separable by powerful heat treatment (heat conditioning, drying or incineration).

The proportion of free water and bound water is therefore decisive in the suitability of a sludge for dewatering. An approximate value can be obtained by **thermogravimetry,** i.e., by plotting the water weight loss curve of a thickened sludge sample at constant temperature under definite handling conditions (figure 30). The point of inflexion of the curve may be determined by drawing the curve V = f(S) where V is the drying rate and S the dryness of the sample (figure 31). A dryness SL is read for each sludge, corresponding to the first critical point: SL is considered to be the dryness of the sludge after loss of the free water: for the sake of practical interpretation, the free water is defined, in thermogravimetry, as the quantity of water capable of being removed at constant drying rate.

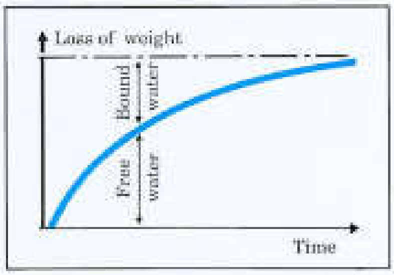


Figure 30. Thermogravimetric analysis of sludge.

With the thermogravimetric method, it is possible to estimate the hydrophilic tendency of a sludge, and also to:

- follow the evolution of the proportion of bound water as a function of the various conditioning processes,
- evaluate fairly accurately the performance of the dewatering units in the laboratory,
- determine a dryness limit for each type of treatment by comparative studies,
- calculate, if required, the binding energy of the various types of water with the sludgy matter.

The interpretation of hydroxide sludge thermograms is more complex because of the presence of rather a large proportion of chemically bound water.

Figure 31. Dewatering curve for sludge dried by evaporation at constant temperature.

6.2.3. Factors characterizing the behaviour of sludge during dewatering

These factors are specific to the dewatering techniques used:

- ability to undergo thickening (see page 158),

- numerical characterization of filterabiliry (see page 177),
- numerical characterization of the compressibility of a sludge
- determination of a dryness limit,
- aptitude to centrifugation (see page 197).

6.3.
SLUDGE PRODUCTION

The quantity of sludge produced directly depends on the amount of SS removed and the amount of treatment reagents used. In biological treatment, however, a large part of the dissolved substances is assimilated by the bacterial population and used in the synthesis of living matter.

Treatment of MWW leads to the production of the average quantities of sludge shown in table 33.

Table 33. Types of sludge produced from MWW treatment.

Treatment"	SS g/inh.day	Volume (2) 1/inh.day
P.S.	40-60	0.4-0.8
P.S. + An. dig.	25-40	0.35-0.7
P.S. + T.F.	65-75	1-1.9
P.S. + T.F. + An. dig.	40-55	0.9-1.8
P.S. + A.S.	75-90	1.3-2.6
P.S. + A.S. + An. dig.	50-65	1.2-2.5

(1) P.S. = primary settling
T.F. = trickling filters
A.S. = activated sludge
An. dig. = anaerobic digestion
(2) After thickening of fresh sludge

6.4.
DISPOSAL OF SLUDGE AND END PRODUCT

Sludge is often difficult to dispose of and its removal is almost always a heavy item in operating costs. From the economic standpoint, the real aim is to limit the cost of sludge treatment and transport. Optimizing this procedure depends on the means of sludge disposal, energy requirements and costs, labour costs, conditioning reagent cost, etc.

On the other hand, the protection of workers' health and of the environment calls for methods which will cause the least nuisance and still be economically feasible.

Sludge and its by-products are disposed of as follows:

6.4.1. Soil improvement

Sludge from the treatment of municipal wastewater and certain kinds of industrial effluents can be used. Encouraging studies have also been run with sludge from the physical-chemical treatment of MWW. The principal agronomic properties of sludge from the MWW biological purification plants are expressed as a percentage of the dry solids as follows:

Table 34.

	Primary settling		Primary settling + biological purification		Extended aeration
	Fresh	Digested	Fresh	Digested	
Organic matter	55-65	40-55	60-80	40-65	55-70
N	2.5-3	2-2.5	3.5-4.5	2-2.5	4-5
P	1-1.5	0.5-1	2-2.5	1-1.5	2-2.5
K	0.2-0.3	0.2-0.3	0.2-0.3	0.2-0.3	0.2-0.3
Ca	5-15	5-15	5-15	5-15	5-15

The value of sludge lies generally more in the humic matter it provides and in the improvement of the water-retention properties of the soil than in its nutritive content alone. The nature of the nutritive matter is equally important since it determines the rate at which it is assimilated: nitrogen, for example, is only partially assimilated the first year: about 30 to 50% for liquid sludge and 20 to 40% for dewatered sludge. The annual assimilation rate then decreases. The use of the sludge depends on the composition of the soil (in particular, the pH, the Ca content), cultivation, what the soil is used for, and the mode of land disposal.

Because of the cyclical needs of crops, a policy of sludge use for agriculture will not be viable until a solution is found that responds to fluctuations in the need for nutritive elements throughout the year: rotation of crops, storage, an alternative means of sludge disposal. In almost all cases, a large and satisfactory storage space is the underlying condition for a solution to sludge use in agriculture. Consistency in quality is also an important factor.

Stabilized sludge has an advantage in that its population of pathogenic germs is greatly reduced, therefore avoiding the problem of bad odours being released during land disposal. The hazards due to bacteria should not, however, be overestimated as microbial decontaminating action in the soil is important.

In addition to excessive amounts of grease and fibres in some cases, the number one potential risk in using sludge for agriculture is the heavy metals it contains. These generally come from industry (in particular, metal surface treatment). The most common dangerous cations found are Zn, Cd, Cu, Ni, Cr, Hg.

The amount of sludge which may be spread depends on current legal regulations which, generally, take into account the duration of land disposal and the amount of heavy metals already in the soil. This amount must not appreciably increase the leachable nitrogen.

Sludge should not be spread on soil in which the pH level leads to a substantial solubilization of trace elements. After land disposal, the pH of the soil should not drop below 6. Although the amounts added each year should be determined by local agronomic testing, a dose of 3 t DS/ ha.yr. may serve as a reasonable guide.

Sludge can be spread:

- in liquid form,
- in a paste-like form (with a thixotropic structure),
- in a plastic solid state (slight adhesion) suitable for shovelling and containing approximately 15% of DS in the case of biological colloidal sludge and less than 50% for very thick inorganic sludge,
- in a friable form leading to a crumbling of residue under mechanical pressure,
- in a granular or powdery form requiring thermal drying in addition to mechanical dewatering. In this case, its value for agriculture may be improved by adding complementary nutrients.

Liquid or paste-like sludge may be spread on the surface or injected. The latter method reduces the release of odours which are especially bad in the case of fermentable sludge containing a lot of water.

In general, the greater the quantity of sludge for disposal, the more it must be dewatered in order to keep down the costs of disposal. This concerns large urban centres with farms lying far outside of town.

6.4.2. Recovery of products

Only some of the constituents of the sludge are recoverable. They include in particular:

- fibres: in the paperboard and timber industries,
- proteins: (in particular in the meat industry) used for livestock feed or pisciculture,
- coagulants: from the treatment of river water (for example, acidification of sludge of Al hydroxides),
- calcium carbonate or lime: in the case of a massive lime treatment. Such is the case, for example, for the sludge coming from the lime softening of drinking water which is used for the conditioning, prior to the dewatering, of organically rich sludge from the biological treatment of MWW,
- zinc, copper, chromium: in the case of the purification of water used in the treatment of metal surfaces,
- inorganic sludge after thermal drying or ash from incineration: can be reused in production of roadsurfacing materials and soil or concrete stabilizers (such reuse continues to have only limited application).

6.4.3. Energy recovery

The use of sludge to generate energy is not generally the main goal of sludge treatment. Sludge is rarely used as a fuel except in the treatment plant. Such may be the case for previously-dewatered sludge obtained from the settling of some types of wastewater containing a very large proportion of fuel (coal dust, for example), or for oily and greasy suspensions obtained by flotation, or even for dry organic sludge in the form of grains or powder. The use of highly organic sludge in granular, or even powdery form, is recommended for the production of transportable fuel. Energy is recovered in two main forms:

- production of methane gas by fermentation. The gas is used for heating or to generate electricity (generator sets) or for the heat conditioning of the sludge itself,

- use of the calorific value of the dry matter in incinerators. The energy generated is used essentially, if not totally, to pre-dewater the sludge. When the initial dryness of the sludge permits, the excess thermal energy may be transformed into electrical energy.

Any recovery of energy is accompanied by a partial or total reduction of pathogenic germs in the sludge.

6 4.4. Tipping

Sludge is most often disposed of in this way. The amount of residue varies, but even after incineration, a substantial amount of by-products remains which usually contains all the heavy metals found in the sludge.

The sludge can be simply discharged into a "liquid sludge lagoon" containing stablized sludge, which takes months or years to drain and evaporate; or dry sludge which can be compacted much more rapidly can be used in sanitary landfill operations (to fill in excavations or low-lying areas).

An approach which is sometimes considered, especially for toxic sludge, is to incorporate solidifying products (silicates, cements, etc.) with the liquid sludge before tipping. This method of treatment has the disadvantage of permanently condemning a large area of ground. Furthermore, the risk of leaching by run-off water cannot be altogether discounted.

Lastly, a yet more frequent practice is the tipping of sludge together with household refuse. The law in this matter varies according to the country. It is necessary to maintain the water content below a maximum level, to keep the product homogeneous and to take the necessary steps to protect the groundwater through collection and treatment of the leachate (see page 591).

6 4.5. Ocean disposal

This expeditious approach usually involves dumping the sludge at intervals from barges or lighters into the sea. In some cases, disposal may involve the use of a sufficiently long and very deep-lying submarine outfall.

The choice of ocean disposal requires a long and detailed prior investigation of currents as well as very thorough bacteriological, biological and fish ecology studies. The destruction of pathogenic bacteria and the breakdown of organic matter are slow in sea water.

All floating matter must be removed from sludge discharged to the sea. Prior anaerobic digestion is the preliminary treatment most often adopted.

6.4.6 Reinjection into the ground

This approach, envisaged primarily for toxic sludge or very concentrated water, involves injecting liquid sludge into porous subsoil pockets separated by pervious continuous strata, at very great depth. Obviously, a thorough geological study is essential.

3

BASIC PHYSICAL-CHEMICAL PROCESSES IN WATER TREATMENT

1. COAGULATION-FLOCCULATION

1.1.

GENERAL

1. 1. 1. Suspended solids and colloids

1.1.1.1. Definitions

Water contains many compounds, which can be classified in three categories (see page 5).

. Suspended solids

These products may be mineral in origin (sand, silt, clays, etc.) or organic (products resulting from the decomposition of plant or animal matter, humic or fulvic acids, for example). Added to these compounds are microorganisms such as bacteria, plankton, algae and viruses. These substances, in particular, are responsible for turbidity and colour.

. Colloidal particles (less than 1 micron)

These are SS of the same origin as the above but of smaller size and with a settling rate that is extremely slow. They are also responsible for turbidity and colour.

. **Dissolved substances** (less than several nanometres)

These are usually cations or anions. Part of the organic matter is also dissolved. Gases are also present (O_2, CO_2, H_2S, etc.).

1.1.1.2. The role of coagulation-flocculation

The coagulation-flocculation processes facilitate the removal of SS and colloids. This occurs in a final stage of solids-liquid separation: settling, flotation or filtration (sub-chapters 3, 4 and 5).

In order to remove dissolved substances, each type of substance requires a specific treatment, which may or may not be preceded by coagulation-flocculation, or even a solids-liquid separation process.

1.1.2. Colloidal suspensions

1.1.2.1. Stability of colloidal suspensions - The necessity for coagulation

Table 35 lists a number of materials and organisms with their size and an indication of the time needed for these particles to settle vertically through one metre of water, at 20°C, under the influence of gravity alone.

Table 35. Settling time for various particles.

(According to Stokes' law)

Particle diameter			Type of particle	Settling time through 1 m of water	Specific Area $m^2.m^{-3}$
mm	µm	Å			
10	104	108	Gravel	1 second	6.10^2
1	103	10'	Sand	10 seconds	6.10^3
10^{-1}	102	106	Fine sand	2 minutes	6.10^4
10^{-2}	10	105	Clay	2 hours	6.10^5
10^{-3}	1	104	Bacteria	8 days	6.10^6
10^{-4}	10-1	103	Colloid	2 years	6.10^7
10^{-5}	10-2	102	Colloid	20 years	6.10^8
10^{-6}	10-3	10	Colloid	200 years	6.10^9

The table also shows that the smaller the particle, the larger its specific area.

Thus colloids are **particles that cannot settle naturally** and for which surface area factors are most important. These factors determine the **stability of colloidal suspensions**. In fact, colloids are subject to two major forces:

- **Van der Waals attraction**, which relates to the structure and form of colloids as well as to the type of medium (E_A),
- **the electrostatic repulsive force**, which relates to the surface charges of the colloids (E_B).

The stability of a colloidal suspension depends on the balance between the forces of attraction and repulsion, the energy level of which is:

$E=E_A+E_B$

This relation is shown in the diagram in figure 32:

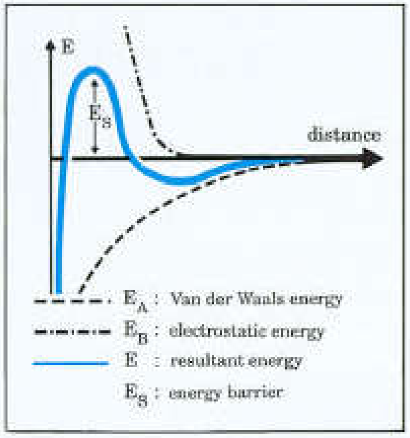


Figure 32. Stability of a colloidal suspension

In order to destabilize the suspension, it is necessary to overcome the energy barrier Es. To accomplish this and, thereby, promote the agglomeration of the colloids, it is necessary to reduce the electrostatic repulsive forces. This destabilization is brought about by coagulation

1.1.2.2. The double layer theory

In raw water, colloids invariably carry a negative charge (imperfections in the crystalline structure, ionization of peripheral chemical groups, etc.). In order to neutralize this negative surface charge, positive ions, which are present in the raw water or are introduced into it, come together to form a layer around the colloid. Various theories have been put forward (Figure 33):

. **The Helmholtz theory**: A layer of positive ions covers the entire surface of the colloid and ensures the neutrality of the entire mass (bound layer).

. **The Gouy-Chapman theory**: The layer of positive ions is spaced unevenly around the colloid; neutrality is obtained at a greater distance (diffuse layer).

. **The Stern theory** brings together the two preceding theories and introduces the idea of a double layer. The first layer, which is attached to the colloid, rapidly loses its potential. The second layer, which is more diffuse, undergoes a slower loss of potential.

1.1.2.3. The zeta potential

The colloid moves with part of its double layer. This layer, which is bound to the colloid, corresponds to the stationary layer in the Stern theory. In this case, the colloid has two potentials (Figure 33):

- E: The surface potential of the colloid or the thermodynamic potential (Nernst, par. 8.1.1).
- Z: The potential at the shear surface or the electrokinetic potential.

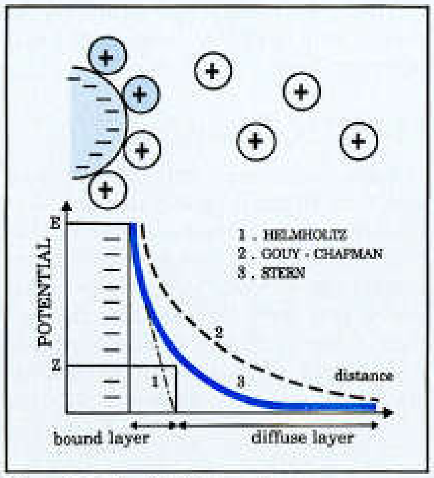


Figure 33. The double layer theory.

Figure 33. The double layer theory.

This Z potential, called the **zeta potential,** determines the moving of the colloids and their mutual interaction. It can be defined through electrophoresis: when a particle is subjected to an electrical field, it almost instantly attains a velocity so that there is a balance between the electrical force of attraction and the friction due to the viscosity of the medium. The following relationship between the zeta potential and the electrophoretic mobility is obtained by calculation:

$$me = \frac{\varepsilon Z}{k\eta}$$

me: Electrophoretic mobility

ε: Dielectric constant of the medium

η Dynamic viscosity

k : 4 or 6, depending on the hypothesis

Those particles that have the same electrokinetic zeta potential possess the same electrophoretic mobility regardless of their diameter.

In the double layer theory, coagulation nullifies the zeta potential.

The equipment used for measuring the electrokinetic potential is the zeta meter (see page 351).

1.1.2.4. The chemical theory

Since the covalent forces of attraction are 20 to 50 times greater than the electrostatic forces, a "chemical theory" has been introduced to interpret the destabilization of colloidal suspensions. This theory puts forth the idea that the primary charge carried by a colloidal particle is due to the direct ionization of chemical groups on its surface (hydroxyl, carboxyl, phosphates, sulphates, etc.). The destabilization is achieved through a covalent reaction between these groups and the polyvalent metallic ions of the coagulants.

This theory shows that the simultaneous precipitation of metallic hydroxides and the interparticular bridging are significant factors in coagulation.

1.1.3. The stages in agglomeration

1.1.3.1. Presentation

There are a number of successive or simultaneous stages involved in the agglomeration of particles (table 36).

Table 36. The stages in agglomeration.

Stage	Factors	Term
ADDITION OF COAGULANT	Reaction with water, ionization, hydrolysis, polymerization	HYDROLYSIS
DESTABILIZATION	Double layer compression	COAGULATION
	Specific absorption of ions from the coagulant on the surface of the particle	
	Specific linkage between ions or species on the surface of the particle	
	Inclusion of the colloid in a hydroxide precipitate	
	Interparticular linking by polymeric species of coagulant	
TRANSPORT	Brownian movement	PERIKINETIC FLOCCULATION
	Dissipated energy (velocity gradient)	ORTHOKINETIC FLOCCULATION

Coagulation is the destabilization of colloidal particles brought about by the addition of a chemical reagent known as a: coagulant.

Flocculation is the agglomeration of destabilized particles into microfloc, and later into bulky floccules which can be settled called floc. The introduction of another reagent, called a flocculant or a flocculant aid may promote the formation of the floc..

Two transport factors determine flocculation:

.**Perikinetic flocculation** is connected to Brownian diffusion (thermal agitation). The flocculation rate or the variation in the number of particles in a period of time is given in the equation:

$$\frac{dn}{dt} = \alpha \frac{4kT}{3\eta} n^2$$

n: Number of particles per unit volume

α: Fraction of efficacious shocks

k: Boltzmann constant

T: Absolute temperature

η: Absolute viscosity

d: Diameter of a particle

This flocculation only occurs in cases where the particles are smaller than 1 micron. It promotes the formation of microfloc.

. **Orthokinetic flocculation** is tied to dissipated energy. The effectiveness of flocculation in this case, which promotes the formation of bulky separable floc, is given by:

	Laminar flow	**Turbulent flow**
$-\frac{dn}{dt}$	$\frac{1}{6}\alpha n^2 G^o d^3$	$KG^0 n^2 d^3$

The velocity gradient G° can only be defined in laminar flow, as the difference in velocity between two adjacent liquid veins in the orthogonal plane with respect to their moving:

$$G^o = \frac{dV}{dz}$$

In practice, a velocity gradient G is used, which corresponds to the turbulent flow.

1.1.3.2 The importance of the velocity gradient

The velocity gradient is defined by:

$$G = \sqrt{\frac{P}{V.\eta}} = K\sqrt{\frac{P}{V}}$$

This definition of G is also applicable to all types of hydraulic processes. G depends on the temperature in particular:

Temperature °C	K
0	23.6
5	25.6
10	27.6
15	29.6
20	31.5
30	35.4
40	38.9

The velocity gradient is an extremely important factor when it comes to determining the probability of the particles coming together. It cannot be increased exaggeratedly. In fact, for the values of G that are too high, the floc formed undergoes a mechanical shearing that leads to its destruction. The values that are usually acceptable for **G** are:

- in coagulation: up to 400, even 1000 s^{-1}
- in flocculation: roughly 100 s^{-1}.

1.1.3.3. The time necessary for coagulation and flocculation

The time required for the coagulation and flocculation reactions to take place is an essential factor. The kinetics are influenced by the type of medium, the temperature, the concentration in colloids, the presence of inhibitors, etc.

These reactions may be characterized by the dimensionless factor G. ξ (ξ = contact time). The value of ξ may be determined by a flocculation test (see page 352).

1.1.4. The coagulants

. Trivalent cations

The neutralization of the negative surface charge of the colloid is accomplished by the addition of cations in the case of inorganic coagulants. The higher the valency, the more effective the coagulating action will be (Schultz-Hardy theory: a trivalent ion is ten times more effective than a divalent ion). When choosing a coagulant, its harmlessness and its cost must be taken into account. Thus, trivalent iron or aluminium salts have been and continue to be widely used in all water coagulation treatments.

. The influence of the pH

Inorganic coagulants, because of their hydrolysis, change the physical-chemical characteristics of water to be treated (pH, conductivity):

$$M^{3+} + 3H_2O \rightleftarrows \underset{\qquad\downarrow}{\underline{M(OH)_3}} + 3H^+$$

Moreover, the pH is a prominent factor in the removal of colloids. The optimum pH is a compromise between the pH necessary for coagulation (according to the type of colloid) and the pH necessary for flocculation (relating to the build-up of iron or aluminium hydroxide floc). Usually it corresponds to the minimum solubility of the hydroxide in question (optimization of the flocculation stage). The pH and the minimal solubility are greatly influenced by the ionic strength and the presence of organic compounds such as humic acids.

Cation	Optimum pH for coagulation-flocculation
Al^{3+}	6.0 - 7.4
Fe^{3+}	> 5

The pH necessary for coagulation may be adjusted by the addition of an acid or a base.

. The treatment rate

The treatment rate is determined by a flocculation test. It may be adjusted by a study of the zeta potential (see page 351).

. Sludge production

The formation of metallic hydroxide causes the production of a substantial amount of sludge. This sludge should be removed in the final solids-liquid separation process.

Organic coagulants may also be used. These are cationic polyelectrolytes which directly neutralize the negative colloids. Thus the amount of sludge produced is considerably reduced.

1.1.5. The flocculants

Inorganic polymers (activated silica) and **natural polymers** (starches, alginate) were the first to be used. But the appearance of the widely varying **synthetic polymers** has changed flocculation results considerably.

As in the case of the coagulant, the treatment rate is determined by a flocculation test. Of chief importance is the timing of the introduction of the coagulant and that of the flocculant. In fact, a flocculant usually does not take effect until the coagulation stage is over. The length of the coagulation stage depends on the type of colloid as well as on the temperature of the raw water. The main factors that should be borne in mind are the size of the floc, its cohesion and its settling rate.

The use of synthetic flocculants often results in a minimum amount of sludge. Combined with modern separation techniques, this can lead to the production of very dense sludge that can be directly treated in a dewatering unit.

1.2. REAGENTS

The reagents used in coagulation and flocculation are inorganic products, natural polymers and synthetic polymers.

1.2.1. Inorganic coagulants

The most widely used coagulants are with an aluminium or iron salt base. In certain cases synthetic products, such as cationic polyelectrolytes which will be discussed later, can be used.

1.2.1.1. Aluminium salts

The basic reaction, when the Al" ion is added to the water, is the formation of a precipitate of aluminium hydroxide with the release of some acidity:

$$Al^{3+} + 3H_2O \rightleftarrows \underset{\downarrow}{\underline{Al(OH)_3}} + 3H^+$$

This acidity can react on some species in solution, especially on the bicarbonate ions:

$$HCO_3^- + H^+ \rightleftarrows H_2O + CO_2$$

This acidity can be compensated for by adding a coagulant in combination with a base (caustic soda, lime, sodium carbonate).

$$Al^{3+} + 3\,OH^- \rightleftarrows \underset{\downarrow}{\underline{Al(OH)_3}}$$

The reactions in this chapter are summarized in a simplified written form. All the resulting products are soluble except $Al(OH)_3$ and $CaCO_3$. The added reagents are in molecular form.

. **Aluminium sulphate** (liquid or solid)

$$Al_2(SO_4)_3 + 6\,HCO_3^- \rightleftarrows$$

$$\underset{\downarrow}{\underline{2\,Al(OH)_3}} + 3\,SO_4^{2-} + 6\,CO_2$$

Dosage: for the clarification of surface water, 10 to 150 g.m^{-3}, expressed as solid commercial grade product ($Al_2(SO_4)_3 . 18H_2O$), depending on the water quality. For treating wastewater, from 50 to 300 gm^{-3}.

. Aluminium chloride (liquid)

$$2\,AlCl_3 + 6\,HCO3^- \rightleftarrows \underline{2\,Al(OH)_3}\downarrow + 6\,Cl^- + 6\,CO_2$$

This product is effective but it is used only under exceptional circumstances.

. Aluminium sulphate + lime

$$Al_2(SO_4)_3 + 3\,Ca(OH)_2 \rightleftarrows \underline{2\,Al(OH)_3}\downarrow + 3\,Ca^{2+} + 3\,SO_4^{2-}$$

Dosage: to compensate for the acidification, the dosage of lime Ca(OH)z needed is about one third of the dose of aluminium sulphate expressed as solid commercial grade product.

. Aluminium sulphate + sodium carbonate

Two types of reactions can take place, depending on the neutralization of the carbonate ions, either as bicarbonates or as free CO_2.

$$Al_2(SO_4)_3 + 6\,Na_2CO_3 + 6\,H_2O \rightleftarrows \underline{2\,Al(OH)_3}\downarrow + 12\,Na^+ + 6\,HCO_3^- + 3\,SO_4^{2-}$$

$$2\,Al_2(SO_4)_3 + 6\,Na_2CO_3 + 6\,H_2O \rightleftarrows \underline{4\,Al(OH)_3}\downarrow + 12\,Na^+ + 6\,SO_4^{2-} + 6\,CO_2$$

Dosage: the amount of sodium carbonate required is between 50 and 100% of the amount of aluminium sulphate as solid commercial grade product.

. Sodium aluminate

In contrast to the preceding case, aluminium, in this case, is in basic form:

$$AlO_2^- + 2\,H_2O \rightleftarrows \underline{Al(OH)_3}\downarrow + OH^-$$

It can displace bicarbonate ions and dissolved CO_2.

$$NaAlO_2 + Ca(HCO_3)_2 + H_2O \rightleftarrows \underline{Al(OH)_3}\downarrow + \underline{CaCO_3}\downarrow + Na^+ + HCO_3^-$$

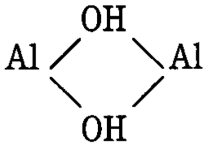
$$2\,NaAlO_2 + 2\,CO_2 + 4\,H_2O \rightleftarrows \underline{Al(OH)_3}\downarrow + 2\,Na^+ + 2\,HCO_3^-$$

Dosage: for the clarification of surface water, 5 to 50 g.m^{-3} of commercial reagent with 50% Al_2O_3.

1.2.1.2. Aluminium polymers

Aluminium polymers are used both for neutralization and bridging of the colloids so that coagulation may take place more efficiently.

Moreover, using polymers promotes the agglomeration of crystallized forms of aluminium hydroxide such as bayerite or gibbsite. The polymerization of aluminium hydroxide in solution presents roughly the same basic structure as these crystals. The basic unit would be $Al_6(OH)_{12}^{6+}$. Polymerization is initiated by a bridging reaction (or olation):



There is a continuous series of polymers the size of which increases with the degree of hydroxylation (molecular ratio R = OH/AI). The more advanced the polymerization, the more the floc approaches the crystalline structure, and the more compact and dense it becomes. However, when these commercial products reach a certain ratio, R, they become very unstable.

Commercial products

The overall formula for these products is:

$$Al_n(OH)_P(C1)_q(S04)_r$$

They are characterized by a molecular ratio OH/Al between 0.4 and 0.6. They are less acid than conventional aluminium salts. Their stability is often ensured by the presence of sulphate ions which inhibit the spontaneous polymerization of the product. Their use often results in a lower treatment rate than that of aluminium sulphate (expressed as A13+). Sludge cohesion is generally better, although adding a flocculant often proves necessary.

The commercial products that are available continue to be improved. Noteworthy are: PAC, WAC, Aqualenc, Alpodar, etc.

. **PCBA** (basic polyaluminium chloride)

In order to obtain a more effective aluminium polymer, it must be prepared on the spot, just prior to its use (Degrémont patent). A much higher OH/Al ratio is obtained by a controlled neutralization of aluminium chloride with the help of a base. The ratio, roughly 2.5, may be adapted, depending upon the nature of the raw water.

The advantages of PCBA compared to a conventional aluminium salt are:

- rapid flocculation,
- efficient removal of organic substances,
- lower treatment rate (expressed as A13+),
- reduced amount of sludge,
- addition of a flocculant

Its preparation in situ is only possible in large facilities.

1.2.1.3. Iron salts

The reaction principle is the same as for aluminium salts with:

$$Fe^{3+} + 3\,H_2O \rightleftarrows \underset{\downarrow}{\underline{Fe(OH)_3}} + 3\,H^+$$

The ferric ion can cause colouring in treated water.

. **Ferric chloride** (liquid, sometimes crystal form)

$$2\,FeCl_3 + 6\,HCO_3^- \rightleftarrows \underset{\downarrow}{\underline{2\,Fe(OH)_3}} + 6\,Cl^- + 6\,CO_2$$

Dosage: for the clarification of surface water, 5 to 150 g.rri 3 of solid commercial grade ferric chloride $FeCl_3.6H_2O$.

For wastewater treatment, 50 to 300 g.m-3 3 of solid commercial grade ferric chloride.

. **Ferric chloride + lime**

$$2\,FeCl_3 + 3\,Ca(OH)_2 \rightleftarrows \underset{\downarrow}{\underline{2\,Fe(OH)_3}} + 6\,Cl^- + 3\,Ca^{2+}$$

Dosage: for the treatment of wastewater, 50 to 500 g.m-3 3 of lime for 50 to 300 g.m-3 3 of solid commercial grade ferric chloride is necessary.

. **Ferric sulphate (solid)**

$$Fe_2(SO_4)_3 + 6\,HCO_3^- \rightleftarrows \underset{\downarrow}{\underline{2\,Fe(OH)_3}} + 3\,SO_4^{2-} + 6\,CO_2$$

Dosage: for the clarification of surface water, 10 to 250 $g.m^{-3}$ of commercial re gent $Fe_3(SO_4)_3.9H_2O$ is necessary.

.Ferric sulphate+lime

$$Fe_2(SO_4)_3 + 3\,Ca(OH)_2 \rightleftarrows \underset{\downarrow}{\underline{2\,Fe(OH)_3}} + 3\,SO_4^{2-} + 3\,Ca^{2+}$$

Dosage: for the clarification of surface water, the amount of lime $Ca(OH)_2$ required is roughly 50% of the amount of commercial grade ferric sulphate $Fe_2(SO_4)_3.9H_2O$

. Chlorinated copperas (liquid)

$$\mathrm{2\ FeC1SO_4 + 6\ HCO_3} \rightleftarrows$$
$$\underline{\mathrm{2\ Fe(OH)_3}}\downarrow \mathrm{+ 2\ C1^- + 2\ SO_4^{2-} + 6CO_2}$$

Dosage: similar to that of ferric chloride expressed as iron.

. Ferrous sulphate (solid)

$$\mathrm{FeSO_4 + 2\ HCO_3^-} \rightleftarrows$$
$$\underline{\mathrm{Fe(OH)_2}}\downarrow \mathrm{+ SO_4^{2-} + 2CO_2}$$

Dosage: for the clarification of surface water, 5 to 150 $g.m^{-3}$ of commercial grade reagent $FeSO_4.7\ H_2O$ is necessary.

For the treatment of wastewater, 100 to 400 $g.m^{-3}$ of commercial reagent $FeSO_4.7H_2O$ is necessary.

In aerated water, ferrous hydroxide oxdizes into ferric hydroxide:

$$\mathrm{2\ Fe(OH)_2 + \frac{1}{2}O_2 + H_2O} \rightleftarrows \mathrm{2\ Fe(OH)_3}$$

. Ferrous sulphate + chlorine

$$\mathrm{2\ FeSO_4 + C1_2 + 6\ HCO_3^-} \rightleftarrows$$
$$\underline{\mathrm{2\ Fe(OH)_3}}\downarrow \mathrm{+ 2\ SO_4^{2-} + 2\ C1^- + 6\ CO_2}$$

Dosage: chlorine requirements are 12% of the amount of ferrous sulphate $FeSO_4.H_2O$

The ferrous sulphate and the chlorine may be introduced separately. Ferrous sulphate, oxidized by the chlorine before use, results in chlorinated copperas (Clairtan, etc.).

. Ferrous sulphate + lime

$$\mathrm{FeSO_4 + Ca(OH)_2} \rightleftarrows$$
$$\underline{\mathrm{Fe(OH)_2}}\downarrow \mathrm{+ Ca^{2+} + SO_4^{2-}}$$

Dosage: for the clarification of surface water, the amount of lime Ca(OH)z required, is about 30% of the amount o£ ferrous sulphate $FeSO_47H_2O$

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In wastewater treatment, 100 to 150 $g.m^{-3}$ of lime is required for 250 to 350 $g.m^{-3}$ ferrous sulphate.

1.2.1.4. Other inorganic coagulants

. Mixed products $A1^{3+}/Fe^{3+}$

Some inorganic coagulants carry both $A1^{3+}$ and Fe^{3+} ions. This is particularly the case with AVR, a mixed sulphate of aluminium and iron (solid). This product is used essentially in the chemical purification of municipal and industrial wastewater, particularly for the removal of phosphates.

. Copper sulphate

$$\mathrm{CuSO_4 + 2\ HCO_3^-} \rightleftarrows$$
$$\underline{\mathrm{Cu(OH)_2}}\downarrow \mathrm{+ SO_4^{2-} + 2\ CO_2}$$

Dosage: 5 to 20 $g.m^{-3}$ of commercial grade product $CUSO_4.5H_2O$ (used in exceptional cases).

This product is mainly used as an algicide.

. Ozone

When water contains organic matter that chelates iron or manganese, ozone can initiate a coagulation-flocculation process. The organic complexes are destroyed by the ozone, and the metal ions which are thus released are oxidized. With the necessary pH conditions, the flocculation of ferric hydroxide results in a floc with a rather low density and cohesion that may be retained by in-line coagulation.

. Chlorine

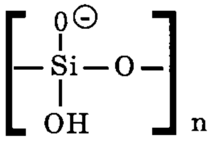
In sea water, free chlorine is necessary to initiate the coagulation reaction

1.2.2. "Natural " flocculants

1.2.2.1. Inorganic flocculants

Activated silica

Activated silica was the first flocculant used. It gives good results, especially when used together with aluminium sulphate in cold water. It is added after the coagulant and is prepared immediately before use by partially neutralizing the alkalinity of a solution of sodium silicate.



$$\left[\begin{array}{c} O^{\ominus} \\ | \\ -Si-O- \\ | \\ OH \end{array}\right]_n$$

The treatment rate is from 0.5 to 4 mg.l^{-1} expressed as SiO_2.

. Aluminosilicate

When the coagulant is aluminium sulphate (or another aluminium salt), the acidity of this product may be used in the place of that of sulphuric acid to activate sodium silicate. Products similar to activated silica, such as aluminosilicate, are obtained. In special cases, sodium silicate may be used alone.

.Other inorganic aids

Before the settling or filtration process, other products are used for raw water containing insufficient suspended solids. These are not flocculants but they play a role in the growth and enlargement of the floc.

Among these are:

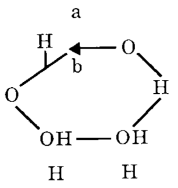
- certain types of clay (bentonite, kaolin);
- pure precipitated calcium carbonate;
- kieselguhr (diatomite);
- activated carbon in powder form (used principally as an adsorbent);
- fine sand.

1.2.2.2. Organic flocculants (natural polymers)

These are natural polymers extracted from animal or vegetable matter.

. Alginates

Sodium alginates are obtained from alginic acid, which itself is extracted from seaweed. The main components of this polymeric structure are mannuronic acid and glucuronic acid. The gramme-molecular weight is in the order of 10^4 to 2×10^5.



	a	b
Mannuronic	COOH	H
Glucuronic	H	COOH

These products are particularly effective as flocculant aids with ferric salts. They may also give good results with aluminium salts. The treatment rate is between 0.5 and 2 mg.l^{-1}

. Starches

Starches are obtained from potatoes, tapioca or extracts of plant seeds. These are glucopyranose polymers that are branched and nonlinear and are sometimes partially broken down (OH^-) or derived (carboxy-ethyl-dextrone). The are used in amounts of 1 to 10 mg.$^{-1}$, preferably together with aluminium salts.

Starches and alginate are solids that must be prepared at concentrations of 5 to 10 g.l^{-1}. Their breakdown in an aqueous solution may be rapid if the out side temperature is high (over 20°C). The preparation tanks must be cleaned on a regular basis to avoid the risk of fermentation.

. Other compounds

There are many other natural organic flocculants, but they are mostly used for specific industrial processes (hydrometallurgy, paper mills, etc.). These are basically polysaccharides:

- galactomannans (gums: guar, carob),
- pectins,
- xanthanes (the aerobic fermentation of sugar by means of a bacterium of the Xanthomonas; for example the Rhodopol).

There are other equally common products such as the derivatives of cellulose(carboxymethyl-cellulose), gelatins and tannins.

1.2.3. Synthetic organic coagulants

These are synthetic organic molecules, cationic in nature, that have an average molecular weight of 104 to 105. They are only available in liquid form, in an aqueous medium.

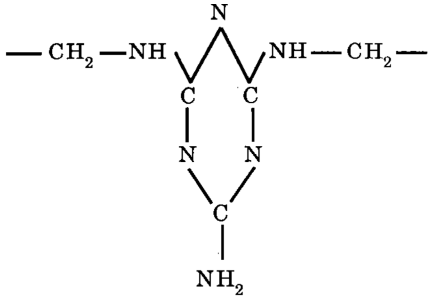
These coagulants may be used directly (without a preparation stage) and totally or partially serve as a replacement for an inorganic coagulant. They must be injected directly following in-line dilution.

The use of organic coagulants leads to a substantial reduction in the amount of sludge produced. The sludge that is extracted is denser and also more sticky. Thus, the organic coagulants are not suitable for every type of separation process. An organic coagulant exerts no more than a negligible effect on the pH value and carries with it a very small amount of additional salinity.

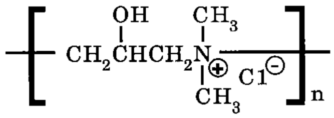
1.2.3.1. Classification

Three main groups may be found:

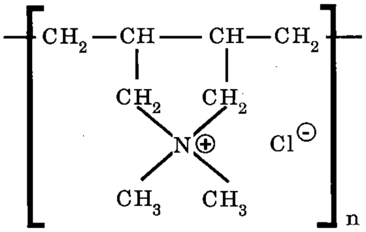
- melamineformaldehyde (or melamineformol)



-epichlorydrin dimethylamine (epiDMA)



poly (chlorure de diallyldiméthyl-ammonium) (POLYDADMAC)



There are also other products which may be encountered such as various polyamines of the epi-DMA and the polyethylenimines, which are basically used in the clarification process of industrial wastewater.

1.2.3.2. Applications

. Clarification

For the treatment of water designed for drinking, it is necessary to refer to the laws of the country concerned. The treatment rates that must be used are in the order of 5-15 $g.m^{-3}$ expressed in terms of the commercial grade product.

. In-line coagulation

In filtering sea water, for certain products, the coagulation reaction may be associated with a premature and detrimental reaction of precipitation of the coagulant because of its high salinity.

. Industrial wastewater

This is a major field of application involving organic coagulants. The treatment rate (5-50 g.m^{-3}) depends substantially on the type of effluent involved.

1.2.3.3. Synergism with an inorganic is coagulant

There are cases in which the organic coagulant alone does not provide the same quality of water as can be obtained with an inorganic coagulant.

The use of the two types of coagulant together provides for a significant reduction in the quantity of inorganic coagulant that is required (40-80%), while at the same time ensuring the production of a minimum amount of sludge.

1.2.4. Synthetic organic flocculants

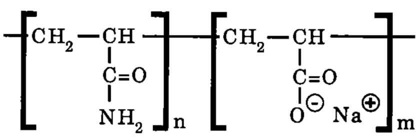
These consist of long-chain macromolecules obtained by the association of synthetic monomers, certain of which possess electrical charges or ionizable groups. These are products that have a very high molecular weight (10^6-10^7), enabling them to attain remarkable performance levels that are usually higher than those attained with natural polymers.

1.2.4.1. Classification

This is established according to the ionicity of the polymer.

. Anionic

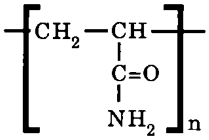
These are usually acrylamide and acrylic acid copolymers.



$$\left[CH_2-\underset{\substack{| \\ C=O \\ | \\ NH_2}}{CH}\right]_n\left[CH_2-\underset{\substack{| \\ C=O \\ | \\ O^{\ominus}\ Na^{\oplus}}}{CH}\right]_m$$

. Neutral (or nonionic)

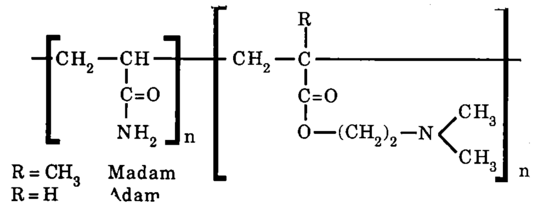
These are basically polyacrylamides.



$$\left[CH_2-\underset{\substack{| \\ C=O \\ | \\ NH_2}}{CH}\right]_n$$

. Cationic

These are copolymers of acrylamide and a cationic monomer, which are usually DMAEM (dimethyl-aminoethylmethacrylate) or DMAEA (dimethyl-aminoethyl-acrylate),



1.2.4.2. Utilization

Organic flocculants are available in three forms:

- solid,
- emulsion (an emulsion of a polymer in an organic solvent),
- solution (at approx. 20 I in an aqueous medium).

The use of flocculants in solid or emulsion form always requires special preparation before being put into solution. A secondary dilution process of these products is always necessary.

1.2.4.3. Fields of application

Surface water

In the clarification process, the synthetic flocculant is used in combination with a coagulant. The best polymer is usually one that is anionic. or non-ionic or very slightly cationic.

The usual dose is between 0.05 and 0.5 $g.m^{-3}$ In some special cases where the water is highly turbid (from sedimentation basins) up to 2 $g.m^{-3}$ of polymer may be used.

Industrial wastewater

In the case of treatment involving an inorganic coagulant, an anionic polymer is usually used in an amount up to 2 $g.m^{-3}$. In some special cases (such as surface treatment, steelworks, gas scrubbing), a cationic flocculant polymer alone is often the best adapted (0.5 to 5 $g.m^{-3}$).

Municipal wastewater (physicalchemical treatments)

In combination with an inorganic coagulant, the best flocculant is usually one of the anionic type (up to 2 $g.m^{-3}$). When only SS removal is desired, a synthetic flocculant may be used alone.

Sludge dewatering

Cationic flocculants are usually adapted to the treatment of organic sludge. Inorganic sludge requires the use of anionic flocculants. Between 0.5 and 7 kg of polymer is consumed per tonne of dry solids.

1.3.
SOLIDS CONTACT FLOCCULATION

Flocculation efficiency may be expressed as follows:

$$e = k\,C^{a}\,G^{\beta}t^{Y}$$

e: flocculation efficiency: this factor relates to the floc formed or to the quality of the settled water,

C: sludge concentration in the flocculation reactor,

G: velocity gradient, t: contact time,

$\alpha,\beta,\gamma > 0$.

In particular, the increase in the contact mass (C) increases the probability that collisions will take place inside the reactor resulting in a more efficient flocculation.

The solids contact units, which create or convey a larger mass of sludge into the flocculation area, utilize this principle.

There are two different techniques that are used. These involve:

- the recirculation of sludge,
- the sludge blanket.

Solids contact units offer a great number of advantages:

- enhanced flocculation: absence of finely divided particles, homogeneous floc, and a shorter flocculation time,
- higher settling rate, hence smaller units,
- completion of specific reactions (precipitation, adsorption on activated carbon, etc.),
- higher organic matter removal by adsorption on the floc,
- savings on chemical reagents (better use, coagulating and flocculating effect of recycled sludge).

The field of application involving solids contact flocculation is very extensive: clarification, specific precipitations (lime softening), colour removal, iron or manganese removal, and aerobic or anaerobic biological treatments.

In the particular case of biological treatment by activated sludge, the introduction of sludge into the reactor also plays another role; it maintains the biomass required for the purification process.

Note: an excessively high sludge concentration in the reactor hinders the settling process.

1.3.1. Sludge recirculation

It is necessary that a regular circulation of sludge be maintained without excessive turbulence, in order to bring about an intimate water-sludge mixture and prevent any sludge deposit.

A built-in or external system continuously conveys sludge into the flocculator upstream from the settling chamber. It is necessary to recirculate the concentrated sludge that has settled down on the bottom of the settling tank. Various recirculation systems are available: injector, propeller, turbine, air lift, external pump, etc.

The settling tank is often equipped with a sludge scraper appliance.

1.3.2. Sludge blanket

In an upward flow unit, an equilibrium is set up between the water velocity and the hindered settling velocity of flocculated particles. When flocculated particles reach a certain concentration, they form a sludge blanket that acts both as a flocculator and as a "fluidized filter", thus ensuring excellent flocculation.

This blanket presents a certain natural cohesion and is able to withstand greater rising velocities than an isolated flocculated particle could. This property of cohesion explains the elasticity of the sludge blanket. It is actually comparable to a spring which tends to compress when weighted down (settling of particles), but which stretches out to a varying degree under the action of an opposing force (upward flow of raw water). The spring mechanism will break if the rising velocity is too great; this must be avoided choosing a suitable velocity.

When the rising velocity of the water is too great, the settling velocity of the particles is no more sufficient to ensure hindered settling of the total mass, and hence the cohesion of the sludge blanket. The flocculent suspension is then carried away with the water.

The cohesion is characterized by the calculation of the **coefficient K of sludge cohesion** (see page 353) which is an essential factor for the understanding and the sizing of a settling tank with a pulsed sludge blanket.

1.4.
THE SPECIAL CASE OF EMULSIONS

The flocculation conditions for the emulsions of hydrocarbons or oils depend on the nature of these substances. They are found in two main forms

- **mechanical emulsions** which are relatively unstable and, after preliminary static settling for one hour, feature a micelle size of a dozen to a hundred microns and concentrations of about 100 to 500 mg.l^{-1},
- **chemical emulsions** that are relatively stable, which is due either to the nature of the hydrocarbons (asphaltenes,

:

naphthenates), or to the simultaneous presence of dispersing agents (alkaline salts, detergents, etc.). Following static settling for one hour, they have a micelle size of 0.1 micron (micro-emulsions) to one dozen microns, and feature a widely variable hydrocarbon concentration that ranges from 100 mg.l-1 (petrochemical complex effluents) to 50 mg.l-' (aqueous cutting fluids).

The coagulation process for these emulsions includes, just as in the case of colloidal particles, neutralization of the zeta potential. However, a coalescence mechanism may predominate in the case of mechanical emulsions. The treatment of the latter may include a phase of destabilization or partial coagulation directly followed by a coalescent filtration process.

The treatment of chemical emulsions must include a complete coagulation process followed by flocculation and separation by settling or dissolved air flotation.

2. CHEMICAL PRECIPITATION

The precipitations most commonly used in water treatment are those of calcium carbonate and metallic hydroxides. These are obtained after the addition of a specific reagent

2.1.
REMOVAL OF CALCIUM AND MAGNESIUM

2.1.1. Main methods

2.1.1.1. Lime softening

The aim is to remove the bicarbonate hardness (or temporary hardness) attributed to calcium and magnesium. The noncarbonate hardness (or permanent hardness: TH - M alk.) is not affected. .

Basic reactions

The chemical reactions for lime softening are as follows:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow \underline{2\,CaCO_3}\downarrow + 2\,H_2O$$

$$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + 2\,H_2O$$

As magnesium carbonate is relatively soluble (solubility about 70 mg.l^{-1}), an excess of lime will bring about the following reaction:

$$Ca(OH)_2 + MgCO_3 \rightarrow \underline{CaCO_3}\downarrow + \underline{Mg\,(OH)_2}\downarrow$$

If the amounts of reagents are accurately adjusted, the alkalinity of the water is reduced to the theoretical solubility of the $CaCO_3$ + Mg(OH)z system, which is between 2 and 3 French degrees under normal conditions of concentration and temperature. This limit value of M alk. may, however, be increased by the presence of dissolved impurities (for example, organic acids, ammonium, etc.).

If, on the other hand, the raw water also contains sodium bicarbonate (M alk. > TH), the water will retain additional alkalinity in the form of sodium carbonate or caustic soda (in addition to the above value), which corresponds to the value M alk. - TH.

. Precipitation mechanism

The reaction of lime in raw water is extremely slow without crystal nuclei. In static settling tanks without a solids contact system, which are hardly ever used these days, the reaction time is several hours.

On the other hand, if the water and lime are brought into contact with a sufficiently large volume of already precipitated $CaC0_3$ crystals, the reaction reaches its equilibrium point in a few minutes. As precipitation takes place on the crystals, these tend to grow in volume; the settling velocities are then increased, and the size of the equipment can be reduced. This is true only if the surfaces of the $CaC0_3$ crystals remain sufficiently clean. Therefore, as the presence of organic colloids is liable to impede crystallization, it is common practice to add coagulant reagents to the raw waters undergoing lime softening treatment in order to coprecipitate these colloids.

Lastly, it should be emphasized that $CaC0_3$, when used alone, tends to form very dense clusters of crystals which settle extremely rapidly, whereas $Mg(OH)_2$, when used alone, always appears in the form of very light floccules. If the percentage of these is substantial, they promote coagulation, but the acceptable settling velocity is much lower than with $CaC0_3$ only.

The assessment of lime softening equipment should, therefore, be primarily based on its ability to produce a homogeneous mixture of raw water, reagent and $CaC0_3$ nuclei, in a reaction zone of a suitable size. In order to increase the settling velocity, an organic flocculant may be injected following the growing phase of the crystals. When the aim is to obtain particularly clear carbonate-free water, lime softening should always be followed by filtration.

2.1.1.2. Use of sodium carbonate

The removal of permanent hardness may be obtained by the cold soda process, with or without lime precipitation of calcium and magnesium bicarbonates. The following reactions are involved:

$$CaSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + \underline{CaCO_3}\downarrow \quad (1)$$

$$CaC12 + Na_2CO_3 \rightarrow 2NaC1 + \underline{CaCO_3}\downarrow \quad (2)$$

This method has some disadvantages; particularly, alkalinity cannot in this way be reduced below 3 to 4 French degrees.

2.1.1.3. Precipitation by caustic soda

The precipitation of calcium and magnesium ions by caustic soda is a variation of the combined lime-soda treatment process, described in 2.1.1.2.

The basic reaction is:

$$Ca(HCO_3)_2 + 2\ NaOH \rightarrow \underline{CaCO_3}\downarrow + Na_2CO_3 + 2\ H_2O \quad (3)$$

Precipitation of calcium carbonate is accompanied by the formation of sodium carbonate, which will react on the permanent hardness according to reactions (1) and (2) above.

If caustic soda is used, therefore, the hardness of a water can be reduced by twice the amount of the reduction of alkaline-earth bicarbonates. The M alk. of the water can be reduced to around 3 to 4 French degrees only if there is enough permanent hardness to combine with the sodium carbonate formed.

2.1.2. Calculation and monitoring of precipitation (obtaining a minimum M alk.)

Notation:

CaH: calcium hardness in French degrees representing the total calcium salts content, MgH: magnesium hardness in French degrees representing the total magnesium salts content, C: free CO_2 content in French degrees calculated as:

$$C = \frac{\text{free } CO_2 \ (mg.l^{-1})}{4.4}$$

2.1.2.1. Amount of lime

.**Positive TH - M alk.**: the theoretical amount of lime required for optimum precipitation of calciu

$$CaO : 5,6 \ (TAC + C) \ g.m^{-3}$$

or

$$Ca(OH)_2 : 7,4 \ (TAC + C) \ g.m^{-3}$$

To precipitate calcium carbonate and magnesium oxide simultaneously, **MgH** being higher than **TH - M alk.:**

$Mg(HCO_3)_2$ hardness = M alk. - CaH:

CaO: 5.6 (2 M alk. - CaH + C) $g.m^{-3}$

or

$Ca(OH)_2$ 7.4 (2 M alk. - CaH + C) $g.m^{-3}$

Negative TH - M alk.:this applies to waters containing sodium bicarbonate. Good precipitation of calcium and magnesium is still possible by calculating the amount of lime on the basis of M alk. + MgH + C, but this gives a water containing great quantities of sodium carbonate and caustic soda, and it may be desirable to use a smaller amount.

Monitoring of results: in any case, the amount of lime must be increased (or reduced) by 5.6 grammes per m^3 (as CaO) or by 7.4 grammes per m^3 as $Ca(OH)_2$ per degree of P alk.measured above or below the theoretical value.

The values 5.6 and 7.4 apply, of course, to 100% pure products. In practice, lime is always impure and contains more or less carbonates, and the industrial values must be increased between 10 and 30% depending on the situation. To precipitate calcium carbonate alone, the ideal setting is when:

$$\text{P alk.} = \frac{\text{M alk.}}{2} \pm 0.5 \text{ French degree}$$

corresponding to a minimum M alk. of about 2 French degrees if the water does not contain magnesium.

If MgH is greater than TH - M alk., application of this rule leads to excessive M alk. values owing to the solubility of magnesium carbonate; the optimum result is obtained when:

$$\text{P alk.} = \frac{\text{M alk.}}{2} \pm 0.5 \text{ to } 1 \text{ French degree}$$

with the lowest possible value for P alk.

2.1.2.2. Amount of sodium carbonate

The required amount of sodium carbonate is:

$$10.6 \ (TH - M \ alk.) \ g.m^{-3}$$

. **Monitoring of results:** theoretically, in a water containing no magnesium, the following must be obtained:

TH = M alk. = 2 P alk.

In practice, in waters where part of the permanent hardness consists of magnesium, this rule may no longer be valid, and each individual case must then be considered separately.

2.1.2.3. Amount of caustic soda

The amount of caustic soda (as pure product) required per degree of M alk. to be precipitated is:

$$8 \ (2 \ M \ alk. - CaH + C) \ gm^{-3}$$

Monitoring of results: in order to lower the M alk. by 1 French degree, the TH must be reduced by 2 French degrees.

In practice, the amount of caustic soda introduced into the water is adjusted to give a minimum residual

2.2.
SILICON PRECIPITATION

The process involves the adsorption of silica on a massive floc of Al, Mg, or Fe hydroxide.

This coprecipitation may be performed either cold or hot. The process is often combined with the $CaC0_3$ process in the lime softening of drilling water.

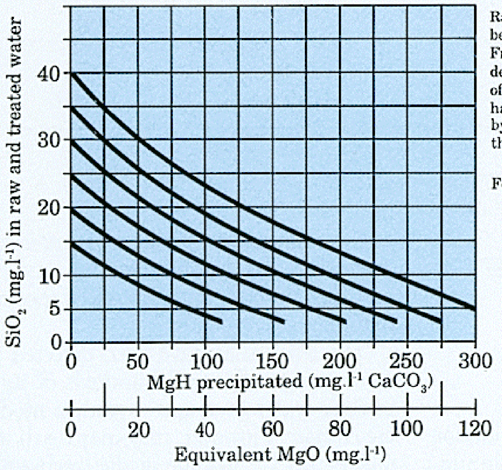
2.2.1. Silica removal with Mg(II)

This treatment may be performed either cold or hot.

Usually, magnesium is already present in the drilling water and precipitates during the lime softening process with part of the silica. Mg may be added in the form of Mg0 powder which solubilizes by cold carbonation into $MgC0_3$, or is simply dispersed at 100°C.

Depending on the analyses of raw water, the temperature and the desired level of removal, graphs make it possible to calculate the amount of Mg0 (see Figure 34) that is reacting, and, by difference, how much must be added.

In the cold process, this varies from 3.2 to 1.8 mg of Mg0 per mg of $Si0_2$ adsorbed, for an initial concentration of 20 to 40 mg.1-1.



Range of water temperature
between 20 and 30°C.
From the water analysis,
determine the quantity
of magnesium
hardness to be precipitated
by the process selected,
then consult the graph.

For example :

- 150 mg.l^{-1} (as $CaCO_3$) of MgH precipitated,
- SiO_2 content in raw water : 30 mg.l^{-1},
- SiO_2 content in treated water : 11 mg.l^{-1}.

Figure 34. Silica removal with magnesium oxide.

2.2.2. Silica removal with sodium aluminate

This treatment should preferably be performed cold (Figure 35).

The residual values obtained are higher than with MgO.

The amount of aluminium, expressed as Al_2O_3, in brine, is in the range of 2 to 2.6 mg per mg of silica coprecipitated.

In the lime-soda softening process for drilling water, silica removal conditions and residual contents obtained for initial levels of 20 to 40 mg.l^{-1} are summarized in the table below:

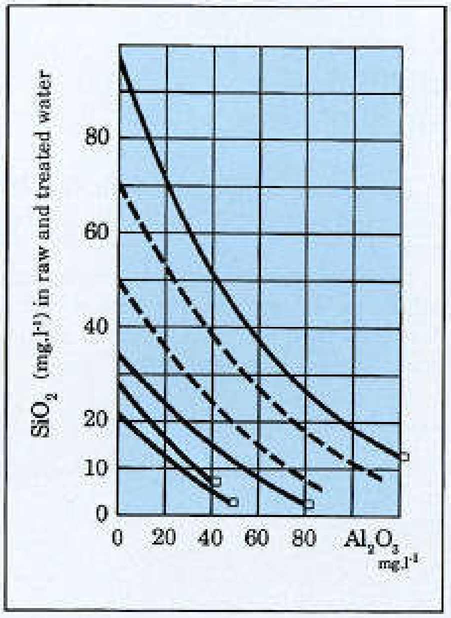


Figure 35. Silica removal with aluminate.

Figure 35. Silica removal with aluminat

Reagent	Temperature C	pH	Residual SiO_2 mg.l^{-1}
MgO	50-55	9.6-10	4-6
NaAlO^{2-}	30-35	8.6-9.5	5-10

The decision as to which of the two reagents to use will be based on the initial level of Mg in the water, the cost of the reagents and the amount of sludge produced.

2.2.3. Silica removal with ferric chloride

FeC13 may be used in combination with aluminate to obtain residual aluminium in the range of 0.2 to 0.3 mg.l^{-1} with a pH of 8.5 to 9, instead of 1 to 3 mg^{-1} with the aluminate alone.

2.2.4. Colloidal silica

Even though its chemical nature is controversial, this would refer to very fine particles of clay with an electropositive nature.

The levels that have been detected are in the range of several hundreds of gg.l^{-1} in river water in countries with a moderate climate. However, they may reach into tens of mg.l-1 in some acidic leachates in hydrometallurgy.

In natural water, the removal maybe obtained:

- by double flocculation with two different pH values with co-adsorption on a metallic hydroxide,
- by precoat filtration, or even better, filtration on an MF or OF membrane

In the case of leachates (in hydrometalurgylurgy), specific non-ionic flocculants that are compatible with the treatments downstream must be used.

2.3.
PRECIPITATION OF METALS

This involves the precipitation of dissolved metals that are mainly found in the effluents resulting from surface treatment, the leachates from hydrometallurgy and the gas scrubbing effluents, after the burning of coal and household refuse.

The usual procedure consists in precipitating the metals in the form of hydroxides by simply neutralizing the acidic effluents. Since none of the pH values for maximum precipitation of all the metals coincide, an optimum reaction zone (see page 516) must be found for the pH, which may range from 7 to 10.5, depending on the minimum values desired for the removal of the most harmful metals.

In the coprecipitation of **carbonates** in the form of less soluble **hydroxycarbonates,** the removal threshold may be improved, as for instance in the case of lead.

The residual values of ionized metals may vary from 0.1 to 2 $mg.l^{-1}$, depending on the metal; this is independent of the hydroxides that may remain in colloidal dispersion depending on the quality of flocculation and settling.

The desirable residual levels for some metals (Cd, Ag, Hg) are becoming more and more strictly limited in some countries and have been reduced to less than 100 $\eta g.1^{-1}$.

Precipitation may thus take place in the form of sulphur compounds, which are hardly ever soluble and which allow the precipitation of weakly chelated metals (ammonium or other organic chelating agents) in a narrow pH range.

This precipitation takes place:

- with Na2S and in the form of colloidal sulphur which requires the copresence of iron hydroxide in order to be flocculated,
- or with derivatives of organic mercaptans which facilitate flocculation.

In cases that are in-between, an excess of a metallic cation, Fe^{3+} or $A1^{3+}$, can be used to promote adsorption (Cd, Se, as well as B, As) or a very strong oxidizing agent can be used as a preliminary step to break strong chelating agents such as EDTA (see page 156).

2.4.
OTHER PRECIPITATIONS

2.4.1. Sulphates

Sulphate precipitation may be induced before the effluents are discharged into the sewers (breakdown of concrete) or recycled (scaling). The sulphates must often be removed from brine or water before distillation.

The usual procedure, applicable in the case of high SO_4^{2-} contents, involves the cold **precipitation of gypsum $CaSO_4.2H_2O$,** by adding Ca^{2+} in the form of lime (usually done with acid water) or $CaCl_2$ (as in the case of brine):

$$SO_4^{2-} + Ca^{2+} + 2\ H_2O \rightarrow \underline{CaSO_4,\ 2\ H_2O}\downarrow$$

In both cases, precipitation in the form of heterogeneous crystals is very slow. To avoid supersaturation and dangerous post-precipitations, the reaction must take place with a very high concentration of nuclei.

The SO_4^{2-} concentrations obtained depend on the salinity, the activity of the medium, and the amount of Ca z+ added, which in the case of lime, is limited by the acidity to be neutralized. The residual levels may be obtained using various diagrams, e.g.:

- 2 to 3 g.l^{-1} SO_4 in brine purification using $CaCl_2$,
- 1.5 to 2 g.l^{-1} SO_4 in neutralizing acidic water without using $CaCl_2$.

A second procedure involves the precipitation of barium sulphate by adding BaC12. The residual solubility obtained is less than 20 mg.L_1, but the reagent is very expensive and rarely used.

2.4.2. Fluorides

Fluoride removal by precipitation is applicable to acidic effluents from gas scrubbing after incineration or from aluminium metallurgy, as well as effluents from the phosphoric acid and glass industries. In the last two cases, the presence of F- is always linked to a high concentration of silica, which changes the precipitation conditions. The neutralizing agent is always lime, to which $CaCl_2$ may be added if it is necessary to obtain low residual values of F-:

$$2\ F^- + Ca^{2+} \rightarrow \underline{CaF_2}\downarrow$$

With a mainly fluoride and sulphuric or hydrochloric pollution, the precipitate has a CaF_2 base. Its crystallization and precipitation show kinetics that lie between those of $CaC0_3$ and gypsum. The size of the equipment is quite similar to that of the equipment for lime softening, although the reaction time is longer.

In the precipitation process that uses only lime, the solubility of CaF_2 depends on the pH for a given salinity (see Figure 36). It also depends on the procedure:

- from 16 to 30 mg.l^{-1} for electroplating effluents,
- from 2 to 5 mg.l^{-1} for phosphoric acid production effluents, owing, however, to the adsorption of F^- on precipitated hydroxyapatite,
- from 20 to 40 mg.l^{-1} for saline effluents.

Dissolved aluminium, when present at a substantial level, is an unfavourable chelating element. Conversely, along with the massive coprecipitation of $AI(OH)_3$ or $Mg(OH)_2$, these hydroxides adsorb fluorides and can reduce their residual solubility.

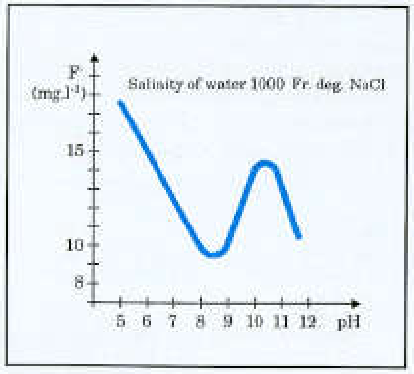


Figure 36. Precipitation of fluoride by lime in an NaCl medium.

With a **substantial amount of silica** present, a parallel reaction is added:

$$SiF_6^{2-} + 4\ OH^- \rightarrow \underset{\downarrow}{\underline{SiOH_4}} + 6\ F^-$$

The F- levels obtained depend on the increase of Ca 2+ in the medium.

The precipitation of great amounts of strongly hydrated silica gel is slow; it is the thickening of the sludge that determines the size of the settling tank.

2.4.3. Phosphates

These salts maybe present in water in variable forms and concentrations:

- phosphoric acid in effluents from phosphate fertilizer factories which contain HF and S102,
- phosphates in domestic wastewater, - phosphates in boiler blowdowns,
- polyphosphates and hexametaphosphates from cooling systems (see page 156).

Two types of precipitation must be considered:

- acidic effluents: by lime,
- non-acidic effluents: by A1 or Fe salts (formation of metallic phosphates).

2.4.3.1. Precipitation by lime

Depending on the initial acidity, two reactions are possible:

- calcium dihydrogen phosphate precipitation at an optimum pH level of 6 to 7:

$$2\ H_3\ PO_4 + Ca(OH)_2 \rightarrow \underset{\downarrow}{\underline{Ca\ (PO_4H)_2}} + 2\ H_2O$$

This compound settles rather rapidly but produces a hi residual solubility (130 to 300 mg.$^{-1}$ P_2O_5 depending on the temperature),

- tertiary calcium phosphate precipitation at a pH level of 9 to 12:

$$2\ Ca\ (PO_4\ H)_2 + Ca(OH)_2 \rightarrow \underset{\downarrow}{\underline{Ca_3\ (PO_4)_2}} + 2\ H_2O$$

The tertiary calcium phosphate presents a residual solubility of several mg.l^{-1} as P_2O_5, however, in a colloidal form. It precipitates slowly without the addition of a flocculant.

The magnesium that may be present has a more complex action:

- below a pH of 9, the solubility of calcium phosphate increases with its concentration,
- above a pH of 10, calcium phosphate coprecipitates with magnesia with residual values below 1 mg.l^{-1}.

2.4.3.2. Precipitation by A1^{3+} or Fe $^{3+}$

$AlPO_4$ and $FePO_4$ are very scarcely soluble salts that precipitate, however, into the colloidal state. The precipitate is removed by adsorption on an excess of metallic hydroxide (see Figure 37).

The residual values of P that are obtained may be below mg.l^{-1}, which implies that the dosages of iron and aluminium salts are relatively high.

pH of phosphate precipitation

Reagent	pH	Notes	Type of precipitate
$Ca(OH)_2$	9 - 12	+ flocculant	Hydroxyapatite
Fe'+	5	+ excess of hydroxide	Phosphates + metal hydroxide
A13+	6		

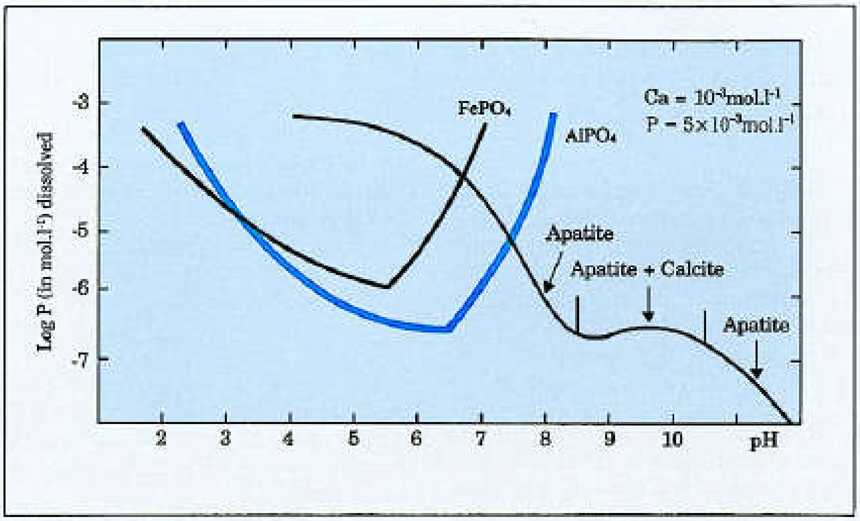


Figure 37. Graph of solubility of Fe, Al and Ca phosphates.

Figure 37. Graph of solubility of Fe, Al and Ca phosphates.

2.5.
PRECIPITATION INHIBITORS

Chemical precipitation may be slowed down by some compounds naturally found in water. It is this natural inhibition which stands in the way if precipitation is desired.

If, on the contrary, precipitation is not desired, inhibition may be induced by adding inhibitors.

2.5.1. Natural inhibition

Inorganic and organic compounds may either form relatively soluble complexes with ions to precipitate, or else disperse precipitation products. When found together they inhibit precipitation by retarding it or by displacing the solubility.

. In carbonate removal

- at the high pH levels used in carbonate removal, NH_4 is converted to NH_4OH, which increases the residual value of M alk.,

- some organic acids, humic or fulvic, form soluble complexes with calcium which increase the residual hardness,

- in the case of surface water which is polluted by municipal effluents, the presence of polyphosphates (chelating agents) slows the nucleation and growing time of crystals and consequently causes them to disperse as colloids.

. **In the treatment of industrial wastewater,** such as gas scrubbing effluents, the presence of both metallic cations (Ni^{2+}, Zn^{2+}, etc.) and NH^{4+} determines the formation of metal-ammonium complexes that are relatively stable.

.**In the physical-chemical iron removal process**, the presence of silica considerably raises the precipitation time of hydroxide.

2.5.2. Induced inhibition-dispersion

2.5.2.1. Main properties

The products used can have different actions.

.**Inhibiting crystallization**

Scale inhibiting action on supersaturated solutions, by the addition of low amounts of inhibitors of the order of mg.l^{-1}. There is an extension of the nucleating time and a slow-down in the growth of nuclei (see Figure 38): this is the threshold effect.

Distortion of the crystalline structure

Action on the growth rate in modifying the facies of the allotropic variety of the precipitate, which results in a lower risk of adhering to the walls and thus forming scale.

. **Dispersing capacity**

The capacity to maintain solid particles in suspension in a divided state when the particles have a tendency to stick together. This is a result of the adsorption of the product on the particles or its action on their electrical charges.

Some products that are used in high amounts have the ability to put back into solution or into suspension salts that have already precipitated on the walls (they enable partial cleaning or help in the descaling process).

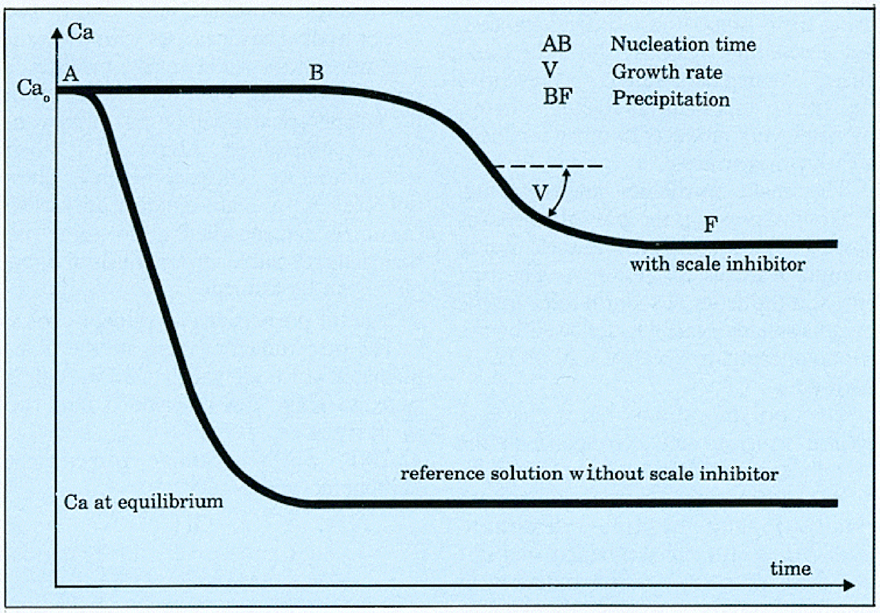


Figure 38. $CaCO_3$ precipitation curve.

. Chelating (or sequestering capacity)

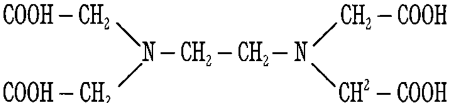
The property of incorporating into their molecule, anions or cations, in order to form new stable soluble compounds despite the presence of a precipitating agent.

Chelating requires great amounts of product, for example in the order of 50 g of phosphate per French degree of Ca for 1000 m3 of water at 20 French degrees of TH.

2.5.2.2. Main compounds

. The chelating agents

Those such as EDTA (ethylenediamine tetraacetic acid) and its sodium salts:



They are mainly used for boiler feedwater water containing traces of hardness or during a descaling operation; however, using them properly is a difficult process. For economic reasons the "threshold effect" is preferably used in preventive treatments, especially in cooling systems, by employing products of other families:

. Polyphosphates

They make up the best known family. Strictly speaking, the polyphosphates possess a linear structure and their overall formula reads as $M_{n+2}Pn.O_{3n+1}$. The first terms in the series of sodium salts are the pyrophosphate: $Na_4P_2O_7$, followed by the tripolyphosphate, $Na_4P_2O_7.NaPO_3$ or $Na_5P_3O_{10}$.

The **polymetaphosphates** have a cyclical structure and correspond to the overall formula $(MPO_3)_n$. The most familiar terms are trimetaphosphate $(NaPO_3)_3$ and hexametaphosphate $(NaPO_3)_6$. Commercial products sold under these names are often mixtures in which the prefix represents the average degree of condensation.

The retarding action is straightforward with regard to calcium carbonate and a little less so with regard to magnesium oxide and calcium sulphate.

Normally, to stabilize water having TH and M alk. levels in the order of 20 French degrees, approximately 2 $g.m^{-3}$ of polyphosphate is used. This dosage increases with the TH, the M alk., the turbidity and the temperature at which it is used. French law governing drinking water has set the maximum level of polyphosphate, expressed as P_2O_5, at 5 $g.m^{-3}$.

Polyphosphates are available on the market in three main forms:

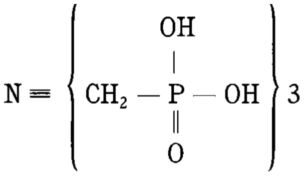
- crystalline polyphosphates, which are readily soluble,
- "vitreous" polyphosphates, -liquid polyphosphates.

The polyphosphates can be decomposed gradually by hydrolysis while giving rise to orthophosphate ions, PO_4^{3-}. The rate of hydrolysis increases with the temperature and the acidity of the medium; a precise threshold, however, above which the polyphosphates will be destroyed, cannot be pinpointed. Above 60°C, their scale inhibiting efficiency becomes questionable. At a high temperature, when calcium is present, there is also some risk that slightly soluble tertiary calcium phosphate will be formed.

. Organic derivatives of phosphorus

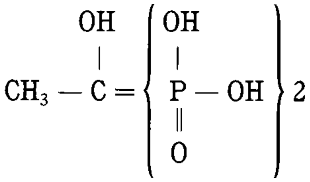
The best known of these are the phosphonates which are widely used in cooling systems. These can be divided into two main types:

- AMP, which is amino trimethylene phosphonic acid



$$N \equiv \left\{ CH_2 - \overset{\overset{OH}{|}}{\underset{\underset{O}{\|}}{P}} - OH \right\} 3$$

- HEDP, which diphosphonic acidis hydroxyethane



$$CH_3-\overset{\overset{OH}{|}}{C}=\left\{\begin{array}{c}OH\\ |\\ P-OH\\ \|\\ O\end{array}\right\}2$$

These compounds are usually sold in the form of concentrated solutions. They are stable at temperatures far exceeding 100°C and are sensitive to the presence of free chlorine. Although they are non-toxic, however, their use in drinking water is governed by standards set by authorities in the field.

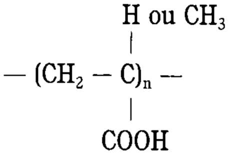
The amounts used vary according to the nature of the water and the conditions under which it will be used; however, they also vary from one commercial product to the other. Amounts average in the order of 1 $g.m^{-3}$ as P_2O_5, to about 10 $g.m^{-3}$ as commercial products.

The P-C-P link, which is more stable than the P-O-P link, makes it possible for them to be used at high temperatures exceeding 130°C, such as is the case with evaporators.

. Synthetic organic polymers

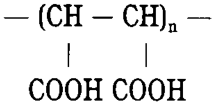
These more recent products have undergone extensive development in the field of water conditioning. The main families involved are:

Acrylic or methacrylic type



$$-(CH_2-\underset{\underset{COOH}{|}}{\overset{\overset{H\ ou\ CH_3}{|}}{C}})_n-$$

Maleic type



$$-(\underset{\underset{COOH}{|}}{CH}-\underset{\underset{COOH}{|}}{CH})_n-$$

Polymers are mixtures of molecules of different sizes. The definition of a polymer depends on the knowledge of its gramme-molecular weight and the distribution of the gramme-molecular weights.

Several properties worthy of note are: - the anionic character,

- the gramme-molecular weights which are close to 10^3 for the scale inhibiting dispersing agents and 10^4 for the dispersing agents,
- a better dispersing capacity than that of polyphosphates and phosphonates,
- adequate stability at a temperature > 150°C and vis-à-vis chlorine,
- easily biodegradable after discharge.

The formulations often contain copolymers or terpolymers in order to increase the efficiency, depending upon the desired application.

. Other dispersing agents

The naphthalene and polystyrene sulphonates possess an anionic character and may be combined with polyphosphates and. phosphonates.

Sodium tannate, derived from wood, is used in low pressure and medium F pressure boilers at a dosage of 2 $g.m^{-3}$ per French degree of calcium

3. SETTLING

Settling is the separation technique ulation often used for SS and colloids (collected in the form of floc after the coagulation-flocculation stage).

3.1.
DIFFERENT TYPES OF SETTLING

There are various types of substances that will settle out:

- **discrete particles** settle independently of one another with a constant velocity,
- **flocculent particles** have varying sizes and settling velocities. When the concentration is low, the settling velocity increases as the size of the floc increases as a result of agglomerating with other particles; this is flocculent settling,
- in the case of higher concentrations, the large quantity of floc causes hindered overall settling with a clearly marked interface between the sludge mass and the supernatant liquid; this is **hindered settling**.

3.1.1. Settling of discrete particles

This is the simplest process, which is the easiest to describe by equations.

3.1.1.1. Theory

When a discrete particle is left alone in a liquid at rest, it is subjected to a driving force FM (gravity) and to a resistant force FT (the fluid drag), resulting from viscosity and inertia:

$$F_M = (\varrho_s - \varrho_l)\, g^V \qquad \uparrow F_t$$

$$F_T = \frac{Cs\, \varrho_l\, v^2}{2} \qquad \downarrow F_M$$

Q_S, Q: densities of the discrete particle and the fluid,

d, s, v: diameter, area and volume of the discrete particle,

V: settling velocity of the particle, g: acceleration of gravity,

C: drag coefficient (dimensionless).

An equilibrium is rapidly set up and the settling of the particle, assimilated to a sphere, takes place at a constant velocity Vo:

$$V_o^{\,2} = \frac{4}{3}\,\frac{(\varrho_s - \varrho_l)\, gd}{C\varrho_l}$$

3.1.1.2. Hydraulic flow

The value of drag coefficient C is defined by the perturbation, which itself is a function of the settling velocity. This perturbation is characterized by the particle Reynolds number, given as:

$$Re = \frac{\varrho_l V d}{\eta}$$

Re = dimensionless

η = absolute viscosity

If Re is low, the forces of viscosity are much higher than the forces of inertia. If Re is high, the viscosity is negligible.

The drag coefficient is given as:

$C = a\, Re^{-n}$, where a and n are constants.

Re	**Flow**	**a**	**n**	**c**	**Formula**
$10^{-4} < Re < 1$	Laminar	24	1	$24\, Re^{-1}$	Stokes
$1 < Re < 10^3$	Intermediate	18.5	0.6	$18.5\, Re^{-0.6}$	Allen
$10^3 < Re < 2.10^5$	Turbulent	0.44	0	0.44	Newton

The table on the opposite page gives the different values of a, n and C, depending on the Reynolds number (charts are also available).

These formulae are the basis of the calculation of the movement of particles in fluids, and are used for settling (of discrete solids in a liquid, drops of water in air), for upward flow (air bubbles in water, oil drops in water), centrifugation and fluidization.

In laminar flow, Stokes' law gives:

$$V_o = \frac{g}{18\eta}(\varrho_s - \varrho_l)\, d^2 \text{ in SI units}$$

3.1.1.3. Sphericity factor

The factor ψ is as follows:

$$\psi = \frac{\text{the volume of a sphere of same area}}{\text{the volume of the particle}}$$

Values of ψ	
Sand	2
Coal	2.25
Talc	3.25
Gypsum	4
Graphite lamellae	22
Mica	170

In the above operation, it is necessary to replace c by $c' = \psi c$.

3.1.1.4. Conditions of capture

Upward flow settling tank

Particles with a settling velocity exceed ing the upward velocity of the liquid will be retained.

. **Horizontal flow settling tank (Figure 39)**

- Let us take a rectangular settling tank of length L and vertical section s (where H is the water depth and 1 is the width), uniformly crossed by flow Q.

- The velocity of a particle entering the tank at the top has two components:

V1: the horizontal velocity of the fluid equal to Q/s,

Vo: the vertical velocity limit given by Stokes' law.

This particle is retained in the tank if:

$$\frac{V_o}{H} > \frac{V_1}{L} = \frac{Q}{H.l.L}$$

i.e.:

$$V_o > \frac{Q}{S_H} = V_H$$

S_H: horizontal area of the tank,

V_H: Hazen velocity (or hydraulic surface loading).

It should be noted that V_H is independent of the depth of the tank.

Theoretically, all particles with settling velocities exceeding V_H will be removed. However, if the feed water is distributed over the entire depth, part of the particles, with a settling velocity V which is lower than the Hazen velocity, will also be retained in the V/V_H ratio. In an upward

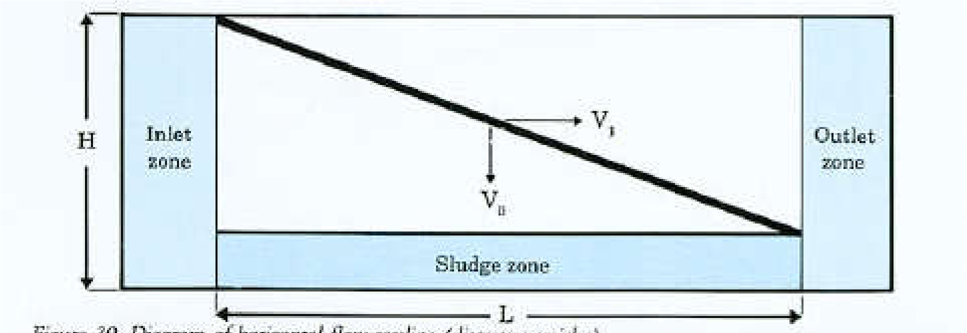


Figure 39. Diagram of horizontal flow settling (discrete particles).

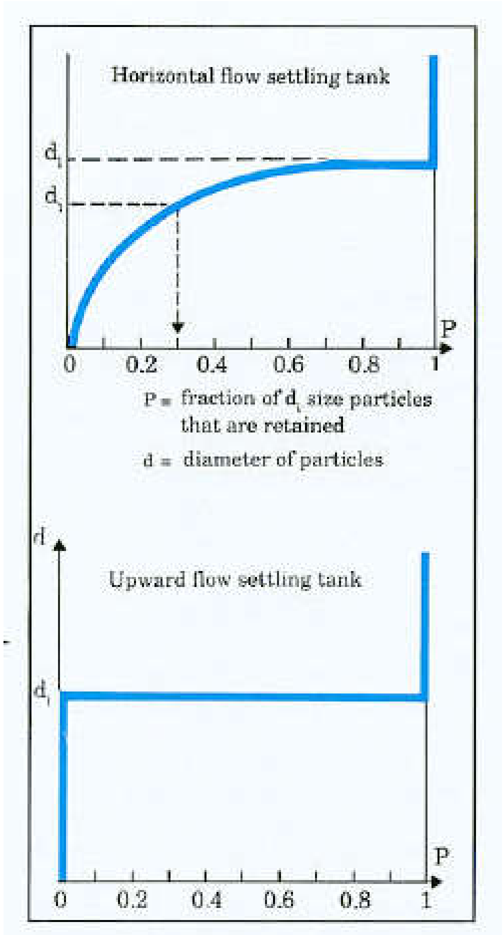


Figure 40. Efficiency of horizontal vs. upward flow settling (discrete particles).

flow settling tank, these particles would not be retained.

Theoretically, for the same horizontal area, a horizontal flow settling tank allows for the separation of a larger number of particles (Figure 40).

In practice, this difference is attenuated or even reversed for the following reasons, which are linked to horizontal flow settling:

- the difficulty of hydraulic distribution on a vertical plane at the inlet as well as at the outlet of the tank,
- the accumulation and collection of sludge,
- in a circular, horizontal flow settling tank, the horizontal component of the velocity of the particle (Vi), decreases as it goes from the centre to the periphery and its settling travel becomes curved.

3.1.2. Flocculent settling

During settling, flocculation is carried on and the settling velocity Vo of particles increases (Figure 41).

This process occurs as soon as the concentration in flocculated matter is higher than about 50 mg.l''.

The efficiency of flocculent settling depends not only on the hydraulic surface loading but also on the retention time.

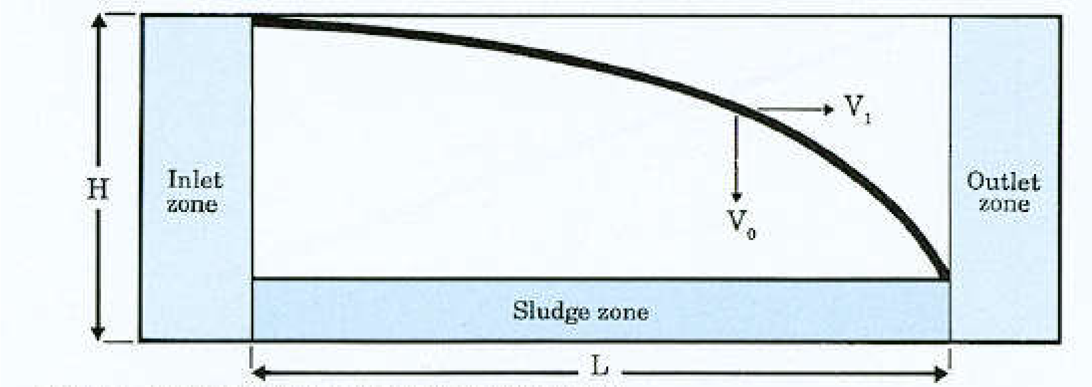


Figure 41. Horizontal flow settling (flocculated particles).

There is no mathematical formula for calculating the settling velocity. Knowledge of this velocity can be gained from laboratory tests and graphs. Figure 42 gives the results of such a test.

3.1.3. Hindered settling of flocculated particles

As soon as the concentration of flocculated particles becomes substantial, interaction between particles becomes more important. Settling is hindered. The particles adhere together and hindered settling causes the formation of an interface between the floc and the supernatant liquid.

This is typical of activated sludge and flocculated chemical suspensions when their concentration exceeds 500 mg.l^{-1}.

<u>3.1.3.1. Visual observation</u>

In the case of hindered settling in a tube of adequate height and diameter (a cylinder of at least one litre), usually four - phases can be seen (Figure 43).

Figure 42. The effect of settling time and depth of settling tank on the removal of flocculated particles in flocculent settling

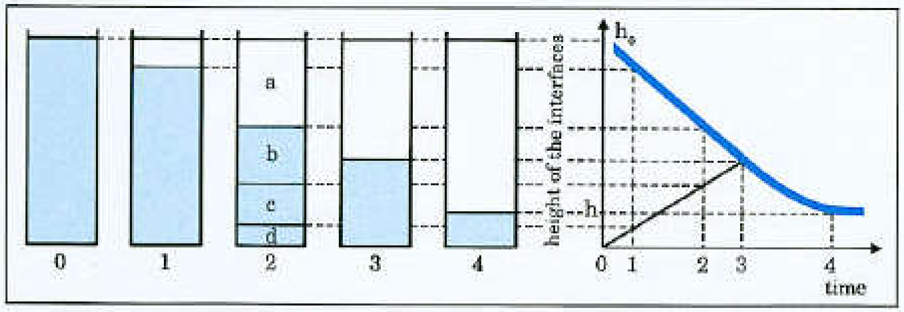


Figure 43. Diagram of hindered settling.

a: Clarification zone where the liquid is clear.

b: Homogeneous suspension zone where the solution appears the same as at the beginning with a clear a-b interface.

c: Transition zone (not always seen).

d: Sludge thickening zone in which the level rises rapidly before it decreases slowly.

At a certain stage, zones b and c disappear; this is the critical point. The change in the height of a-b, then a-d interface, measured as a function of time, is shown by **Kynch's curve**.

3.1.3.2. Kynch's curve (Figure 44)

Kynch's basic hypothesis is that the falling velocity of a particle depends solely on the local particle concentration C.

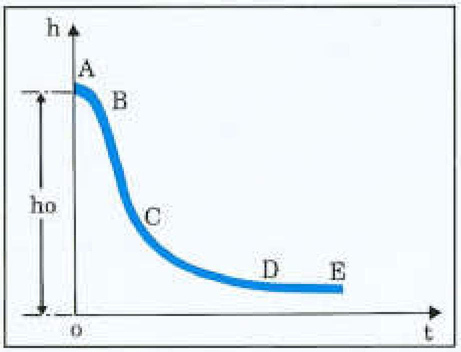


Figure 44. Kynch's curve.

From A to B, the interface is more or less clear; this is the floccule coalescence phase. This phase does not always exist.

The straight section from B to C represents a **constant falling velocity Vo** (slope of straight line). For a tube of given dimensions, Vo depends on the initial concentration of SS and the flocculation properties of the suspension. As the initial concentration Co increases, the settling velocity Vo of the mass drops. For example, for a municipal activated sludge with a concentration of SS varying from 1 to 4 $g.l^{-1}$, Vo varies from 6 to 1.8 $m.h^{-1}$.

The concave section CD corresponds to a gradual slowing down of the falling velocity of the top layer of the deposit.

From D onwards, the floccules come into contact with one another and exert a compressive action on the lower layers.

Kynch's theory applies to sections BC and CD which cover the most important field of settling of activated sludge.

3.1.3.3. Interpretation

Let us take a suspension which has no coalescence phase when settling (Figure 45). The calculation shows that:

- in the triangle BOC, the concentration and falling velocity ate constant and are respectively equal to the initial values at B,
- in the triangle COD, the equiconcentration curves are straight lines passing

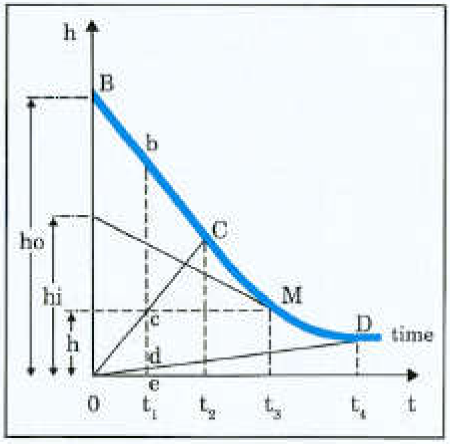


Figure 45.

through the point of origin, which means that from the first moments of settling, the layers closest to the bottom go through all the concentrations between the initial concentration and that corresponding to point D, where compression starts.

The sludge medium of depth eb, at time ti, therefore, has three separate zones:

- a top zone bc, where the **concentration and falling velocity are uniform** and have retained their initial values Co and Vo,
- an intermediate zone cd, where the concentration gradually increases from c to d and the falling velocity drops accordingly;
- a lower zone de, where the sludge floccules come into contact with one another and are subject to compression.

In the medium considered in time tz, the top zone disappears, and in that considered in time t_4, only the lower zone remains.

For point M in section CD, two concentrations can be defined:

CM`: concentration at the interface CM: average concentration

According to Kynch's hypothesis:

$$C_M^i = C_O \frac{ho}{hi}$$

And also:

$$C_M = C_O \frac{ho}{h}$$

The three sections BC, CD and DE of Kynch's curve (Figure 44), are applied in sizing the units for hindered settling. The phase BC corresponds to solids contact settling tanks. The phase CD pertains to installations in which sludge thickening is desirable (thickened sludge recirculation units). The phase DE is applied in sludge thickening.

Sludge Volume Index or SVI (Mohlman index)

On Kynch's curve there is a special point used to define a sludge: it is the 30 minute abscissa. The SVI is intended mainly to define the types of biological sludge.

$$SVI = \frac{V}{M}$$

V: Volume of sludge after 30 minutes of settling (CM). M: SS present in this volume (g).

For the same sludge, the SVI partly depends on the geometric characteristics of the test cylinder as well as on the initial concentration of the sludge. For this reason, it is recommended that whenever necessary, the sludge be first diluted with purified water so that the final volume is about 250 ml (in a one litre cylinder). Maintaining a slow agitation during the test is prescribed for some operations, although this seems questionable. Activated sludge that settles easily has an SVI of 50 to 100 $cm^3.g^{-1}$.

3.2.
SIZING SETTLING TANKS

The surface area of a settling tank is based on two criteria:

- the hydraulic surface loading, which corresponds to the volume of effluents to be treated per unit of surface area and time ($m^3/m^2.h$),
- the solids loading, which corresponds to the quantity of SS to settle per unit of surface area and time ($kg /m^2.h$).

3.2.1. Influence of the hydraulic surface loading

This loading is directly related to the settling velocity of SS. The preceding paragraphs show that this velocity can be calculated by Stokes' law for discrete particles and can easily be measured in the case of flocculent settling.

In these cases the dimensions of the settling tank depend only on the hydraulic surface loading.

3.2.2. Influence of the solids loading

In the case of hindered settling of flocculated particles where the thickening factor is involved, the solids loading (or flux rate) is usually the determining factor used to calculate the settling tank area.

A settling tank of section S is fed by an inflow QE that has an SS concentration CE. Sludge at a concentration Cs is drawn off from the bottom at a rate Qs.

In the absence of chemical or biological reactions influencing the SS concentrations, and considering a removal yield of 100%, the result is:

- treated flow $Q = Q_E - Q_s$
- assessment of suspended solids QsCs = $Q_E C_E$

or a solids loading of:

$$\frac{Q_S C_S}{S} = \frac{Q_E C_E}{S}$$

Kynch's curve indicates the settleable solids loading. For a particular point on Kynch's curve of concentration C_i, the settling velocity V_i is given by the tangent to this point. At this level the flux rate is $F_i = C_i V_i$.

To this figure F; must be added the draw-off flux rate F_s given by $C_i V_s$ with $V_s = Q_s/S$. The total solids loading is $F = C_i V_i + C_i V_s$.

Figure 46 indicates the changes of these various flux rates. F shows a minimum FL associated with a critical concentration CL, which imposes a minimum section Sm for the settling tank so that:

$$Sm = \frac{Q_E C_E}{F_L}$$

A particular point L may be determined directly on the solids loading F (Figure 46 c) by:

$$\left(\frac{dF}{dC_i}\right)_L = \left(\frac{dF_i}{dC_i}\right)_L + V_S = 0$$

The point L is, therefore, the point of the F_i curve where the tangent is equal in absolute value to the draw-off rate Vs (Figure 46 a). These results can be expressed differently considering Kynch's curve. The limit flux rate FL at point L is given by:

$$F_L = C_L\,(V_L + V_S) =$$

$$C_L\left(V_L + \frac{Q_E C_E}{S} \text{ x } \frac{1}{C_S}\right)$$

where:

VL is the settling velocity at point L.

Thus, in order for settling to occur:

$$\frac{Q_E C_E}{S} < \frac{V_L}{\frac{1}{C_L} - \frac{1}{C_S}}$$

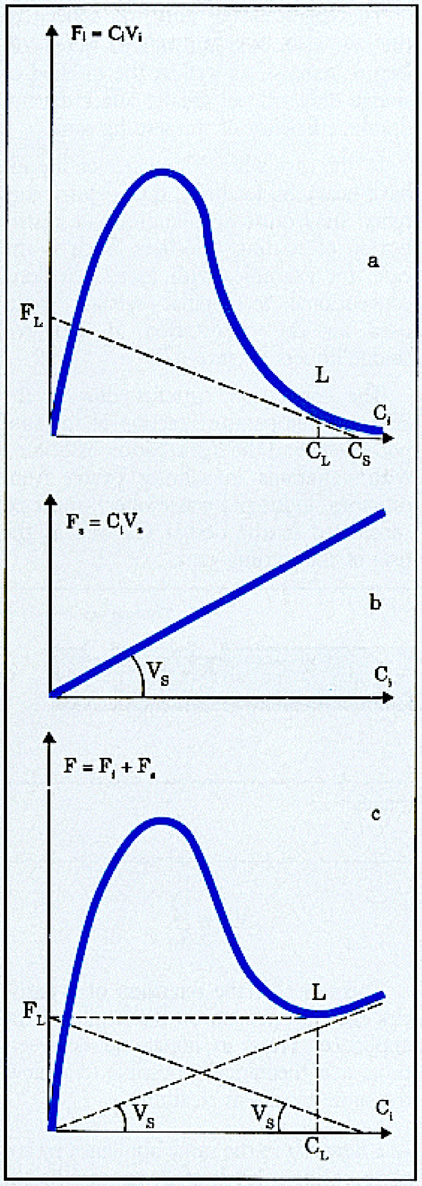


Figure 46. Solids loading curves.

Figure 46. Solids loading curves,

3.2.3. Structure of the settling tanks

In practice, there is no ideal settling tank, for eddies can occur in the liquid, the wind may create waves on the surface, and the convection currents caused by local temperature (action of the sun) and density differences may affect the settling efficiency. Every effort must be made to obtain a laminar and steady circulation with suitable values for the Reynolds number as given by:

$$Re = \frac{V\, d_h}{\nu}$$

Re: Reynolds number (characterizing thefluid flow),

V: velocity of circulating water, in m.s^{-1},

dh: equivalent hydraulic diameter, in m,

ν: kinematic viscosity of the water, in m.s^{-2}

$$\text{with } d_h = 4\,\frac{\text{Wetted area}}{\text{Wetted perimeter}}$$

Note: the hydraulic radius of a conduit is given as:

$$r_h = \frac{\text{Wetted area}}{\text{Wetted perimeter}}$$

In the case of a circular conduit running full, the hydraulic diameter is the same as the diameter of the conduit. The numerical values of the Reynolds number depend on the choice of rh or do in the definition. In practice, the flow is considered laminar if Re < 800 (with d_h).

Moreover, the **Froude number** makes it possible to assess the stability of a circulation process when the flow is affected primarily by gravitation and the forces of inertia.

$$Fr = \frac{V^2}{g d_h}$$

The more stable the circulation, the more uniform the velocity distribution over the whole section of the tank. Stable circulations have high Froude numbers.

In practice, H/L or H/R ratios can be defined, where H is the wetted depth of rectangular settling tanks of length L and circular tanks of radius R. With a retention time of two hours in the tank, Schmidt-Bregas gives:

- for horizontal flow, rectangular settling tanks:

$$\frac{1}{35} < \frac{H}{L} < \frac{1}{20}$$

- for circular settling tanks:

$$\frac{1}{8} < \frac{H}{R} < \frac{1}{6}$$

The shape of the tank, the design of the raw water feed and treated water collecting systems, as well as the method of sludge draw-off, all greatly affect the hydraulic efficiency of the settling tank.

In the case where the water or liquids have heavy SS loadings, the "density currents" may cause an inappropriate distribution of settling velocities. Such is the case, for example, with excessively long conventional rectangular settling tanks used for the clarification of activated sludge liquors (Figure 47).

The convection currents due to the effects of temperature (action of the sun, hot water) and the disturbances associated with variations in salinity (water from estuaries, industrial wastewater), must be considered in the design (as well as the use) of the settling tank.

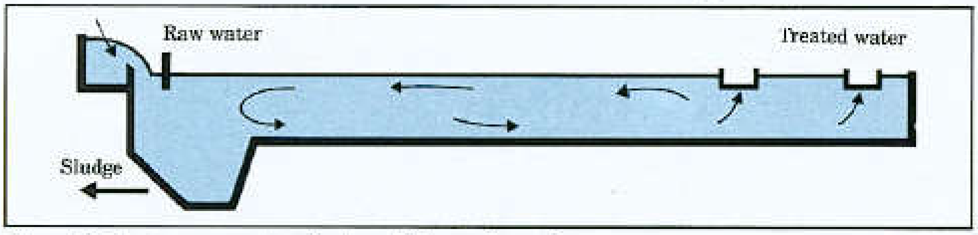


Figure 47. Density currents in a horizontal flow settling tank.

3.3. LAMELLAE SETTLING

3.3.1. Principle

For horizontal flow settling tanks, the only basic size factor is the horizontal set tling area S_H (see 3.1.1).

A discrete particle is retained if its settling velocity is higher than the Hazen velocity VH.

$$V_H = \frac{Q}{S_H}$$

Theoretically, the retention of a particles does not depend on the height of the appliance. Thus, in horizontal flow set

ding, it is theoretically possible to achieve - the same results in treating:

- a flow nQ in the same appliance by superimposing n levels of elementary heightH/n (Figure 48 a and b),

- the same flow Q by superimposing n levels of elementary height H/n and of length L/n (Figure 48 a and c).

In practice, superimposing horizontal settling tanks without a scraping system does not allow for efficient sludge removal,and thus leads to reduced performance

3.3.2. General

The use of lamellae settling consists in multiplying the surfaces of water-sludge separation in one unit. Therefore, positioning lamellae packs (parallel tubes or plates) in the settling zone creates a large number of elementary separation cells. In order to provide for the evacuation of the sludge, it is necessary to incline the lamellae at an angle 9 to the horizontal.

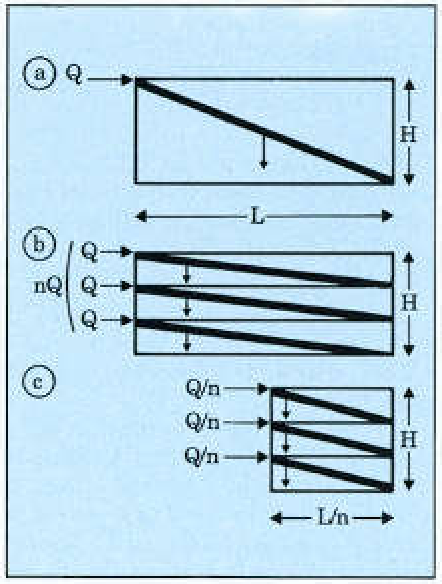


Figure 48. Horizontal flow settling.

By analogy with Hazen's theory, and at first analysis, the limit settling velocity ui in an element is:

$$u_l = \frac{Q}{n.S_L \cos \theta}$$

S_L: area of each element,
n: number of lamellae.

There are three types of lamellae settling (Figure 49):

. **countercurrent** settling (sludge and water circulate in reverse flow):

$$u_l = \frac{Q}{n.l. (L \cos \vartheta + e \sin \vartheta)}$$

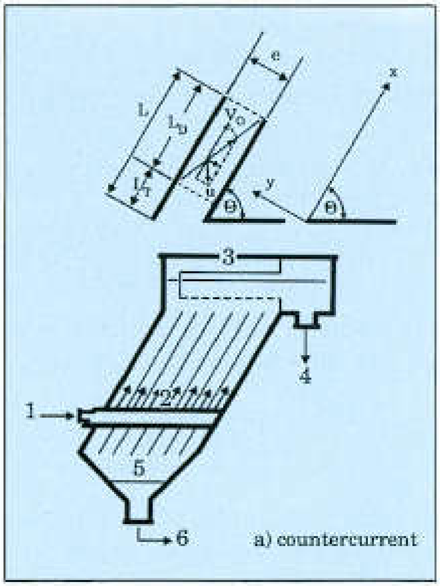


Figure 49 a. Countercurrent lamellae settling.

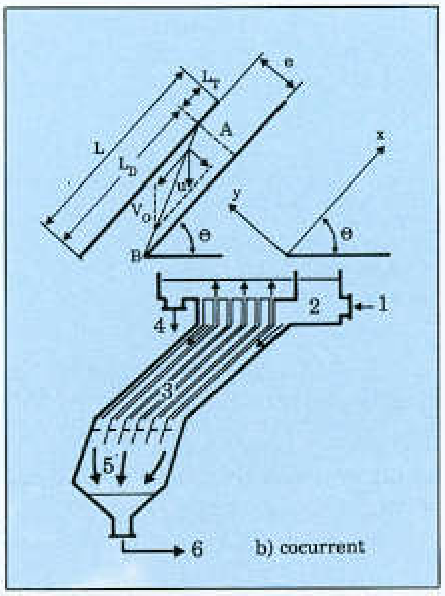


Figure 49 b. Cocurrent lamellae settling.

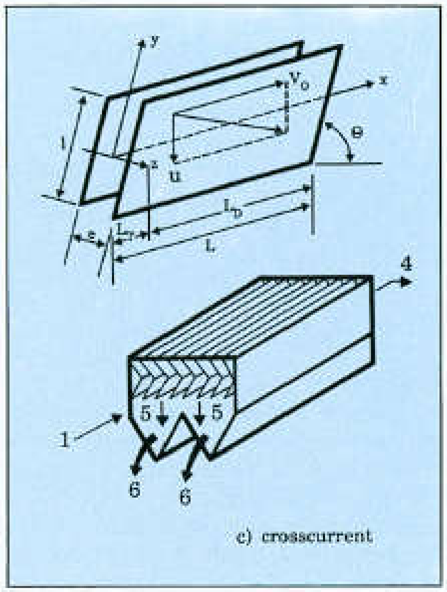


Figure 49 c. Crosscurrent lamellae settling.

1 - Inflow of flocculated water.
2 -Distribution zone.
3 - Clarified water collection.
4 - Clarified water outlet.
5 -Sludge pit.
6 - Sludge draw-off.

Figure 49. The three types of lamellae settling.

. **cocurrent** (sludge and water circulate from top to bottom):

$$u_l = \frac{Q}{n.l. \, (L \cos \delta - e \sin \delta)}$$

. **crosscurrent** (sludge and water circulate in a perpendicular direction):

$$u_l = \frac{Q}{n.l. \; L \cos \theta}$$

where:

$\left.\begin{array}{l}\text{L: length of the lamella}\\ \text{l: width of the lamella}\end{array}\right\} S = L.l$

e: space between two lamellae (orthogonal distance)

These formulae do not take into account hydraulic limits or the limits connected with the inflow and outflow of settled solids.

3.3.3. Theoretical study

The uneven distribution of velocities

Let us take a system of lamellae packs arranged in a settling tank. The distribution of velocities in a laminar system is parabolic, which in the chosen system of coordinates results in the following formulae for a countercurrent system (Figure 50):

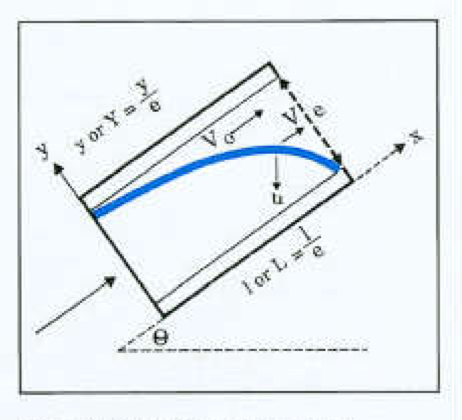


Figure 50. Travel of a retained particle.

$$\frac{V}{V_o} = A\,(Y - Y^2)$$

$$S_c = \frac{u_l}{V_o}\,(\sin\theta + L\cos\theta)$$

where:

V: fluid flow velocity at a given point,

V_o average velocity of fluid in direction Ox,

u_o average upward velocity (vertical component of Vo, i.e., V(, sin),

u1 minimum settling velocity necessary for a particle to be retained in the system,

L: 1/e ratio, 1 being the length of the element in the direction of the flow, also called reduced length,

Y: y/e, ordinate of the particle in direction Y, also called reduced ordinate,

e: orthogonal distance between two packs,

A and S_o: factors that depend on the type of plates or tubes used.

	A	S_o:
Circular tubes	8	4/3
Parallel plates	6	1
Square tubes	Unexplicit	11/8
Hexagonal tubes	Unexplicit	4/3

The length l_D settling required to separate particles with a settling velocity u1 is:

$$l_D = e\left(\frac{S_c}{\cos\theta.\sin\theta}\times\frac{u_o}{u_l} - tg\,\theta\right)$$

. Setting up a laminar flow

The preceding formula is based on a laminar flow from the bottom of the lamellae. In practice, a transition length IT must be added so that the fluid passes from a turbulent flow to a laminar flow. IT is defined as:

l_T : ad_hRe

where:

a: constant (0.028 according to Schiller),
d_h hydraulic diameter,
Re: Reynolds number.
Thus, the total length required is:

$$l = e\left(\frac{S_c}{\cos\theta.\sin\theta}\times\frac{u_o}{u_l} - tg\,\theta + \frac{0{,}028\,d_h^2}{\nu\ .\sin\theta}\cdot\frac{u_o}{3600}\right)$$

- l,e in m,
- u_o, w in $m.h^{-1}$
- V in $m^2.s^{-1}$

Inversely, the removal capacity of an existing settling tank with a given flow pattern can be calculated from this formula.

3.3.4. Practical application

.Choosing the type of lamellae settling

Countercurrent settling uses a simpler and more viable hydraulic system. Cocurrent settling, however, runs into great trouble in the recovery of clarified water. With crosscurrent setting, distributing the hydraulic flow equally is a delicate matter.

Choosing the type of lamellae packs

There are many models available: corrugated plates, round tubes, square tubes', herring-bone elements, hexagonal modules.

In order to compare the various lamellae packs, it would be interesting to examine the approximate factor u1 which is defined on page 167, i.e.:

$$u_l = \frac{Q}{n.S_L.\cos \delta} = \frac{u_o.S_H}{n.S_L.\cos \delta}$$

$$\text{soit } \frac{u_l}{u_o} = \frac{S_H}{n.S_L.\cos \delta}$$

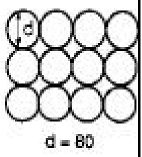
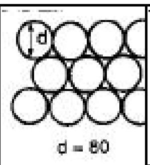
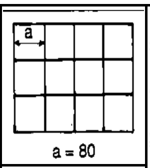
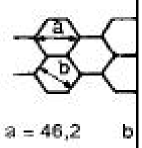
This ratio depends on the specific type of pack. Thus, with an equivalent hydraulic diameter, for packs 1.5 m in length and inclined at a 60° angle, the hexagonal modules have the greatest projected surface area (see table below).

The packs of parallel plates can also develop large surface areas while maintaining reasonable heights; however, this is only possible by substantially reducing the space between the plates, which seriously compromises the viability of the installation. Moreover, installing plates is a critical procedure; it requires putting up props and braces, which often disturb the hydraulic flow and promote the adhesion of sludge.

3.3.5. Conclusion

The hydraulic efficiency of hexagonal modules is greater than that of tube and plate packs. The modules limit the risk of clogging considerably while providing a large surface area.

(Degrémont uses such modules with hydraulic diameters of *80* and 50 mm, depending on their application.

Type of lamellae pack	**Circular tube in aligned rows**	**Circular tubes in staggered rows**	**Square tubes**	**Hexagonal modules**
Equivalent hydaulic 80 diameter (mm)	80			
Shape				
$\frac{u_l}{u_o}$	$\frac{1}{6,4}$	$\frac{1}{7,4}$	$\frac{1}{8,1}$	$\frac{1}{10,8}$

4. FLOTATION

4.1.

FLOATABILITY AND RISING VELOCITY

4.1.1. General

As opposed to settling, flotation is a solids-liquid or liquid-liquid separation procedure which is applied to particles whose density is lower than that of the liquid they are in.

- If the difference in density is naturally.sufficient for separation, this type of flotation is called natural.

- **Aided** flotation occurs when external means are used to promote the separation of particles that are naturally floatable

- **Induced** flotation occurs when the density of the particle is originally higher than that of the liquid and is artificially lowered. This is based on the capacity for certain solid and liquid particles to link up with gas (usually air) bubbles to form °partide-gas" composites with a density less than that of the liquid in which they form the dispersed phase. The phenomenon involved is of the three-phase type (usually gas-liquid-solid), and depends on the physical-chemical properties of the three phases and especially on their interfaces.

In industrial operations there is always some overlapping between the different procedures.

4.1.2. The size and velocity of bubbles

The rising velocity of a gas bubble in a laminar flow system is shown in Stokes' equation (see page 159).

$$V = \frac{g}{18\eta} \cdot (\varrho_1 - \varrho_g) \cdot d^2$$

in which:

d : diameter of the bubble,

ρ_g: density of the gas,

ρ_1, : density of the liquid,

η: absolute viscosity

. **Terminology**

In the field of water treatment it is standard practice to reserve the term "flotation" (in its strictest sense) for induced flotation which uses very fine air bubbles, or "microbubbles", 40 to 70 microns in diameter, similar to those present in the "white water" running from a tap on a high pressure main. This procedure is called dissolved air flotation (DAF).

In the minerals industry, however, the term mechanical flotation is used to describe the use of dispersed air to produce bubbles that measure 0.2 to 2 mm in diameter; their use is also very different.

Figure 51 indicates the variation of the rising velocity of air bubbles depending on their diameter. Bubbles measuring 50 microns have a rising velocity of about 6 $m.h^{-1}$, while those bubbles measuring several millimetres in diameter have velocities that are about 100 times higher.

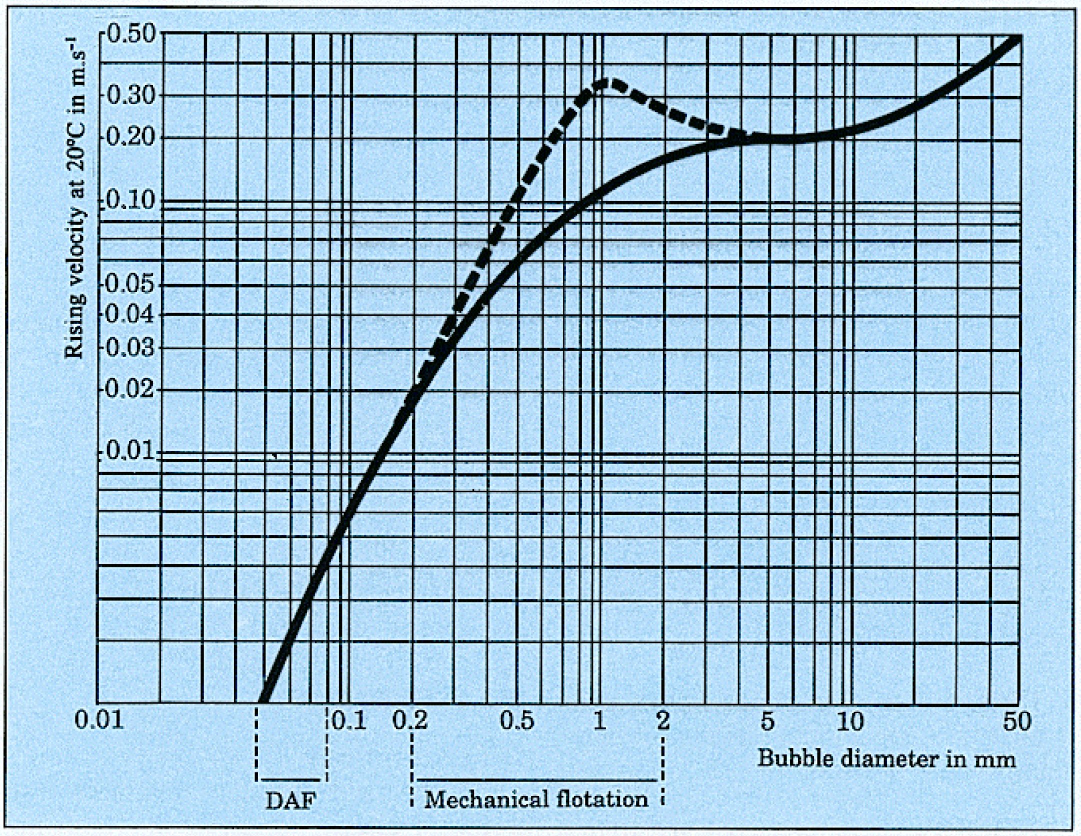


Figure 51. Rising velocity of gas bubbles in water.

4.1.3. Particle-bubble composites

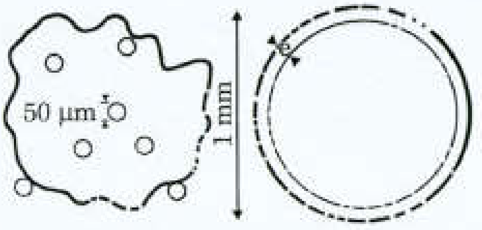


Figure 52. Diagrammatic representation of a particle-bubble composite.

4.1.3.1. Rising velocity

Stokes' equation is still applicable, where :

d is the diameter of the particle-bubble composite,

ρ_g, is replaced by ρ_s, density of the particle-bubble composite.

The shape or the sphericity of the "particle-bubble of gas" composite must also be taken into account.

The favourable effect of the size (assimilated to the diameter of a sphere) of the "particle-bubble of gas" composite should not conceal the fact that, in the case of flotation of particles heavier than the liquid, the specific area, i.e., the ratio

$$\frac{\text{area}}{\text{volume}} \text{ or } \frac{\text{area}}{\text{weight}}$$

diminishes as the diameter increases. Given the same quantity of air fixed per unit of surface area, this will result in a reduction of the factor $(\rho g - \rho s)$. Therefore optimization is necessary

4.1.3.2. General considerations on the size of bubbles

In order to separate flocs it is necessary to use microbubbles for the following reasons:

- in case a good distribution of bubbles all over the cross-section is desired, using bubbles that measure several millimetres in diameter would result in an air flow rate much greater than with microbubbles. At the same time, this increase in air flow would set up disturbing eddy currents,
- increasing the concentration of bubbles increases the likelihood of collision between the solid particles and the bubbles. Moreover, the low rising velocity of bubbles in comparison to the fluid mass allows them to adhere to the fragile floc particles. This assumes that their diameter is less than the diameter of the suspended solids or floc.

A flotation process using larger bubbles is used to separate particles that are bulkier than the floc and lighter than water. Such is the case in the separation of greases.

4.1.3.3. Minimum volume of gas, required to cause flotation.

The minimum volume of gas Vg of density p, needed to bring about the flotation of a particle of weight S and density & in a liquid with a density p, is given by the expression:

$$\frac{V_g}{S} = \frac{\varrho_s - \varrho_g}{\varrho_l - \varrho_g} \times \frac{1}{\varrho_g}$$

4.1.3.4. The importance of the quay of floc

. **Physical-chemical floc**: flotation is often combined with preliminary flocculation: the flocculated form of the particles is an indispensable condition for an efficient floc-bubble adhering process. By incorporating a flocculant (see pages 141 and 142), the floc can be enlarged, if necessary, and the particle area increased. This leads to improved adhesion of the bubbles and an increase in the rising velocity of the composites.

. **Biological floc**: the quality of bioflocculation has a definite effect on flotation (hydration, surface activity, SVI, floc size, etc.). Bulking activated sludge is particularly difficult to float.

4.2.

NATURAL AND AIDED FLOTATION

4.2.1. Natural flotation

Natural flotation is generally used for all preliminary oil separation processes. This (two-phase) flotation maybe preceded by a coalescing process (in which the microdroplets adhere to one another) to achieve a minimum size promoting separation.

Figure 53 shows the rising velocities of hydrocarbon droplets of various sizes; these values are used as a basis for the sizing of static oil separators.

Natural flotation may take place as a result of a release of gas from fermentation. This is the case with the scum

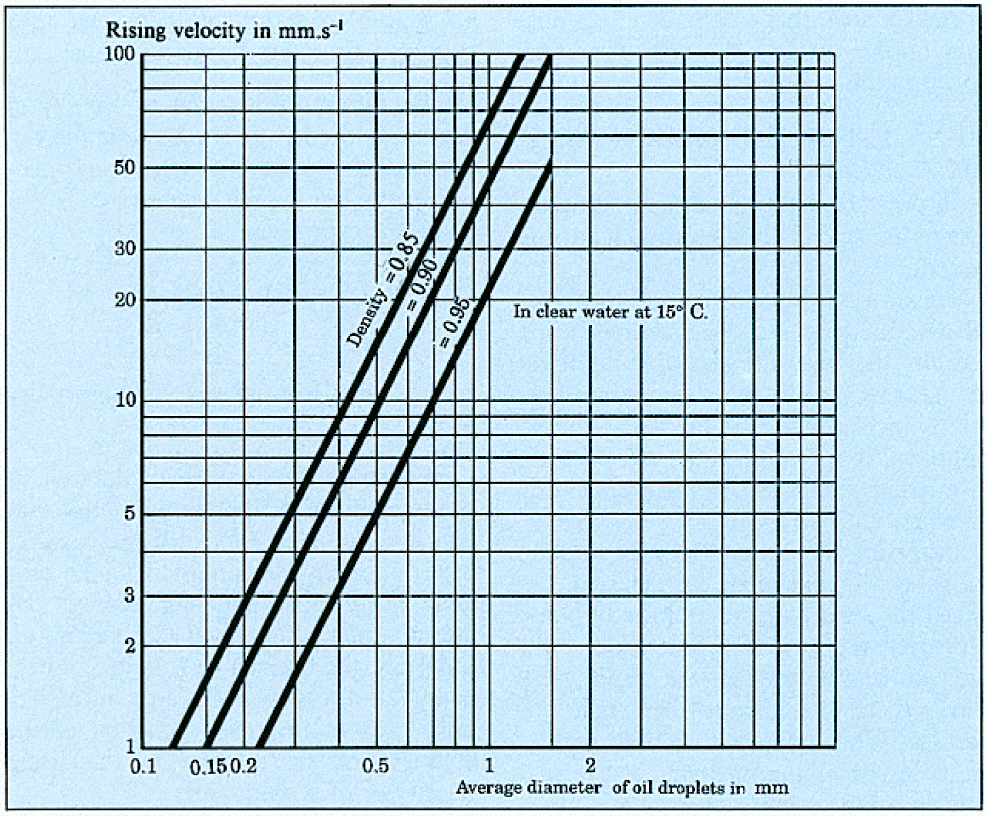


Figure 53. Rising velocity of oil droplets in water.

in digesters which can contain 20 to 40% of SS even though its density is only 0.7 or 0.8 kg.l^{-1}.

4.2.2. Aided flotation

This is natural flotation improved by blowing air bubbles into the liquid mass. This procedure is particularly used with the separation of greases (solid particles) that are dispersed in a turbid liquid (sewage). Two separate zones are generally provided in the units; one is for mixing and emulsifying; the other, a calmer zone, is for flotation proper.

In the rough oil separation stage, medium size bubble diffusers (2 to4 mm) are arranged so as to produce local turbulence designed to separate heavy particles, both organic and inorganic, which adhere to the grease (Figure 54).

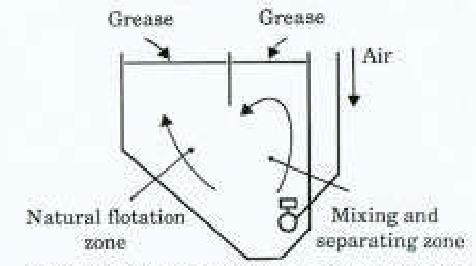


Figure 54. Principle of oil separation by aided flotation.

For more thorough oil separation, air is diffused in fine bubbles (0.5 to 1 mm) by an underwater mechanical aerator. The moving element of the unit assures that the greases are mixed and separated while the air lift effect of the air bubbles carries the particles to the surface, thus aiding their accumulation.

4.3.
MECHANICAL FLOTATION AND FROTH FLOTATION

This procedure takes place under conditions very different from those . of dissolved air flotation: size and thickness of solid particles, size of the bubbles and mixing process. Certain reagents are used to change the surface tension.

This process of mechanical dispersion of air bubbles 0.2 to 2 mm in diameter is mainly used for the separation and differential concentration of **ore pulp.** The crushed ore, in the form of particles generally less than 0.2 mm in diameter, is put into suspension in water to which a collector agent, and an activator or a depressor have been added. The procedure requires a large number of cells in series. Each cell is equipped with a stator-rotor unit that uses substantial energy which hydroxide floc cannot resist.

In treating **oily water** (from oil refineries), the separation of oil by mechanical flotation is called froth flotation. It is achieved by adding an organic coagulant or demulsifying agent. Flotation units are constructed with three or four cells in series.

Froth flotation by mere injection of air may also be used for the separation of surfactants.

4.4.
FLOTATION BY MICROBUBBLES

As can be seen on page 171, this usually involves dissolved air flotation (Figure 55).

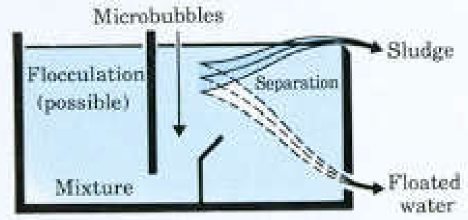


Figure 55. Diagram of dissolved air flotation.

4.4.1. Production of microbubbles

The most widely used technique for producing microbubbles is **pressurization.** The bubbles are obtained by the expansion of a solution that is enriched with dissolved air at several bar pressure. The type of pressure release system has a determining effect on the quality of the sludge bubbles produced. The curve shown in Figure 56 indicates the air concentration of an air-saturated water for different pressures at 20°C. The pressurized liquid used is either raw water (full-flow pressurization) or recycled treated water (recycle pressurization).

- In the clarification of surface water or industrial wastewater, recycle pressurization is applied; the flow rate of the pressurized water is only a fraction of the nominal flow of the plant, i.e., 10 to 50% of .the flow to be treated, at pressures of 3 to 6 bar. Air is dissolved at a rate of about 70% of saturation at the considered pressure. Hence, the compressed air requirements vary between 15 and 50 Nl.m^{-3} of water under treatment.

Figure 56. Solubility of air in water (20°C).

- In the case of sludge thickening (at a drinking water or wastewater facility), pressurization takes place on a full-flow or recycle basis, and air requirements are greatly increased.

Electroflotation is another technique in which bubbles (Hz and Oz) are produced by electrolysis of water using appropriate electrodes. The anodes are highly sensitive to corrosion, and the cathodes to scaling by carbonate removal. When protection of the anodes requires the use of protected titanium, it is not possible to periodically reverse the electrodes for the purpose of self-cleaning. A preliminary chemical treatment of the water or periodic descaling of the cathodes must take place in that case. The current densities used are of the order of 80-90 ampere-hours per in' of flotation unit area. The production of gas is about 50-60 litres per hour per mz of area. The rising velocities that are possible are less than those of dissolved air flotation because of the nature of the bubbles and their method of generation.

4.4.2. Fields of application

The applications of DAF in the field of water treatment are various:

- separation of flocculated matter in the clarification of surface water (for water with a low SS content),
- separation and recovery of fibres in paper mill effluents,
- separation of flocculated or non-flocculated oils in wastewater from refineries, airports and steelworks,
- separation of metallic hydroxides or pigments in the treatment of IWW,
- thickening of sludge from biological wastewater treatment or from drinking water clarification (using for example a Pulsator),
- clarification of activated sludge liquor.

The separation or downward velocity of the water used in the flotation units varies according to the nature of the suspensions to be treated, and also according to the method of generation and distribution of the microbubbles.

For a given flotation unit, the acceptable downward velocity (or the specific solids loading in the case of thickening) and the concentration of the floated sludge are strongly influenced by the value of the ratio:

$$\frac{\text{quantity of air dissolved}}{\text{quantity of material to be floated}}$$

Usually, the greater this ratio, the greater the rising velocity imparted to the particles and the higher the downward velocity. The lower the sludge's bulk density, the greater its concentration in dry solids.

In the case of wastewater, it is usually not possible to float all the suspended solids. Inevitably, a fairly large and very heavy part of the materials will finally accumulate on the floor of the unit. The flotation units must therefore always be equipped with a system for the removal of bottom sludge (a steeply conical bottom or floor scrapers).

The conditions for the application of the different flotation processes in water treatment are summarized in the following table.

Flotation proces	**Air flow used Nl.m^{-3} water**	**Size of bubbles**	**Input power per 3 m treated Wh.m^{-3}**	**Theoretical retention time min**	**Hydraulic surface loading m.h^{-1}**
Aided flotation (grease removal)	100-400	2-5 mm	5-10	5-15	10-30
Mechanical flotation (froth flotation)	10,000	0.2-2 mm	60-120	4-16	
Dissolved air flotation (clarification)	15-50	40-70 gm	40-80	20-40 (excluding flocculation)	3-10

5. FILTRATION

5.1.
BASIC EQUATIONS

Filtration is a separation process that consists in passing a solid-liquid mixture through a porous material (filter) which retains the solids and allows the liquid(filtrate) to pass through

5.1.1. General rule

Since filtration is the flow of a liquid through a porous medium, it is governed layer.by Darcy's law for the rates usually applied in water treatment:

$$V = \frac{K}{\eta}\,\frac{\Delta P}{\Delta H} = \frac{1}{R\eta}\,\frac{\Delta P}{\Delta H}$$

where:

V : filtration rate,

K : permeability of the filtering layer,

ΔP: head loss through the filtering layer,

ΔH: depth of considered layer,

η : dynamic viscosity of water,

R : resistance to filtration of the filtering

The *head loss* OP is proportional to the filtration rate V, the dynamic viscosity of water, the layer depth, and inversely proportional to the permeability of the medium.

5.1.2. Filtration of a turbid liquid with formation of a filter cake

Filtration of sludge-laden liquid through a support with the formation of a filter cake of increasing thickness will now be examined (Figure 57).

According to Darcy's law, R consists of two resistances in series, the resistance Rg of the cake and the initial resistance Rn, of the membrane:

$$R = R_g + R_m$$

$$\text{avec } R_g = r\frac{M}{S} = r\frac{Wv}{S}$$

in which:

M is the total weight of the deposited cake,

W is the weight of SS deposited per unit volume of filtrate,

v is the volume of filtrate after a given time t,

S is the filtration area,

r is the specific resistance to filtration of the cake under pressure P.

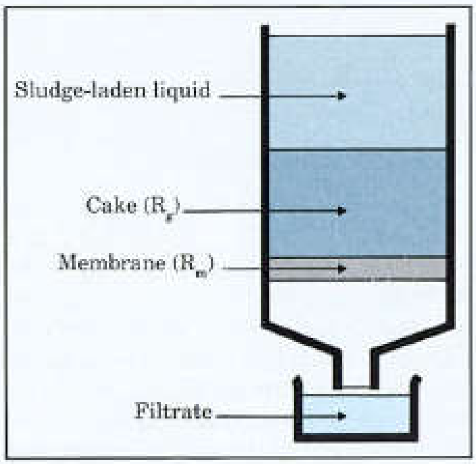


Figure 57.

$$\text{Hence: } V = \frac{1}{S}\frac{dv}{dt} = \frac{P}{\eta(r\frac{Wv}{S} + R_m)}$$

the integration of which produces an equation of the type

$$t = av^2 + bv \text{ or } \frac{t}{v} = av + b$$

$$\text{with } a = \frac{\eta rW}{2PS^2} \text{ and } b = \frac{R_m}{PS}$$

The graph showing this equation is a straight line which enables r to be defined as the slope a = tan θ (Figure 58).

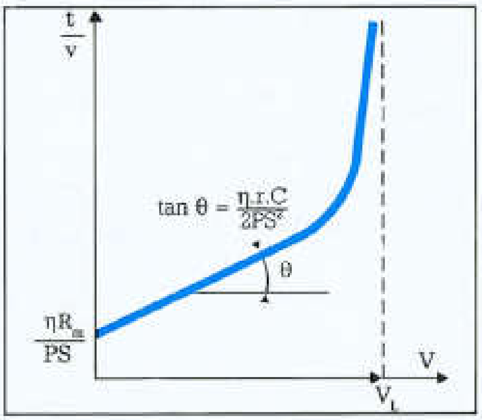


Figure 58.

Note: This integration is correct only if r remains constant throughout the filtration - and this only holds true for incompressible sludges.

If the filtration of a given volume of filter cake is continued for a fairly long period, we encounter first of all a break in the curve beyond which the dryness increases very slowly until it reaches the limit value of dryness of the cake. The value of r increases with the pressure in accordance with a law given by the expression r = to + r 'p^s in which to and r' are respectively the limit specific resistance where P = 0 and the specific resistance where P = 1 bar; s, known as the compressibility coefficient of the sludge, is a dimensionless number; r, the filtration coefficient or specific resistance, is expressed in m.kg^{-1}. The resistance ro.5, measured under a pressure of 49 kPa (0.5 bar), is generally used when comparing various sludges

5.2.
GENERAL

There are three general types of filtration processes, depending on themethod used:

- filtration on a support,
- filtration through a granular filter bed,
- filtration with a filter cake.

Membrane filtration, a kind of filtration on support, will be studied in subchapter 9. The filtration of sludge, which includes various filtration techniques with the formation of a cake, will be examined in chapter 19, subchapter 2

5.2.1. Filtration mechanisms

According to the characteristics of the particles to be filtered out and the filtration material used, one or more of the following principal mechanisms can be involved: retention, attachment and detaching.

5.2.1.1. Retention mechanisms

There are essentially two types:

Mechanical straining: this retains all particles larger than the mesh size of the filter or the mass of the particles already deposited which themselves form filter material. The finer the mesh of the filtering material, the more marked this phenomenon will be: it is of little significance in a filter bed composed of relatively coarse material, but is of great importance in filtration through a finemesh media: strainer, filter sleeve, etc.

Deposit on the filter material: the suspended particle follows a line of current in the liquid; depending on its size in relation to the pores, it may be able to pass through the filter material without being retained. However, various phenomena cause its travel to change and bring it into contact with the material.

The following phenomena can be identified:

- direct interception by rubbing,
- diffusion by Brownian movement,
- inertia of the particle,
- settling: particles may settle on the filter material by gravity, whatever the direction of filtration.

These retention mechanisms occur mainly during the process of in-depth filtration.

5.2.1.2. Attachment mechanisms

The attachment of particles to the surface of the filter material is promoted by a slow rate of flow, and is caused by physical forces (jamming, cohesion), and by adsorption forces, mainly Van der Waals forces.

5.2.1.3. Detaching, mechanisms

As a result of the mechanisms referred to above, the space between the walls of the material covered with particles that have already deposited, decreases. Consequently, the velocity of flow increases. The retained deposits may become partially detached and be driven deeper into the filter material or may even be carried off in the filtrate.

The solid particles in a liquid and the colloidal particles that are flocculated to a greater or lesser degree do not have the same characteristics and do not react to the same extent to the above mechanisms. Direct filtration of a liquid in which the suspended solids retain their original state and electrical charge will therefore be very different from filtration of a coagulated liquid.

5.2.2. Clogging and washing of the filter material

Clogging is the gradual blocking of the interstices of the filter material. Clogging causes the head loss to rise.

If a constant intake pressure is main tained, the flow of filtrate will decline. To keep output constant, the initial pressure must be increased as the filter becomes clogged.

The clogging rate depends on:

- the matter to be retained: the more suspended solids there are in the liquid, the greater the cohesion of these solids, and the more liable they are to proliferate(algae, bacteria),
- the filtration rate,
- the characteristics of the filter material: size of the pores, uniform particle size, roughness, shape of the material.

The filter becomes clogged when it reaches the maximum design head loss .It must be restored to its original condition by efficient and economic washing; the method used depends on the type of filter and the type of matter it retains.

5.2.3. Choice of 'nterstices method

Several different criteria govern the choice between the different types of filtration on support and filtration through a filter bed:

- characteristics of the liquid to be filtered, its impurities and their evolution with time,
- the desired quality of filtrate and the permissible tolerances,
- the quality of the mass of retained material when the object is to recover it,
- installation conditions,
- facilities available for washing.

In selecting a filter, the possibility of easy, efficient and economical washing is as important as obtaining the best filtration quality, since this quality will only . It be maintained if the washing process allows the filter material to remain intact.

5.3.
FILTRATION ON SUPPORT

We can distinguish:

- straining, which is surface filtration in which the mesh openings are relatively large (larger than approximately 30 microns),
- fine filtration, in which filtration through thin support of the coarsest particles occurs together with in-depth filtration of the finest ones.

One aspect of surface filtration should be emphasized: it removes particles that are larger than the filter pores **insofar as they cannot change in shape.** Under pressure and with substantial head losses, it is possible that larger particles can pass through.

5.3.1. Straining and microstraining

This involves a relatively coarse filtration or filtration through a thin support made of metal or plastic fabric, or filtering elements with regularly shaped pores. Depending on the size of the openings, the process is referred to either as microstraining or as macrostraining, of which the latter is covered in the area of fine screening (see chapter 9).

Mesh or pore openings	25-150 gm	0.2-4 mm	2-6 mm
Method Operation	Microstraining Gravity or under pressure	Macrostraining Gravity	Fine screening Gravity

The "removal capacity" is defined by the mesh void: the system retains all particles which are bigger than the mesh size. During the operation, strained particles may partially obstruct the mesh, and the filter may retain particles that are smaller than the size of the actual removal capacity.

In gravity operation, the maximum head loss designed for these filters is usually low - in the area of several dozen centimetres. This is due to the fragility of the cloth used, which may tear under the pressure applied and/or when washed.

5.3.1.1. Free surface microstraining

The main objective of microstraining is to remove the plankton from surface waters. This process will, of course, also remove suspended solids of large size and plant or animal debris from the water. It may also be used after biological purification or lagooning to remove residual suspended solids.

Optimum efficiency is obtained by maintaining a more or less constant total head loss that results from partial clogging by the particles to be retained. However, the efficiency of such an installation will always be limited by a number of factors:

- the washed filter cloth does not carry an effective deposit at the start of the filtering cycle, and filtration is then limited to the size of the mesh alone,

- plankton removal is never complete. The plankton can grow again, particularly when the temperature rises,

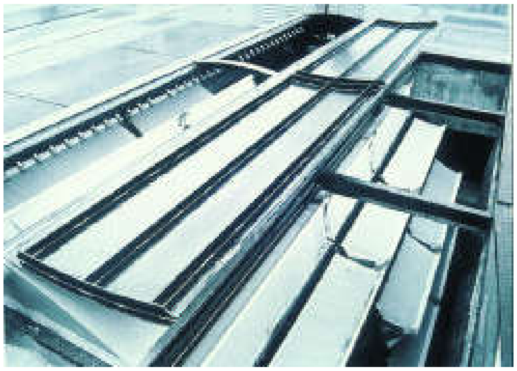


Figure 59. Microstrainer with dihedral filtering elements shown out of the water

Figure 60. Microstrainer with dihedral filtering elements. Washing the filter cloths.

- certain very small eggs can easily pass through the filter cloth and hatch in the downstream tanks, where crustaceans visible to the naked eye may develop,
- because of the risk of corrosion of the microstrainer cloth or its supports, it cannot be used for continuous treatment of heavily prechlorinated water,
- microstrainers have to be fairly large to cope with peaks of plankton growth which occur several times a year. If they are too small, the output of the plant could be reduced significantly during these peaks and during alluvial highwater periods.

The smaller the mesh, the more important the straining area has to be. Thus, with a 35-micron mesh size, the filtration rate should be 35 m.h-1 at the most, calculated over the total area of the strainer (50 m.h^{-1} on the real submerged area).

The reduction in clogging capacity of the water by microstraining ranges from 50 to 80% with an average of about 65%. As a comparison, a good settling tank gives a reduction of 80 to 90% without prechlorination and 95 to 99% with prechlorination. The microstrainer should be used only for water containing few suspended solids. It has no effect on colour and on dissolved organic matter, and only removes the coarsest proportion of the suspended particles.

For a really effective disposal of plankton, clarification preceded by oxidation is essential.

5.3.1.2. Microstraining under pressure

In industry, water may be strained under pressure. The aim is to assure:

- either protection against the clogging of relatively large openings (several mm) with a straining threshold of 0.15 to 2 mm. This is the case with once through or open recirculating cooling systems,
- or **continuous removal of fine solids**. The straining threshold can be lowered to 50-75 microns, if not lower, and the unit becomes part of a treatment line. This may be the case where sea water is injected to obtain secondary recovery of oil.

These filters, used mainly for filtering industrial water, are called automatic regeneration rotary filters or, sometimes, pressure mechanical filters. They are used with differential pressures of 0.5 to 2 bar. The initial head loss should be small (0.15 to 0.5 bar).

5.3.2. Filtration using cartridges and candles

5.3.2.1. The goal

In the treatment of water, filters are used to solve one of the following problems:

Very high quality of the filtrate
from water containing a very small amount of particles and without the release of support:

- condensates from HP boilers, whether starting up or in steady operation,
- the feeding of systems with ultrapure water,
- protection of reverse osmosis membranes.

The aim is to remove increasingly finer particles down to 0.5 microns (bacteria). Disposable supports may be used despite their cost.

Protection of hydraulic systems preventing the carrying away of discrete particles:

- injection of sea water for secondary recovery,
- cooling systems or process water systems.

It is necessary to prevent the loss of all filtering materials (fibres, resins, activated carbon, etc.) and any input of particles by the air. The level of filtration ranges from 10 to *200* microns. The use of regenerable supports is now in the preliminary phase.

5.3.2.2. Choice of media

This depends on the desired efficiency and the parameters of use.

Criteria for filter efficiency

- **The nominal removal threshold** has been determined by the manufacturer for a given support and suspension to be treated. It corresponds to the dimensions of the finest particles retained without giving a strict removal percentage.
- **The "absolute" removal threshold** is the diameter of the smallest particle for which the (3 index reaches the value desired for a given application. This (3 index, 500 i.e.:

$$\frac{\text{Number of particles in the water to be filtered}}{\text{Number of particles in the filtrate}}$$

is measured by the filtration of a reference suspension made up of silica powder ACFTO for suspended solids larger than 1 µm, or of a bacterial suspension less than 1 µm.

Calculations are carried out by means of an electronic laser counter. Figure 61 shows (ß depending on the diameter of the particle) the result obtained with a test filter. Depending on the industry, the desired ß index can be:

$$\frac{5000}{1} \text{ or } \frac{2000}{1} \text{ or even } \frac{200}{1}$$

It should be emphasized that passing from a nominal removal threshold to an absolute removal threshold may raise the cost by several dozen times, and it is not always worth it.

- **Fouling Index FI** (see page 359). The lowering of this index relates to a reduction of the fouling potential of water; it is often far more significant (in colloidal water) than the size of the particles alone, which are theoretically removed.

Parameters associated with use

- **Regeneration** or consumption of support material.
- Head loss or admissible filter run.

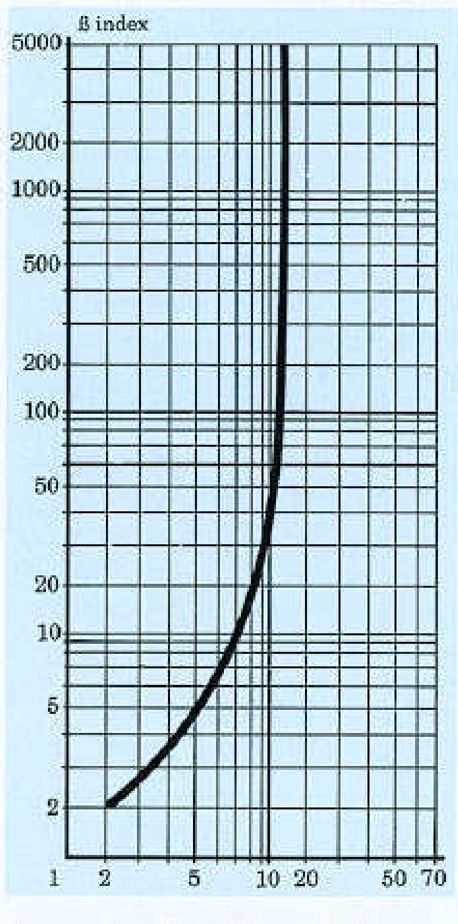


Figure 61. Example of measuring the β index.

- Suspended solids concentration in the to be treated.
- Risks of releases: supports or retained matter.

5.3.2.3. Types of filters

Differentiating between a thin support and a thick support becomes deceptive in view of the removal thresholds currently desired. Different ones are:

. **Expendable cartridges** which are equipped with:

- pleated membranes made of paper, polycarbonate or Nylon 66 films, unwoven, heat-welded fabrics (polypropylene), which are usually not subject to release. They may have absolute removal thresholds between 0.1 and 20 µm, and can be distinguished by their filtering areas,
- felt, unwoven or wound textiles, plastic composites, which can be released.

. **Cartridges backwashable with water,** equipped with:

- fibres and sintered metals with nominal thresholds ranging from 6 to 100 µm, - fabrics made of monofibre horsehair (polyester) with nominal thresholds of between 20 and 100 gym.

Backwashing is only possible with cartridges with a high nominal threshold used in water with a low SS content.

. **Regenerable candles** equipped with:

- sintered metals or ceramics,
- agglomerated plastic materials.

Regeneration is less often ensured by backwashing using filtered water than by other methods that are especially suited for, and compatible with, the supports (steam, acids, ultrasounds, etc.).

Generally speaking, whether it concerns backwashable cartridges or regenerable candles, the increased fineness of the filtering supports and the filtration of clogging water result in a progressive deterioration of the supports; they must be replaced after a certain number of cycles.

5.3.3. Filtration on precoated sup port

This is in-depth filtration through a transitory media maintained by a thin support and formed either by the introduction of an exterior precoat (a filter aid) or by the slurry to be filtered itself.

In the initial phase of the operating cycle, precoating takes place, which consists in recirculating the filter aid or the slurry itself on the filter in such a way that the coarsest particles can mix and form arches over the apertures of the thin support, the openings of which are several times larger than the diameters of the particles. Thus a filtering precoat can form and build a filter cake, the thickness of which determines the filter run between washings.

During the filtration cycle, it may be necessary to continuously inject a filter aid, either to slow down the increase in head loss or to improve the filtrate. This is called feeding.

. **Applications**

Filtration through a precoat is used for liquids that are usually only slightly loaded with SS, and filter runs progress from several days to several weeks:

- power station condensates,
- oily condensates from heating,
- beers and wines,
- aqueous cutting fluids from truing process,

- hydraulic fluids,
- syrups from sugar and glucose mills.

Filtration with a self-forming precoat is used with slurries containing 0.5 to several $g.l^{-1}$ SS, and a filter run can be limited to a few hours. For instance:

- cloudy juice from carbonation in sugar refining;
- wort from brewing operations, settled product in vats,
- pulps from hydrometallurgy.

. **Precoat and feed materials**

Depending on the application, different materials can be used:

- **cellulose**, in the form of high-purity fibres, has a filtering capacity comparable to that of a slow filter paper, but it has a very low adsorbent capacity. It is insoluble in cold or warm water, and starts to hydrolyse at 85°C,
- **diatomaceous earth** consists of fossilized siliceous shells of marine origin; it is very fine (5 to 100 µm) and has some adsorbent capacity. In the presence of water loaded with colloids, *it* provides better clarification than cellulose.

It is also able to adsorb emulsified impurities such as oils or hydrocarbons. The silica of the diatomaceous earth is slightly soluble in demineralized water (especially when alkaline),

- activated carbon, because of its very high adsorbent capacity, can be used on a supporting layer of cellulose or diatomaceous earth for colour removal and for almost complete removal of organic matter of vegetable origin,
- ion exchange cation and anion resins in powder form, mixed in varying proportions, provide filtration with thorough removal of colloidal iron or total demineralization of condensates in thermal and nuclear power stations.

. **Washing**

Backwashing is carried out when the design permissible head loss reaches the maximum. In order for washing to be

Figure 62. Support plate equipped with candles.

Figure 63. A Shell facility in Brent (North Sea). Flow: 2100 mj.h-'. Precoat filters.

effective, the precoat and the suspended completely detached from the support

solids retained on the precoat must be without causing progressive clogging.

5.4.
FILTRATION ON A GRANULAR BED

5.4.1. Principle and monitoring

Water to be treated passes through a filter bed made of a granular material; the layer depth is an important parameter that depends on the type of filter used. Suspended solids are retained in the intergranular spaces throughout the greater part of the layer depth. The operation of the filter is usually monitored in two ways.

5.4.1.1. Measurement and evolution of the quality of the filtered water

Figure 64 shows the evolution of turbidity in a filtrate and defines the typical periods of a filter's operation:

c = maturing period,

b = period of normal operation,

d = initiation of filter breakthrough,

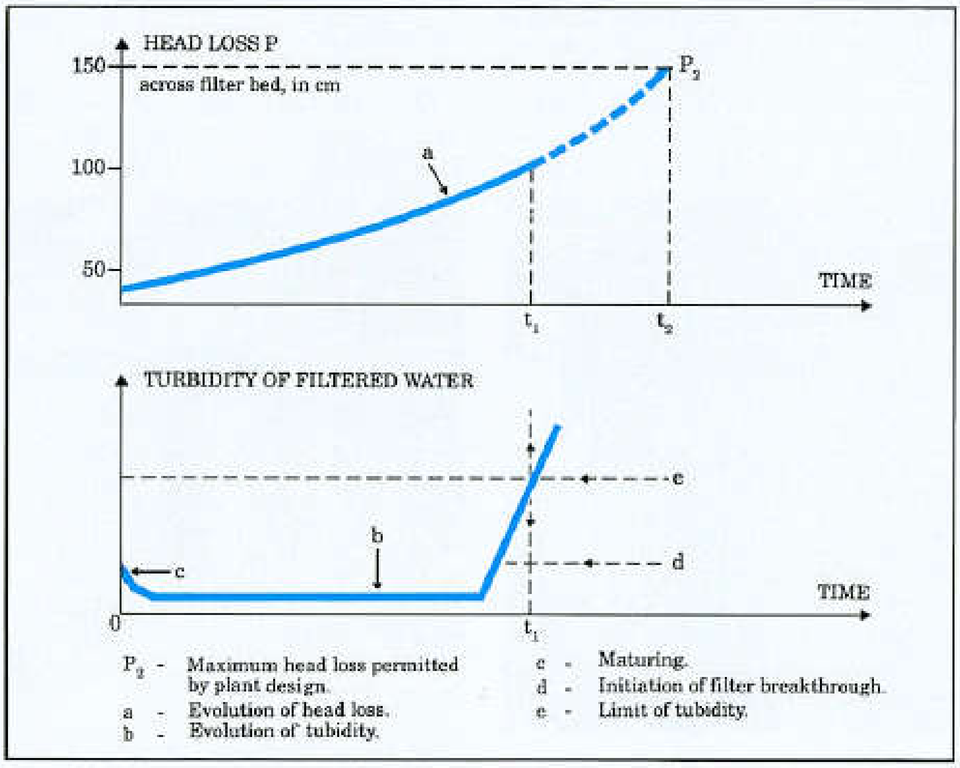


Figure 64. Filtration curves on a granular bed.

e = acceptable limit of turbidity; the turbidity of filtered water reaches this value for a time ti.

5.4.1.2. Measurement and evolution of head loss

The graph in figure 64 shows the variation of head loss P with time. The design of the unit allows for a maximum head loss that the filter should not exceed; for example, P_2 = 150 hPa (= 150 cm WC). This head loss is reached after a time t_2, which is an important characteristic of filter operation.

5.4.1.3. Optimizing filter operation

In order to obtain optimum operation of the filter, it is important that the filter attain a head loss P_2 corresponding to time (t_2) before breakthrough at time (t_1), which is :

$$t_1 > t_2.$$

For water coagulated with a metallic salt, ti and t_2 are given by the following test formulae (Richard and Croce-Spinelli), which indicate the variation of t_1 and t_2 as a function of operating characteristics:

$$t1 = a.v^{-0,95}.K^{0,75}.D^{-0,45}.L^{0,95}.V^{1,85}$$

$$t2 = b.v^{-0,75}.K^{-0,7}.D^{1,5}.P^{0,9}.V^{0,65}$$

with:

D: effective size of the material,

L: layer depth,

P: rise in head loss,

V: filtration rate,

K: cohesion of retained floc,

v: volume of flocculated suspended solids in the water to be treated.

The effective size of the filtering material and the cohesion of the retained floc are essential factors in the variation of ti and t2. The coefficients a and b are experimental. After a single filtration test, the formulae make it possible to predict the different times ti and t2 corresponding to various operating conditions.

5.4.1.4. Pressure curves

The graphs in Figure 65 represent an open filter, with a sand depth BD and a water depth AB. On the right hand graph, the levels of the pressure take-offs A, B, C, D as measured from the floor D of the filter are plotted on the Y-axis, and the pressures represented as water head are plotted on the X-axis with the same scale as on the Y-axis. Thus at point B of the filter, at the top of the filter bed, the pressure is always equal to the water depth AB, plotted as B'b. At point C of the filter bed, when the filter is shut down, the pressure takes the value AC, plotted as Cc.. Likewise, the static pressure at floor level equals AD, plotted as D'do.

All the points representing the static pressure at different levels of the filter are on the 45° straight line A'do.

With the filter in operation, according to Darcy's law, the head loss in homogeneous, clean sand is proportional to the depth of the sand and to the flow rate, which is taken as constant for this analysis. The pressure at point C of the filter becomes equal to $C'c_1$, with the value c_oc_l representing the head loss of the sand between levels B and C; likewise, at floor level, the pressure at D becomes equal to $D'd_1$, with dodl as the head loss in clean sand.

The line bc_ld_l is a straight line since cocl and dodl are proportional to the depth of sand (Darcy's law).

When the sand is completely matured, the plotting of the pressures $C'c_2$ and $D'd_2$ at the various levels of the sand gives the curve bc_2d_2, which represents the pressures in the filter; it has a curvilinear section

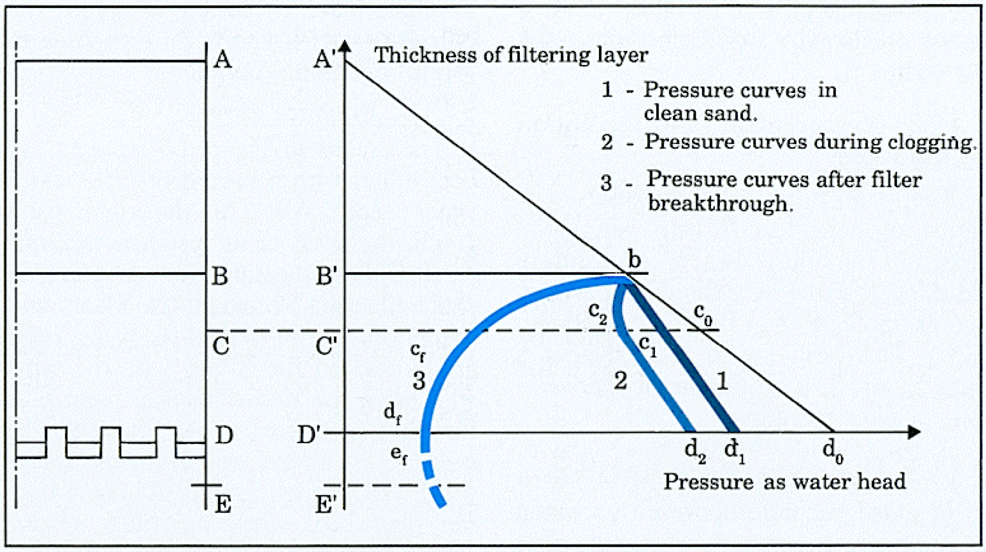


Figure 65. Pressure distribution in a filter bed.

and a linear section parallel to the straight line bd1 which represents the head loss with a clean filter. Point C_2 that shows the start of the linear head loss, indicates the level C reached by the impurities in the sand; below C, when the head loss is linear, the sand is clean. Point C defines the depth BC of the **"filtration front"** at the time considered.

Therefore, the minimum sand depth and minimum head loss anticipated before clogging are BC and c_0c_2 respectively.

The shifting of point C during clogging represents the progress of the filtration front. In Figure 65, where the filter no longer gives clear water once the maximum head loss P_2 is reached, the curve representing the pressures at different points in the filter is given by bcfdfes it reaches the floor without having a straight section, which means that the filtration front has passed the floor and filter breakthrough has occurred.

If a filter with a greater depth of sand had been used, the curve representing the pressure at the different points of the filter for the maximum available head loss would have become linear at point ef: this immediately gives the minimum depth DE of sand that should have been added to make $t_1 = t_2$.

Finally, experience shows that the values of ti that correspond to different depths of a specific sand are fairly proportional to the corresponding thicknesses.

5.4.1.5. Maximum removal capacity of a filter

Suspended solids lodge between the grains of the filter material. Given the fact that sufficient space must always be left for the water to flow, on the average the sludge can hardly fill more than a quarter of the total volume of voids in the material.

For a 1 m layer depth and 1 m^2 filtering area, that is, a volume of 1 m^3 of material, there are approximately 450 litres of empty spaces whatever the particle size; the volume available for the removal of particles is about 110 litres, provided that the effective size of the filter media and the head loss anticipated by the design of the unit are suited to the nature of these particles.

When the filters operate by gravity (open filter), and the suspended solids to be retained have a hydroxide floc base, their DS content does not exceed 10 $g.l^{-1}$ the quantity that can be removed per m^3 of filter material is therefore no more than 110x 10= 1100g.

This figure increases when the floc contains dense mineral matter (clays, calcium carbonate). For a sludge containing 60 $g.l^{-1}$ DS, it can reach:

$$110 \times 60 = 6600 \text{ g}$$

In the case of pressure filtration of industrial impurities, the layer depth may reach 2 m and the head loss, 0.5 bar or even 2 bar. Thus, the filter can retain a quantity of matter as high as:

- $CaCO_3$: 4 to 15 kg per m^2 of filtering area,
- oily slime: 10 to 25 kg,
- mill scale: 20 to 100 kg.

These values indicate the maximum permissible content of suspended solids in raw water entering a filter once its filtration rate and the run between two washing operations' have been determined.

For example, a filter with a 1 m deep bed operating at a rate of 10 m.h-1 that requires washing every eight hours (80 m3 water per m3 filter bed between washing operations) cannot cope with more than:

$\frac{1100}{80}$ = 13.75 $mg.l^{-1}$ flocculated suspended solids, or more than

$\frac{6600}{80}$ = 82.5 $mg.l^{-1}$ dense mineral suspended solids.

For suspended solids in river water, the figure will be midway between the above two values.

5.4.2. The porous media

5.4.2.1. Physical properties

A filtering material is generally defined by the various factors dealt with in chapter 5, page 378:

- **grain size,**
- **effective size (ES),**
- **uniformity coefficient (UC),**
- **grain shape:** angular (crushed material) or round (river and sea sand). The same filtered water quality is obtained using an angular material whose effective size is smaller than that of a round grain material.

Given an equal size, the head loss increase is less with coarse grains than with round grains for, contrary to what might be expected, coarse grains bed down less easily than round grains, and leave larger spaces for the water to pass through,

- **friability:** it allows suitable filter materials to be selected without the risk that the washing operations will produce fines.

A material that is too friable is unacceptable, especially with downflow filters where the washing ends with an expan sion phase with water only, as the fines formed clog the filter surface,

- **loss in acid**: obviously, a high loss in acid cannot be tolerated when the water is likely to contain corrosive carbon dioxide gas or any mineral acidity,
- **the density of the grains** making up the filter media,
- **their bulk** densities in air and water.

There are other properties specific to adsorbent materials such as activated carbon; they will be examined in chapter 5, page 383.

5.4.2.2. Nature of the porous media

Quartz **sand** was the first material that was used for filtration, and it is still the basic material in many existing filters.

Anthracite or **marble** can be used instead when any trace of silica must be avoided in industrial processes or when they are easier to obtain.

For some methods of treatment, such as polishing, tertiary treatment of effluents, etc., it.,is advantageous to use **materials with a large specific area,** e.g., expanded schists, Biolite, pozzuolana or other similar material.

Some filters use a combination of different materials (multi-media filters). In this case, the sand may be combined with anthracite, garnet, schists of varying porosity, etc., provided that these materials have low friability and low loss in acid.

Finally, filtration may be effected through sufficiently strong granular activated carbon in the following cases:

- to replace sand after settling treatment both to remove the residual floc and to combat pollution by adsorption,
- in a second filtration stage for polishing treatment only or dechlorination.

5.4.2.3. Choice of grain size for a filter media

This choice must be made while also taking the depth of the layer and the filtration rate into account. It depends on the nature of the water to be filtered (direct filtration of raw water, filtration of settled water, biological filtration of secondary or tertiary wastewater), and on the desired quality of water. It also depends on the type of filter used (pressure filter or gravity filter) and on the available head loss. The following table shows the influence of various parameters on the quality of water and the filter runs.

	Diameter of the grains	**Layer depth**	**Filtration rate**	**Available head loss**
Quality of filtered water	↘	↗	↘	=
Filter run	↗	↗	↘	↗
Loading per m^2	=	↗	=	↗

The direction of filtration is generally downward. Depending on the type of washing system selected (see page 192), there are three types of filtration which correspond to a choice of different grain sizes:

. **filtration on a layer of homogeneous material**. This material is washed with air and water without hydraulic expansion during the final rinsing phase. This results in a perfect homogeneity of the filtering layer; the size of the grains in the filter material is the same at the bottom and the top of the filtering layer. During the filtration cycle, the filtration front is formed and progresses regularly; this helps control the filtration cycle. Figure 66 shows the pattern of pressure curves in a filter bed,

. **filtration on a layer of heterogeneous material**. When the washing process uses water alone or when there is a final rinsing phase with hydraulic expansion of the material, classification of filter material occurs. Here, the coarsest grains are at the bottom of the filter while the finest are at the surface. During the filtration cycle, the fine filtering material receives the water to be purified which contains all the matter to be retained, while the coarsest filter material receives a cleaner water. Thus, controlling the filtration cycle is more difficult; the cycles are shorter given the fact that the fine material screens the water at the surface of the filter. Figure 67 shows the pattern of pressure curves in the filter bed,

. **filtration through a multi-media filter:** the observations mentioned above have led to the setting up of a filtration process using two filter layers (dual-media

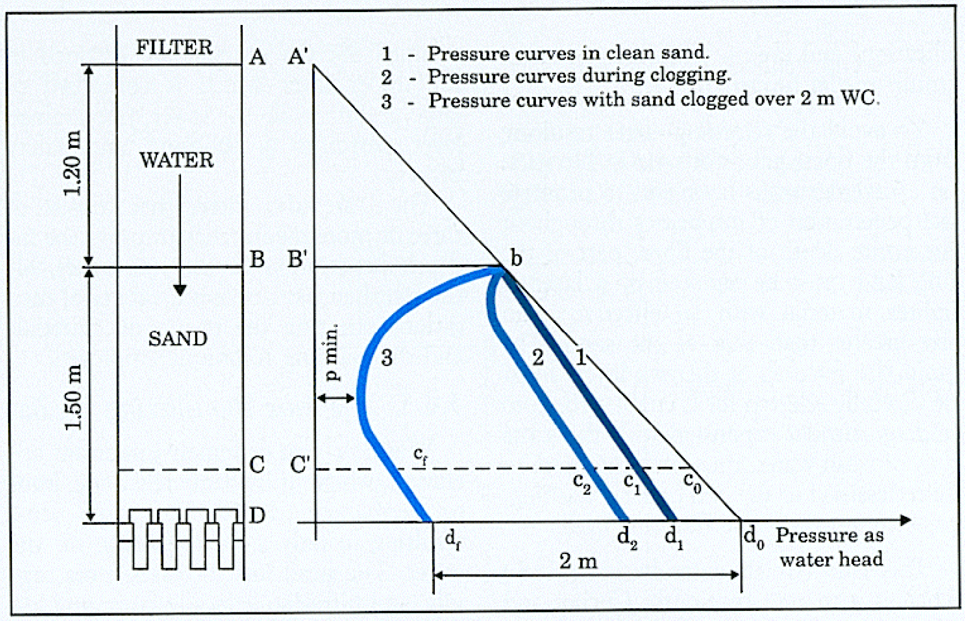


Figure 66. Pressure curves in a single homogeneous media Aquazur V type filter.

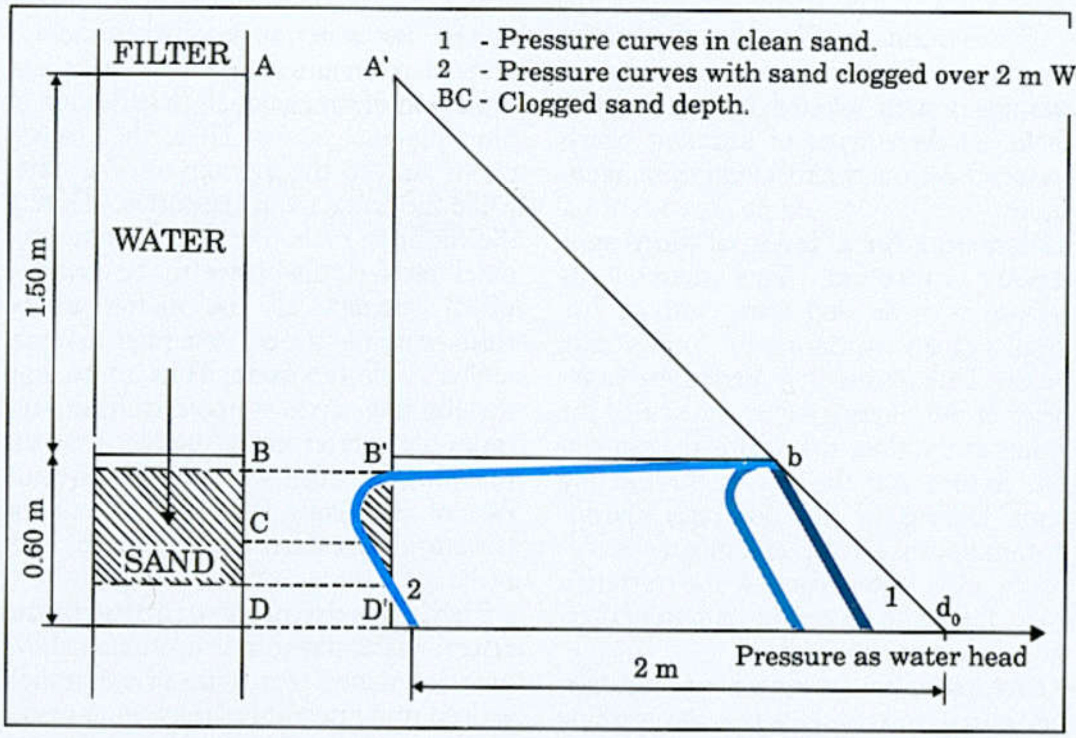


Figure 67. Pressure curves in a filter with a single heterogeneous layer (the shaded portion of sand is under vacuum).

filtration) and even several filtering layers (mufti-media filtration).

To avoid the screening effect resulting from the finest grains of sand in filtration on a heterogeneous layer and to promote the penetration of impurities throughout the entire depth of the filter, part of the fine sand must be replaced by a layer of lighter material with an effective grain size greater than that of the sand. The grain size for each of the two layers must be carefully selected for it enables them to undergo similar expansion with the same flow of wash water, thus enabling them to be reclassified at the end of each washing, prior to resuming the filtration cycle.

This rule (which dates back to 1880 when it was used by Smith, Cuchet and Monfort), allows distribution of the retained SS: the coarsest are retained in the upper layer which is composed of large grains, while the lower, fine-grained layer performs a polishing and safety process.

There are also filters that consist of three or more media; they improve the indepth penetration of the impurities, although their use imposes a variety of conditions affecting the choice of materials and the washing technique employed.

5.4.3. Washing the filtering media

Washing is an extremely important operation, which, if inadequately done, leads to permanent clogging of some areas resulting in only a small passage for the water. The head loss increases more rapidly, and filtration is locally faster and less effective.

The filtering material is washed by a current of water flowing from the bottom upwards, in order to dislodge the impurities and convey them to a discharge channel. At the same time the filtering material needs to be agitated in the current of water. A number of methods can be employed to achieve this result.

5.4.3.1. Washing with water alone to expand the filter bed

The current of water must be sufficient to expand the filtering material, i.e., to bring about an increase in its apparent volume of at least 15%.

As the viscosity of water varies according to temperature, it is desirable that asystem should be provided for measuring and regulating the flow of wash water so as to keep the degree of expansion desired constant over time.

The expanded layer then becomes subject to convection currents; in certain zones the filtering material moves downwards and in other neighbouring zones upwards.

Because of this, portions of the compact layer of sludge encrusting the surface of the filtering material are carried deep down to form hard and bulky **mud balls** as a result of the action of eddy currents. This is partly overcome by breaking up the surface crust with powerful jets of high-pressure water ejected from fixed or rotating nozzles (surface washers).

This method requires considerable care and makes it necessary to measure the expansion of the filtering material exactly. Its greatest drawback is that it results in a size grading whereby the finest filtering material is concentrated on the surface; it is therefore an unsatisfactory method for downward filtration.

5.4.3.2. Simultaneous air and water washing without expansion

A second method, which is now widespread, is to use a low backwash flow rate which will not cause expansion of the sand, and at the same time to stir the sand by an injection of pressurized air. Thus, the sand remains stable, and the surface crust is completely broken up by the air; in this way, mud balls cannot be formed; in fact, they do not occur with this type of washing process.

During this period of **air scour,** the higher the flow rate of the wash water, the more rapid and effective the washing will be. The minimum value for a washing to be effective and the maximum value not to be exceeded so as to avoid a loss of filtering material both depend on the material and on the filter parameters.

When the impurities have been removed from the filtering material and collected in the layer of water between the sand and the discharge channel, "rinsing" must take place, i.e., the layer of dirty water must be replaced by clear water.

Rinsing may be carried out by various methods after air scour has stopped, such as the following:

- continuing the backwash at a constant flow rate until the discharged water runs clear. The time this takes is inversely proportional to the flow rate of water (which must always be higher than 12 $m^3/ h.m^2$), and proportional to the depth of the layer of water above the filtering material,
- increasing the flow rate of water during rinsing to at least 15 $m^3/h.m^2$,

- sweeping the surface of the filter with a horizontal current of raw or settled water combined with the backwash,
- draining off the dirty water above the sand and sweeping the filtering material surface as above.

5.4.3.3. Washing with air and water in succession

This method of washing is used when the filtering material is of such a nature that it is impossible to use air and water simultaneously without running the risk that the wash water will carry off the filter media to the drain. This applies to filter beds composed of fine sand or low-density materials (anthracite, activated carbon or Biolite, etc.). This type of washing is also used for dual-media filter beds.

In the first stage of the washing operation, air is used alone to detach the retained impurities from the filtering material. In the second stage, a backwash of water with a sufficient velocity to bring about the expansion of the filtering materials) enables the impurities detached during the first stage to be removed from the bed and to be carried away. In the case of impurities which are heavy or particularly difficult to remove (for example wastewater), this cycle may be repeated several times.

5.4.3.4. Washing by sections

Usually, washing involves the entire surface of a filtering unit. In some types of filters it may be done by sections (see Figure 68).

In the filter, the fixed walls mark off the cell units for washing. An apparatus moves into place above each of the cells at a time. The dirty water is drawn up through the sand layer of the section and the water is sent into a side discharge channel. The water to wash a cell comes directly from neighbouring cells. The cells are washed one after the other.

This type of washing may be continuous. Its major drawbacks are:

- the washing takes place with water alone, i.e., without air,
- it is impossible to limit the flow of water filtering through the cell that resumes filtration; thus, the velocity is higher because there is no cellular regulating system and, in certain cases, this can result in a deterioration of the quality of filtered water,
- there is a risk of cell isolation being insufficient.

This type of washing can be justified in certain cases (filtration of cooling system water, of wastewater, etc.). However, it is not safe for the filtration of good quality water (drinking water, etc.).

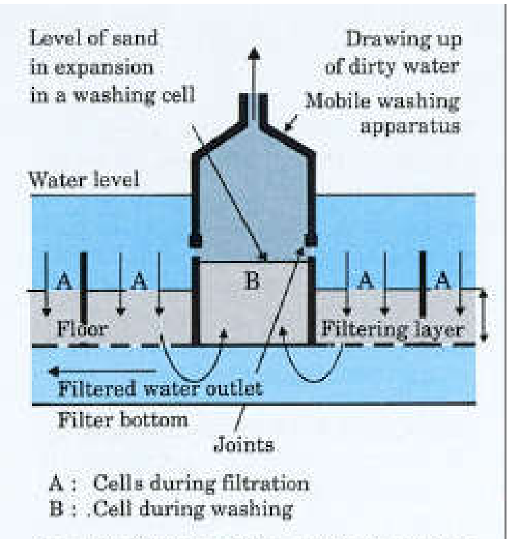


Figure 68. Principle of filter washing by sections.

5.4.3.5. Frequency of washing and wash water requirements

The frequency of washing depends on the nature of the water to be filtered as well as on the nature and the quantity of the SS to be retained. Washing must begin as soon as the head loss reaches its maximum value or when filter breakthrough occurs. In practice, the washing operation is often carried out after a certain volume of water has been filtered, according to operating conditions and usage experience.

The amount of wash water consumed depends essentially on the character and weight of the particles retained per m3 of filtering material. The combined use of air scour and settled water makes it possible to reduce water requirements by some 20 to 30% as compared with washing with water alone.

Wash water requirements are greater:

- the deeper the layer of water above the filtering material,
- the lower the flow rate of the backwash water alone,
- the greater the distance separating the sludge discharge channels,
- the larger the quantity of sludge to be removed, and
- the greater the cohesion and density of the sludge.

Water requirements are also increased by surface washers.

5.4.4. Slow filtration and rapid filtration

5.4.4.1. Slow filtration

The object of slow filtration is to purify surface waters without prior coagulation or settling. The colloidal matter is coagulated by the enzymes secreted by algae and by microorganisms which are retained on the sand (biological membrane). In order to get satisfactory results, three stages of filtration are usually necessary:

- roughing filters working at a rate of 20 to 30 $m^3/h.m^2$,
- prefilters working at a rate of 10 to 20 $m^3/d.m^2$,
- filters working at a rate of 2 to 5 m^3 $/d.m^2$.

The slow filtration rate ensures a fairly low head loss at each stage, and the filters are washed an average of once a month. Roughing filters and prefilters are washed more often according to the turbidity of the raw water.

After washing, the quality of the filtered water is not yet satisfactory; the filter must be allowed to discharge to drain until the biological membrane forms; this takes several days.

Slow filtration gives good clarification results provided that the water does not contain large quantities of SS, and that a low final filtration rate is maintained. However, when the suspended solids in the water increase, roughing filters and prefilters are not sufficiently efficient, and the turbidity of the treated water is likely to rise well above the values permitted by the appropriate standards unless the filtration rate is further reduced.

These filters are also particularly sensitive to a high plankton growth which may clog their surface.

Moreover, if slow filters are used for surface water with a high content of organic matter and chemical pollutants, the filtered water may still have an unpleasant taste.

Furthermore, the biological action of slow filters is not effective when it comes to removing all micropollutants (phenols, detergents, pesticides). For instance, they can only remove about 50% of organochlorinated pesticides. Moreover, they are not successful in retaining heavy metals.

5.4.4.2. Raid filtration

Rapid filtration takes place at rates ranging from 4 to 50 $m^3/h.m^2$ depending on the application.

. **In the treatment of drinking water,** biological action is weak; at the most, there is some nitrification in cases when the velocity is limited, when the oxygen content is adequate and when the nitrifying bacteria find favourable nutritive conditions in the water.

The principal methods are:

- direct filtration, in which case no reagents are added to the water to be filtered,
- filtration with in-line coagulation of water not previously settled; the reagent used may be a coagulant, a flocculant aid or an oxidizing agent,
- filtration of coagulated and settled or floated water.

In the latter case, the filters are in an ideal situation when they receive water of nearly constant quality that contains a low SS content. The filtration rates are tied to the desired quality of the filtrate; they may range from 5 to 20 $m^3/h.m^2$, depending on the quality of settled water and the nature of the filters used.

It is also possible to use two consecutive filtration operations, with each filtration stage preceded by coagulation in which an aid and an oxidizing agent are added.

. **In the treatment of wastewater** (municipal or industrial), filtration is always connected to a biological activity because of the substantial amount of organic pollution, the possible input of oxygen and the temperature.

5.4.5. Filtration direction

Water to be filtered usually passes through the filtering material in a downward direction, whereby the filtering material is completely submerged. The water flows either by gravity or under pressure.

In some filters, the filtering material is not completely submerged and the water trickles into the filtering media; this type is called a "dry" filter and is especially useful for some biological treatments (see page 312).

Other filters use an upward filtration flow; the water percolates through the filtering material from the bottom to the top. With this method the storing capacity may be higher but the head loss is limited by the weight of the filtering material. Beyond this limit the material is pushed upward and breakthrough occurs. In order to avoid this drawback it is necessary to provide for a blocking unit in the filtering material (grid, etc.). This unit permits the use of a material to be used that is lighter than water.

A double filtration direction can also be used. The water to be filtered penetrates the filtering material from the top as well as from the bottom. The recovery of the water takes place in the core of the filtering media.

A variation of upward filtration method uses floating materials. This is still being studied.

Lastly, tests have been carried out to develop a filter which would allow water to flow through the filtering material in a horizontal direction. The difficulties inherent in clogging and washing this type of filter have limited the use of this method.

6. CENTRIFUGATION

6.1. DEFINITIONS

Centrifugation is a **separation** process which uses the action of **centrifugal force** to promote accelerated settling of particles in a solid-liquid mixture. Two distinct major phases are formed in the vessel during centrifugation:

- the sediment, resulting from centrifugation, which usually does not have a uniform structure. In fact, classification occurs between the particles with a high density (bottom of sediment) and the lighter particles (organic colloids, for example),

- a supernatant liquid **called centrifugate or centrate,** resulting from a single phase that is often clear though sometimes cloudy, due to the presence of very fine colloidal particles that are not readily settled. However, it may also contain two or more phases if the mixture's interstitial liquid contains elements with different densities, such as oils for example.

Centrifugal force

In a cylindrical vessel (Figure 69) that turns at an angular speed ω of (rad.s^{-1}) or N (rpm) and contains a liquid ring of mean radius R (in m), the centrifugal acceleration γ (in m.s^{-2}) to which the particles are subjected is given by the equation:

$$y = ?^{2}R = 0,011\ N^{2}R$$

The acceleration generated by centrifugal separation is always expressed by reference to the earth's gravitational field as a multiple of g:

$$G = \text{multiple of } g = \frac{\omega^2 R}{g} = 11.2 \times 10^{-4}\ N^2.R$$

($g = 9.81$ m.s^{-2})

While a static settling tank clarifies a suspension according to the laws of sedimentation using gravitational pull of the earth alone, rotary machines (centrifuges) built on an industrial scale enable accelerated sedimentation to take place under the action of centrifugal fields that range from 800 to 4,000 g depending on the size of the machine.

The force exerted on a particle of unit weight is expressed by:

$$Fc = 0.011\ N^2R\ (\varrho_S - \varrho_L) \times \frac{1}{g} = G\ (\varrho_S - \varrho_L)$$

where:

ϱ_s: density of particle

ϱ_L: density of interstitial liquid.

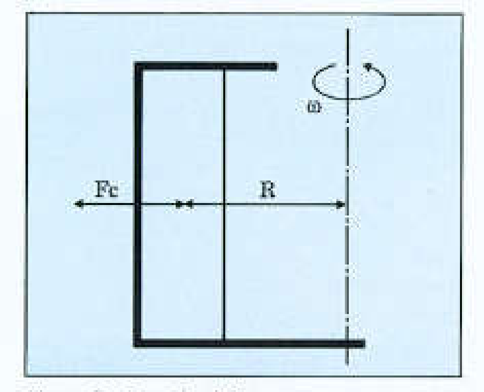


Figure 69. Centrifugal force.

6.2.

FIELDS OF APPLICATION IN WATER TREATMENT

.Separation of solid substances from highly concentrated suspensions

This is the most common use of centrifugation. Used this way for the treatment of sewage sludge, it enables:

- dewatering with the production of a more or less consistent sediment depending on the nature of the sludge to be treated,
- accelerated thickening of low concentration sludge with a view to optimizing the sludge treatment lines (main application: light biological sludge and possibly certain metallic hydroxide sludges).

Industrial units used in these applications are called continuous centrifuges, which are rotary machines with a solid bowl, as distinguished from other machines featuring a basket and sieve, which are dewatering units used specifically for crystalline chemicals.

Sometimes centrifugal force may also have applications in the following fields:

. Separation of oily suspensions with a low SS content

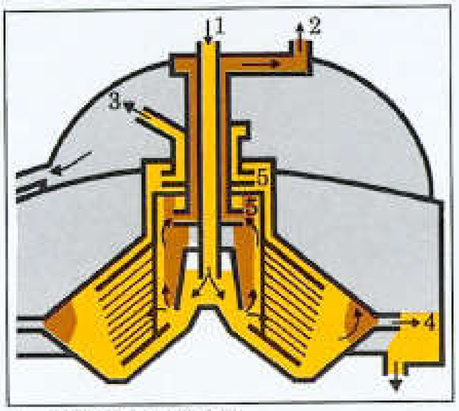
In this case disc centrifuges (see Figure 70) are used. These are rotary machines that consist of a horizontal solid bowl and are able to create very high centrifugal fields (3,000 to 8,000 g) (applications mainly in the automobile industry).

The solid phase is discharged by calibrated orifices with a small diameter (1 to 2 mm), called nozzles, which are located around the edges of the bowl. In the case of small machines, however, discharge takes place by the periodic opening of the bowl (autocleaners). Disc centrifuges are also used for water-oil separation.

. Separation of oily concentrated sludge

When the volume occupied by the sediment becomes too great it is possible to separate the three phases - solid/water/ oil - by horizontal, three-phase, continuous centrifuges.

The separation of the three phases can only take place efficiently and regularly if the physical-chemical properties of the sludge are relatively stable, as the location of the various clarified water and oil recovery ports is an essential parameter. Thus, the regularity of the treatment depends on a constant volume of sediment/water/oil respectively (refinery applications).



1 - Oily suspension feed.
2 - Light oil phase outlet.
3 - Water phase outlet.
4 - Sediment outlet.
5 - Centripetal turbines.

Figure 70. Three-phase disc centrifuge. Cross-sectional diagram.

. **Separation of heavy particles and large-sized grains by cycloning**

Cycloning uses the effect of centrifugal force created by the tangential feed of a liquid into a fixed cylindroconical vessel without moving mechanical parts. The acceleration created is low. This method is primarily used for the desanding of water from gravel pits, some surface water of torrential nature, and sludge.

6.3.

THE CENTRIFUGABILITY OF SEWAGE SLUDGE

When a sample of fresh sludge from municipal sewage (primary sludge + colloidal biological sludge) is subjected to a centrifugal field of 1,500 g in a laboratory centrifuge for 1 to 2 min, the following appear in the centrifugation bowl (see Figure 71):

- a cloudy supernatant liquid containing fine colloids in suspension,
- a sediment which can be divided into two zones:
  . a concentrated lower zone of dense matter:
  DS content: 25 to 35%
  VS/DS ratio: 55 to 65%
  . a less concentrated upper zone of hardly cohering matter that is, therefore, of a rather paste-like consistency:
  DS content: 10 to 18%
  VS/DS ratio: 75 to 85%

When the same experiment is repeated with a flocculated sludge, especially if an organic polyelectrolyte has been used, the following formation is observed:

- a clear supernatant liquid containing verylittle DS,
- a completely homogeneous sediment with substantial cohesion.

This capacity of the sludge suspension to separate in a laboratory centrifuge into two distinct phases is known as the "centrifugabiliry" of the sludge which polymer conditioning aims to improve. It is featured by:

- the clarification of the centrate, depending on the centrifugal field, the duration of the centrifugation process and the dosage of polymer,
- the volume taken up by the sediment, for it conditions the potential specific flow of the industrial machine,
- the consistency of the sediment, can be measured by penetrometry. More than the DS content, it is this parameter that makes it possible to predict whether the sediment can be easily extracted.

A centrate from a centrifuge can never be totally free of fine colloids (internal hydraulic perturbation inside the machine).

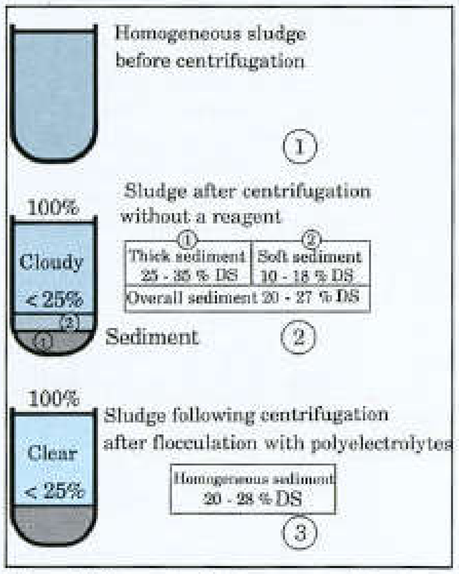


Figure 71. Example of laboratory centrifugation of municipal sludge.

6.4.
CONTINUOUS CENTRIFUGES

These are currently the only centrifuges used for clarifying sewage sludge (Figure 72). Centrifuges of this type consist basically of a horizontal, cylindroconical bowl (1) rotating at a high speed. Inside this bowl, a helical extraction screw, or scroll (2) is placed coaxially so that it perfectly fits the internal contour of the bowl, only allowing clearance between the bowl and the threads of the scroll. These two rotors, the bowl and the scoff, rotate at different speeds, and it is this difference in speeds that is known as the **relative velocity,** or $\mathbf{V_R}$.

The product to be treated (3) is introduced **axially** into the unit by an appropriate distributor (4). It is propelled into the ring space ,(5) formed by the internal surface of the bowl and the body of the scroll.

The separation process basically takes place inside the cylindrical section of the bowl. The relative velocity of the scroll in relation to the bowl pushes the settled product (6) along into the bowl. The conveyance of the solids along the length of the cone enables the sediment to pass out of the clarified liquid phase. As the feed is continuous, a liquid level (7) is established in the unit following a cylindrical surface which constitutes the internal surface of the liquid ring.

Once the solid has passed out of the liquid ring, the remaining section of the cone all the way up to the diffuser-ejector provides for final draining: this section is known as the **drying zone** (8). The clarified liquid (9) is collected at the other end of the bowl (the side with the large diameter) by flowing over the adjustable thresholds (10) which restrict the liquid ring in the unit. The rotor is protected by a cover which enables the clarified liquid as well as the sediment to be collected.

Continuous centrifuges used in industry for the separation of crystalline products have undergone some modification so that they can also be used for the treatment of sewage sludge. These centrifuges have been chosen for the following reasons:

- they operate on a completely continuous basis (sludge feeding and sediment discharge),
- the phases are separated by accelerated settling, and the sediment is conveyed by the scroll, thus avoiding any risk of clogging because the liquid phase does not pass through a filter medium,
- a homogeneous sediment and a high separation efficiency are obtained through the utilization of polyelectrolytes.

Continuous centrifuges are characterized

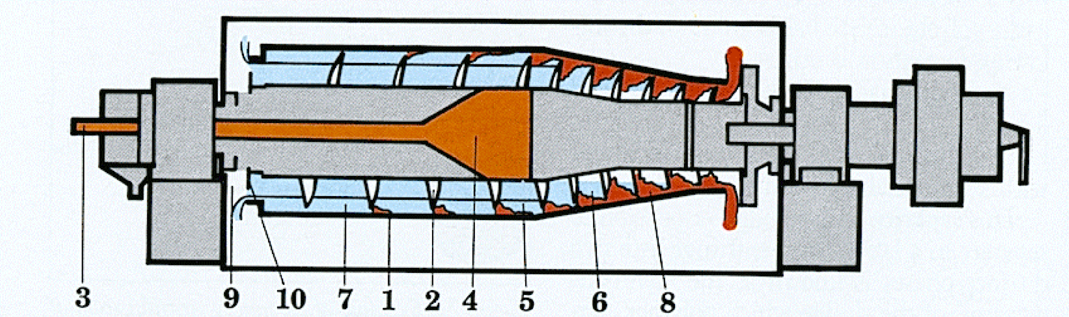


Figure 72. Cross-section of a continuous centrifuge.

6 4.1. Cocurrent and countercurrent 74), the sludge is introduced at the level systems (see Figures 73 and 74)

Continuous centrifuges are distinguished first of all by their respective directions of travel of the sludge suspension and of the sediment.

In the **cocurrent** system (Figure 73), the sludge is introduced at the beginning of the cylindrical section so that the liquid and the solid are conveyed in the same direction throughout the entire cylindrical section. The sedimentation process takes place along a longer route with less hydraulic turbulence, hence:

-better adaptation to difficult products involving low density and concentration with a more limpid centrate,

- often reduced polymer requirements.

However:

- there is a greater sensitivity to abrasion (the entire rotor is in contact with the sediment),

-usually the hydraulic capacities are lower and the sediment is a little less dry, - there is more strain between the scroll and the bowl (the sediment travels the entire length of the bowl).

In the **countercurrent** system (Figure of the joint between the conical and cylindrical sections where there is a rapid separation of solid substances, hence:

- better adaptation to thicker sludge,

- more localized abrasion (the conical section only),

- higher hydraulic capacities (however, with the risk of a lower quality of clarification owing to turbulence).

Mixed versions incorporating the two systems are also available.

6.4.2. Angle of conicity

This angle is usually between 8 and T2°. When the sediment enters the conical section, it is subjected to a backflow force that is as low as the angle of the bowl is reduced. This force also depends on the intensity of the centrifugal field. It _is maximum when the sediment passes out of the liquid ring. At this stage the cohesion of the thickening sludge has to be preserved or extraction will be unsuccessful and the clarified solids will flow back toward the cylindrical section resulting in a substantial drop in separation efficiency.

It is possible to reduce this backflow

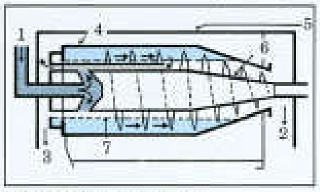


Figure 73. Cocurrent centrifuge.

1 – Sludge feed.
2 – Sediment outlet.
3 – Clarified liquid outlet.
4 – Bowl.

.

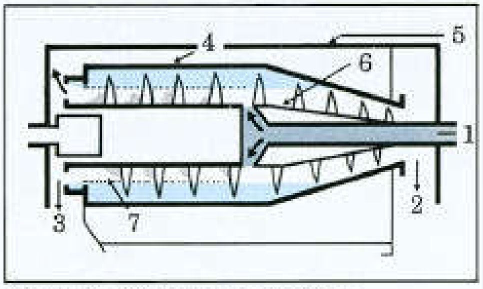
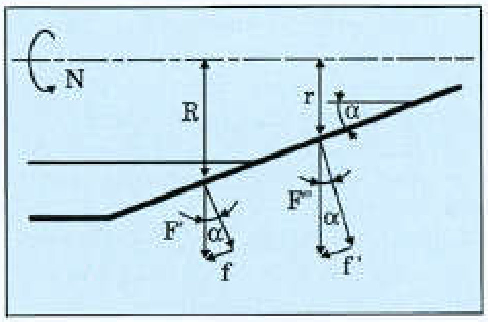


Figure 74. Countercurrent centrifuge.

5 – Enclosure.
6 – Helical scraper.
7 – Liquid ring.



$f = F'_c \sin \alpha \ (d_S - d_L) = F' \sin \alpha$
with $F'_c = 11.2 \times 10^{-4}\ RN^2$
$f' = F''_c \sin \alpha \ d_S = F'' \sin \alpha$
with $F''_c = 11.2 \times 10^{-4}\ rN^2$

Figure 75. Incidence of the conicity of the bowl and of the rotation speed on the backflow force f.

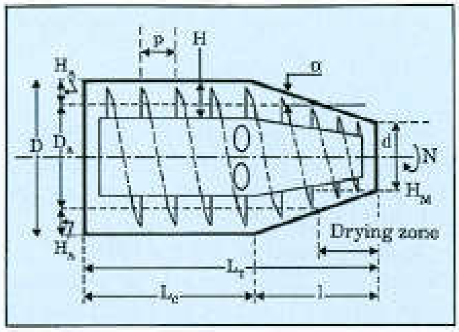
force by decreasing the speed of the bowl (or **absolute velocity** VA). However, in order to avoid reducing the final DS content (Figure 75), some compromise should be found. However, great angles of conicity (higher internal sediment storage volume) and high speeds allow the hydraulic capacity of centrifuges to be substantially increased.

6.4.3. Other parameters (Figure 76)

6.4.3.1. Diameter of the bowl: D

Units range in diameter from 0.15 to as high as 1.7 m. The treated flow Q depends, of course, on D, but to the same extent on the relation L_T/D. Long units (L_T/D larger than 3 or 4) must have the same hydraulic capacities with smaller diameters in order to improve energy consumption and acceleration. Moreover, it is above all the cylindrical section that is extended (Lc/D larger than 2 or even 3).

However, in treating paste-like sludge, the cohesion of the sludge often hinders performance.



N: bowl speed,
D: bowl diameter on the cylindrical side,
d: cone outlet diameter,
L_T: total length,
L_c: straight length (separating length),
α: angle of conicity,
l: conical length,
H: height of thread between scroll and bowl,
p: scraper pitch,
H_A: depth of liquid ring,
H_M: depth of liquid ring at overflow,
D_A: internal diameter of liquid ring.

Figure 76. Characteristic parameters.

6.4.3.2. Clarification area S with maximum liquid ring

This important parameter defines the maximum clarification area. It is calculated as follows:

$$S = p.D_A.L_c \text{ in } m^2$$

The Q/S ratio may be used to determine the size. However, it does not take into account the hydraulic turbulence inside the bowl.

6.4.3.3. E factor (Figure 77)

This expresses the equivalent settling area of a centrifuge operating at 1,000 g in relation to a simple settling process. A simplified calculation of this parameter is:

$$\Sigma = \frac{2k\pi\omega^2.L_c}{g} (3/4R^2 + 1/4r^2) \text{ in } m^2$$

In order to compare the two units, Σ is calculated at normal operating speed (N):

$\Sigma N = \Sigma . G . 10^{-3}$.

As a rule, ΣN is used to extrapolate the hydraulic capacity of units of different ranges.

However, one has to be careful when using the parameter ΣN in the treatment of creeping sludge because it does not take into account the turbulence caused by the helical scraper or the turbulence which occurs at the outlet outside of the liquid ring.

6.4.3.4. Hydraulic throu hg flow

This flow characterizes the turbulence and energy engendered across the restricted passageway located between the body of the scroll and the bowl which is agitated by a helical scraper which is moving at a high speed. The minimum throughflow is often of crucial importance when used on the many sewage sludges leaving a sediment that is difficult to compact.

. Longitudinal speed VT across the liquid ring is defined by:

$$V_T = \frac{Q}{S_A} \ m^3/m^2.h$$

Q = the flow in $m^3.h^{-1}$,

S_A = the cross-section of the liquid ring in m^2.

For hardly coherent sludge it is recommended that a limit of 100 to 180 m^3/m^2.h not be exceeded.

. **The sludge volume loading F_T** in the liquid ring is defined by:

$$F_T = \frac{Q}{V_c} \ m^3/m^3.h$$

V, = the clarification volume,

i.e., Sn.L.m3.

High H values (height of thread) lead to a calmer transfer. If the properties of the sludge permit, an increase in clarification volume can usually result in higher sludge volume loadings.

6.4.3.5. Settling time: T

$$T = 3600 \times \frac{V_c}{Q} \text{ in seconds}$$

(It usually lies between 40 and 100.)

6.4.3.6. Scroll

The height of the thread of the scroll as well as the scroll pitch exert a certain influence on the hydraulic capacities of the unit. It is the mechanism that is the most sensitive to abrasion, and the thread is usually protected: Stellite (48-50° Rockwell), ground tungsten carbide (62-65° 203 Rockwell), chromium-plating or even ceramic tiles or tiles made of sintered tungsten carbide. For some applications, the scroll may have a decreasing pitch in the conical section in order to better compact the sediment. Sometimes it also has perforated threads in the cylindrical section in order to ensure less turbulent transfers.

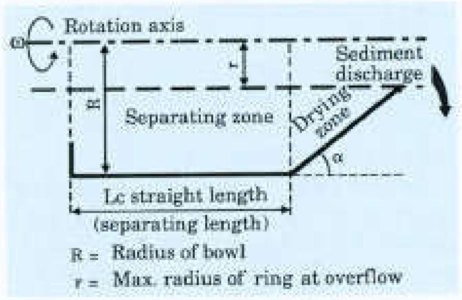


Figure 77. Determination of Σ factor.

7. FLUIDIZATION

This technique is used in various water treatment units:

- fluidized bed biological reactors,
- granular bed biological filters and reactors (washing),
- fluidized bed driers and furnaces.

In a reactor, which is usually a twophase system and contains solid particles through which fluid passes from the bottom toward the top, each particle is subjected to gravitational force on the one hand, and, on the other hand, to the frictional force due to the passage of the fluid. This results in an equilibrium which defines a velocity limit: if the rising velocity of the fluid is less than this velocity limit, the particle has a tendency to settle,

whereas if is higher, the particle has a tendencyto be carried upward by the fluid.

In fact, the "fluidized bed" is not made up of merely one particle, but rather of a group of particles; moreover, the particles are not all the same size. In practice, when a granular mass inside a column is subjected to increasing rising velocities, the results summarized on the graph in Figure 78 are attained. The material expands at the same time as the rising velocity increases. The same is true for head loss until a certain minimum velocity of fluidization V_{mf} is attained. This velocity also depends on the temperature.

Beyond this value, the head loss remains constant. This value is well defined for a material that has a uniformity coefficient equal to 1. Ibis is not true for materials used in practice. In this case the V.f is determined by the intersection of the extension of the two linear portions of the curve (Figure 78 a). Beyond a V_f velocity, the material is carried away by the rising current (Figure 78 b).

In order to facilitate the fluidization in the biological treatment process, materials are used that have a small effective size and develop a large specific area. The advantage of this large area is that it allows the fixation and development of a large bacterial mass. Thus it is possible to obtain a volume of bacterial activity that is substantially higher than that obtained with free bacteria. The development of bacteria on the surface of particles leads to the formation of a film whose activity is greater as its thickness is negligible. Furthermore, the particle-film combination constitutes a new particle whose real average specific gravity is lower than the real specific gravity of the original particle: for

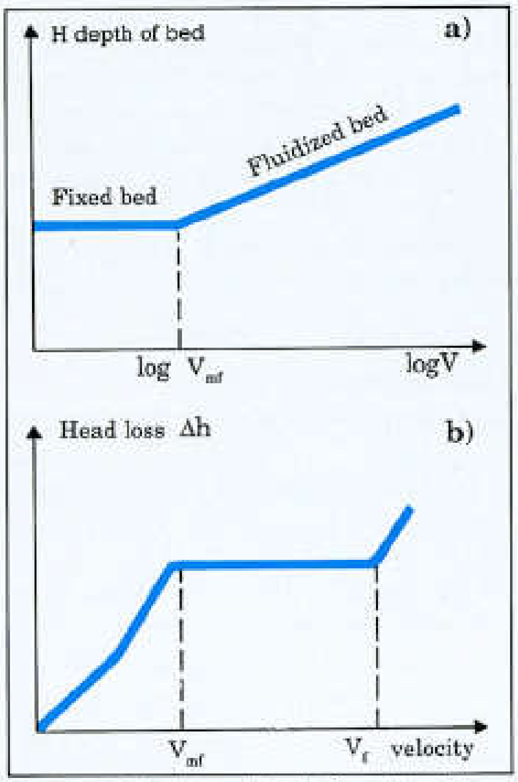


Figure 78. Behaviour of a bed of particles subjected to a rising current.

the same rising velocity the expansion of the material grows as the thickness of the film increases.

Proper operation of a fluidized bed reactor depends

- proper distribution of the fluid at the base of the reactor
- a contact material that is uniform and resistant to abrasion,
- the employment of an adequate washing system which permits excess sludge to be evacuated while maintaining enough seed material to enable the reactor to restart. Usable materials include sand, pumice stone, Biolite, etc.

Table 37 gives several fluidization velocities for commonly used materials.

Table 37. Minimum fluidization velocities for various filtering media
(t = 20°C).

	Sand (round grains)		**Anthracite** 1.4-2.5 mm			
Material	**ES 0.55**	**ES 0.95**	**Heat treated**	**Natural**	**Pumice stone**	**Biolite L** 2.7 mm
ES, mm	0.53	0.95	1.62	1.16	1.38	2.58
V_{mf}, m.h^{-1}	21	47	65	38	37	125

NES: nominal effective size,[2] ES: measured effective size.

8. ELECTROLYSIS

8.1.

BASIC PRINCIPLES - DEFINITIONS

Applying a potential difference between two electrodes immersed in an electrolytic bath (solution containing ions), creates an oriented electrical field in which the ions begin to move: the canons move in the direction of the cathode, the anions move in the direction of the anode. When sufficient voltage is applied, the following reactions occur at the electrolyte-electrode interfaces:

- at the anode: oxidation with loss of electrons: $A- - A + e^-$

- at the cathode: reduction with gain of electrons: $C^+ + e^- \rightarrow C$

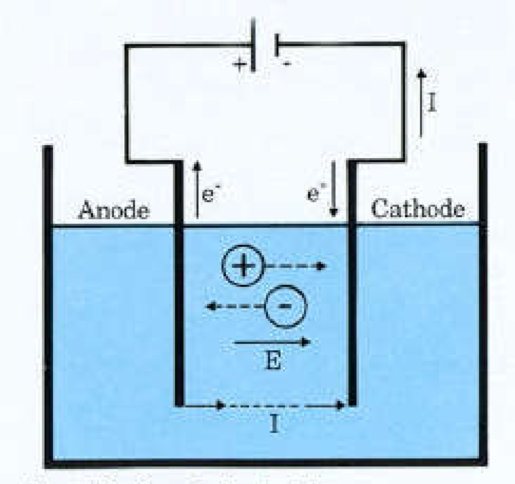


Figure 79. Electrolysis principle.

8.1.1. Nernst equation

When plunged into an electrolytic solution (with nil current), an electrode takes an Eo voltage. This voltage, which corresponds to an equilibrium between the species present, is known as the equilibrium potential and follows Nernst equation:

$$E_0 = E_0^0 + \frac{RT}{nF} \ln \frac{Aox}{Ared}$$

where:

E_0: equilibrium potential of the electrode,

E_0^0: equilibrium potential of the electrode in standard conditions (activities of oxidizing and reducing species equal to the unit),

R: constant of ideal gases,

F: Faraday constant,

T: absolute temperature,

n: number of electrons brought into play in the electrochemical procedure,

Aox: activity of the oxidizing species, Ared: activity of the reducing species.

The activities can be assimilated to concentrations in the case of ideal solutions. The E^0_o and E_o potentials are expressed in relation to a reference electrode, usually a standard hydrogen electrode (s.h.e.).

Table 38 gives the standard equilibrium potentials for a number of electrochemical couples (at 25°C measured against the s.h.e.).

8.1.2. Electrolysis voltage.

In the normal operation of an electrolytic cell, the V voltage obeys a law of form:

$V = (E_0 + ?)_{anode} - (E_0 + ?)_{cathode} + rl$

with:

E_0: the equilibrium potential of the electrodes,

η: the overvoltage of the electrodes,

rI: the ohmic loss owing to the resistivity of the electrolyte.

8.1.3. Faraday's law

Faraday's law expresses the equation that links the amount of electricity passing through an electolytic cell to the amplitude of the reactions which take place at the electrode-electrolyte interfaces:

$$P = R_F \frac{M}{n} \frac{It}{N.e_o}$$

P: weight of substances involved during the reaction (g),

R_F: current efficiency,

M: molecular weight of the substances

It: amount of electricity passing through the cell (C),

n: number of gramme-electrons exchanged during the reaction,

N: Avogadro number = 6.02×10^{23} for one mole,

eo: the electron charge = 1.6×10^{-19} C.

8.2.
FULL-SCALEAPPLICATIONS

8.2.1. Electrochlorination

Electrochlorination involves manufac turfing a dilute sodium hypochlorite solution in situ from a sodium chloride solution (sea water or brine).

<u>8.2.1.1. Reactions</u>

The formation of hypochlorite from chloride may be summarized by the over all reaction :

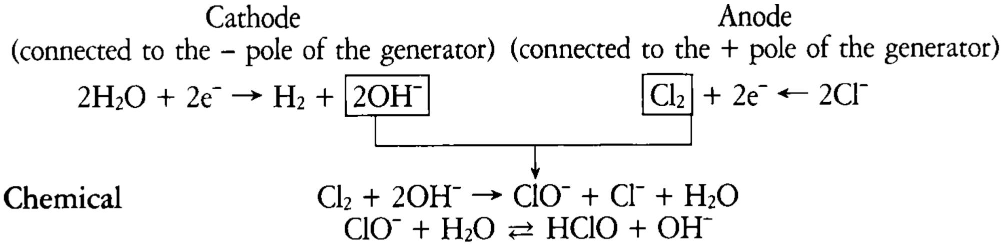
$2NaCl + H2_0 - >NaClO + NaCI + H_2$

Table 38. Nernst scale of standard a equilibrium potentials.

Metal	Electrode reactions	Equilibrium potential (volts)
Magnesium	$Mg= Mg^{2+} + 2e^-$	-2.34
Beryllium	$Be = Be^{2+} + 2e^-$	-1.70
Aluminium	$Al = Al^{3+} + 3e^-$	-1.67
Manganese	$Mn = Mn^{2+} + 2e^-$	-1.05
Zinc	$Zn = Zn^{2+} + 2e^-$	-0.76
Chromium	$Cr = Cr^{3+} + 3e^-$	-0.71
Iron	$Fe = Fe^{2+} + 2e^-$	-0.44
Nickel	$Ni = Ni^{2+} + 2e^-$	-0.25
Lead	$Pb = Pb^{2+} + 2e^-$	-0.13
Hydrogen	$H2 = 2 H^+ + 2e^-$	-0.000
	$CU = Cu^{2+} + 2e^-$	by convention
Copper	$Cu = Cu^+ + e^-$	+0.34
Copper	$Ag= Ag^+ + e^-$	+0.52
Silver	$Pt = Pt^{2+} + 2e^-$	+0.80
Platinum	$Au = Au^{3+} + 3e^-$	+1.20
Gold	$Au = Au\ 3+ + 3^e$	+1.42

. Main reactions

Electrochemical



. Parasitic reactions

- Migration and oxidation of the OH^- at the anode: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$,

- Reduction of the ClO^- at the cathode:

$ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$

- Formation of hydroxides, mainly

$Mg(OH)_2\ Mg^2 + 2OH^- \rightarrow \underline{Mg(OH)_2}\downarrow$

8.2.1.2. Fields of application

Sodium hypochlorite has a strong residual oxidizing capacity which promotes the destruction of organic matter. It constitutes an ideal reagent in water treatment. Its generation in situ according to the electrochlorination process eliminates the safety and supply contingencies resulting from chlorine storage.

Thus, the electrochlorination process has been developed basically to protect the cooling systems of offshore platforms, electric power stations or factories using sea water against the proliferation of algae and mollusks.

The energy consumption of full-scale

units is somewhere around 4 kWh per kg of equivalent chlorine produced. The concentration of hypochlorite solutions produced usually ranges from 1 to 3 g per litre

8.2.2. Electrocoagulation

This electrochemical process used on some wastewaters basically results in flocculation according to the following processes:

- the creation of an electrical field between the electrodes which promotes the collision between the charges present in the effluent,
- the release of metallic ions (Fe, Al) when the sacrificial anodes dissolve; these ions generate hydroxides which enable floc. equivalent chlorine. of to form

The energy consumed in this process varies from one application to another but often ranges from 2 to 4 kWh per m3 treated.

8.2.3. Other applications

- electroflotation: see page 176,
- electrodialysis: see page 219,
- electroplating: see Chapter 26, section 10.

9. SEPARATION BY MEMBRANES

The procedures of separation and concentration by membranes have been known for a hundred years or so. Never theless, we had to wait until the 1960s to see the industrial application of such techniques by the development of synthetic membranes. Since the 1970s, these procedures have developed considerably with regard to:

- the number of membranes developed and marketed,
- the performance and thus, potential industrial applications in treatment of water as well as of other fluids.

At the risk of being simplistic, these new membranes may be grouped either according to the type of separation they are able to perform or according to their structure. Here the discussion will be limited to membranes and procedures that have to do with the treatment of aqueous solutions and suspensions.

9.1.
GENERAL

A membrane is any **material** which forms a thin wall (0.05 mm to 2 mm) and is capable of putting up a selective resistance to the transfer of different constituents of a fluid, thus allowing the separation of some of the elements (suspensions, solutes or solvents) making up this fluid.

9.1.1. The structure of the membranes

Ever since the first reverse osmosis membranes made of acetate or cellulose were used, a large number of organic (polymer) membranes, or even inorganic membranes (for instance obtained by the heating of ceramic particles such as Al_2O_3, carbon, silicon carbide, zirconium oxide), have been slowly added to the list. They may be characterized by their structure (Figures 80 and 81).

. Homogeneous membranes

These membranes have been pierced with holes, which are quasi-cylindrical in shape, through a bombardment process followed by a chemical attack (some of these membranes are used in microfiltration, as for instance Nuclepore membranes).

. Asymmetrical membranes

These membranes are made in one stage using the same polymer material. However, in this case, the selectively permeable layer has been reduced to a very fine "skin" in order to limit the resistance to transfer in proportion to the thickness of the layer. This layer rests upon another, thicker substrate that has much slacker pores which intends to provide the membrane with satisfactory mechanical properties without significantly impeding the flow of water. These properties can be artificially improved even more by anchoring the membrane onto a fabric support, thus reinforcing the slack substrate.

. Composite membranes

These membranes enable a permselective skin to be placed on a preexisting porous support which is, itself, often asymmetrical; this is a more recent addition. Since the two materials placed together are usually of different types, the properties of each, mechanical in one, selective in another, are used to their fullest extent.

9.1.2. Mechanisms of transfer through the membranes

They can be divided into three groups (Figure 82).

. Filtration

In this case membranes called semipermeable membranes are used. The solution is concentrated due to selective passage of the water ("convective" transfer of the solvent through the porous

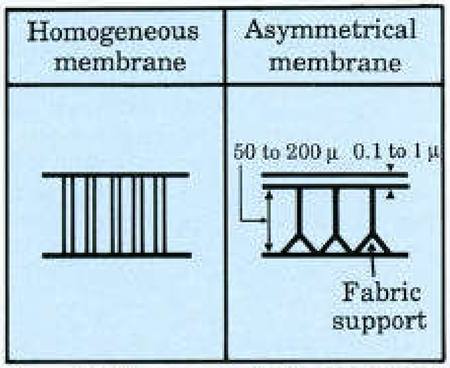


Figure 80. The structure of homogeneous and asymmetrical membranes.

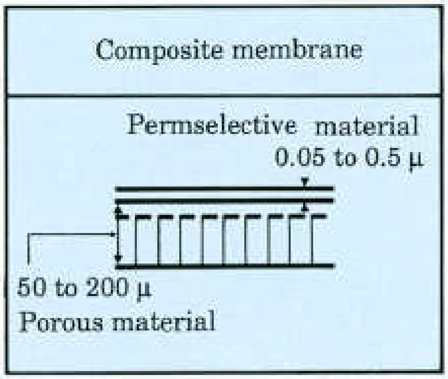


Figure 81. The structure of a composite membrane.

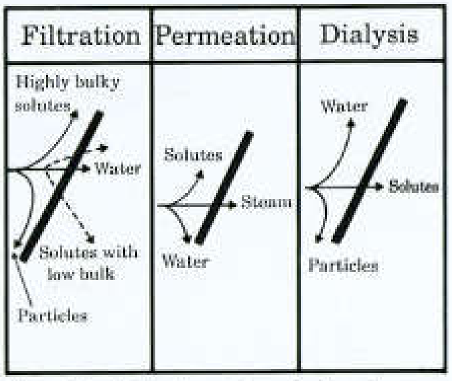


Figure 82. Mechanisms of transfer through membranes.

medium), whereas the other constituents of the fluid are sometimes retained at the surface of the porous medium, depending on their size. The ideal membrane would only allow the passage of water (perfect osmosis).

. Permeation

It is possible to divide up a mixture by allowing the selective passage of one of the constituents **in gas phase** through the membrane. .

. Dialysis

The membranes used, which allow the passage, selective or not, of ions, do not permit the passage of water. These membranes may be neutral or charged. If they are charged (the material being identical to that used in ion exchange resins, in layer form), they become selective in allowing the transfer of ions carrying opposite charges; membranes can thus be cationic, which permits the passage of cations only, or anionic, which allows the passage of anions only.

9.2.
SEMI-PERMEABLE AND CLARIFICATION MEMBRANES

With these membranes, water is the preferred transfer phase under the effect of a pressure gradient. They are usually described as filtration membranes and classified according to the size of their pores (Figure 83).

However, this customary classification is somewhat at fault because:

- from the moment the field of ultra filtration, and a fortiori, osmosis, is reached, it becomes difficult to define the size of the pores correctly by the usual methods (bubble points, mercury porosimetry, optical microscope, electron microscope),
- the traditional transfer techniques of filtration (convective transfer of water through a porous medium and filtration/ screening of particles that are larger than the pores), which work so well in microfiltration and ultrafiltration, are inadequate when it comes to membranes used in nanofiltration and hyperfiltration which is also called reverse osmosis.

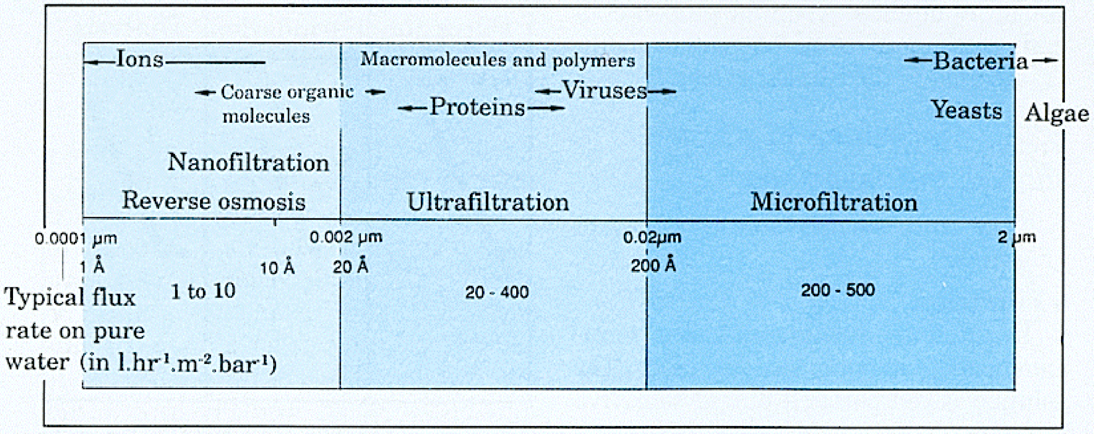


Figure 83. Types of membrane filtration.

9.2.1. Reverse osmosis (RO)

Reverse osmosis makes use of the properties of semi-permeable membranes which allow water to pass through while solutes are retained except for certain organic molecules very similar to water (with a low molecular weight and strong polarity).

If a concentrated saline solution is separated from a more dilute solution by such a membrane, the difference in chemical potential tends to promote the passage of water from a compartment with a low potential to that with a higher potential in order to dilute it (natural osmosis). In order to stop this diffusion, a pressure must be exerted on the "filtered" fluid. At equilibrium, the pressure difference established in this way is known as the **osmotic pressure of the system** (Figure 84).

A simple equation relates osmotic pressure to concentration: $\Pi = \Delta$ C.R.T.

Π: osmotic pressure in Pa,

ΔC: difference in concentration in mol.m^{-3}

$$\text{mol.m}^{-3} = \frac{\text{concentration in kg.m}^{-3}}{\text{molecular weight in kg.mol}^{-1}}$$

R: constant of an ideal gas = 8.314 (J/mol.K),

T: the temperature in K.

Example: concentration in solution:
100 kg.m^3; T: 300 K; for a compound with a molecular weight of 0.050 kg.mol^{-1}:

$$\Delta C = \frac{100}{0.050}$$

$$\pi = \frac{100}{0.050} \times 300 \times 8.314 = 50 \times 10^5 \text{ Pa,}$$

i.e., 50 bar.

Similarly:
for a compound with a molecular weight of 0.5 kg.mol^{-1}, $\pi = 5$ bar,
for a compound with a molecular weight of 50 kg.mol^{-1}, $\pi = 0.05$ bar.

Clearly, the smaller the molecule (i.e., the lower the molecular weight), the greater the osmotic pressure set up by the same difference in concentration. This explains why ultrafiltration leads to an osmotic backpressure which is much lower than that experienced with reverse osmosis.

This is illustrated in Figure 85, which shows that the theoretical law does not apply to higher concentrations.

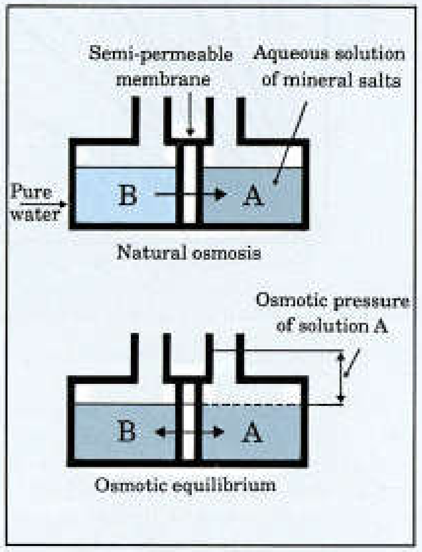


Figure 84. Osmosis phenomenon.

Figure 84. Osmosis phenomenon

In fact, to produce "pure" water from a saline solution, the osmotic pressure of the solution must be exceeded. In the same way, it may be said that in order to obtain economically viable flows, at least twice the osmotic pressure must be exerted; for instance, for a brine containing several grammes of salt per litre, pressures of 5 to 30 bar would be needed, and for sea water, pressures of 50 to 80 bar would be needed.

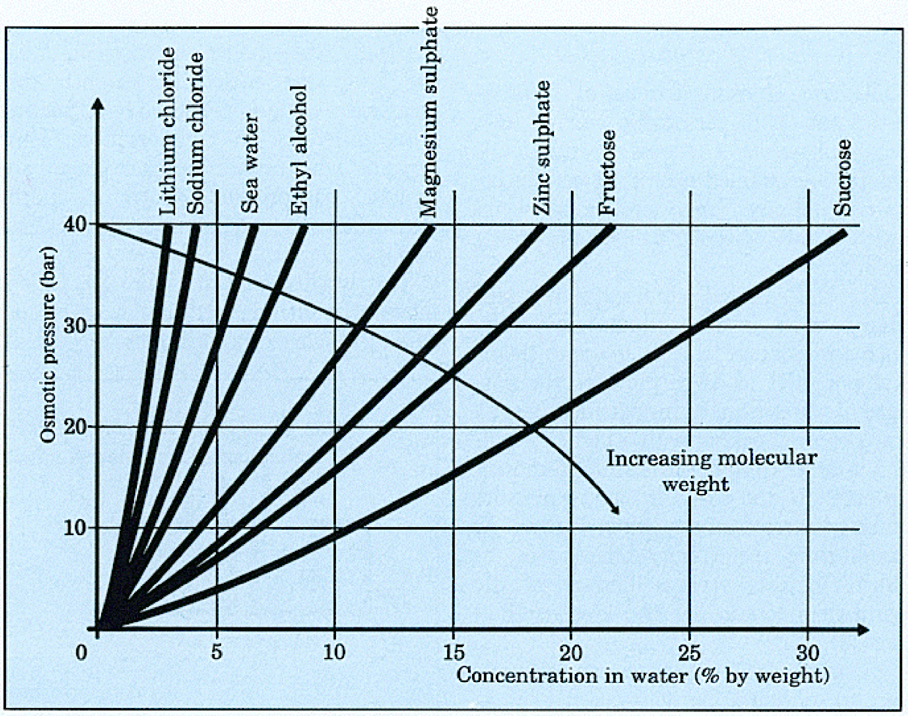


Figure 85. Osmotic pressure of various solutions.

A second phenomenon can amplify this effect. As Figure 86 illustrates, when water is transferred, the molecules and ions retained by the membrane tend to accumulate along its entire surface, thereby increasing both the salinity actually "treated" by the membrane and the osmotic pressure that must be "overcome" in order to desalinate the solution. This results in higher energy costs, as well as in the risk of causing precipitation if the solubility product of one of the canon-anion couples is exceeded in the boundary layer all along the membrane.

This phenomenon is known as **concentration polarization** of the membrane and is defined by the coefficient:

$$\psi = \frac{C_m}{C_e}$$

with:

C_m: concentration of the liquid in contact with the membrane,

C_e: concentration of the liquid to be treated.

This phenomenon can be reduced to a minimum by maintaining a circulation flow across the upstream surface of the membrane, which limits the thickness of the boundary layer and facilitates the reverse diffusion of the rejected solutes; however, this limits the fraction of desalinated water. This technique is used in industrial systems to maintain the coefficient ? between 1 and 1.4.

To describe the phenomena observed, best models call upon the laws of diffusion, water being considered dissolved by

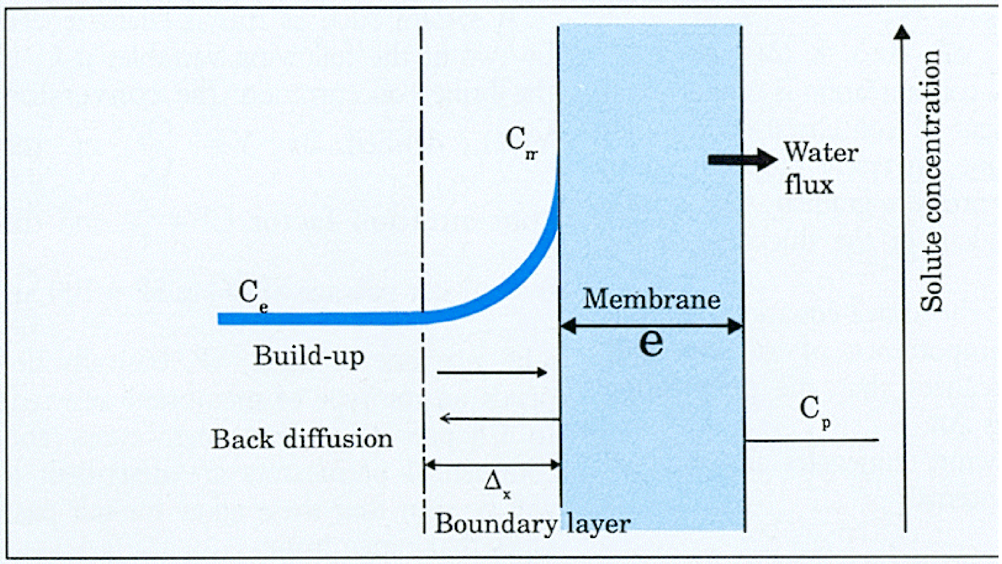


Figure 86. The concentration polarization.

the polymer making up the membrane (water used for swelling the polymer); this water moves under the effect of the pressure gradient, while the salts move under the effect of their concentration gradient alone.

For a saline solution, the water and salt *flux* rates may be obtained by Fick's and Henry's laws.

For water:

$$Qp = Kp.\frac{S}{e}.(\Delta P - \Delta\pi).K_t$$

with:

Qp: flow of water through the membranes,

Kp: membrane permeability coefficient for water,

S: membrane surface area, e: thickness of the membrane,

ΔP: hydraulic pressure differential across the membrane,

Δp : osmotic pressure differential across the membrane,

K_t : temperature coefficient.

Thus, the *flow* of water through the membrane is directly proportional to the effective pressure gradient, represented by the difference between the hydraulic and the osmotic pressure.

The coefficient Kt takes the viscosity of water into account. The latter decreases when the temperature rises. Therefore, the *flow is* greater when the temperature rises (2.5 to 3% difference per degree at about 15°C).

For salts:

$$Q_s = K_s.\frac{S}{e}.\Delta C.K_t$$

with:

Q_S: flow of salt through the membrane,

K_S: membrane permeability coefficient for solutes,

S: membrane surface area,

e: thickness of the membrane,

ΔC: ion concentration differential across the membrane:

$$C_m - C_p \text{ or } Ce.\psi - Cp$$

K_t : temperature coefficient.

The flow of salt is directly proportional to the gradient of concentration through the membrane; for a given membrane and a given solution, its value is independent of the applied pressure.

The salt concentration in the product is given by the relation of the two preceding equations.

$$C_p = \frac{Q_s}{Q_p} = \frac{K_s}{K_p}\frac{C_m - C_e}{\Delta P - \Delta\pi} = \frac{K_s \psi C_e}{K_p (\Delta P - \Delta\pi) + K_s}$$

Thus, this concentration is proportional to the gradient of concentration through the membrane, inversely proportional to the effective pressure gradient ($\Delta P - \Delta\Pi$), and independent of the thickness of the membrane.

Moreover, the above equations demonstrate the importance of ψ, especially when one realizes that the polarization also increases $\Delta\Pi$.

The following tendencies are observed in all RO systems:

	Product flow Q_P	Product salinity C_P
Pressure ↗	↗	↘
Temperature ↗	↗	=
Salinity ↗	↘	↗
ψ ↗	↘	↗

In practice, the simplest osmosis System contains the following elements:

- a high pressure pump to supply energy to the system,
- a permeator (module) or group of permeators,
- a valve on the discharge line circuit to maintain pressure in the system:

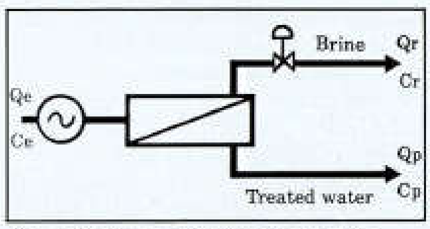


Figure 87. Design of a reverse osmosis unit.

Figure 87. Design of a reverse osmosis unit.

A system such as this is characterized by two of the following variables if C_r is the brine concentration: the **conversion** Y(%), defined by $Y = \frac{Q_P}{Q_e}$, or the **concentration factor** $CF = \frac{C_r}{C_e}$ and the **overall salt passage** SP(%) as $SP = 100 \frac{C_P}{C_e}$.

. In fact, one of these, SP, basically depends on the type of membrane selected. In Chapter 15, where membranes and commercial permeators are described, it will be seen that these allow for salt passages that range from:

0.5 to 15% on monovalent ions,

0.05 to 8% on bivalent ions.

It will be observed that these values are rather low. So, as a first approximation, C_P often tends to be overlooked in favour of C_e or C_r, a step which simplifies the equations mentioned above.

. The others, Y or CF, depend on the choice the project director makes as to the use of more or less raw water. This choice is fundamental:

- if Y rises, the energy cost pet m3 product E decreases, since less water is pressurized for the same amount of production, - however, the CF rises at the same time, since using the same approximation as mentioned above, the salt evaluation gives:

$$FC = \frac{1}{100 - Y}$$

In the same period:

- the quality of product CP decreases, since the mean concentration in front of the membrane grows in a permeator, this concentration varies between Ce at the inlet to G at the outlet, which means that in the preceding equation, Ce must be replaced by

$$\frac{C_e + C_r}{2},$$

average concentration in the permeator,

- Q_P decreases; as a result, the osmotic pressure p, proportional to $\frac{\psi C_r + C_r}{2}$ increases.

The influence of the choice of the conversion may be summarized in the table below:

If Y ↗ , then E (kW/m^3) ↘ but also Q_P ↘ , C_P ↗ , CF ↗ .

Note: the positive effects (less brine to be rejected) and, often, the negative effects (scale formation, fouling) resulting from the increase in CF, will be seen in Chapter 15.

9.2.2. Nanofiltration

This is a variation of the RO membranes that has recently been introduced, which features:

- passage of monovalent salts that is relatively high: 30-60%,
- passage of bivalent salts that is substantially lower: 5-15%,
- passage of organic solutes of the same type as with RO membranes.

Thus, the main advantage of these membranes is that by allowing a higher passage of monovalent salts (which contribute most to the osmotic pressure), they limit ΔΠ, hence the energy required to achieve:

- partial desalination in combination with adequate softening of a moderately saline water (TDS less than 2 g.l^{-1}),
- "cheap" purification of water as far as organic pollutants are concerned.

9.2.3. Ultrafiltration (UF)

The membranes used in ultrafiltration possess a slacker structure (asymmetric or composite), which allows only the coarsest solutes (macromolecules) to be rejected, and a fortiori all types such as viruses and bacteria.

They are usually characterized by their **removal threshold,** i.e., the size of the lowest molecular weight protein rejected by the membrane. There are industrial membranes which have a removal threshold ranging between 2 x 103 to 105 daltons.

This concept is only meaningful in view of the variations in the steric configuration of the same protein depending on the salinity, the pH, etc., and a fortiori of two macromolecules of identical molecular weight.

The unit flows indicated for OF membranes range from 0.1 to 1 m^3/h.m^2.bar for clean water, but these decrease considerably when colloids are present for two basic reasons: concentration polarization and fouling.

The first phenomenon has already been shown in the case of reverse osmosis. In ultrafiltration, it is responsible for the presence of a boundary flux when the pressure across the membrane increases (Figure 88).

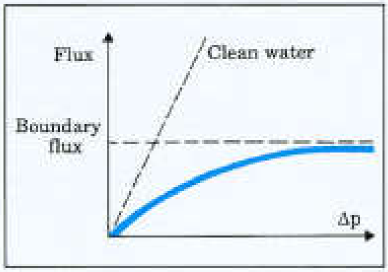


Figure 88. Influence of pressure across membrane on flux in ultrafiltration.

The overconcentration of solutes near the membrane leads in fact to a substantial increase in osmotic pressure; the resistance to transfer of the substances in this very concentrated boundary layer (the polarization coefficient often exceeds 102) becomes preponderant. The values of the flux are often in the order of several dozen litres per m^2, i.e., 10 to 100 times lower than the flux of clean water.

The only way of increasing the flux is to work at a higher tangential velocity, which involves substantial energy consumption.

The second phenomenon is fouling which, at a constant concentration, is evidenced by a lowering in flux in the long term, which can end in a complete blockage of the membrane (Figure 89).

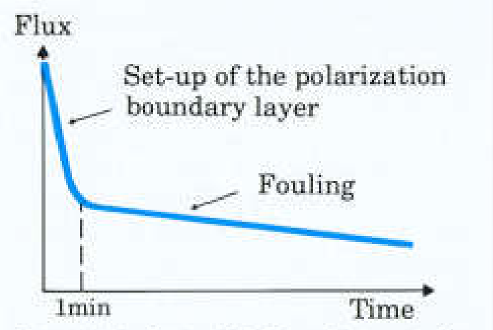


Figure 89. Evolution of the flux with time in ultrafiltration.

Fouling is due to the formation of a deposit of colloidal particles on the surface of the membrane. It is also due to the adsorption of varied solutes and the most finely divided colloidal particles in the pores. The first phenomenon is easily reversible by means of backflushing (detaching of the cake and transfer). The second, however, is very often unaffected by backflushing or by a higher circulation velocity, etc.; the membrane can only be cleaned by a suitable chemical treatment.

This illustrates that the chemical nature of the membrane is an important criterion for ultrafiltration as well as microfiltration. For each use, a type of material should be chosen that remains little affected by the adherence of solutes to be treated and that is thus more easily flushed clean by hydraulic means.

9.2.4. MicroFltration (MF)

These membranes do not change the composition of the solution in any way; only suspended solids, colloids, bacteria, etc., are rejected (or filtered).

In this case, the phenomena described above as a consequence of the rejection of solutes (osmotic pressure - polarization concentration) disappear and their place is taken by the phenomena already described in filtration through rather thin, porous media: clogging from the accumulation of a cake or internal clogging of the pores.

Thus, two types of operations are taking place at the same time:

9.2.4.1. Dead end filtration

In this case (Figure 90 a), the water is forced through the membrane and the retained particles build up in the form of a filter cake which grows thicker and less porous, which causes a reduction in the specific flow, a condition known as "fouling" of the membrane.

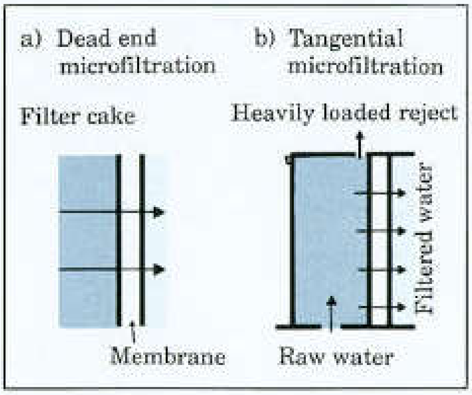


Figure 90. Microfiltration modes.

In most operations, equipment employed includes:

- flat laboratory microfiltration membranes (to measure SS, the fouling index FI, etc.),
- filtration cartridges on flat or pleated membranes, etc.

These elements are disposed of once they become fouled. Sometimes they are "regenerated" by a countercurrent washing device.

9.2.4.2. Tangential filtration

In this case (Figure 90 b), as in the case of all other semi-permeable membranes, the membranes are designed in such a way as to allow part of the inflow to be used as a circulation flow across the active side of the membrane; this limits the build-up of cake by continuously carrying away the substances discharged out of the system.

This continuous cleaning method has been designed for most of the systems equipped with "regenerable" membranes. Generally, this makes any membrane unclogging or washing operation unnecessary.

In fact, in industry the amount of energy expended is too great to achieve this goal and a compromise involving "the circulation energy/unclogging frequency" still remains to be reached (see Chapter 15).

These membranes and the technology that they incorporate ought to replace the process of coagulation-flocculation as well as that of solids-liquid separation described at the beginning of this chapter. They are also being developed for use in the fine filtration procedure involving various substances and processes such as:

- acids or solvents used in the microelectronics industry,
- the "sterilizing" filtration process for beverages such as beer, fruit juices, wines, or liquid substances used in the pharmaceutical industry and in biotechnology.

9.3.
PERMEATION PROCESSES

The following can be mentioned:

9.3.1. Gas permeation

A gas mixture is weakened or enriched by acting on the differences in diffusion rates of its constituents through the dense matrix of the membrane under the influence of a pressure gradient. Examples of this are:

- hydrogen recovery in a hydrocarbon mixture (Figure 91 a - petroleum industry) or in the blown off gases from an ammonia synthesis operation,
- enriching the air with nitrogen or oxygen.

9.3.2. Pervaporation

If on the downstream face of a pervaporation membrane one creates a partial vacuum in such a way that it is situated below the vapour tension of one of the solutes of the solution in contact with the upstream face of the membrane, one may observe through it a selective transfer of these solutes in their gaseous form. Gas condensation provides for the possible recovery of the solutes mentioned. For example:

- the dehydration of alcohol; in this way, an absolute alcohol may be recovered by selectively transferring water vapour through a hydrophilic membrane (Figure 91 b),
- the removal of THM from drinking water; in the same way, these solvents can be forced to be diffused selectively

through a silicone membrane for instance. It has already been shown, at the pilot level, that this technique could be competitive with current techniques of stripping and/or adsorption on activated carbon if permeators with a large surface area were manufactured industrially.

9.3.3. Distillation on membranes

By creating a partial vacuum on the downstream face of a microporous membrane, a system may be created which:

- counteracts the displacement of the liquid phase applied to its upstream face, on the condition that the difference in pressure across the membrane remains lower than the capillary pressure across it. In practice, a porosity lower than 0.8 µm on hydrophobic membranes results in differences of one bar of pressure to be applied, - on the other hand, allows the passage of water vapour through the membrane. When it condenses, this vapour lends water a substantial purity; in fact, only other volatile compounds may pass through at the same time as water.

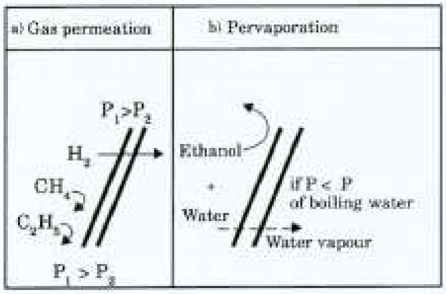


Figure 91. Permeation processes.

Several full-scale systems operate on this principle. Nevertheless, they retain the energy-consuming character of singleeffect distillation systems. However, by using organic membranes, corrosion which is usually found in the evaporators may be avoided.

Possible application: the concentration of industrial effluents (toxic, etc.) before incineration or crystallization (Figure 92).

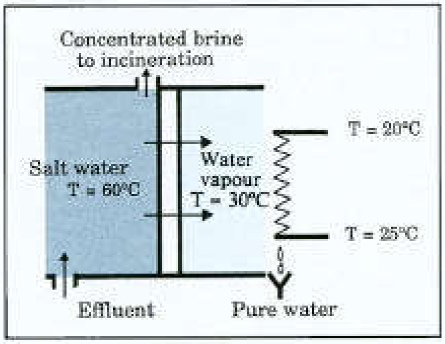


Figure 92. Distillation on membranes.

9.4.
DIALYSIS MEMBRANES

The **passage of solutes** through the membrane may be obtained by means of a pressure gradient, a chemical potential gradient or an electrical potential gradient.

9.4.1. Piezodialysis (pressure gradient)

Has no industrial application.

9.4.2. Simple dialysis (chemical potential gradient)

The impurities migrate in order to equalize the chemical potential (salts and organic solutes of low molecular weight) on the two sides of the membrane. If the phase which is being concentrated is sufficiently renewed, a nearly total removal of impurities may be obtained.

The main application is hemodialysis (Figure 93 - artificial kidney functioning), which results in a purification of the blood (the removal of salts, urea, etc.) in cases of renal deficiency, by placing it in contact via a dialysis membrane with plasma containing solutes that must remain in the blood while excluding those that must be removed.

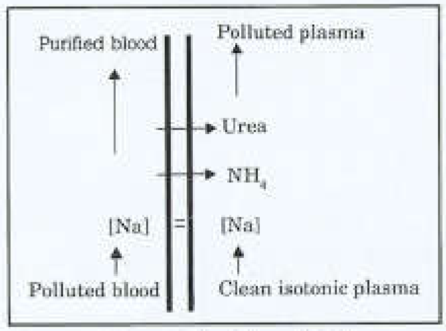


Figure 93. The principle of hemodialysis.

9.4.3. Electrodialysis

. Principle

If a liquid that is rich in ions, is subjected to an electrical field by means of two electrodes with a continuous potential difference applied between them, the cations will be attracted to the negative electrode (cathode) and the anions will be attracted to the positive electrode (anode). If nothing impedes their movement, they will each lose their charge on the opposite sign electrodes and thus, electolysis takes place.

However, if a series of selective dialysis membranes is placed between the electrodes:

- cation membranes, permeable only to the cations,

- and anion membranes, permeable only to the anions,

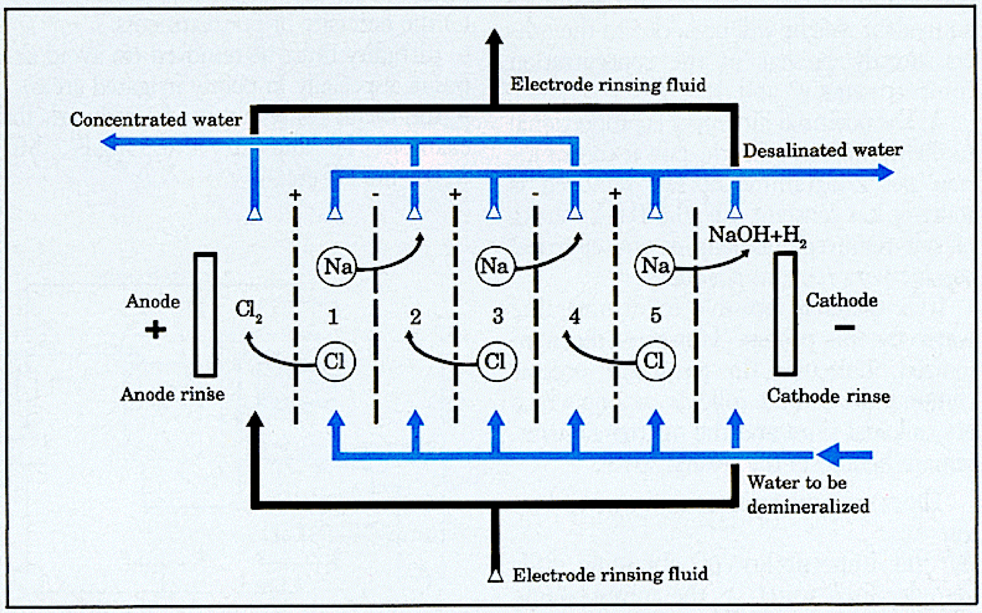


Figure 94. The principle of electrodialysis.

Figure 94. The principle of electrodialysis.

and arranged alternately as shown in the diagram in Figure 94, the migration of ions is restricted as the anions cannot pass through the negative membranes and the cations cannot pass through the positive membranes.

Thus, in the case of the cell in the diagram, which has three pairs of membranes, of which compartments 1, 2, 3, 4 and 5 are fed by a flow consisting of a sodium chloride solution, the ions in compartments 1, 3 and 5 pass into compartments 2 and 4 under the influence of the electrical field created by the electrodes.

It is easy to see that in this way the water in compartments 1, 3 and 5 becomes low in salt (becomes "demineralized"), while the water in compartments 2 and 4 becomes concentrated.

The introduction into the system of each coulomb will therefore result in one gramme-equivalent weight of anion and cation leaving each of the demineralization compartments (1, 3 and 5). This gramme equivalent weight will be added to the others already present in the concentration compartments (2 and 4).

As the potential difference is proportional to the number of cells, the power consumption per kilogramme of salt removed is more or less constant (i.e., 0.6-0.8 kWh/kg of salt removed), as long as the electrical conductivity remains adequate.

It is therefore possible to demineralize water by this process. However, the non-ionized molecules (in particular organic compounds) and the colloids, among which are colloidal silica and the microorganisms, remain behind in the treated water.

The main **limitations** to this method are due to:

A) the impossibility of obtaining fully demineralized water, as the corresponding compartments would have an excessive electrical resistance leading to ohmic losses. Generally speaking it is unrealistic to try to reduce the TDS of the treated water below 300 mg.l^{-1},

B) the cost of the treated water, which increases rapidly with the TDS of the feed: - on the one hand, as has been already seen, the power consumed is proportional to the quantity of salts removed,

- on the other hand, if we wish to avoid a fall off in selectivity and a back diffusion of ions caused by an excessive chemical gradient between the two sides of the membrane, this concentration gradient must be restricted.

Depending on the internal hydraulic conditions in the electrodialysis units (turbulence all along the membranes) the optimum level of salt removal that can be achieved ranges from 40 to 66% per processing stage (i.e., the salt passage is between 60 and 34%). It is for these reasons that most units are built up of several stages (see Figure 95),

C) the necessity of pretreatments:

- turbidity must be removed (to avoid deposits, especially in poorly irrigated areas),
- the metal content must be reduced, for example: Fe and Al < 0.3 mg.l^{-1}, Mn < 0.1 mg.l^{-1}, etc.,

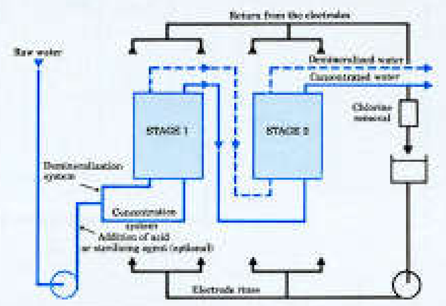


Figure 95. Two-stage electrodialyis installation.

Figure 95. Two-stage electrodialyis installation.

- there must be a reduction in salts which are liable to precipitate in the concentration compartments. The phenomenon of polarization must be taken into account, which, in the case of electrodialyis, tends not only to cause excessive concentration of the ions present in the water to be treated but also to change the pH value (due to the overconcentration of OHor H^+ ions, which may reinforce the tendency of some compounds to precipitate,

D) limitations of use: membranes, that have the same chemical make-up as ion exchange resins, also have the same limitations as the latter (see page 235): in particular, sensitivity to oxidizing agents ($C12 < 0.1$ $mg.l^{-1}$), and especially the risk of irreversible poisoning of anionic membranes if the water to be treated contains organic macromolecules that are liable to be adsorbed on the membranes.

. **Polarity reversal electrodialysis (EDR)**

In order to avoid the risk of scale formation, an ideal solution consists in reversing the polarity of the electrodes on a regular basis (for instance for five minutes every 30-60 minutes), thus instantaneously switching the concentration and desalination compartments, and thereby the position of the polarization layers that change sides on the membrane. The water "produced" during these phases must therefore be discharged.

This technique is planned for all modern electrodialysis installations, for it results in a simplification of the pretreatment process, although it should be admitted that the price for this involves complex additions of major importance:

- automatic valves to allow for discharge to drain during the reversal phases,
- electrodes to impede anodic corrosion.

The main **area of application of electrodialysis** is the production of drinking water from brackish water with a low mineral content (0.8 to 2 $g.l^{-1}$), and here it remains competitive with reverse osmosis. It also offers advantages for the desalination of colloidal and organic solutions (e.g., for demineralizing whey). In this field, it competes with the ion exchangers alone. In fact, the use of reverse osmosis would involve the attendant concentration of all the species present and would produce demineralized water, whereas electrodialysis only removes the ionized species.

10. ADSORPTION

10.1.
THE MECHANISM

Adsorption refers to the ability of certain materials to retain molecules (gas, metallic ions, organic molecules, etc.) on their surface in a more or less reversible manner. There is a mass transfer from the liquid or gas phase to the surface of the solid. The solid thus acquires superficial (hydrophobic or hydrophilic) properties liable to modify the state of equilibrium of the medium (diffusion, flocculation).

The adsorptive capacity of the solid depends:

. on the developed surface area or **specific surface area** of the material. Natural adsorbents (clays, silica, etc.) possess specific surface areas that vary with the physical-chemical state of the liquid medium (pH value, nature of the bound cations, surface saturation by organic molecules, etc.). Thus, certain clays such as bentonites (Montmorillonite for instance) have a surface area which is accessible to most molecules and ranges from 40 to 800 $m^2.g^{-1}$. Their adsorptive capacity is quite variable but constitutes the main parameter in the regulation of transfers and in the mobility of elements in the natural environment.

Industrial adsorbents (mainly activated carbon) develop extensive surface areas (roughly between 600 and 1200 $m^2.g^{-1}$) which are characteristic of a very strong microporosity. Other adsorbents such as metallic hydroxides that are formed in the course of the coagulation-flocculation process also develop very large surface areas whose expanse is closely dependent on the pH value;

. on the **nature of the adsorbateadsorbent bond,** in other words, on the free energy of interaction G between the adsorption sites and that part of the molecule which is in contact with the surface. This energy is directly measurable in the case of the adsorption of gases. However, in a liquid medium, the calorimetric methods only record the differential enthalpy of adsorption which corresponds to the difference between the adsorption energy of adsorbed molecules and the desorption energy of bound water at the interface;

. on the **contact time** between the solid and the solutes. At equilibrium, there is a dynamic exchange between the molecules of the adsorbed phase and those that remain in solution. Many theories have attempted to model the relation that exists between the number of molecules adsorbed ($g.g^{-1}$ or $g.m^{-2}$, etc.) and the number at equilibrium. One of the most commonly employed theories in the field of adsorption on activated carbon is Freundlich equation:

$$X/m = Ce^{1/n} \text{ (cf. Figure 96)}$$

where:

- X/m is the weight of pollutant retained per unit weight of the adsorbent,
- Ce is the equilibrium concentration of pollutant molecules in the aqueous phase,
- K and n are energy constants depending on the adsorbate/adsorbent couple at a given temperature which is kept constant during the operation (isotherm). In fact, no modelling, no matter how "complex", can cover the structure of the isotherm, and a fortiori explain the mechanisms of adsorption. The basic reason for this is that any surface is heterogeneous both as regards physical aspect and energy.

Mainly, the Van der Waals type attraction and the Coulomb electrostatic type attraction are the basis for adsorption. For instance, it can be seen that there is a strong affinity of aromatic molecules for the graphitic structure of carbon and a repulsion of the nonaromatic polar molecules.

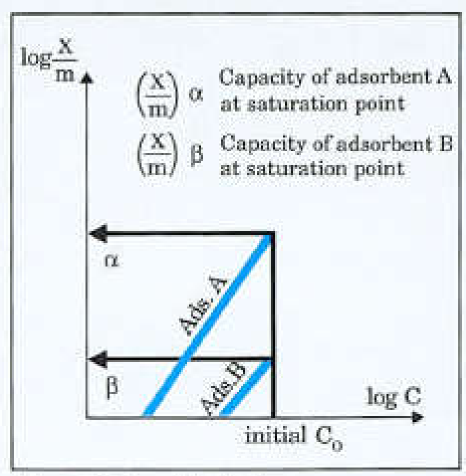


Figure 96. Freundlich isotherms.

10.2.
MAIN ADSORBENTS

10.2.1. Activated carbon

Experience shows that activated carbon has a broad spectrum of adsorptive activity, as most organic molecules are retained on its surface; the hardest to retain are the molecules which are the most polar and the linear ones with a very low molecular weight (simple alcohols, primary organic acids, etc.). Molecules that are **slightly polar,** generating taste and smell, and molecules with a relatively **high molecular weight** are for various reasons well adsorbed on carbon.

Beyond these adsorbent properties, activated carbon is also a bacteria support that is capable of breaking down a fraction of the adsorbed phase. Thus, a part of the support is continuously being regenerated and capable of freeing sites, allowing new molecules to be retained.

10.2.1.1. Main applications

Activated carbon is used:

. **in the polishing treatment** of drinking water or very pure industrial process water; in this case the activated carbon will retain the dissolved organic compounds not broken down by natural biological means (self-purification of waterways): micropollutants, substances determining the taste and flavour of the water; it will also adsorb traces of certain heavy metals;

. **in the treatment of industrial wastewater,** when the effluent is not biodegradable or when it contains certain organic toxic elements that rule out the use of biological techniques. In this case, the use of activated carbon often allows the selective retention of toxic elements and the resultant liquid can thus be degraded by normal biological means;

. **in the "tertiary" treatment** of municipal and industrial wastewater. The carbon retains dissolved organic compounds which have resisted upstream biological treatment, and thus removes a large part of the residual COD.

10.2.1.2. Catalytic action

One property of activated carbon is its catalytic action, particularly on the oxidation of water by free chlorine:

$$Cl_2 + H_2O \rightarrow 2\ HCl + \frac{1}{2}\ O_2 \nearrow$$

This is the method used for the **dechlorination** of water subjected to excess chlorination treatment. This dechlorination is characterised by the **half-dechlorination length,** that is, the depth of the filter bed which for a given velocity causes the reduction by one-half of the amount of chlorine in the water measurement (see page 385). The pH level has a considerable influence on this depth. According to the temperature, the free chlorine content and the tolerance allowed on the residual chlorine, loads of between 5 and 15 volumes of water per volume of activated carbon per hour are used.

This same type of catalytic action is used to break down the chloramines into nitrogen and hydrochloric acid. However, the kinetics are slower than in the case of free chlorine (the half-dechlorination length is much greater); therefore, the load must be greatly reduced in volume if comparable results are to be obtained.

The dechlorination capacity of a carbon is affected by any factor that might interfere with the contact between the carbon and the water to be treated, such as deposits of calcium carbonate, surface saturation through adsorption of various pollutants, etc.

10.2.2. Other adsorbents

Apart from a few natural adsorbents already mentioned, new adsorbents have been developed:

. **inorganic adsorbents:** alumina and other metallic oxides; they can have a very large specific surface area (300400 mz.g 1), but these solids adsorb more selectively than carbon. Their capacity depends very much on the pH value andtheir mesoporosity. Below the isoelectric point only negatively charged molecules are adsorbed on positive charge sites. In the current state of their development, they are unable to be competitive with activated carbon. However, some of these solids such as the alumina or the ferric oxyhydroxides have the advantage of removing fluoride, phosphates, nitrates, etc.,

. **organic adsorbents:** macromolecular resins with specific surface areas of between 300 and 750 $m^2 g^{-1}$; their adsorptive capacity is poor compared with that of activated carbon; however, these resins have better adsorptive kinetics (use ranges from 5 to 10 vol./vol.h) and are often easier to regenerate (low binding energy).

Here the "scavengers" should also be mentioned, which are highly porous anion resins (see page 239). However, these resins have a smaller specific surface area and their action on polar substances (such as humic acids, anionic detergents) is partly due to their ionic charge, which distinguishes them from other adsorbents.

10.3.
MAIN USES OF ACTIVATED CARBON

Activated carbon is available in two forms: powdered carbon and granular carbon.

10.3.1. Powdered activated carbon

Powdered activated carbon (PAC) takes the form of grains between 10 and 50 gm and its use is generally combined with a clarification treatment. If it is added continuously to the water together with flocculating reagents, it enters the floc and is then extracted from the water with it.

It is recommended that this extraction be carried out by means of a sludge recirculation clarifier (Densadeg) or by a sludge blanket clarifier (Pulsator, Superpulsator). These clarifiers considerably increase the time during which the water and carbon are in contact, thereby making it easier to reach equilibrium. (Thus, by using a Pulsator instead of a static settling tank, a savings of 15 to 40% of carbon can be achieved, while still obtaining the same result.)

10.3.1.1. Advantages

- Powdered activated carbon is about 2 to 3 times less expensive than granular activated carbon.
- Extra quantities of powder may be used to handle pollution peaks.

- Investment costs are low when the treatment involves only a flocculationsettling stage (an activated carbon feeder is all that is needed).
- Adsorbtion is rapid since the large surface area of the powder is directly accessible.
- The activated carbon promotes settling by making the floc heavier.

10.3.1.2. Disadvantages

- The activated carbon cannot be regenerated when mixed with hydroxide sludge and must then be regarded as expendable. - It is difficult to remove the final traces of impurities without adding an excessive amount of activated carbon.

Figure 97. Facility in the city of Nantes (western France). Flow: 11,700 m^3.h^{-1}. PAC feed unit.

- In order to use the carbon during pollution peaks, it is indispensable that the pollution peaks be identified beforehand. - Therefore, powdered activated carbon is mostly used when intermittent or small quantities are required (smaller than 25 g.m-3 3 depending on the case).

10.3.2. Granular activated carbon

10.3.2.1. Physical characteristics of granular activated carbon

The physical characteristics of granular activated carbon (GAC) vary considerably depending on the products (see table 39).

Table 39. Physical characteristics ofgranular activated carbon.

Raw material	Peat, bituminous schists, anthracite, wood, coconut
Form	Crushed, extruded
Grain size ES mm UC	0.25 - 3 1.4 - 2.2
Friability 750 strokes 1500 strokes	10 - 50% 20 - 100%
Bulk density (compacted)	0.20 - 0.55
Specific surface area m^2.g^{-1}	500 - 1300
Ash content %	4 - 12

Bearing these parameters in mind is fundamental when selecting the activated carbon and using it for a specific application.

10.3.2.2. Adsorptive capacity of carbon

Granular activated carbon is used as a filter bed through which the water to be treated passes, leaving behind its impurities which are thus extracted methodically: the water, as it progressively loses its pollutants, encounters zones of activated carbon which are less and less saturated and therefore more and more active.

Whether treatment using activated carbon is economical or not largely depends on the adsorptive capacity of the carbon, expressed in grammes of retained COD per kilogramme of activated carbon, which characterizes the "carbon requirements" for a given result. For a given polluted water-carbon system, this capacity depends on:

- **the depth of the bed**: the deeper a bed, the easier it deals with extended adsorptive fronts without excessive leakage (a principle similar to that of ion exchange described on page 230) while still ensuring thorough saturation of the upper layer,
- **the exchange rate**: experience shows that three volumes of water per volume of carbon per hour can seldom be exceeded when treating high levels of pollution. In the case of drinking water, in which the content of adsorbable products is very low, any decision as to the economic optimum has to take the high investment costs into account, with the result that higher bed volumes are used: 5 to 10 vol./vol.h, with a smaller degree of carbon saturation.

The theory only gives an indication of the trend of the laws of adsorption. It still remains indispensable to call upon the experience of the expert and to carry out dynamic tests on columns of sufficient size so that results can be extrapolated.

There are laboratory models which provide information on which to base the anticipated adsorptive capacity of carbon.

10.3.2.3. Functions of a carbon bed

A compact bed has four functions:

. filtration: this must often be reduced to a minimum in order to avoid clogging of the bed which is unavoidable without efficient washing systems to break up the layers completely after each cycle. In addition the carbon tends to extract adsorbable products from the floc with which it is in contact, causing premature saturation. This is why it is often advisable to use sand filtration as a preliminary step;

. **biological media:** this phenomenon can contribute to the process of purification, but can also be very dangerous if not properly controlled (fermentation, giving off odours, clogging of the bed, etc.);

. **catalytic action** (as a reminder);

. **adsorption:** this must remain the basic role of the carbon.

There are three possible arrangements:

- **simple fixed beds**: this technique is widely used in drinking water treatment (see Mediazur filters, Chapter 13, par. 3.2);
- **fixed beds in series**: a series of several columns is used which are regenerated by permutation (Figure 99). Thus, a countercurrent extraction system is organized. The Mediazur filter which involves a biflow (see Chapter 13, par. 4.2) is a variation of this and uses two cells;
- **moving beds**: these make use of the countercurrent principle (Figure 100). The base of the bed can be fluidized.

Figure 98. Vity-Chdtillon facility, Paris area (France) - LE-Dumez. Flow: 4,000 m3.h^{-1}.
6 Mediazur T filters and 9 Mediazur V filters.

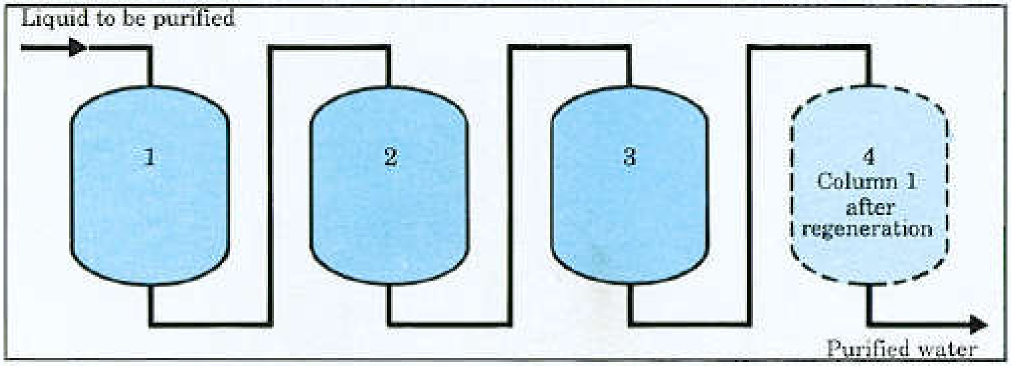


Figure 99. Diagram of fixed beds in series.

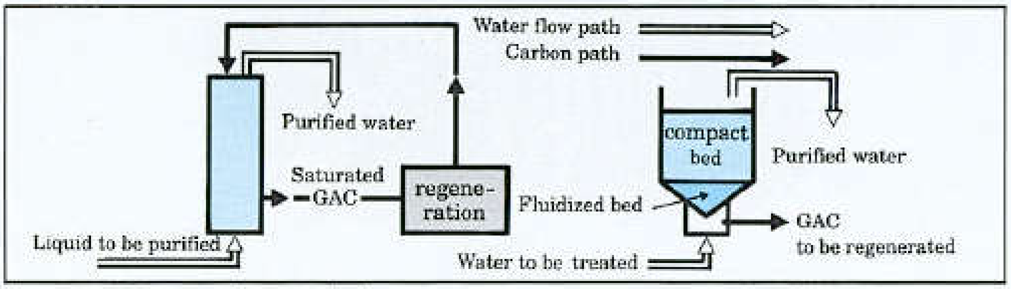


Figure 100. Diagrams of moving beds.

10.3.2.4. Regeneration

Activated carbon (like artificial adsorbents) is an expensive product. In most cases the cost of replacing the saturated carbon would be prohibitive. It should therefore be regenerated, and three methods have been developed for this purpose:

. **Steam regeneration:** this method is restricted to regenerating carbon which has only retained a few very volatile products; however, steam treatment can be useful in unclogging the surface of the grains and disinfecting the carbon.

. **Thermal regeneration:** by pyrolysis and burning off of adsorbed organic substances (Figure 101). In order to avoid igniting the carbon, it is heated to about 800°C in a controlled atmosphere. This is the most widely used method and regenerates the carbon very well, but it has two disadvantages:

- it requires considerable investment in either a multiple-hearth furnace, a fluidized bed furnace or a rotary kiln. The furnace must have monitoring devices for atmosphere and temperature, a dewatering system at the inlet and a carbon quenching system at the outlet;
- it causes high carbon losses (7-10% per regeneration), so that after 10 to 14 regenerations, the GAC volume will, on average, have been entirely replaced.

The use of electrical heating (infrared furnace, induction furnace) reduces these losses. However, these methods, which are expensive, are only used for the recovery of costly metals.

. **Chemical regeneration:** (Degrémont has developed a process based on the action of a solvent used at a temperature

Figure 101. Taif facility (Saudi Arabia). Flow: 12,600 $m^3.d^{-1}$. GAC regeneration furnace. Capacity: 6 $t.d^{-1}$.

of approximately 100°C and with a high pH.

The advantage of this process is that for the same capital outlay, only minimum carbon loss occurs (about 1% of the quantity treated). However, the use of chemical reagents for regeneration (alkaline reagent and solvent) leads to the formation of eluates from which the solvent must be separated by distillation. The pollutants are then destroyed by incineration unless they can be recovered. The process is less widely used than thermal regeneration.

Biological regeneration: this method of regeneration has not yet been applied on an industrial scale.

11.ION EXCHANGE

11.1.
GENERAL

11.1.1. Principle

Ion exchangers are insoluble granular substances which have in their molecular structure acidic or basic radicals that can exchange, without any apparent modification in their physical appearance and without deterioration or solubilization, the positive or negative ions fixed on these radicals for ions of the same sign in solution in the liquid in contact with them. This process, known as ion exchange, enables the ionic composition of the liquid being treated to be modified without changing the total number of ions in the liquid before the exchange.

The first ion exchange substances were natural earths (zeolites); they were followed by synthetic inorganic compounds (aluminosilicates) and organic compounds; the latter materials are used today almost exclusively under the name of **resins.** This term has been wrongly extended to cover any kind of exchanger.

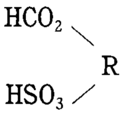
They are either in the form of granules, as is usually the case, or in the form of beads.

There are two categories: the resins of the gel type and those of the **macroporous** or loosely cross-linked type. Their basic structure is identical: the macromolecular structure is obtained in both cases by copolymerization of, e.g., styrene and divinylbenzene. The difference between them lies in their porosity. Their high cross-linking degree increases their mechanical strength to both physical (pressure - negative pressure) and chemical (change in the ionic saturation, or exhaustion, state) stresses.

Gel type resins have a natural porosity that results from the polymerization process and is limited to intermolecular distances. It is a microporous type structure.

Macroporous type resins have an additional artificial porosity which is obtained by adding a substance designed for this purpose. Thus, a network of large canals known as macropores is created in the matrix. These products have a better capacity for adsorption and desorption of organic substances.

The chemical structure of the exchangers is such that in their molecule they have one or more radicals that are either acidic or basic. For a better understanding of exchange phenomena, cation exchangers can thus be assimilated to an R-H form acid, and anion exchangers to an R-OH form base. The strength of this acid or this base depends on the nature of the molecular nucleus and the radicals that are attached to it, such as HCO_2, HSO_3, NH_3OH, etc. The exchanger is known as monofunctional if there is only one variety of radicals, as for instance HCO_2 or HSO_3. It is called polyfunctional if the molecule contains various types of radicals at the same time, and thereby radicals of various ionic strengths such as for instance:



11.1.2. The ion exchange reaction

11.1.2.1. Use of a reversible reaction of the softening -type:

$$R\text{-}Na_2 + Ca^{2+} \rightleftarrows R\text{-}Ca + 2\,Na^+$$

As is the case with any chemical equilibrium, it is governed by the law of mass action, the reverse reaction of which corresponds to the regeneration of the exchanger.

If the liquid to be treated is brought into static contact with the exchange material, the reaction stops when equilibrium is reached between the liquid and the resin.

Therefore, in order to achieve substantially complete exchange, it is necessary to create successive equilibrium stages by percolating the water through superimposed layers of exchange material. There is always a varying degree of **leakage of the ion** that one wants to remove.

Laws governing a reversible ion exchange: for each reaction involving two ions A and B, the equilibrium between the respective concentrations A and B in the liquid and in the ion exchange substance can be shown graphically (Figure 102).

Under conditions of equilibrium, and for a concentration B of X% in the solution, the exchange material becomes saturated up to a concentration of Y%. When the two ions A and B have the same affinity for the exchange material, the equilibrium curve corresponds to the diagonal of the square. The more marked the exchange material's preference for ion B, the further the curve moves in the direction of the arrows.

The form of the curve for a given system of two ions depends on a number of factors: nature and valency of the ions, concentration of ions in the liquid, and type of exchange material. In a system $Ca^{2+} \rightleftarrows 2\,Na^+$ applied to a sulphonated polystyrene, the exchange material always

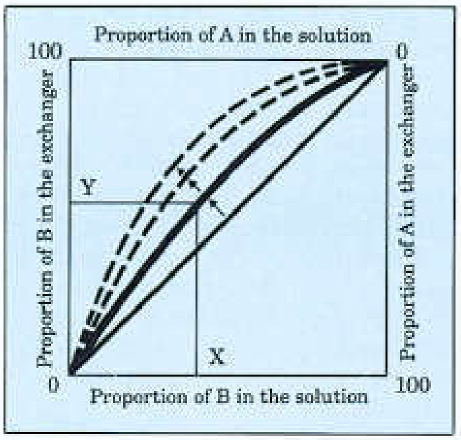


Figure 102. Ion exchange curves.

has a greater affinity for calcium than for sodium, and the more dilute the solution the more this will be the case.

As mentioned above, static batch treatment effected by bringing the liquid and the exchange material into contact in a tank would reach a certain point on the curve and remain there.

If the treatment is to be continued until one ion is effectively removed in favour of another, the point of equilibrium must be progressively shifted by passing the liquid through a series of successive layers of the exchange material containing fewer and fewer ions to be retained, thereby moving along the equilibrium curve almost to the zero concentration point for the unwanted ion. If we take a layer of exchange material entirely in form A, and if a liquid containing ion B is passed through it, the successive equilibrium points between A and B give a series of isochronous concentration curves that can be represented by Figure 103 a for two ions of similar affinity and by Figure 103 b where the exchange material has a much greater affinity for ion B' than for ion A'. The "leakage point" is reached when the isochronous curve leaves the vertical right-hand axis (positive concentration of B in the liquid outlet curve). The curves for the two cases of different affinity are represented in Figure 103 c.

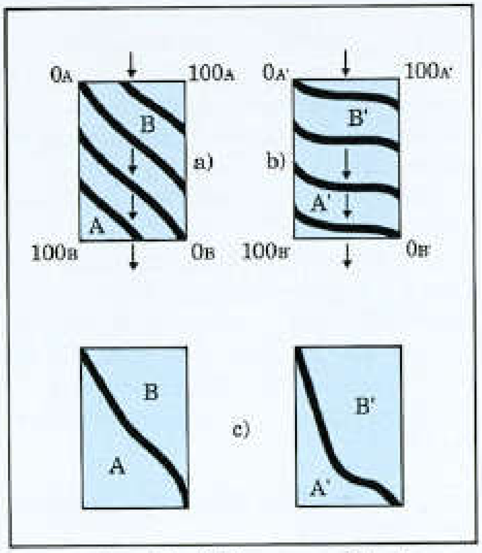


Figure 103. The displacement of isochronous curves.

If the area $\frac{B}{A+B}$ represents the fraction of the total exchanger capacity used when the leakage appears, it is clear that this fraction is much greater for B' than for B.

This is also obvious with the treated liquid in the form of "the exhaustion curves" (Figure 104).

The form of the exhaustion curves depends not only on the static equilibrium curve mentioned above, but also on the exchange kinetics,, between the liquid and the exchange material; these kinetics involve the penetration of solutes into the exchanger, and are governed by laws known as the "Donnan equilibrium laws°.

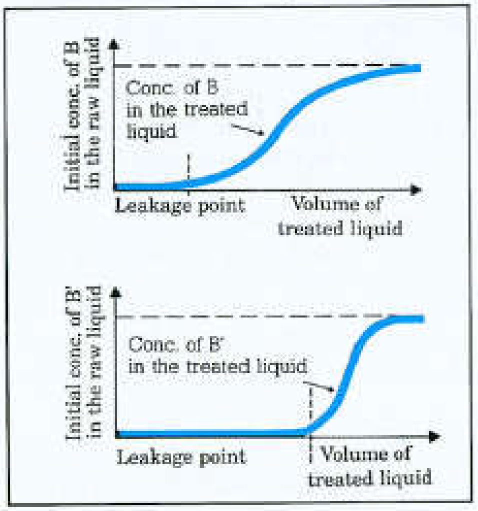


Figure 104. Exhaustion curves.

These phenomena are very complex; they involve both the degree of dissociation and concentration of ions, the temperature, the nature of the exchange material/liquid interface, and the kinetics of penetration into the solid that constitutes this exchanger.

The total capacity of an exchanger, i.e., the total number of equivalents available for exchange per litre of exchange material, is only of very relative practical value; for commercial application it is the "useful capacity" defined from the isochronous graphs or exhaustion curves described ear her which is of importance.

Another important point in industrial applications becomes clear when we examine these graphs.

Accepting the existence of an exchange material-liquid equilibrium curve, the quality of the liquid treated by an exchange layer depends on the quality of **the last layer through which the liquid passes,** whatever the qualities of the preceding layers.

If we consider a reversible reaction of the type:

$$R - A + B \rightleftarrows R - B + A$$

that represents "service" from left to right and "regeneration" from right to left, it is necessary to examine the state of the exchanger at the start of a treatment cycle following a regeneration cycle. It is clear that at the beginning of the treatment cycle the quality of the treated water, characterized by the ion leakage, will essentially depend on the degree of regeneration of the last layer of exchange material.

These factors must be borne in mind during the examination of the different qualities of exchange materials and their industrial applications.

11.1.2.2. Non-reversible reaction

This applies to the removal of a strong acid by a strong base anion exchanger:

$HCl + R - OH - R - Cl + H_2O$

The reverse reaction (hydrolysis) is virtually non-existent; the exchange is complete and can be obtained just as well under static contact or percolation conditions. In this case ion leakage may be zero, provided that the contact time between the water and the resin is long enough.

Equilibrium reactions that give rise to an insoluble compound can be likened to this type of exchange. For example, if sea water is treated with an exchanger saturated with silver ions, the following reaction is obtained:

$R - A + NaCl \rightarrow R - Na + AgCl$

Since AgCl is insoluble it precipitates.

Under these conditions, and according to Berthollet's law, the equilibrium shifts completely and the reaction is complete, even under static conditions.

Ion exchange is not instantaneous, and the rate of reaction depends upon the type of resin. In practice this type of exchange" exhaustion curves similar to those in Figure 104.

The two types of reaction mentioned above can be used:

- to remove one or more unwanted ions from the liquid under treatment,
- to select and concentrate in the exchanger one or more ions that will be bound later in the purified and concentrated state in the regeneration or elution liquid.

11.1.2.3. Use of a previously-attached complex anion

This complex ion is liable to cause secondary reactions, for instance oxidation-reduction phenomena affecting the ions in the water or liquid to be treated, without itself dissolving in the liquid.

For example: absorption of dissolved oxygen by oxidation of a sulphite anion resin R - NH_3 -HSO_3 into a sulphate resin R - NH_3 - HSO_4.

11.1.2.4. Other uses

The ion exchange laws do not concern the use of ion exchangers for other purposes (catalysis, adsorption).

11.1.3. Methods of regeneration

In the case of softening and demineralization processes, the end of the cycle is reached when the exhaustion curve corresponds to that shown in Figure 103 (compounds A' and B'). It can then be assumed, at least as far as the upper layers are concerned, that the ion exchanger is saturated with B' ions and is in equilibrium with B' concentration in the inflowing solution.

Regeneration is carried out by causing a concentrated solution of A' ions to flow through the exchanger either in the same direction as the exhaustion (cocurrent regeneration) or in the opposite direction (countercurrent regeneration).

. **Cocurrent regeneration:** in this operation (Figure 105) the concentrated solution of A' ions is initially brought into contact with those layers of the ion exchanger saturated with the B' ions which are expelled from the resin; these B' ions are then carried to those layers of the ion exchanger which are at a lower level of exhaustion and where the conditions are favourable to their capture; during the first stage of regeneration it is therefore mainly the A' ions which are eluted from the column.

Therefore it appears that, in order to achieve total regeneration of the ion exchanger, it is necessary to subject a quantity of ions corresponding to the ratio A'/B' to a double exchange process.

Finally, if the quantity of regenerating solution is limited, the B' ions will not be completely eluted from the ion exchanger and the bottom layers will not be fully regenerated.

Consequently, during the following cycle, the B' ions will undergo selfregeneration by the A' ions displaced from the upper layers.

. **Countercurrent regeneration:** the course of events will be different when the regenerating reagents are made to flow upwards from the bottom. In this case,

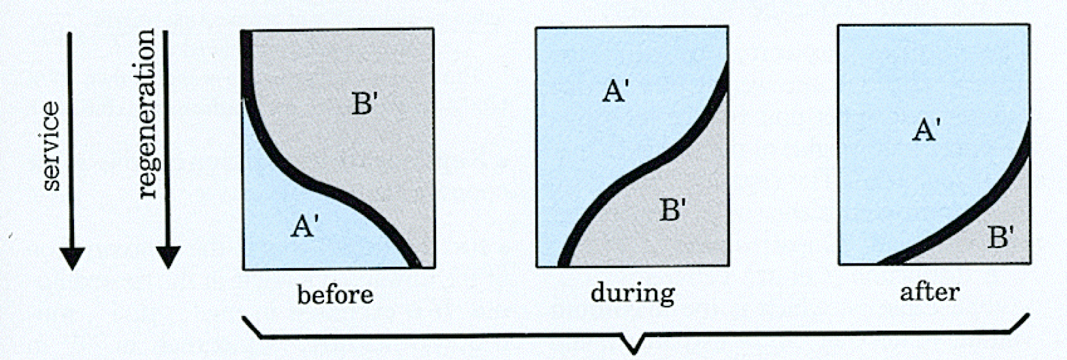


Figure 105. Cocurrent regeneration.

the concentrated A' ions first of all encounter the resin layers with a low concentration of B' ions, the elution of which therefore takes place in favourable conditions; what is more, the B' ions cannot be recaptured in the exhausted upper layers (Figure 106).

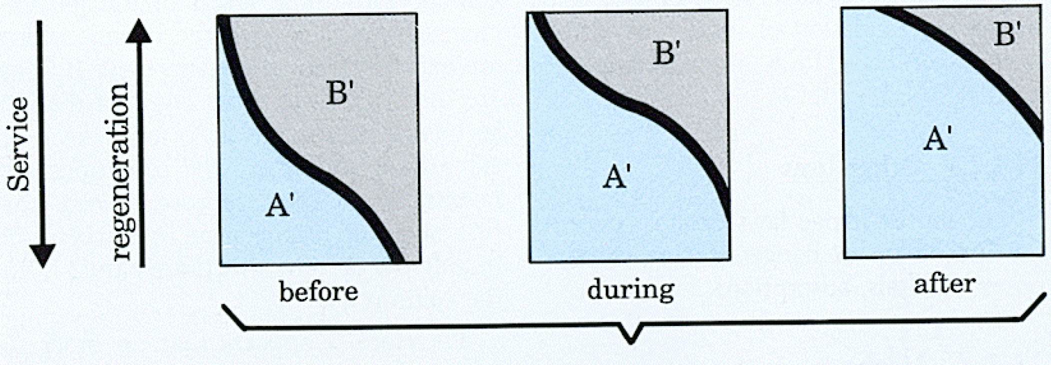


Figure 106. Countercurrent regeneration.

Regeneration therefore takes place in far more reversible conditions than when the cocurrent technique is used, and from a thermodynamic point of view, this means greater efficiency.

Two important advantages of the principle of countercurrent regeneration should be emphasized:

- higher efficiency, and consequently reduced reagent requirements, given equal quality,
- better quality of the treated water thanks to the fact that the bottom layers are regenerated with a large excess of reagent.

11.1.4, Ion exchange vocabulary

. **Exchange capacity of an exchanger**: this is the weight of ions that can be retained per unit volume (or sometimes per unit weight) of the exchange material concerned. The capacity is expressed in gramme-equivalents or in degrees per unit volume of compacted resin.

A distinction is drawn between:

- total capacity, which is the maximum volume of ion that can be exchanged, and which characterizes a given resin,
- breakthrough capacity, which is the usable fraction of the above, depending on the hydraulic and chemical conditions of each individual application.

Bed volume:

$$\frac{\text{volume per hour of liquid to be treated}}{\text{volume of resin}}$$

Ion flux:

bed volume x salinity of water

.

Regeneration level:

$$\frac{\text{weight of reagent used}}{\text{volume of the ion exchange material}}$$

Regeneration rate:

$$\frac{\text{gramme-equivalents of regenerating reagent}}{\text{gramme-equivalents of eluted ions}} \times 100$$

This ratio is always equal to or greater than 100%

(100% corresponds to the stoichiometric efficiency).

.

Regeneration efficiency: this is the opposite ratio to the above.

. **Ion leakage**: this is the concentration of the unwanted ion left in the treated liquid. It is expressed in $mg.l^{-1}$, $\mu g.l^{-1}$, milliequivalents/litre, sometimes in % in relation to the inflowing liquid.

. **Breakthrough:** this is the maximum permissible ion leakage requiring the production cycle to be shut down.

Attrition: mechanical wear of the exchanger grains as they are being used.

11.2.
MAIN TYPES OF ION EXCHANGERS

11.2.1. Properties of an ion exchange material

An ion exchange material for industrial use must meet the following requirements:

The product must be insoluble under normal conditions of use.

In practice, all the exchange materials in current use meet this requirement, and their true solubility at ambient temperatures is not detectable by the usual methods of analysis under normal conditions of flow and temperature. This is no longer true of certain exchange materials once a certain temperature is reached.

The product must be in the form of grains of maximum homogeneity and of dimensions such that their head loss in percolation remains acceptable.

Ion exchange materials used for the applications described below take the form of grains 0.3 to 1.2 mm in size. Powdered resins of between 5 and 30 microns, known as "microresins", are available for certain special uses (treatment of condensates, waters from nuclear systems).

The changes in the state of the exchange material must not cause any deterioration in its physical structure.

The exchange material may be required to retain ions or ionized complexes of highly varied dimensions and weights.

In some cases this causes an obvious contraction or swelling (up to 100% for some carboxylic resins (HCO_2-R) between the H and NH_4 phases). This swelling and contraction, obviously, should not cause the grains to burst. In the most difficult cases the design of the apparatus should allow for this expansion without causing excessive stresses in the bed.

It should never be forgotten that there are certain (all too often disregarded) limitations on the use of ion exchangers:

- ion exchangers can function only in the presence of a liquid phase of limited concentration,
- ion exchangers are made to retain ions and not to filter suspended solids, colloids or oily emulsions. The latter substances can only shorten the life of the exchange materials,
- the complex problem of removing soluble organic substances must be the subject of a detailed study,
- the presence of large quantities of dissolved gases in the water can cause serious disturbances in the activity of the exchangers,
- the powerful oxidizing agents Cl_2 and O_3 affect some resins,
- generally speaking, great caution should be used in the practical application on an industrial scale of laboratory results, and also when reading the documentation produced by ion exchanger manufacturers.

The rules for the design and use ofthe appliances are just as important as the knowledge of the theoretical performance of the exchange materials themselves

11.2.2. Cation exchangers

. **Inorganic exchangers and sulphonated carbons:** these products are merely of historical interest.

. **Synthetic exchangers:** these products can be divided into two groups:

- strong acid cation exchangers,
- weak acid cation exchangers

11.2.2.1. Strong acid cation exchangers

They are characterized by having HSO_3 sulphonic radicals and acidities close to that of sulphuric acid. In current use these are **sulphonated polystyrenes** obtained by:

- copolymerization of styrene and divinylbenzene in emulsion form to obtain perfect spheres on solidification,
- sulphonation of the beads thus obtained.

The products obtained by this process are virtually monofunctional. Their physical and chemical properties vary depending on the percentage of divinylbenzene to styrene, known as the degree of crosslinking, which generally varies from 6 to 16%.

The second column in table 40 lists a number of products in current use for fixed beds with a moderate percolation rate and for the treatment of waters of average properties.

These products are not suitable for treatment (continuous or batch processes) at high rates or with frequent cycles, or for the treatment of oxidizing water. There are specially designed resins on the market, generally with a high degree of cross. linking and frequently of the "macroporous" type.

The best known resins are listed below:

Strong acid cation exchangers.

	NAME OF PRODUCT	
Supplier	Gel type	Macroporous type
Bayer	Lewatit S 100	Lewatit SP 112
Duolite	Duolite C 20	Duolite C 26
Dow Chemical	Dowex HCR-S	Dowex MSC-1
Rohm & Haas	Amberlite IR 120	Amberlite IR 200

11.2.2.2. Weak acid cation exchangers

These are polyacrylic resins characterized by the presence of **HCO_2 carboxyl** radicals that can be likened to organic acids such as formic or acetic acid. They differ from strong acid exchangers in two respects:

- they retain only the Ca, Mg, Na, etc., cations that are bound to bicarbonates, but they cannot exchange canons at equilibrium with strong anions (SO_4, Cl, NO_3),
- they can be regenerated more easily and their regeneration rates are close to those of stoichiometric efficiency.

The best known carboxylic resins in current use are listed below:

	NAME OF PRODUCT	
Supplier	Gel type	Macroporous type
Bayer		Lewatit CNP 80
Duolite	Duolite C 433	Duolite C 464
Dow Chemical	Dowex CCR 2	
Rohm & Haas	Amberlite IRC 50 IRC 84	

11.2.3. Anion *exchangers*

Anion exchangers can be divided into two main groups:

- weak or intermediate base anion exchangers,
- strong base anion exchangers.

The two types can be distinguished in practice as follows:

- the weak base types do not retain very weak acids such as carbonic acid or silica, but the strong base types retain them completely,
- the strong base types alone are able to release the bases from their salts by the following typical reaction:

$$R - OH + NaCl \rightleftarrows R - Cl + NaOH$$

- the weak base types are more or less sensitive to hydrolysis, in the form of the displacement by pure water of the anions previously attached to the resin:

$$R - Cl + H_2O \rightleftarrows R - OH + HCl$$

whereas the strong base types are practically unaffected by this phenomenon,

- the weak base types are regenerated more easily.

11.2.3.1. Weak or intermediate base anion exchangers

All these products consist of a mixture of primary, secondary, tertiary, and sometimes quaternary, amines. The nucleus of the molecule is highly varied in nature and may be aliphatic, aromatic or heterocyclic.

A list of this type of resins (nonexhaustive) is shown below. Some of these resins have a macroporous structure.

	NAME OF PRODUCT	
Supplier	Gel type	Macroporous type
Bayer		Lewatit MP 64
Duolite		Duolite A 378
Dow Chemical	Dowex WGR 2	Dowex MWA 1
Rohm & Haas	Amberlite IRA 68	Amberlite IRA 93

11.2.3.2. Strong base anion exchangers

The existence of quaternary ammoniums in the molecule is typical of these products. All the strong base resins used for demineralization purposes belong to two main groups commonly known as type I and type II. The former consists of simple quaternary ammonium radicals, the latter of quaternary ammonium radicals with alcohol function. Each type has its own field of application, depending on the nature of the water to be treated and the conditions applying to the regeneration cycle.

The two types differ in the following respects:

- in type I, the basicity is strong and the capacity low; the regeneration efficiency is poor,
- in type II, the basicity is weaker and the capacity higher; the regeneration efficiency is also better.

The following list of resins used for ordinary applications is not exhaustive:

	Gel type		**Macroporous type**	
Supplier	Type I	Type II	Type I	Type II
Bayer	Lewatit M 500	Lewatit M 600	Lewatit M 500	Lewatit MP 600
Duolite	Duolite A 101	Duolite A 102	Duolite A 161	Duolite A 162
Dow Chemical	Dowex SBR	Dowex SAR	Dowex MSA 1	Dowex MSA 2
Rohm & Haas	Amberlite IRA 400	Amberlite IRA 410	Amberlite IRA 900	Amberlite IRA 910

11.2.4. Some numerical data

11.2.4.1. Total capacity

The table gives data on the total exchange capacities of various categories of exchange materials expressed in grammeequivalents per litre of resin:

Nature of exchange material	Gel type	Macro-porous type
Weak acid cation	3.5-4.2	2.7-4.8
Strong acid cation	1.4-2.2	1.7-1.9
Weak base anion	1.4-2.0	1.2-1.5
Strong base anion		
- type 1	1.2-1.4	1.0-1.1
- type 11	1.3-1.5	1.1-1.2

11.2.4.2. Regeneration levels

They have little to do with the nature of resin but mainly depend on the **conditions of use,** which explains the disparities that have been observed. The values listed below are expressed in grammes of pure product per litre of resin.

Strong acid cation	NaCl	80-300
	H_2SO_4	80-250
	HCl	40-200
Weak acid cation	110% of the capacity used	
Weak base anion		
Strong base anion	NaOH	40-100
	NH_3	30-60
	Na_2CO_3	60-130
	NaOH	40-200

11.2.5. Adsorbent and special resins

11.2.5.1. Adsorbent resins

These are products that are designed to retain nonionic compounds (basically organic molecules) in solution in polar and nonpolar solvents by means other than ion exchange and by a reversible technique.

This process of adsorption on solids is very complex and involves various types of interaction between the adsorbent surface and the adsorbed molecules.

For this reason, the adsorptive capacity of the resins depends on numerous factors, of which the main ones are:

- the chemical composition of the skeleton (polystyrenic, polyacrylic, formophenolic),
- the type of functional groups of polar adsorbents (secondary and tertiary amines, quaternary ammonium),
- the degree of polarity,
- the porosity (usually macroporous materials with pore sizes up to 130 nm),
- the specific surface area: up to 750 $m^2.g^{-1}$,
- hydrophilic nature,
- the shape of the grains.

Possible uses include:

- protection of the ion exchange system by retaining the pollutants present in feed water (humic acids, detergents, etc.),
- decolourization of sugar syrups, glycerin, grape musts, whey, etc.,
- separation, purification and concentration processes in the pharmaceutical industry and synthetic chemistry.

The regeneration method of adsorbent resins basically depends on the product adsorbed. The traditional eluants are: acids, bases, sodium chloride, methanol, adapted organic solvents and, in certain cases, pure water or steam.

The choice of the correct adsorbent presents some difficulty; it must be guided by the properties of each adsorbent and the products to be retained. Therefore, laboratory or pilot studies are indispensable in the majority of cases.

11.2.5.2. Special resins

. **Polyfunctional resins:** these are products that combine the properties of strong resins with those of weak resins. This is the case with anion resins which are able to remove all the anions including silica and COz while ensuring a high exchange capacity and an excellent regeneration efficiency due to their weak-base function.

o **Chelate resins:** these comprise special functional groups (aminophosphoric, aminodiacetic, aminodioxime, mercaptan) which permit the selective retention of heavy metals from various effluents (zinc, lead, mercury, etc.), gas chromatographic separations of metals, and also the final softening of brine from the electrolysis process.

. **Resins for nuclear use:** this involves products with a higher degree of purity than that of resins used in common operations. Among these are strong acid cation resins in H+ form that are regenerated to 99%, and strong base anion resins in OHform with less than 0.1% of Cl-.

Catalyzing resins:

- conventional resins used in a basic or acidic catalyst process (for example, the inversion of glucose in the manufacture of liquid sugar),
- resins with a metallic catalyst (for example, a palladium resin for deoxygenation of demineralized water or sea water).

11.3. CONVENTIONAL TECHNIQUES

11.3.1. General

It is important to emphasize that the techniques related to ion exchange processes should not be used unless the raw water has been subjected to a form of preliminary treatment suited to its type, which must include the removal of suspended solids, organic matter, residual chlorine and chloramines, etc. The preliminary treatment varies with the type of ion exchanger used.

The conventional systems are made up of fixed-bed ion exchangers regenerated ated on a cocurrent basis: the water to be treated as well as the regeneration solution pass through the resin bed from top to bottom.

The complete cycle of exchange

consists of the following phases:

- **service** (or production): the operating cycle of an exchanger is determined by the exchange capacity of the layer. This corresponds to an exchangeable mass of ions, and consequently, to a certain volume of water treated between two regeneration operations,
- **loosening:** an upward flow of water loosens the resin bed and provides for the removal of particles and resin debris that may have risen up to the surface,
- **regeneration:** the diluted regenerant passes slowly through the resin bed from top to bottom,
- **displacement** (or slow rinse): water is introduced at the same rate of flow and in the same flow direction as the regenerant until nearly all of the latter is washed out and removed,
- **fast rinse:** water is introduced at the production rate of flow until a quality of treated water is obtained that is suitable for use in the production process.

Description of an ion exchange unit: whatever the type of exchange, whether for softening, carbonate removal or demineralization, each appliance normally consists of a vertical, closed, cylindrical vessel holding the resin. The latter can be placed in direct contact with the treated water collection system, which may consist either of nozzles evenly distributed over a tray, or of a system of perforated tubes of a suitable number and size. The resins may also be supported by a layer of inert granular material such as silex, anthracite or plastic beads. The layer itself is drained by the collection system (Figure 107).

Sufficient free space is left above the resin bed to allow it to expand normally (between 30 and 100% of the compacted volume depending on the type of resin) during countercurrent expansion.

Both the water to be treated and the regenerant are admitted at the top of the vessel by a distribution system of varying complexity.

The appliance has an external set of valves and pipes for the various operations of service, expansion, regeneration and rinsing. The valves may be manually or automatically controlled, or can even be replaced by a central multiport valve.

Note: to simplify matters, the reactions in the following description are taken as complete. In practice, a slight ion leakage always occurs.

11.3.2. Softening

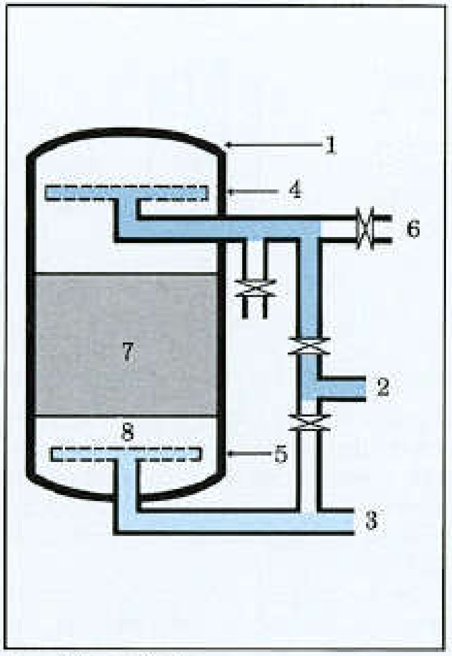
A cation exchanger regenerated with a sodium chloride solution is used for this purpose (Figure 108).

All the salts in the water under treatment are transformed into sodium salts. The hardness of the treated water is virtually nil. Its pH and alkalinity values remain unchanged. Softening can be done after preliminary purification by lime, which removes the bicarbonates and reduces the M alk. to a value generally between 2 and 4 French degrees. In this case, the water obtained is both free from carbonates and softened (Figure 109).

11.3.3. Carbonate removal

This process uses a carboxylic resin which is in the R-H form, having been previously regenerated by an acid (Figure 110). This resin has the property of retaining metallic cations and releasing the corresponding anions in the form of free acid, until the pH of the treated water reaches a level of between 4 and 5, at which point all the carbonic acid from the bicarbonates is released. The cations associated with the anions of strong acids (chlorides, nitrates, sulphates) are not retained by the resin.

Under these conditions, the treated water contains all the original salts of strong acids and an amount of dissolved CO_2 which is equivalent to the bicarbonates in the raw water. The alkalinity of this water may be nil, and its hardness



1 – Exchanger body.
2 – Raw water inlet.
3 – Treated water outlet.
4 – Raw water distributor.
5 – Treated water collector.
6 – Regenerant discharge.
7 – Resin.
8 – Support layer.

Figure 107. Softener.

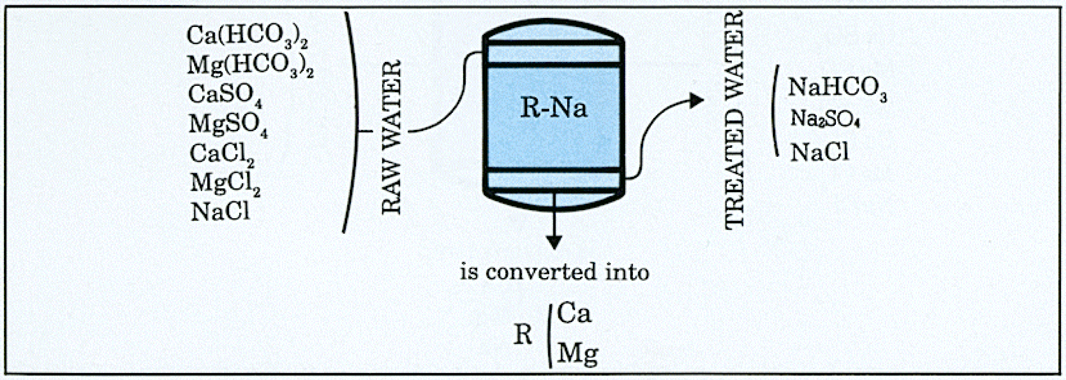


Figure 108. Softening.

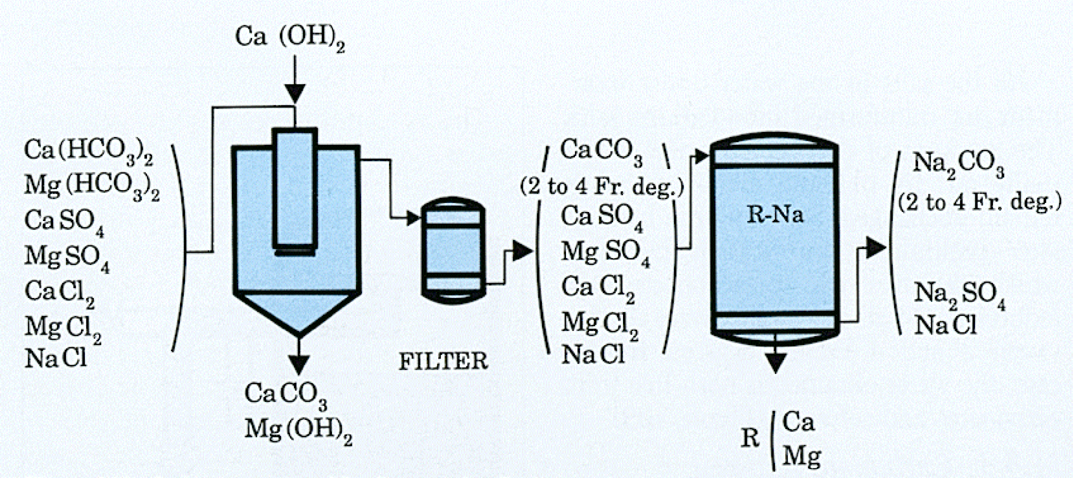


Figure 109. Carbonate removal by lime, and softening.

equal to the TH - M alk. value of the raw water; the hardness value may therefore fall to zero if the TH is equal to or less than the M alk., since the alkaline-earth ions are exchanged rather than the alkaline ions.

In the opposite case, a zero hardness may be obtained by combining in the same vessel a layer of carboxylic resin and a layer of sulphonic resin, regenerated in turn with a strong acid and a solution of sodium chloride. The carboxylic resin works in the H cycle and retains the TH in a quantity which is equivalent to the M alk. The sulphonic resin exchanges the sodium ions for permanent hardness which is equal to TH - M alk. In this way a carbonate-free and softened water is obtained.

With **water containing sodium bicarbonate,** the efficiency of carboxylic resins is poor, and the H-Na method is sometimes used instead: a sulphonic resin in H form is placed in parallel with another in Na form and while the former retains all the canons and releases the corresponding acids, the latter produces softened water. A mixture of decationized and softened water in suitable proportions provides treated water of the same composition as the first method.

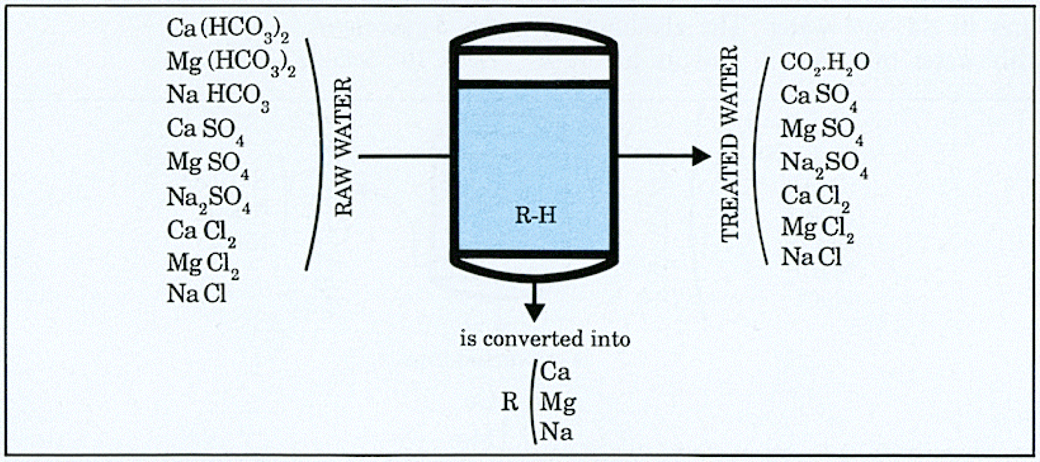


Figure 110. Carbonate removal.

However, this method has the disadvantage of requiring the acid water to be kept strictly proportional to the water containing bicarbonate alkalinity, as otherwise an acid, and thereby corrosive, mixture is obtained.

With these systems it is generally advisable to remove the dissolved C02 produced by the ion exchange process.

11.3.4. Demineralization

A number of various demineralization processes have been studied which are essentially based on the following factors: the quality of water to be obtained, the composition of the water to be treated and the consumption of regeneration reagents. Other considerations such as capital outlay, installation, etc., may also influence the composition of the system.

The description given below of the various combinations of exchangers most frequently employed, uses the terminology:

- WCR: weak acid cation resin
- SCR: strong acid cation resin
- WBR: intermediate or weak base anion resin
- SBR: strong base anion resin
- $|CO_2|$: CO_2 removal
- MB: mixed bed.

11.3.4.1. Partial demineralization

This is comprised of a unit **filled with strong acid cation exchanger** (SCR), regenerated by a strong acid, which operates in series with a unit filled with weak (or intermediate) base anion ex**changer** (WBR), regenerated by caustic soda or ammonia. The water produced is used as is as long as the carbonic acidity is not damaging; otherwise it is deaerated on a C02 removal unit (decarbonator) that is placed either upstream or downstream from the anion exchanger (Figure 111).

The treated water contains the totality of the silica present, and when it is deaerated, the level of carbonic acid is approximately 15 mg.l-'; depending upon the regeneration rate adopted for the cation exchanger, the conductivity can range between 2 and 20 gS.cm'. The pH level is in the order of 6 to 6.5 as long as the removal of carbon dioxide is done correctly.

This type of system produces boiler feedwater for medium pressure boilers and water for various industrial processes.

11.3.4.2. Total demineralization

. **SCR + SBR systems:** all ions, including silica, are removed (Figure 112). In the majority of cases it is advisable to reduce the flux of ions passed to the anion

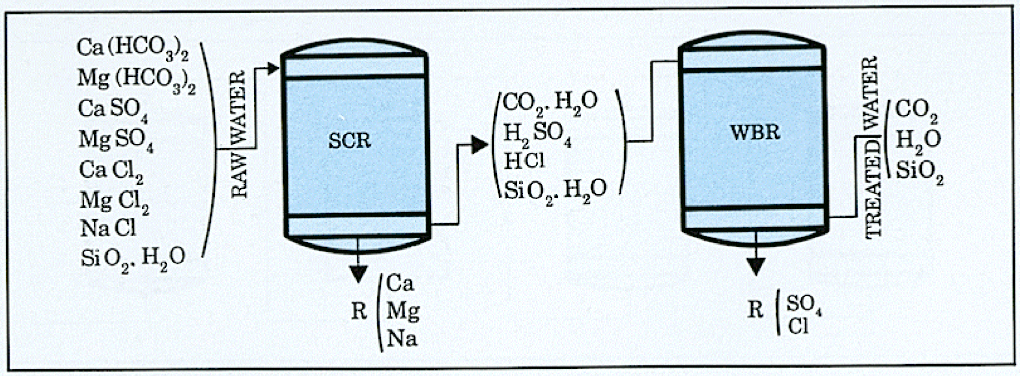


Figure 111. Partial demineralization.

exchanger by installing, between the anion exchanger and the cation exchanger, a CO_2 removal unit intended to reduce the CO_2 content to a few mg.l-'. This brings about a reduction in the volume of strong base anion resin and in the regeneration reagent requirements.

The quality of demineralized water essentially depends on the regeneration rate of the cation exchanger. The ion leakage takes the form of a trace of caustic soda (or of lime, if the raw water contains no sodium) from the cation exchanger. A reduction in the level of silica itself depends on the level of caustic soda that remains in the demineralized water. In practice, in most of the cases the water obtained by this method has a conductivity of 3 to 20 µS.cm^{-1} a silica level of 0.05 to 0.5 mg.l^{-1} and a pH ranging between 7 and 9.

This is the simplest arrangement and a demineralized water that may be used in a wide variety of applications can be obtained with it.

. **SCR + WBR + SBR system:** this combination (Figure 113) is a variation of the previous one. It provides exactly the same quality of water, while offering economic advantages in the case where the water to be treated contains a high proportion of strong anions (chlorides and sulphates). In this system, the water, after

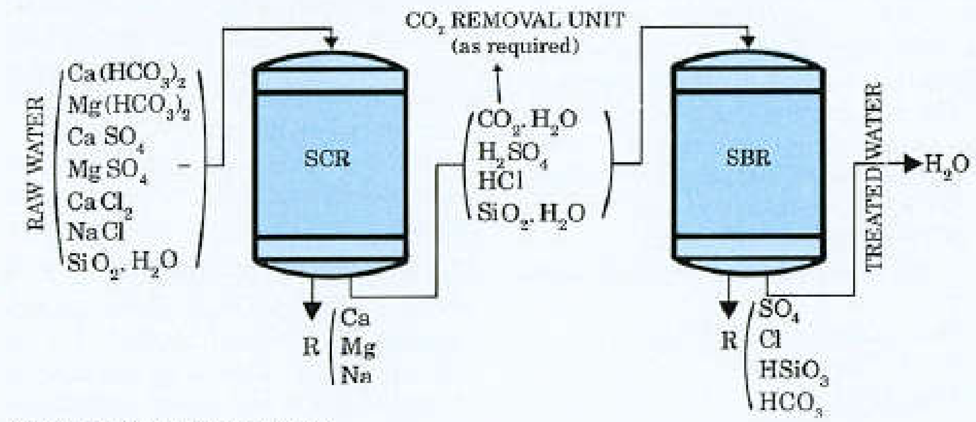


Figure 112. Total demineralization.

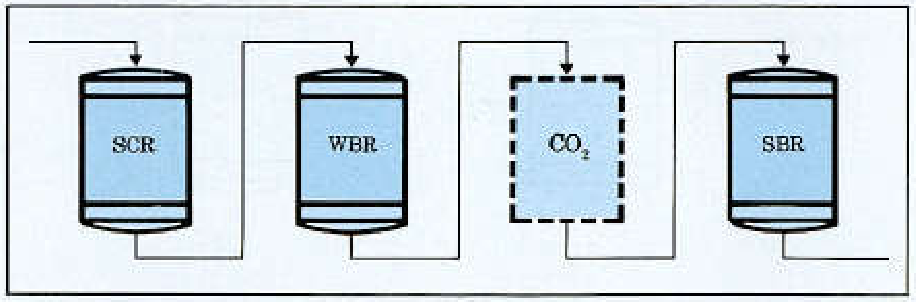


Figure 113. Total demineralization with two anion exchangers.

Figure 113. Total demineralization with two anion exchangers.

first passing through the weak base anion exchanger, in turn passes through the strong base anion exchanger. The optional COz removal unit may be installed either between the cation exchanger and the first anion exchanger, or between the two anion exchangers.

The regeneration of the anion exchangers takes place in series with the caustic soda solution first passing through the strong base resin and then through the weak base resin. This method requires the use of much less caustic soda than was used in the previous one, because the excess caustic soda remaining after normal regeneration of the strong base resin is usually sufficient to regenerate the weak base resin completely.

Moreover, when raw water contains a high proportion of organic matter, the weak base resin protects the strong base resin.

. **Systems with WCR + SCR grouping:** this combination is advantageous in cases where the water contains a high proportion of bicarbonates. In this system, regeneration is effected in series first passing through the sulphonic exchanger and then through the carboxylic exchanger.

Since the carboxylic resin is regenerated more or less stoichiometrically, from the excess free acid that remains after the regeneration of the sulphonic resin, the total regeneration rate is considerably lowered.

Figure 114 shows a system permitting minimum consumption of reagents.

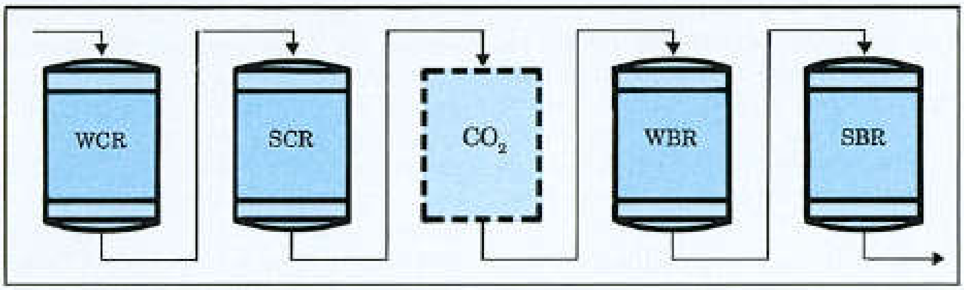


Figure 114. Total demineralization with two cation exchangers and two anion exchangers.

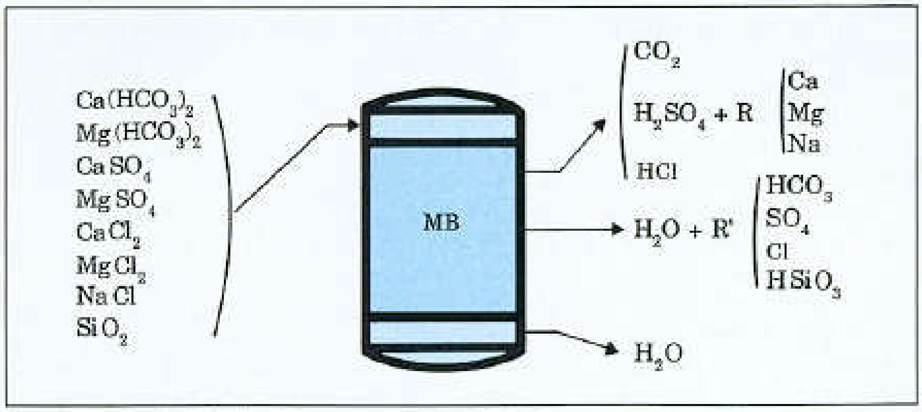


Figure 115. Total demineralization with a mixed bed.

. **Mixed bed installations (MB):** this process differs essentially from the separate bed system in that the two strong resins, the cation and the anion, are joined in a single vessel. The two resins are intimately mixed by agitation with compressed air. The grains of resin are thus arranged side by side, and the whole bed behaves like an infinite number of anion and cation exchangers in series (Figure 115).

To carry out regeneration, the two resins are separated hydraulically during the loosening phase. As the anion resin is the lighter, it rises to the top, while the heavier cation resin falls to the bottom.

When the resins have been separated, each of them is separately regenerated in turn with caustic soda and a strong acid.

Any excess regenerant is removed by rinsing each bed separately. After partial emptying of the vessel, the two resins are remixed with compressed air. Rinsing is completed and the vessel is then ready for a fresh cycle.

The advantages of mixed bed systems as compared with separate bed systems are as follows:

- the water obtained is of very high purity and its quality remains constant throughout the cycle (its conductivity is below 0.2 $\mu S.cm^{-1}$, its silica level is less than 20 $\mu g.l^{-1}$),
- the pH is almost neutral,
- rinse water requirements are very low.

The disadvantages of mixed bed systems are a lower exchange capacity and a more complicated operating procedure because of the requirement that the separation and remixing processes be carried out absolutely correctly.

Mixed bed exchangers can be used directly on raw water as long as it contains very few ions (water which has undergone prior treatment by reverse osmosis or distillation, condensed water, nuclear pool water in closed loops, etc.). A complex system of ion exchangers can be replaced by a single mixed bed.

Special layouts have also been used as follows:

- SCR + | C02 | + MB, -softener + MB,
- SCR + WBR + | C02 | + MB: useful arrangement for a water containing many strong anions.

However, the mixed bed exchangers are most often used in polishing treatment.

.Installation equipped with a polishing system: the quality of water flowing out of a primary system, whatever its composition, is determined by the ion leakage from the cation exchanger. This ion leakage varies, depending upon the properties of the raw water and the rate of regeneration. The quality of the demineralized water obtained is not sufficient for certain uses such as that of feedwater for very high pressure boilers and various applications in the chemical, nuclear or electronics industries. Therefore, it has to be further treated in a system known as a polishing plant.

The ion leakage from the cation exchanger is converted to a free base on the anion exchanger, which therefore entails a silica leakage from the latter. As a result, a polishing system must necessarily contain a strong acid cation exchanger and a strong base anion exchanger.

The polishing system may be arranged so that there are two columns in series with regeneration taking place in the direction SBR2 - SBR1 and SCR2 - SCRl. In these arrangements the polish ing exchangers are perfectly regenerated and the quality of the demineralized water is excellent (the conductivity is less than 1 gS.cm ', its silica level ranges between 5 and 20 µg.l^{-1}).

This system, however, is being used less and less frequently. Mixed bed exchangers that produce water with a conductivity in the order of 0.05 gS.cm^{-1} at 25°C, and have silica leakages that are considerably below 10 gg.l^{-1}, are preferred. A polishing mixed bed, due to the low volume of inflowing ions, is regenerated only every 5 to 10 cycles of the primary system.

In some applications, it may be sufficient to have as a polisher a weak or a strong acid cation exchanger designed to neutralize the caustic soda leakage from the anion exchanger in the primary system. By using this polishing exchanger, known as a "buffer filter,„ it is possible to obtain water that is virtually free of cations (with a conductivity below 1 µScm) and has a pH value of between 6 and 7.

11.4.

SIZING A DEMINERALIZATION SYSTEM

The following data are necessary for sizing:

- M alk. of the raw water in French degrees,
- SSA of the raw water in French degrees $(SO_4 + Cl + NO_3)$,
- silica content as $TSiO_2$ (1° = 12 mg.l^{-1} SiO_2,
- content of carbon dioxide, TCO_2, in the water after passing through the cation exchanger and, where appropriate, after CO_2 removal,
- volume V of water to be supplied between regeneration processes, in m^3, including service water if appropriate,
- hourly flow rate Q in m^3,
- exchange capacity C of the resins expressed in degrees-litres per litre of compacted resin (the degrees may be replaced by milliequivalents, where 1 millequivalent = 5 French degrees).

In the case of conventional systems, the exchange capacity is calculated for each resin, with the aid of information furnished by the manufacturer.

The anion exchanger is calculated first for capacity C: the volume to be used is given by the formulae:

$$V_a = \frac{V \times SAF}{C}$$

in the case of a weak base exchanger, and:

$$V_a = \frac{V \times (SAF + TCO_2 + TSiO_2)}{C}$$

in the case of a strong base exchanger.

The cation exchanger is calculated next, allowing for the additional water αVa necessary to rinse the anion exchanger, where a may vary from 5 to 20 depending on the type of resin. This results in:

$$V_c = \frac{(V + \alpha\, V_a)\,(SAF + TAC)}{C}$$

The volumes calculated must then be compared with the hourly flow rate to be treated. There are upper limits to the flow rate or to the bed volume.

If Vc or Va are too low, they should be readjusted, possibly by increasing the cycle volume V.

11.5.

MONITORING AND MAINTENANCE OF A DEMINERALIZATION PLANT

11.5.1. Checking the treatment

The checks to be made on a demineralization plant essentially include the following measurements:

- conductivity (or resistivity),
-silica concentration,
- hardness where necessary,
-sodium concentration,
- pH.

The maximum reliability can be obtained by continuous automatic checks, especially those relating to the conductivity, the silica and the pH.

For the correct interpretation of the conductivity measurement and the consequent deduction of the ion leakage value, it should be borne in mind that normally, in a properly designed installation, the demineralized water only contains traces of caustic soda (see Chapter 8, par. 3.2.2).

11.5.2. Disinfection of resins

Operating difficulties sometimes occur due to the presence of microorganisms:

- fouling of the bed that is invaded by bacterial colonies (especially on carboxylic resins),
- internal contamination of the resin pores (especially on anion exchangers).

The remedies, which should not be applied until an expert has been consulted, are of two types:

- preventive, by prior continuous or intermittent chlorination of the raw water,
- curative, by disinfection of the resin bed with formol, or with a solution of a quaternary ammonium-based product, or else with a brine of 200 g.1- in NaCl, alkalinized to a pH of 12 with the aid of caustic soda.

11.5.3. Storage of resins

11.5.3.1. In their original packaling

Protection against dehydration: it is necessary to preserve the resins in their packaging, which should be kept intact. They should be kept away from sunlight and at a temperature not exceeding 40°C. From time to time it is important to check the packaging for water tightness, and to maintain the moisture level of the resin in cases where the packaging has been opened, by irrigating it with water whenever necessary before reclosing the packaging.

. **Protection against freezing:** the resins can either be stored in a site protected from freezing conditions or be treated with a saturated brine.

11.5.3.2. Inside a plant

.Protection against dehydration: it is necessary to keep the columns filled with water at all times.

Protection against freezing: water should be replaced with a saturated brine which will ensure that the resin is protected at a temperature down to -17°C. For lower temperatures, it is necessary to use a water/glycol mixture in appropriate proportions.

Protection against bacterial growth: before shutdown, it is important that suspended solids be removed by means of a prolonged washing operation on a countercurrent basis. The cation and anion resins must be maintained in a saturated state; for anion resins, this is also a means of avoiding the hydrolysis of strong base groups into weak base groups and into nonionic groups, which leads to losses in capacity.

Cation exchanger beds can be filled with a 0.5% formol solution. It is advised that this concentration be checked periodically to ascertain that it does not fall below 0.2 % .

Anion exchanger beds can be filled with a 0.1% solution of a quaternary ammonium salt

It is equally effective to fill the unit with a brine with a minimum concentration of 200 g.l^{-1}; moreover, it constitutes a protection against freezing and hydrolysis.

12. OXIDATION-REDUCTION

12.1.

PRINCIPLE - THE REDOX POTENTIAL

Some substances are found either in oxidized or in reduced form, and are converted from one to the other by gaining electrons (reduction) or by losing electrons (oxidation). A system comprising an acceptor and a donor of electrons is known as an "oxidation-reduction" system.

$$\text{Red} \rightleftarrows \text{Oxyd.}^{n+} + ne^-$$

for example, iron:

$$Fe^{2+} \rightleftarrows Fe3^+ + e^-$$

It should be noted here that, apart from the "oxygen" and "hydrogen" elements which are respectively able to act only as an oxidizing and a reducing agent, there are no substances which are oxidizing agents or reducers in an absolute sense.

The possibility of such interaction is determined by the concept of oxidation-reduction potential or redox potential, which depends on the activity of the oxidized and reduced forms according to theformula (see page 206):

$$E_o = E_o^o + \frac{K}{n} \log \frac{|\text{ oxidized form }|}{|\text{ reduced form }|}$$

where n is the number of electrons involved in the oxidation-reduction reaction, and Eo is the so-called "normal" potential corresponding to the equilibrium: | (oxidized form) | = | (reduced form) |.

The oxidation-reduction potential is measured by a pair of electrodes. One electrode is usually made of non-corrodible material (platinum or gold) while the other is a reference electrode that is normally a KCl-saturated calomel electrode (Figure 116). The measured potential EHg, which is positive or negative compared to the calomel electrode, and is expressed in volts, must be compared with the potential of the hydrogen electrode EH; it should be recalled that the former is positive i.e. at 20°C:

$E_H=E_{HG}+0.248V$

. The rH, or oxidation-reduction potential, is calculated from an equation derived from Nerst equation:

$$rH = \frac{E_H}{0,029} + 2pH = \frac{A \pm E_{Hg}}{0,029} + 2pH$$

The various substances can be classified by comparing their Eo potential. A substance A that has a higher normal potential than a substance B will oxidize the latter. Thus, the substance B is the reducing agent for substance A.

By definition zero potential is that of a hydrogen electrode. Listed in table 40 are the normal potential values at 25°C of a number of substances found in water.

In fact, conversion of a substance from an oxidized form to a reduced form usually takes place by means of another substance which itself is converted from the reduced form into the oxidized form:

$$aOx_1 + bRed_2 \rightleftarrows aRed_1 + bOx_2$$

(redox equation)

Thus, we see a combination of the two couples. By mixing equal quantities of the oxidizing agent of one of the couples and of the reducing agent of another couple, a(Oxi) = b(Red2), the point of equivalence can be reached. The potential of the system is then expressed by:

$$E = \frac{bE_1 + a\,E_2}{a + b}$$

On a titration curve (potential vs. concentration of oxidizing agent) this is identified by the point of inflection.

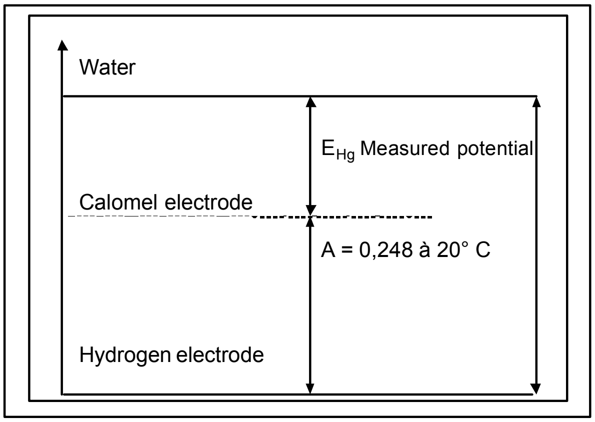


Figure 116. Measurement of the oxidation-reduction potential.

Table 40. Normal oxidation-reduction potential values of oxygenated and halogenated compounds.

(E_H = 0 volt)

		E_o volt
$OH^0 + H^+ + e^-$	$\rightarrow H_2O$	2.76
$O_3 + 2H^+ + 2e^-$	$\rightarrow O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.76
$Cl_2 + 2e^-$	$\rightarrow 2Cl^-$	1.36
$HBrO + H^+ + 2e^-$	$\rightarrow Br^- + H_2O$	1.33
$O_3 + H_2O + 2e^-$	$\rightarrow O_2 + 2OH^-$	1.24
$ClO_2 + e^-$	$\rightarrow ClO_2^-$	1.15
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.07
$HIO + H^+ + 2e^-$	$\rightarrow I^- + H_2O$	0.99
ClO_2 aq $+ e^-$	$\rightarrow ClO_2^-$	0.95
$ClO^- + H_2O + 2e^-$	$\rightarrow Cl^- + 2OH^-$	0.90
$HO_2^- + H_2O + 2e^-$	$\rightarrow 3OH^-$	0.87
$BrO^- + H_2O + 2e^-$	$\rightarrow Br^- + 2OH^-$	0.70
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$I_3 + 2e^-$	$\rightarrow 3I^-$	0.53
$IO^- + H_2O + 2e^-$	$\rightarrow I^o + 2OH^-$	0.49

Depending on experimental conditions, water can take part in oxidation-reduction reactions (see page 206).

12.2.
THE GOAL

Oxidation-reduction reactions are used in the treatment of water:

- for disinfection of water,
- to convert an element from its dissolved state to a state in which it may be precipitated (Fe, Mn, sulphur removal, etc.).

The definition and monitoring of the pH value in a reaction is very important. Figure 117 graphically represents the state of various forms of iron and of manganese and their evolution depending on the pH and the redox potential, in order to:

- convert an element from its dissolved state to its gaseous state (for example, denitrification),
- break down a substance into several simpler substances the presence of which is acceptable in water (for example, phenols, etc.),
- break down a non-biodegradable substance into several simpler substances which can be removed by bacterial assimilation during a later treatment phase (for example, micropollutants).

Oxidation can take place by means of chemotrophic bacteria such as in the oxidation of iron and manganese, the oxidation of sulphur compounds, the oxidation-reduction of nitrogen compounds and methane-forming reduction.

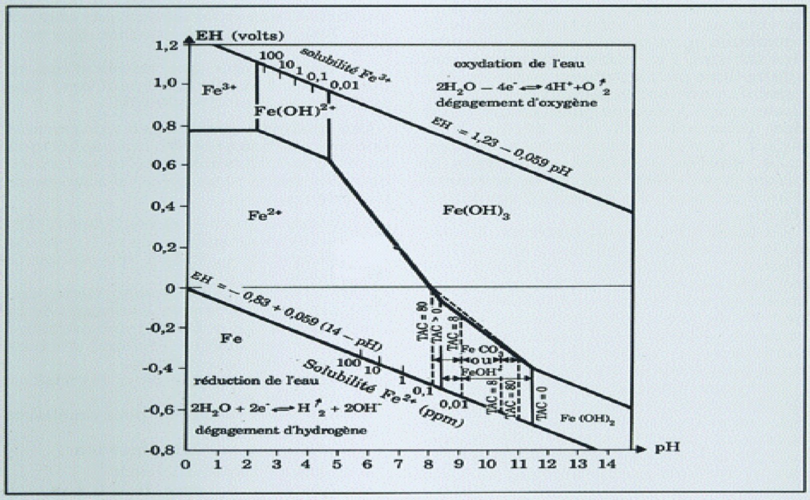


Diagramme "potentiel-pH" du fer (domaines d'existence des ions et des précipités) d'après HLM, 1961.

Figure 117. Diagram ofiron 'potential pH" (areas where ions and precipitates are located), so called: diagram of stability from MrPourbaix.

12.3. MAIN OXIDATION TECHNIQUES

12.3.1. Oxidation by physical means

using air

This consists in dissolving oxygen of the air in water. After being dissolved oxygen may oxidize some compounds as for example ferrous iron to ferric iron according to the reaction:

$$4Fe^{2+} + O_2 + 8\,OH^- + 2H_2O \rightarrow \underline{4\,Fe\,(OH)_3}\downarrow$$

The techniques employed are those developed in Chapter 17.

Aeration by physical means has as secondary effect the removal of dissolved gases that are in excess with regard to the composition of the air used for aeration:

- the removal of H_2S,
- the removal of excess CO_2 (thus raising the pH level). It must be noted that an overly extensive aeration can lead to an excessively high pH level (see the carbonate balance, page 262).

using oxygen

Whenever the oxygen demand is great it may be of interest to replace air with pure oxygen when aeration takes place under pressure. The partial pressure of oxygen is thus multiplied by five for a same pressure of air injection which makes it possible to increase the quantity of dissolved 02 in the water at this pressure. This technique is primarily used in the treatment of wastewater.

12.3.2. Oxidation by chemical means

12.3.2.1. Gaseous reagents

The reagents used are chlorine and ozone.

A) Chlorine. Chlorine is the most commonly used reagent for the disinfection of water. Chlorine cannot be used directly in its gaseous state. It must first be dissolved in water. It reacts in water according to the reaction:

$$Cl_2 + H_2O \rightleftarrows HClO + HCl$$

which is accompanied by the secondary reaction:

$$HClO \rightleftarrows ClO^- + H^+$$

Figure 118 illustrates this latter balance depending on the pH level. If the pH level is below 2 all the chlorine is in its molecular form. At a pH level of 5 molecular chlorine disappears and all the chlorine is in the form of HC10. At a pH level of above 10 all the chlorine is in the form of hypochlorite ions ClO^-.

The **bactericidal effect** of chlorine is maximum when the chlorine is in the HC10 form. Figure 118 demonstrates how to **calculate** the quantity of chlorine present in the form of HCIO for a given pH level of between 5 and 10 and a given dosage of free chlorine measured in a water. The quantity of chlorine is thus called **free available chlorine** which is not directly measurable. Chlorine possesses a significant residual power.

Chlorine also reacts with organic matter in water and with ammonia. If increasingly large dosages of chlorine are introduced into several receptacles containing the same water, and the total residual chlorine in each receptacle is measured at the end of a given contact period (2 hours for example), the curve in figure

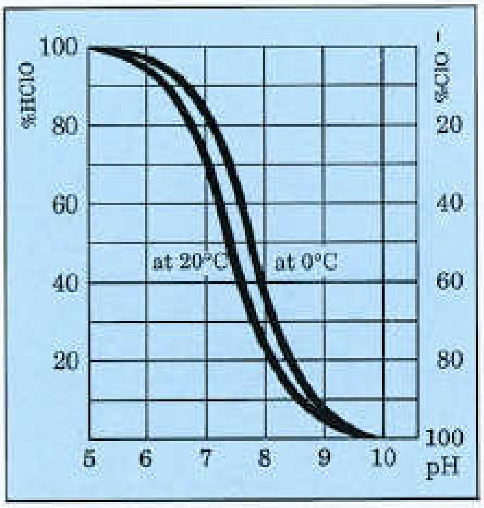


Figure 118. The dissociation of HClO in water.

119 is obtained. The dotted line curve represents the quantity of free chlorine.

The chlorine reacts with compounds containing ammonium according to the following reactions:

$HCIO + NH_3 \rightarrow NH_2Cl + H_2O$, monochloramine

$NH_2Cl + HCIO \rightarrow NHCl_2 + H_2O$, dichloramine

$NHCl_2 + HCIO \rightarrow NC1_3 + H_2O$, trichloramine

$2NH_3 + 3HClO \rightarrow N_2 + 3HCl + 3H_2O$

From the beginning of the curve up to point M, mono- and dichloramines are formed by reaction with the amount of residual chlorine. Beyond point M, the chlorine added reacts with the mono- and dichloramines to give trichloramines that do not react with the amount of residual chlorine. This is point P. The amount of chlorine added p corresponds to the **breakpoint.**

Beyond the breakpoint, the amount of total residual chlorine increases in the same proportions as the chlorine added. The residual chlorine is then found mainly in the form of free chlorine.

The kinetics of the reaction of chlorine on a water containing ammonium and of the formation of byproducts depend on a number of parameters (pH, temperature, form of ammonium); a model of this has been made (Saunier, 1976).

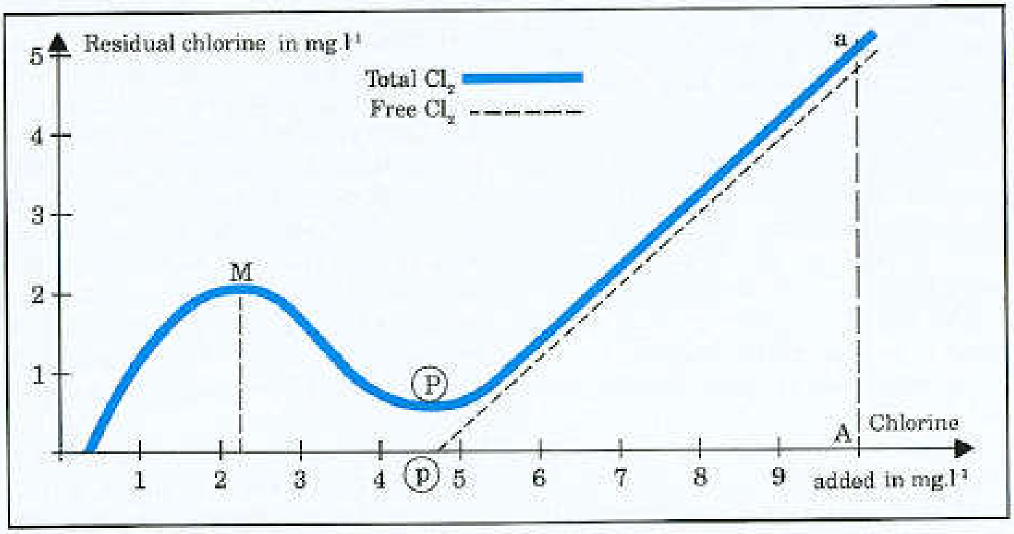


Figure 119. Chlorine absorption curve.

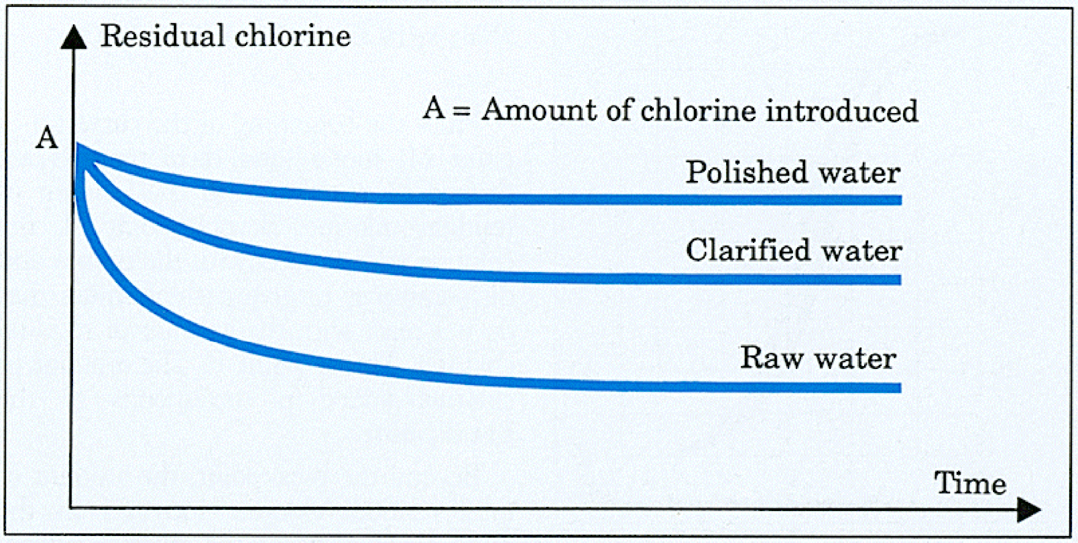


Figure 120. Network test – Chlorine absorption vs. time.

Network test: this test shows chlorine consumption by water versus time (Figure 120). From this graph can be deduced the quantity of chlorine necessary to obtain a given residual chlorine at the end of a system, whose retention time is known. This test also shows the efficiency of the treatment applied to raw water: a clarified water absorbs less chlorine than a raw water but more chlorine than a polished water.

B) Ozone. In practice, ozone is the most powerful oxidizing reagent used in the treatment of drinking water. It is a gas which is produced on the site of its use (see Chapter 17, sub-chapter 4).

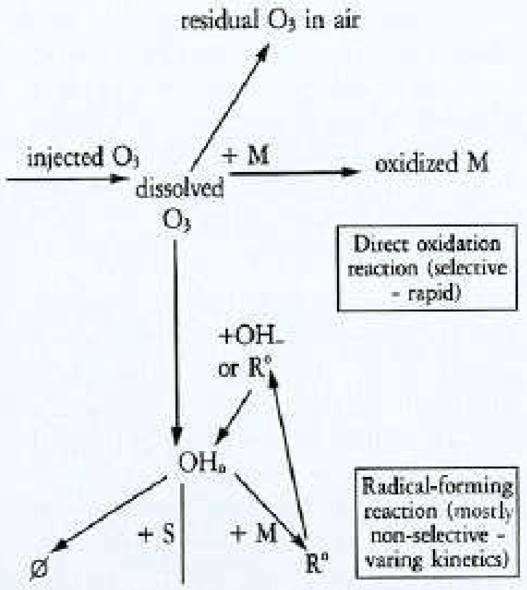
The action of ozone in water is the result of two successive phenomena:

- the dissolution in water (transfer from gas to water),
- the action of dissolved ozone on the body to be oxidized.

Hoigné demonstrated (Figure 121) that the action of ozone is actually two fold. Ozone may act by direct reaction of the ozone molecule: these reactions are usually very selective.

Ozone may also be induced to act through secondary species such as OH^0 radicals, formed when the ozone molecule decomposes in water. This OH^0 species may react with compounds known as "scavengers" resulting in reaction products without acting on the ozone dissolved in the water. The OH^0 species may also react with solutes M, resulting in R° radicals which will themselves promote the breakdown of the ozone molecule in water. The presence of OH^- also allows the ozone molecule to break down. This indirect or radical-forming action of ozone is **not very selective,** but the kinetics of the reaction vary widely depending on the substances to be oxidized.

Due to its oxidizing properties, ozone is also used for disinfecting water. It acts rapidly and efficiently but does not have any residual power.



M: solute
oxidized M: oxidized solute
R°: free radical catalyzing the breakdown of ozone
S: scavenger
Ø: product not catalyzing the breakdown of ozone

Figure 121. Diagram of the action of ozone (from Hoigné).

.Ozone and UV rays

In combination with ultraviolet rays the formation of OHO radicals can result according to the reactions:

$$O_3 + hv \rightarrow O^* + O_2$$

$$O^* + H_2O \rightarrow 2OH^\circ$$

OH^O radicals are formed. The combined action with UV rays and ozone facilitates the radical-forming action of ozone.

12.3.2.2. Liquid reagents

These are mainly certain compounds of chlorine and hydrogen peroxide.

. Chlorine compounds

Chlorine dioxide has a high oxidizing power (see table 40). It reacts according to the reaction:

$$C1O_2 + 5e^- \rightarrow Cl^- + 2O^{2-}$$

It is produced on site using the reaction of sodium chlorite either with chlorine or with hydrochloric acid (see Chapter 20, par. 6.3.2).

Chlorine dioxide reacts very slowly with water:

$$2\,ClO_2 + H_2O \rightleftarrows ClO_2^- + ClO_3^- + 2\,H^+$$

It is sensitive to photochemical breakdown according to the following dismutation reaction:

$$2CI0_2 + hv + H_2O \rightarrow C10_3^- + Cl^- + O_2$$

Depending on the conditions of application, chlorine dioxide may result either in an oxidation reaction (excess of $C1O_2$) or in a chlorination reaction (low excess of $C1O_2$).

Although the chlorine dioxide is sometimes regarded as useful for oxidizing some organic products, its principal application, owing to its residual power, is in disinfecting drinking water at the end of the treatment line.

Javel water. After being dissolved in water, sodium hypochlorite NaClO breaks down into:

$$NaClO \rightleftarrows ClO^- + Na^+$$

The preponderance of the pH reaction will thus be in the oxidizing or bactericidal action of this oxidizing agent.

Chloramines. Chloramines result from the reaction of chlorine on ammonium according to the reaction cited above. Chloramines have a bactericidal power that is far lower than in the preceding examples but they are more stable and they have a residual effect that is useful in the case of large systems that supply water at a high temperature.

. **Hydrogen peroxide**

Hydrogen peroxide is a strong oxidizing agent (see table 40) which breaks down in water according to the reaction:

$$H_2O_2 + H_2O \rightleftarrows HO_2^- + H_3O^+ \ (1) \qquad pK = 11{,}6$$

However, its high cost limits its use for specific purposes. As a bactericide, it may be used to disinfect pipes in a system supplying ultrapure water (placed in contact with water containing several hundred milligrammes per litre of H_2O_2 for about one hour). The advantage of this oxidizing agent is that it does not cause the formation of halogen compounds.

It is sometimes used to oxidize sulphur compounds which cause foul odours during sewage treatment.

It may also be used in combination with other oxidizing agents. **With ozone:** the reaction of ozone on hydrogen peroxide is very slow. Ozone would react with the HO^{2-} ion in reaction (1) according to the following overall reaction:

$$2O_3 + H_2O_2 \rightarrow 2OH^\circ + 3O_2$$

The result is the formation of OH^O radicals, the action of which has been cited above.

12.3.3. Applications

12.3.3.1. Drinking water

. **Disinfection of water:** this is the primary reason for using oxidizing agents in treating water for consumption. The conditions generally accepted governing their use are the following:

- chlorine: a rate of 0.5 $mg.l^{-1}$ of free chlorine must be maintained for a contact period of at least 30 minutes at a pH level of below 8,
- ozone: a rate of 0.4 $mg.l^{-1}$ of residual ozone must be maintained for 4 minutes - chlorine dioxide: a rate of 0.2 $mg.l^{-1}$ must be maintained for 15 minutes.

These conditions ensure the effectiveness of the bactericidal action of these oxidizing agents. To achieve proper disinfection, it is furthermore indispensable that the water's turbidity be lower than 1 NTU.

Ozone is particularly effective in removing viruses (virulicidal effect).

.Other possible applications

Table 41 summarizes the stages in which the various oxidizing agents commonly employed during the production line of drinking water might be used.

The directives governing the use of the most important of these oxidizing agents are as follows:

- ozone may be used advantageously at any point in the treatment line. It does not however have a residual effect. Thus it does not prevent the growth of algae in tanks and on gravity filters. It does not ensure a residual effect in the system,
- chlorine ensures that a percentage of residual oxidizing agent remains following its use; thus its bacteriostatic effect is noteworthy. If chlorine is applied at the start of the treatment line with a higher dosage than the breakpoint (see Figure 119), it provides for the removal of ammonium. On the other hand, it leads to the formation of organochlorinated compounds that must be avoided as far as possible (see page 44). Therefore it is rec

Table 41. Introduction of oxidizing agents into the treatment line.

	Air	Cl_2	O_3	ClO_2	Chloramines
Preoxidation	+	(+)	++	(+)	0
Intermediate oxidation	+	+	++	(+)	-
Final oxidation	0	+	+	+	-
Disinfection	0	+	++	+	-
Residual effect (safety disinfection)	0	+	0	+	+

++: Recommended use
+ : Possible use
(+): Possible use with caution
- : Use not recommended
0 : No effect or no appreciable effect

ommended that the introduction of chlorine be delayed so that it comes as far downstream as possible in the treatment line,

- chlorine dioxide is an equally excellent bacteriostatic compound. Introduced at the end of the treatment line, its level must not exceed 0.4-0.6 mg.l-' to preclude the water from tasting bad owing to the chlorite ion which appears after the oxidation-reduction reaction of dioxide with organic matter. The following reaction takes place:

$$\text{OM of water} + C1O_2 \rightarrow \text{oxidized OM} + C1O_2 + Cl^-$$

When the dioxide is introduced at the start of the system, this same reaction causes a substantial amount of C102 to appear which must not be allowed to remain in the treated water. It can be removed by ozonation (resulting in the production of the chlorate ion C103) or by filtration on GAC (resulting however in a shortening of the service life of GAC). Chlorine dioxide does not remove ammonium.

As a guide, table 42 lists the relative effectiveness of oxidizing agents with regard to a variety of parameters.

12.3.3.2. Municipal wastewaters

Except for oxygenation phases in which the aim is to ensure oxidation and assimilation of organic matter and ammonium by bacteriological means, chemical oxidizing agents are not used other than for disinfection which is generally partial.

While the disinfection of water for consumption has as its aim the total removal of pathogenic germs (which show up in the fecal contamination indicator germs), the aim of partial disinfection is to reduce the concentration of pathogenic germs which is controlled by a reduction in the number of fecal contamination indicator germs. The desired reduction most often corresponds to a lowering of 2 or 3 logarithmic units.

It is clear that the amounts used depend on the quality of the effluent. Special emphasis should be placed on removing the SS to the greatest extent possible before disinfection (tertiary filtration).

Table 42. The efficiency of oxidizing agents.

Element considered	Usable oxidizing agent				
	Air	C12	C102	03	KMn04
Iron	++	++	++	+++	+
Manganese	0	+	++	+++	+++
Colour	0	+	+	++	0
Odour and taste	+	±	+	+++	0
Ammonium	0	+	0	0	0
Organic matter	0	+	+	+	0
Reducing substances	0	++	++	++	+
Biodegradability	0	-	-	++	0
Disinfection	0	++	++	++	(+)

12.3.3.3. Industrial waters and effluents.

This mainly concerns the following industrial waters and effluents.

. **Using oxidizing reagents** - cyanide-laden waters from electroplating or gas scrubbing, -hydrazine-laden condensates: oxidation by H_2O_2 catalyzed on specific resins, - nitrite baths from electroplating: oxidation by H_2O_2 + Cu^{++} (Fenton reagent), NaClO or H_2SO_5,

- solutions of thiosulphates oxidizable from H_2O_2

.

. **Using air or oxygen** - spent caustic soda, rich in S^{2-},

- waters from pickling, loaded with Fe^{2+},
- uranium leachates U^{4+}.

Most of these reactions present a high enough potential and rapid enough kinetics to permit regulation except in the case of thiosulphates. If other less dangerous reducing agents co-exist, a posteriori monitoring to limit the overconsumption of a costly oxidizing agent, as in the case of cyanide-laden effluents from gas scrubbing, is considered adequate.

The use of air and oxygen in the equipment known as "oxidizers" requires high temperatures and pressures in order to achieve adequate kinetics and efficiency.

. Using ozone

- effluents containing low CN or phenol concentrations,
- effluents from methionine units or those containing refractory compounds.

. An example of oxidation: treatment of cyanides

The oxidation of cyanides in an alkaline environment theoretically comprises two successive stages: the cyanate state in which there is practically no toxicity; then the nitrogen and bicarbonate state. The powerful oxidizing agents employed are sodium hypochlorite, chlorine and permonosulphuric acid (Caro's acid). In practice, for economic reasons only the first stage is employed.

1st stage (cyanates)

The overall reactions that come into play are:

- using sodium hypochlorite:

$NaCN + NaClO \rightarrow NaCNO + NaCl$

- using chlorine gas:

$NaCN + Cl_2 + 2NaOH \rightarrow NaCNO + 2NaCl + H_2O$

- using Caro's acid:

$NaCN + H_2SO_5 \rightarrow NaCNO + H_2SO_4$

The first two reactions occur almost instantaneously where the pH level is above 12, but the reaction speed drops rapidly if the pH level falls (critical threshold: pH 10.5). Whatever the pH level, an intermediate compound which is formed is cyanogen chloride CNCI which is just as dangerous as hydrocyanic acid:

$NaCN + NaClO + H_2O \rightarrow CNCI + 2NaOH.$

With a pH level starting at 10.5, however, cyanogen chloride is hydrolyzed the moment it is formed according to the reaction:

$CNCI + 2NaOH \rightarrow NaCl + NaCNO + H_2O$

With Caro's acid, an adequate reaction speed is observed for pH level above 9.5.

2nd stage (nitrogen)

The passage of cyanate into nitrogen occurs according to the reaction:

$2NaCNO + 3Cl_2 + 6NaOH \rightarrow 2NaHCO_3 + N2 + 6NaCl + 2H_2O$

It also takes place at a pH level of 12 259 but requires three times the amount of reagent and a reaction time of about one hour, as it is impossible to regulate the potential.

Table 43 shows the amounts of reagents required to oxidize as far as the cyanate stage one gramme of CN^- present in an effluent that has already been brought to a pH level deemed optimal for reaction.

Table 43. Oxidation of free cyanides.

Reagents	**Stoichiometric amount** for 1 g of CN	**Industrial practice** for 1 g of CN
NaClO in ml (1)	18.2	21 (3)
H2S5 in ml (2)	22	24 (3)
NaOH in g	3.1	3.5 (3)

(1) NaClO commercial solution at 47-50 chlorometric degrees, i.e., 150 $g.l^{-1}$ of active chlorine.

(2) H_2SO_5, commercial solution at 200 $g.l^{-1}$.

(3) Normal excess for cyanide concentrations less than 100 $mg.l^{-1}$ (in the case of rinse water).

12.4.
REDUCTION BY CHEMICAL MEANS

The most common examples involve the reduction of oxygen, that of hexavalent chromium, as well as the destruction of residual oxidizing agents employed in disinfection. It is also necessary to mention the reduction of nitrites in the process of surface treatment (sulphamic acid or $NaHSO_3$).

12.4.1. Chemical reduction by oxygen

Sodium sulphite or ammonium bisulphite is used, for, even though it is more expensive, it is simpler to use and provides a greater buffer effect
The reactions are:

. Using sodium sulphite
$O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$
16 g of $Na_2SO_3.7H_2O$ are needed per mg of oxygen.

. **Using ammonium bisulphite**
$1/2O_2 + NH_4HSO_3 \rightarrow NH_4HSO_4$
6.2 mg of bisulphite are needed per mg of oxygen.

Three applications are common: in treating boiler water, conditioning oncethrough cooling systems and conditioning waters used for secondary recovery.

12.4.2. Reduction of hexavalent chromium

The reduction of toxic hexavalent chromium into trivalent chromium which is less toxic and can be precipitated in the form of hydroxide occurs in an acid medium through the action of sodium bisulphite or ferrous sulphate.

. **Using sodium bisulphite**
$H2Cr_2O_7 + 3NaHSO_3 + 3HzSO_4 \rightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 4H_2O$

. **Using ferrous sulphate**
$H_2Cr_2O7 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fez(SO4)3 + 7H2O$

The first of these reactions occurs almost instantaneously where the pH level is below 2.5, but the reaction speed falls rapidly when the pH level rises (critical threshold is a pH level of 3.5).

The reduction of ferrous iron has fewer restrictions and may occur with a pH level below 6, with monitoring. It is less used.because a significant amount of hydroxide sludge is produced during the final neutralization stage.

Table 44 shows the amounts of reagents required to reduce 1 g of Cr(VI).

12.4.3. Reduction of residual chlorine during disinfection

This process may be necessary at the end of a system supplying drinking water over a long distance or in the case of discharge, into a sensitive zone, of municipal sewage which has been chlorinated. The most commonly used agents are NaHS03 and SOz which act according to the following reactions:

$$SO2 + HC1O + H_20 \rightarrow H_2SO_4 + HCl$$
$$NaHSO_3 + HC1O \rightarrow H_2SO_4 + NaCI$$

Table 44. The treatment of hexavalent chromium.

Reagents	Stoichiometric amount for 1 g of Cr(VI)	Industrial practice for 1 g of Cr(VI)
NaHS03 in ml (1)	5.7	6.5 (2)
H2S04 in g	0.95	1
FeS04.7H20 in g	16	20 (2)
H2S04 in g	1.90	2

(1) $NaHSO_3$, commercial grade solution at 530 $g.l^{-1}$, sp. gr.: 1.33.

(2) Normal excess for the treatment of rinse water.

13. NEUTRALIZATION – REMINERALIZATION

Treatments designed to correct the pH are often referred to as neutralization treatments and consist in bringing the pH of water into line with a defined value. They may be employed in the following areas:

- the neutralization of various effluents with a pH often close to neutral before being discharged into the environment: industrial effluents that are acidic or alkaline, acidic waters from mine drainage, etc.,
- the correction of the pH before a further biological or physical-chemical treatment stage (adjustment of the flocculation pH, for example),
- the correction of the carbonate balance in order to protect the supply pipelines from corrosion or scale formation.

This last point in particular will be expanded upon because it constitutes an important stage in the treatment of drinking water and industrial waters.

In fact, water with calcium bicarbonate corrective treatments:

- aeration,

capable of initiating the formation of a natural protective film known as Till- 261 man's film (see page 425). The conditions surrounding the formation of this film may involve all or part of the following

- neutralization of carbonic acidity until the saturation pH is achieved for aggressive waters or, on the contrary, acidification of scale-forming waters,
- remineralization of waters short of calcium bicarbonate.

In the absence of conditions necessary for the formation of the protective carbonate film, the protection of the supply network may also be insured:

- against corrosion by a film-forming treatment based on corrosion inhibitors,
- against scale formation, notably that due to salts other than calcium carbonate, by a chemical conditioning of water (involving the formation of soluble compounds which is adequately oxygenated pounds) apart from methods of precipand in carbonate balance is, when cold, nation, ion exchange or demineralization.

13.1.
THE CARBONATE BALANCE

Natural water is not pure and contains various dissolved chemical elements, the most common of which is calcium bicarbonate (or hydrogen carbonate).

The practical balance of this salt with carbon dioxide is governed by rather complex laws, and shifting it can provoke chemical reactions causing the dissolution of calcium carbonate (or aggressiviry), or the precipitation of calcium carbonate (or scale formation) which can add to simple electrochemical corrosion reactions particular to the metals.

13.1.1. General study of balance Concepts of aggressivity and corrosivity

All studies of carbonate balance are based on the following equations:

- the equality of positive and negative electrical charges:

$$\underbrace{H^+ + 2Ca^{2+} + 2Mg^{2+} + Na^+ + K^+ + \dots}_{P}$$

$$\underbrace{OH^- + HCO_3^- + 2CO_3^{2-} + Cl^- + NO_3^- + 2SO_4^{2-} + \dots}_{N} \qquad (1)$$

– the dissociation of the water:

$$(H^+)\ (OH^-) = pK'_e = pK_e - \varepsilon \qquad (2)$$

– the balance of the water and H_2CO_3:

$$(H^+)\ (HCO_3^-) = K'_1\ (H_2CO_3)$$

where $pK'_1 = pK_1 - \varepsilon$ (3)

$$(H^+)\ (CO_3^{2-}) = K'_2\ (HCO_3^-)$$

where $pK'_2 = pK_2 - 2\varepsilon$ (4)

– solubility product of $CaCO_3$:

$$(Ca^{2+})\ (CO_3^{2-}) = K'_s$$

where $pK'_s = pK_s - 4\varepsilon$ (5)

The H^+, OH^-, HCO_3^-, CO_3^{2-}, Ca^{2+} ions and carbonic acid are **fundamental factors** of the carbonate balance. The N and P ions which essentially involve the ionic strength of the solution are secondary factors with regard to the balance and are defined by Legrand and Poirier as **characteristic elements**

Temperature is also an important factor influencing the value of dissociation constants.

The term E depends on the ionic strength ~1 of the solution according to the equation:

$$\varepsilon = \frac{\mu}{1 + 1{,}4\ \sqrt{\mu}}$$

and the ionic strength ~t expressed in moles by litre is defined by the relation:

$$\mu = \frac{1}{2} \sum C_i\, z_i^2$$

Ci and zi are respectively the concentrations in moles per kg and the valences of the various ions present in the solution.

Using the preceding equations the **saturation pH** may be calculated by substituting in equation (4) of water at equilibrium the value of C03 2- by one obtained from equation

$$(H^+) = \frac{K'_2}{K'_s}\ (HCO_3^-)\ (Ca^{2+})$$

i.e.:

$$pH_s = pK'_2 - pK'_s - \log\ (Ca^{2+}) - \log\ (HCO_3^-) \qquad (6)$$

Thus, it is necessary that pH = pH, for the water to be unaffected by calcium carbonate scale; consequently, it will not attack the walls of the cisterns, the tanks or the pipelines. The concentration of CO_2 which corresponds exactly to pH, is known as equilibrium CO_2.

The pHs corresponds to the saturation pH of the water under consideration for identical values of bicabonates and calcium, that is, saturation pH achieved by the addition or escape of carbon dioxide.

If the pH is lower than the pHs, the water has a tendency to dissolve the lime and attack the cement, the concrete, etc. It also renders impossible the formation of a protective carbonate film on the metal pipelines because of the redissolution of $CaCO_3$ which progresses at the same rate as it is precipitated. Such a water is known as **aggressive;** the fact that the pH level is too low is due to an excess of carbon dioxide, which is referred to as aggressive CO_2. The total concentration of dissolved CO_2 in this case is therefore equal to the some of the equilibrium CO_2 + the aggressive CO_2. It is this excess of CO_2 that must be removed or transformed during the treatments known as neutralization treatments.

Distribution of CO_2 in water

total CO_2

free CO_2 CO_2 of bicarbonates

aggressive CO_2 equilibrium CO_2

If the pH is higher than the pHs, the water has a tendency to precipitate limestone in contact with $CaCO_3$ nuclei, and the water is referred to as **scale-forming;** in this case, its free CO_2 concentration is lower than the theoretical value of equilibrium CO_2. To combat scale formation, either the pH must be lowered to bring it in line with the equilibrium value or a softening or carbonate removal treatment must be carried out (see page 146).

Thus, regulating the saturation pH is a necessary condition although it is not sufficient to avoid corrosion in some cases.

13.1.2. Techniques for calculating aggressivity – Diagrams

In practice it is interesting to study the evolution of the six constituents H^+, OH^-, CO_3^{2-}, HCO_3^-, Ca^{2+} and H_2CO_3 and to show this by means of graphs. Any two basic constituents are taken as coordinates, and the graph enabling the curves representing the various elements linked to the carbonate balance of water to be simply constructed is selected on the basis of fundamental equations of equilibrium.

Using different variables a large number of diagrams may be drawn up from which the most commonly used may be referred to.

13.1.2.1. Langelier's method

Using the general equation (6) to calculate the pHs, Langelier devised a calculation graph incorporating alkalinity and calcium expressed as $mg.l^{-1}$ $CaCO_3$, the total salinity (dry residue in $mg.l^{-1}$) which influences, through the ionic strength, the value of the apparent coefficients involved in the dissociation of balances, and temperature.

The pHs may be calculated from the diagram (see Figure 122) by the equation: $pHs = C + pCa = pAlk$ with $C = pK'^2 - pK'S$

Langelier also established index SI, **the saturation index,** equal to the difference between the measured pH in a considered water and its calculated pHs:

$$SI=pH-pHs$$

If pH G pHs, SI is negative and the water is aggressive.

If pH > pHs, SI is positive and the water is scale forming.

This resolution takes into account a salinity of up to about 3 $g.l^{-1}$ and temper ature, but does not permit amounts of neutralization reagents to be calculated.

In the case of brackish water, and especially sea water, the correction proposed by Stiff and Davis in the pHs calculation (see Figure 123) is employed.

pHs = K + pCa + pAlk where K = pK'z - pK's

13.1.2.2. Hallopeau and Dubin method

These authors have devised a graphic method of determining the aggressive action of water on limestone and of calculating the amounts of neutralizing reagents, by expressing the saturation pH in terms of the logarithms of alkalinity (measured by the M alk. and expressed in moles.l^{-1}) and of calcium hardness (in moles.l^{-1}):

$$pH_s = \log K'_s - \log K'_2 - \log(Alk) - \log(Ca^{2+}) + \log p$$

where:

$$p = 1 + \frac{2K'_2}{(H^+)}$$

In this graph (see Figure 124), free CO_2 and pH are therefore represented by two sets of parallel straight lines.

Free CO_2 can be determined when the pH and alkalinity of a water are known.

The graph contains two curves representing physical dissolution of the CO_2 and neutralization by lime and limestone.

Figure 124 a shows an example of a water in which the representative point M, defined by its coordinates (M alk., pH), is located in an aggressive zone. In order that it be brought in line with the balance, three solutions are possible:

- No. 1: escape of CO_2 by aeration; the M alk. and calcium remain unchanged; the saturation pH thus corresponds to the pHs of the initial water,
- No. 2: neutralization by a base (caustic soda or lime); the M alk. rises and, if lime is used, calcium rises in the same proportion,
- No. 3: neutralization by an alkaline (Na_2CO_3) or alkaline-earth ($CaCO_3$) carbonate; the M alk. and possibly (in the case of $CaCO_3$) the calcium increase approximately twice as much as in the preceding case.

This demonstrates that on the one hand the saturation pH is different in the three cases studied, and that on the other hand the higher the final M alk., the lower the saturation pH.

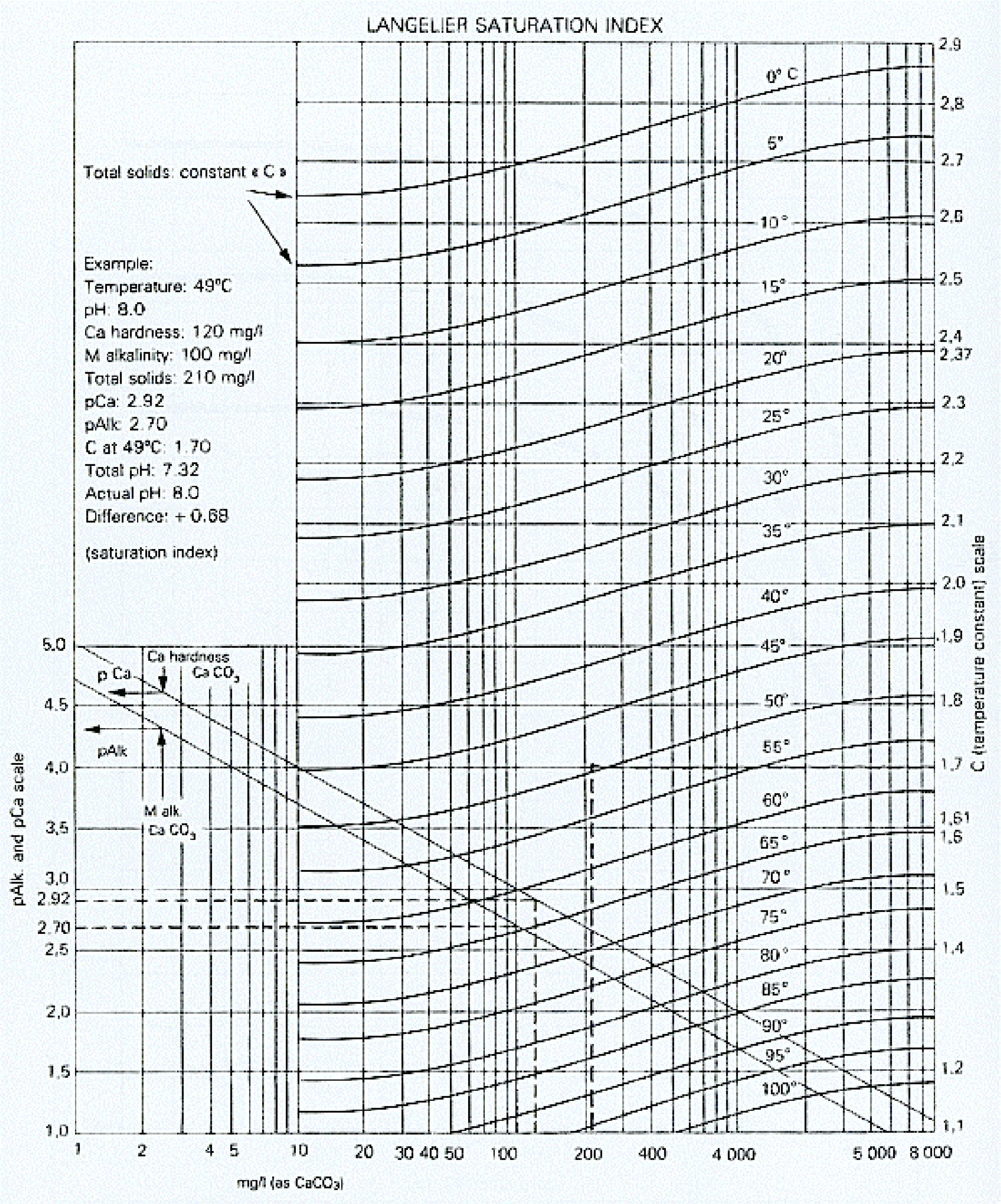


Figure 122. Langelier diagram.

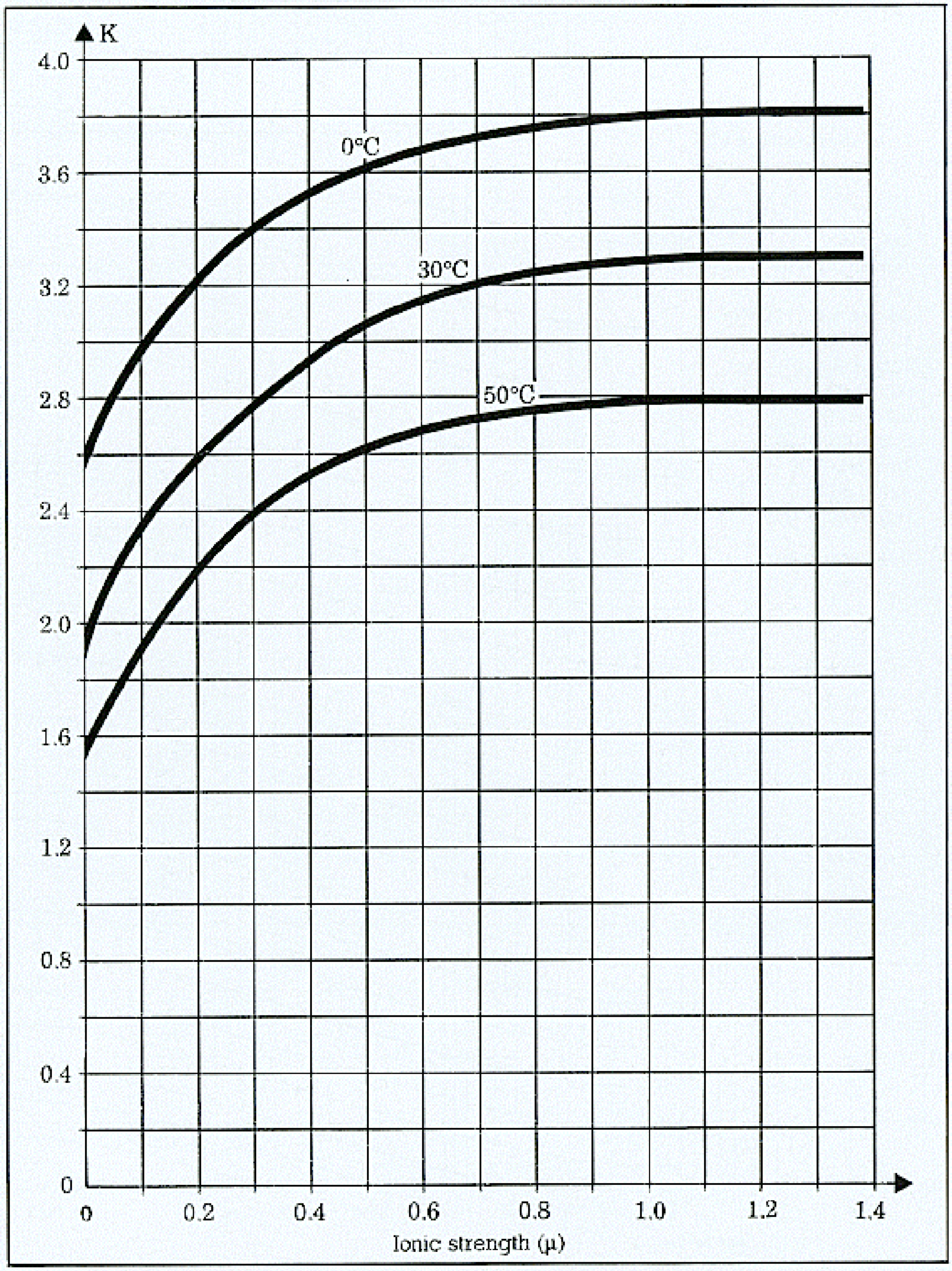


Figure 123. Value of Stiff and Davis coefficient K relating to ionic strength.

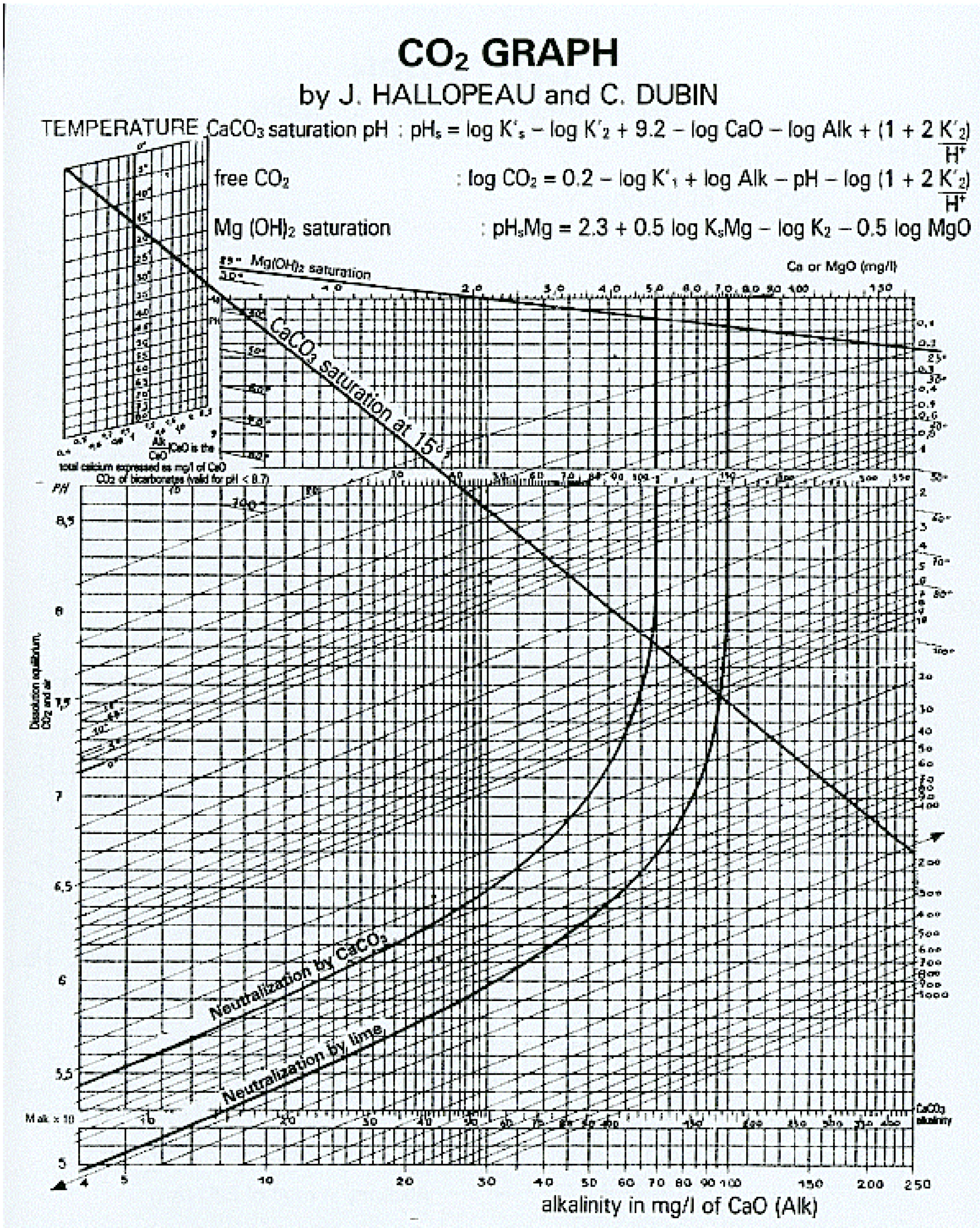


Figure 124. CO₂ graph

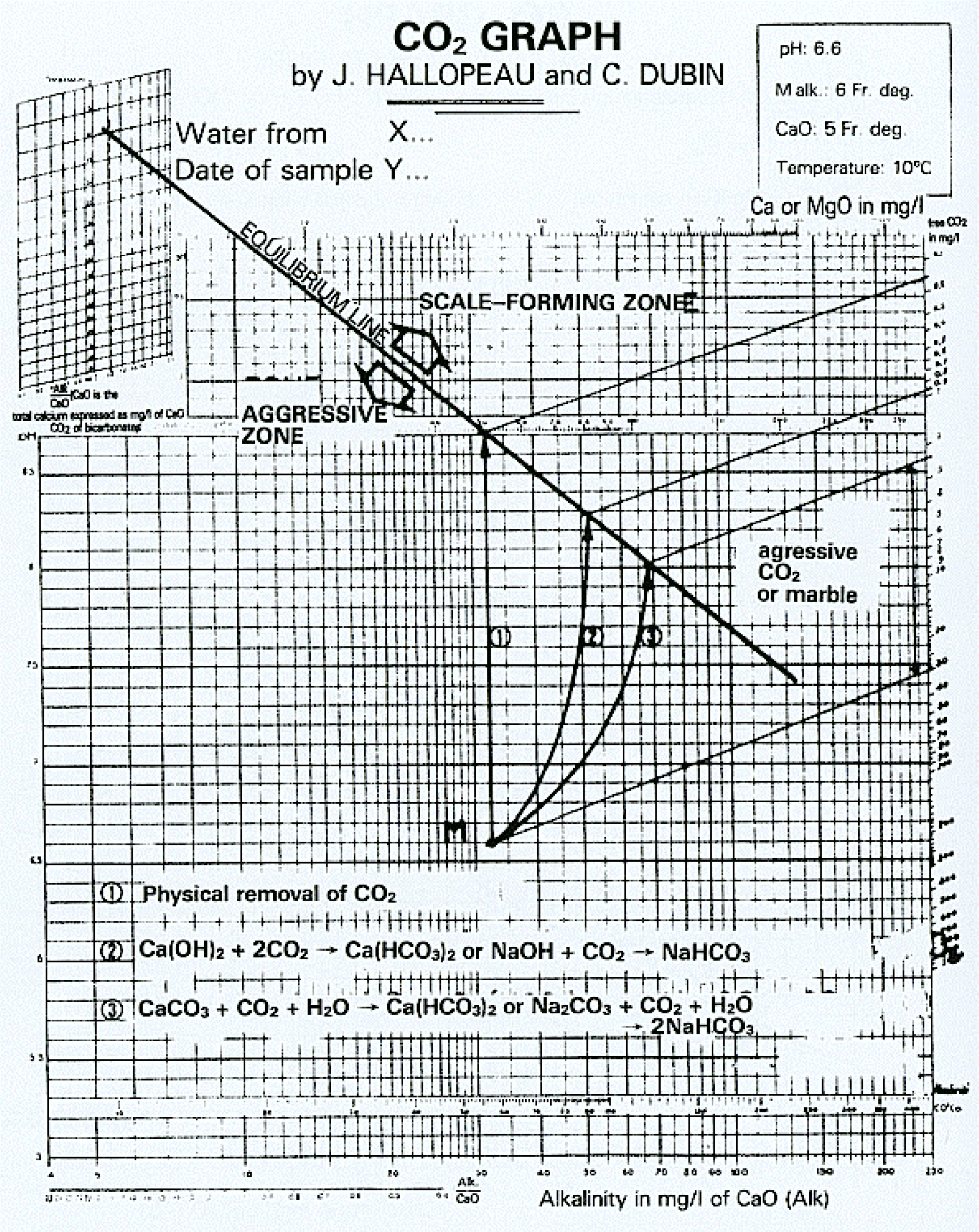


Figure 124 a. CO₂ graph.

In cases numbers two and three, the difference between the final M alk. and the initial M alk. makes it possible to determine the amount of alkaline reagent to be used after an evaluation of the shifting of the equilibrium line which is tied to the variation in the alkalinity/calcium ratio during the neutralization process.

Although it introduces concepts of calcium and total hardness, this method does not take the total salinity or the alkaline waters into account and only covers waters with a low or moderate mineral content.

13.1.2.3. Legrand and Poirier method

These authors considered the system of coordinates. plotting Ca^{2+} on the X-axis and total CO_2 on the Y-axis (see Figure 125).

They justified this choice with the advantages it presented: the steps are arithmetic (as a rule in millimoles.l^{-1}), which prevents the origins being shifted to the infinite; the concentrations of all basic elements show up immediately; the shifting of the representative point of water occurs almost always following the

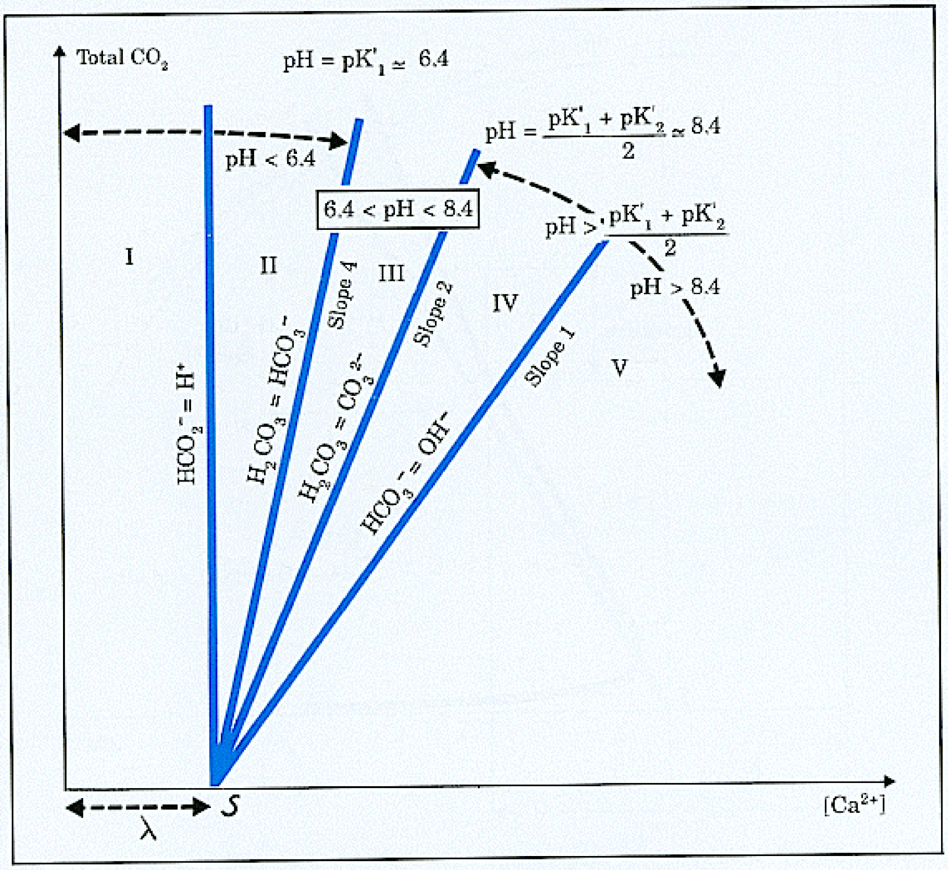


Figure 125. Delimitation of the various zones of the plane (example shown for water at 20°C).

lines or following the equilibrium curve. Finally, the treatment process is shown on this graph either by a displacement of the representative point or by a change in the equilibrium curve or by both at once.

Taking , $\frac{N\text{-}P}{2} = \lambda$

the equation of the electric neutrality (1) becomes: $(HC0_3^-) = 2\,[(Ca^{2+}) - ?] - 2\,(C0_3^{2-}) - (OH^-) + (H^+)$ and adding to each element of the equation $(H_2CO_3) + (CO_3^{2-})$:

total CO_2 =

$2\,[(Ca^{2+}) - \lambda] + (H_2CO_3) - (CO_3^{2-}) - (OH^-) + (H^+)$

In adopting the coordinates mentioned above, a graph is obtained whose plane is divided into areas limited by the main particular cases (corresponding to the set of curves pH = constant, which is a set of lines coming together at point S of abscissa ~,): Figure 125 illustrates these areas; practice demonstrates that the near totality of natural water (before or after treatment) is comprised in area III, that

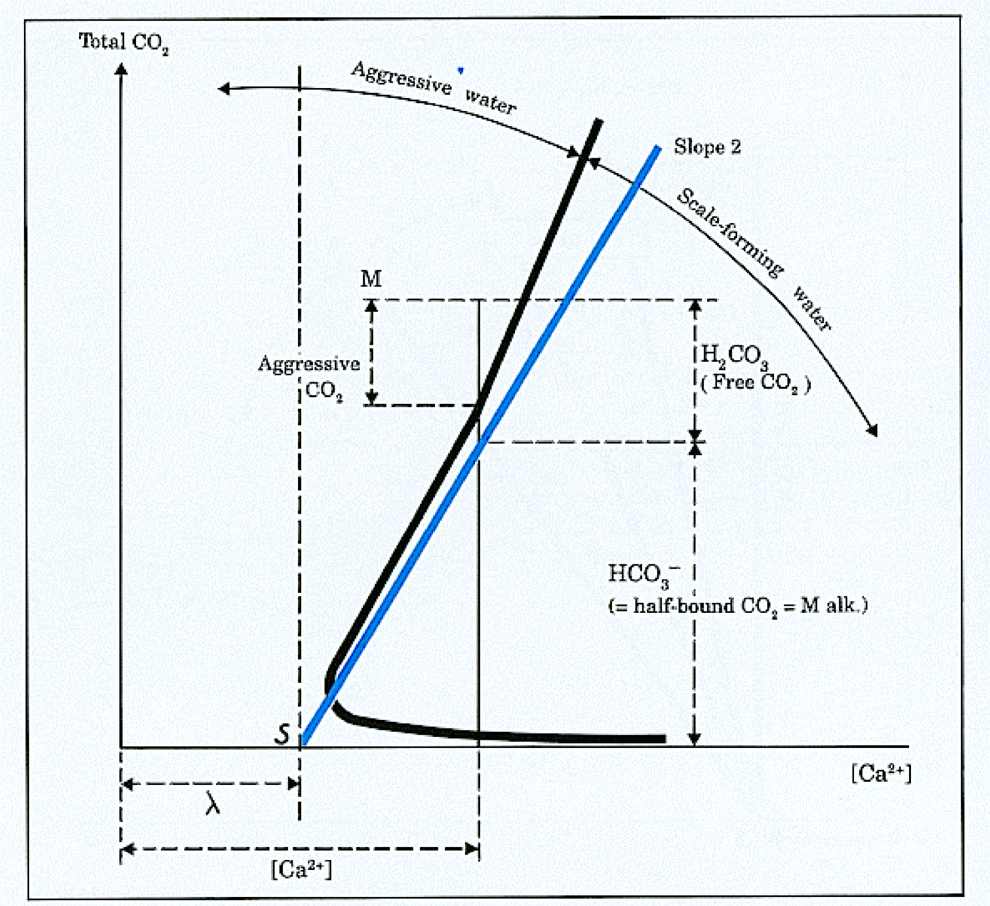


Figure 126. Representative point (M) and equilibrium curve.

is to say between the line of slope 4 (which corresponds to pH = pK'i = about 6.4 at 20°C) and the line of slope 2 (which corresponds to

$$pH = \frac{pK'_1 + pK'_2}{2} = \text{about } 8.4 \text{ at } 20°C).$$

The curve to which all the waters at equilibrium relate for given values of temperature and parameter λ, is the type shown in Figure 126; this figure, among other things, shows an example of figurative point M of a given water, which is assumed to be aggressive, with its position relative to the equilibrium curve and data which may be deduced as regards the characteristics of the ater (particularly the proportion of aggressive CO_2 in the total free CO_2 content).

The use of the graph makes it possible to predict the development of the system in all possible cases (with the amount of reagent doses if necessary) with or without changes in the equilibrium curve.

Apart from the Legrand and Poirier method, there are hardly any other methods that provide such thorough results. However, this method involves long calculations. Nonetheless, its use has been simplified and expanded through the use of the micro data processing.

13.2.
ACHIEVING CARBONATE BALANCE

First, it should be remembered that it is sometimes possible to correct the pH value by physical techniques involving gas and liquid phase mass transfer.

Particularly the processes involving the physical removal of carbon dioxide by aeration are described in sub-chapter 14, and so, only those cases which involve a chemical reaction in water to be treated will be considered here.

13.2.1. Addition of reagents

13.2.1.1. Neutralization through the addition of alkaline or alkaline-earth reagents

In the case of water intended for human consumption, the reagents most commonly used are caustic soda, lime or sodium carbonate. The reactions of aggressive CO_2 neutralization are therefore the following:

$2CO_2 + Ca(OH)_2 \rightarrow Ca(HCO_3)_2$

$CO_2 + NaOH \rightarrow NaHCO_3$

$CO_2 + Na_2CO_3 + H_2O \rightarrow 2NaHCO_3$

These same products are used in the treatment of industrial water, which also uses other specific reagents:

- lithium hydroxide in the nuclear industry,
- neutralizing amines (ammonia, cyclohexylamine, ethanolamine, morpholine, etc.) in boiler feedwater: during vapour condensation they combine with the dissolved carbonic acid to form an amine bicarbonate; the coefficients of the division of CO_2 between vapour and water phases are such that the applied dosages may be much lower than the stoichiometric amounts calculated based on the CO_2 actually released in the boiler; at low and medium pressures the dosage is in the order of 1 g per g of released CO_2; at high pressure following thermal deaeration, the dosages are about 1 g per m_3 of water,

- calcium carbonate in powder form for the neutralization of industrial wastewaters.

With carbonic acid these reagents cause the formation of bicarbonates. With strong acids from some industrial effluents, neutral salts are obtained.

Because of its low price, lime is the reagent most frequently used. When lime is used for the final adjustment of the pH value in drinking water, it is useful to employ a lime saturator to trap impurities and to provide a limpid lime water, whereas milk of lime always lends water a turbidity whose intensity depends on the degree of purity of the commercial product and the required amount of lime.

All neutralization treatments must be carefully monitored. It is often desirable to slave the reagent dosage to the result ant pH value in treated water. The efficiency of the treatment also depends on how well the neutralizing reagent is mixed with the water to be treated: thus, it is important to obtain an even mixture in reaction vessels equipped with stirrers.

This type of neutralization in drinking water treatment plants is carried out:

- either at the end of the treatment,
- or partly at the beginning. of the treatment (adjustment of the flocculation pH value for example) and continuing at the end of the treatment line,
- or sometimes entirely at the plant inlet (particularly in some cases of iron-manganese removal).

13.2.1.2. Acidification

The main applications of this technique are as follows: correction of scaleforming water, "vaccination" of industrial systems, treatment prior to desalination, neutralization of alkaline effluents and pH adjustment after softening by lime.

When CO_2 is used, the plant comprises: storage tanks or cylinders, a gas flowmeter and a dissolving tower. In other cases sulphuric acid and sometimes hydrochloric acid are used and these are fed by metering pumps.

13.2.1.3. Reciprocal neutralization

In some cases a chemical reagent may be dispensed with, when using the interaction of two or more waters with opposite characteristics:

- aggressive waters and scale-forming waters (however, additional reagent often has to be added to achieve the exact carbonate balance conditions),
- acidic and alkaline effluents (surface treatment, for example).

In this category we can also include those cases where acidic and alkaline waters are passed alternately through carboxyl resins.

13.2.2. Filtration on alkaline-earth products

This type of treatment which uses materials with a base of calcium carbonate mixed, where appropriate, with magnesium carbonate (dolomite) or magnesium oxide, is most often applied to the neutralization of aggressive carbon dioxide; the latter forms bicarbonates during the filtration process.

In the past it was common practice to use marble as the filtering material. However, because of its slow rate of reaction other products known under the commercial names of Neutralite, Neutralg, Magno, Akdolit, etc., are now preferred. The reaction kinetics of these agents give complete effectiveness with a relatively small compact mass.

Some of the products available on the market are calcined during their manufacture and therefore contain a high proportion of alkaline-earth oxides and give the treated water a high degree of alkalinity when they are first put into service which gradually diminishes in the course of time.

Neutralite and Neutralg, with no free bases, do not have these disadvantages and are indefinitely stable. They are available in various grain sizes and are composed of calcium and magnesium carbonates. Their special structure insures a rapid and uniform solubility which is always proportional to the amount of C02 to be neutralized.

Filtration through alkaline-earth materials is employed very often in deep-lying water where no other treatment is required, while the addition of products in slurry or solution form is generally incorporated in a complete treatment line (removal of iron and manganese from deep-lying water, clarification of surface water, etc.).

However, with this procedure the saturation pH cannot be exceeded to speed up the formation of the protective film which may require the additional injection of an alkaline reagent.

13.2.3. Consumption of reagents in the adjustment of carbonic acidity

Reagent	**Consumption of pure product per g of aggressive CO_2**	**Increase of hardness aggressive CO_2, in Fr. degrees**
Lime	0.84 g $Ca(OH)_2$ (0.85-1 g of commercial grade product)	0.11
Caustic soda	0.91 g NaOH	0
Sodium carbonate	2.4 g Na_2CO_3	0
Marble	2.3 g $CaCO_3$	0.23
Magnesium oxide	0.45 g MgO	0.11
Neurralite	2-2.2 g	0.23

13.3. REMINERALIZATION

13.3.1. Purpose

Remineralization results in an increase in the M alk. and/or the CaH. It is also referred to as recarbonation. It is most often used to promote the formation of a protective film inside a pipeline. It may also be used as an aid to help process water to meet the standards of quality or to improve the organoleptic (and sanitary) quality of some waters used for consumption (evaporator water).

This stage of treatment is generally designed to take place at the end of the line (fresh ground water or water having undergone desalination treatment). It may also be of use to enlist this treatment step at the beginning of the line for fresh and coloured surface water requiring a complete clarification treatment. This enables a better monitoring of the flocculation pH value and, if necessary, an improvement in the flocculation quality.

13.3.2. Process

To achieve the recommended and CaH values, various techniques may be used depending on the initial quality of the water, the size of the plant and the treatment materials that are locally available.

13.3.2.1. Carbon dioxide and lime

This is the technique most commonly used when the quality of water requires that there be a simultaneous increase of M alk. and calcium in medium and largesize plants.

About 8.8 g Of CO_2 + 5.6 g of CaO or 7.4 g of $Ca(OH)_2$ should be added per degree of M alk. and per m^3 of water.

The carbon dioxide is usually introduced into the contact tower through porous diffusers under a head of water several metres high. In the case of water for industry, CO_2 may be taken from engine exhaust or a flue and, if necessary, scrubbed in a trickling column. It is also possible to use submerged burners to burn a liquid or gaseous hydrocarbon in the liquid itself.

The quantities of fuel required to generate 1 kg of CO_2 are: coke 350 g, fuel oil 450 g. However, only commercial liquid CO_2 ensures a higher-purity product (such as in the case of drinking water).

The lime must be prepared in a saturator in the form of lime water when a clear water is being remineralized at the end of the treatment line. Depending on the initial M alk. of the water to be treated, it is sometimes preferable to inject the lime following the carbon dioxide to avoid removal of carbonates from the water at the point of lime injection.

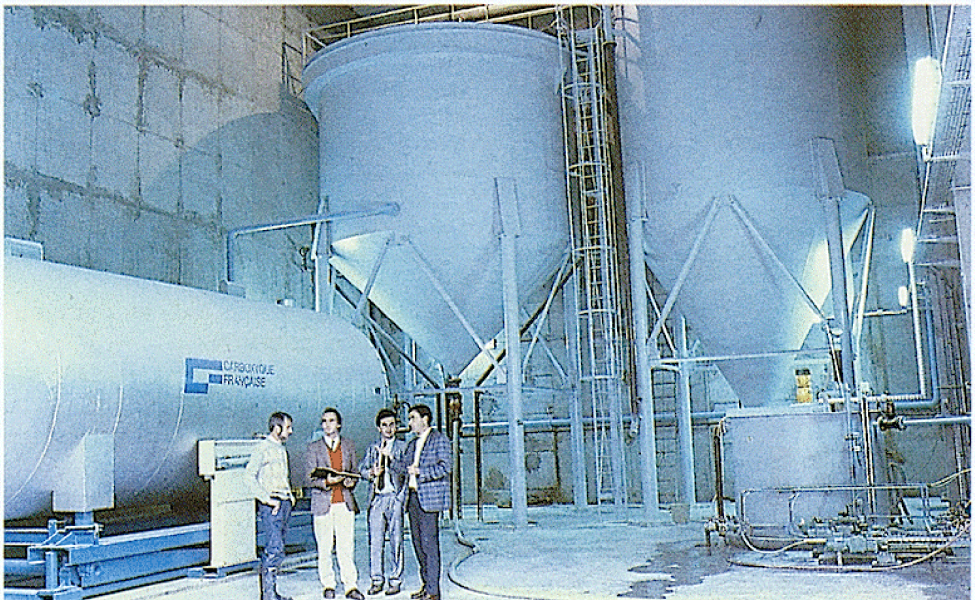


Figure 127. Treatment plant at Dorlay (Central France). Flow: 625 $m^3.hr^{-1}$. Facility for remineralization by injection of CO_2 and lime.

13.3.2.2. CO_2 and filtration through neutralizing materials

In this case carbon dioxide consumption is reduced (4.4 $g.m^{-3}$ 3 per degree of remineralization) and the process runs more smoothly. However, contrary to the CO_2 and lime processes, the saturation pH cannot be exceeded, even when this is necessary.

13.3.2.3. Sodium bicarbonate and calcium salt

HCO_3 bicarbonate ions (as sodium bicarbonate) and Ca 21 calcium ions (generally as calcium chloride, though sometimes as calcium sulphate) are introduced into the water simultaneously.

To obtain an increase of 1 French degree in 1 m3 of water, 16.8 g of sodium bicarbonate must be used with either:

- 11.1 g of calcium chloride (as $CaCl_2$),
- or 13.6 g of calcium sulphate (as$CaSO_4$).

For this last process, unfired gypsum may be placed in contact with the water in order to prepare a saturated solution containing 2.3 g of $CaSO_4.2H_2O$ or 1.8 g of $CaSO_4$ per litre.

Calcium chloride has the advantage of being easier to use due to its solubility. However, it introduces Cl^- ions into the water which, when added to a pre-existing concentration that is already high, may reverse the effects of the remineralization treatment by exerting an influence on the corrosion processes.

Unless a high degree or remineralizationization has been achieved, this type of treatment usually must be completed by an injection of an alkaline reagent in order to reach the saturation pH. These treat-

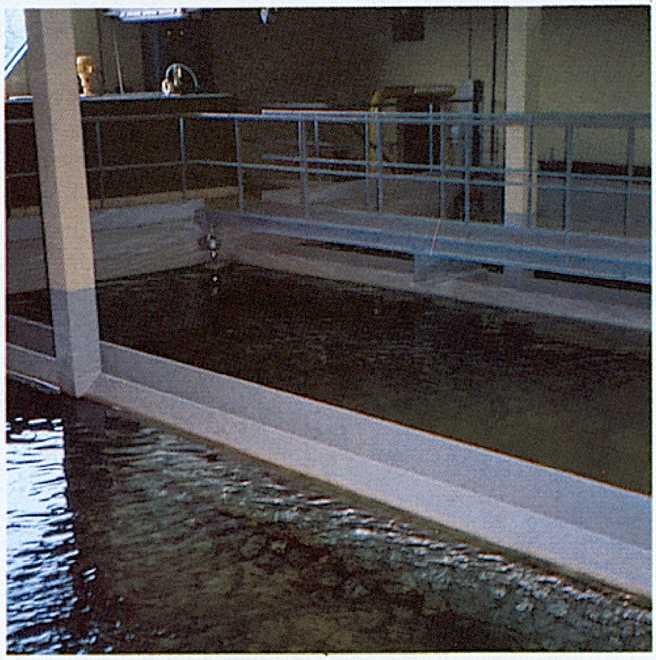


Figure 128. Epinal treatment plant (Eastern France). Flow: 300 $m^3.hr^{-1}$. Mineralization treatment by CO_2 injection and filtration through Neutralite. 3 filters of 28.5 m^2.

ments which require a small initial outlay (preparation tanks and metering pumps) lead, however, to high operating costs. These techniques are usually used with small and medium-size plants.

13.3.2.4. Miscellaneous

Depending on the quality of the water and the availability of local materials, the following techniques may sometimes be employed:

- sodium bicarbonate + lime or sodium carbonate
- sodium carbonate and carbon dioxide,
- sulphuric acid and calcium carbonate.

14. GAS AND LIQUID PHASE MASS TRANSFER

Among the techniques of water treatment there are many which cause the transfer of water between two phases, the liquid and the gas phases.

These mass transfers consist in causing a constituent (referred to as a solute) to change from one phase to the other. They may be divided into two categories:

- **absorption** involves the transfer of constituents from the gas phase into the liquid phase. It involves either the dissolving of a gas (air, oxygen, ozone, chlorine) in water in order to treat the latter: biological purification, iron removal, disinfection; or the dissolving of a polluting gas (H_2S, SO_2 and sulphur products, NOx, NH_3 and volatile organic products, HCl, etc.), in a liquid solution in order to purify the gas phase: gas scrubbing.

Absorption is often associated with a chemical reaction;

- **desorption** involves the reverse process whereby volatile gases such as CO_2, O_2, H_2S, NH_3, chlorinated solvents, which are dissolved in liquid are made to change to the gas phase such as in stripping and deaeration

The desorption process takes place without a chemical reaction.

The liquid-gas system, however, always follows the laws of mass transfer from one phase to the other until a state of equilibrium is ultimately reached.

14.1

THEORETICAL BASES OF GAS AND LIQUID PHASE MASS TRANSFER

The principal laws governing gas and liquid phase mass transfer are:

- in the liquid phase, **Henry's law** which, for a given temperature, links the partial pressure p of a gas to its mole fraction x in the liquid phase:

$p = Hx$ with H being Henry's constant.

Henry's constant for the main gases is given in Chapter 8, page 509:

- in the gas phase, **Dalton's law** and the law of ideal gases.

Hence, for a mixture of gases occupying a volume V at a temperature T under a pressure P and consisting of $m_1, m_2, \ldots, m_n$

specific amouns of gases of respective molecular weights Ml, Mz ... M,, exerting partial pressures pl, pz ... p,,, the following may be expressed:

$$P = p_1 + p_2 + p_3 ... + p_n$$

$$\frac{p_1\, M_1}{m_1} = \frac{p_2\, M_2}{m_2} = ... \frac{p_n\, M_n}{m_n}$$

- for the transfer: **Whitman and Lewis theory** calculates the overall flux N of gas transferred through the exchange surface area S when there is no accumulation at the interface:

$$N = k_L.S.\,(C_{il} - C_l) = k_g.S.\,(C_g - C_{ig})$$

(see Figure 129).

Cl and Cg are the gas concentrations in the liquid and gas phases respectively. Only C_l and C_g are accessible to measurement.

Cd and Cig are the concentrations at the interface, with kL and kg being the transfer coefficients in the liquid and gas phases depending on the interface and the state of turbulence.

These laws point out the essential factors involved in an efficient transfer:

. maintaining a strong concentration gradient between the liquid and gas phases and the interface. This gradient acts as a driving force,

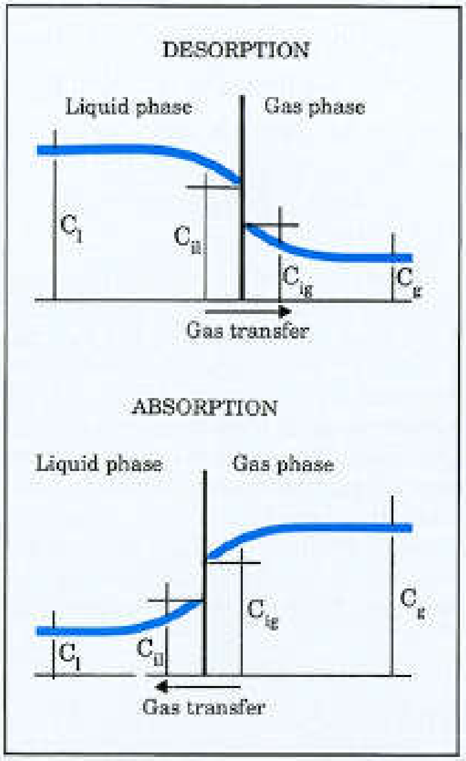


Figure 129. Gas and liquid phase mass transfer.

. creating a gas/liquid interface that is as extensive as possible,

. using a powerful state of turbulence and stirring.

14.2.
GAS DISSOLUTION (ABSORPTION)

The purpose of this process is to treat a water (iron removal, disinfection, biological purification) or to purify a polluted gas. The gases to be dissolved are usually not very soluble and their resistance to transfer comes from the liquid film, so that the following equation may be written:

$$N = \frac{dm}{dt} = k_L.S\;(C_s - C_l)$$

where:

M: mass of gas transferred,

Cs: saturation concentration of the gas and the liquid, G: concentration of the gas in the liquid. If

V is the volume of the liquid, then:

$$\frac{dm}{dt} = V\,\frac{dC}{dt}$$

hence:

$$\frac{dC}{dt} = k_L\,\frac{S}{V}\,(C_l - C_s)$$

In practice, this factor $k_L \frac{S}{V}$ is referred to as KL a **coefficient of mass transfer.** $a=\frac{S}{V}$ is the specific exchange area.

If CS and G are expressed in $mg.l^{-1}$, K_L a is expressed in s .

Usually in water treatment, absorption takes place with a chemical reaction that is often an oxidation reaction of varying speed (e.g.: Fe" oxidation, disinfection, the oxidation of organic matter with or without bacterial respiration, etc.). In the case where the gas reacts strongly with some of the constituents present in the water, the coefficient of mass transfer is higher than that found in pure water. Not only should the solubility and the diffusion ability of gas be taken into account but also the chemical kinetics.

The main two types of dissolution to be considered are:

- that which occurs entirely within the liquid itself, requiring a large volume of compressed gas which is diffused by **bubbling.** This type is mainly used for oxidation and disinfection with ozone, and oxygenation of activated sludge (biological purification),
- that which occurs entirely at the surface of the liquid by the multiplication of interfaces by means of **Contact media or Packed** columns usually operating at near atmospheric pressure such as in the case of gas scrubbers.

Mixed techniques that combine these two dissolution processes also exist: for example iron removal columns, Nitrazur N and Biofor reactors.

14.3.
STRIPPING (DESORPTION)

This involves extracting gases dissolved in water so as to transfer them to a gas phase in order to obtain a deaerated water with very low level of dissolved gas. The gases extracted from the liquid phase are stripped by a large countercurrent of gas known as stripping gas. In order to implement the degasification process the content of gas to be removed in the stripping gas must be virtually nil. Application of the laws of transfer illustrates that to obtain a very low level of dissolved gas, it is necessary to:

-lower the mole fraction of the gas considered in the gas phase: stripping of CO_2 using air,

-lower the total pressure involved in the gas phase: vacuum deaeration of oxygen and CO_2,

- increase Henry's constant, such as in thermal deaeration at a high temperature (O_2, CO_2).

Most of the dissolved gases previously mentioned are slightly soluble in water and it is the transfer into the liquid phase that determines desorption. In the case of highly soluble gases, such as NH3, desorption is controlled by the gas phase. The industrial equipment most commonly used is the packed columns, the calculation of which is similar to that of the distillation columns.

The packing height H required for stripping may be calculated either:

- by the product H = HTU x NTU (as in the case of slightly soluble gases),

HTU is the height equivalent to a transfer unit and depends on the parameters of the packing, NTU is the number of transfer units and depends solely on the initial and final concentrations and on the interface at the various stages,

- or by the product H = HETP x NTP (in the case of highly soluble gases),

NTP is the number of theoretical plates as determined by analytical or graphic calculation,

HETP is the height equivalent to one theoretical plate, which mainly depends on packing.

In order to remove oxygen the number of transfer units (or stages) varies according to the saturated waters at 15°C, from 8 to 12 for final concentrations of 50 to 10 $\mu g.l^{-1}$.

The desorption of CO_2 is not so extensive. In a demineralization facility a reduction in CO_2 concentration of 70 down to 10 $mg.l^{-1}$ requires less than two stages.

15. LIQUID/LIQUID EXTACTION

The liquid/liquid extraction process is a basic operation that allows a component (solute) to be extracted from an inert liquid by another liquid known as a solvent:

Inert liquid + solute:	liquid phase 1 ↘	Extraction	↗ Solute + solvent
Solvent:	liquid phase 2 ↗	Liquid-liquid	↘ Inert liquid + traces of solute

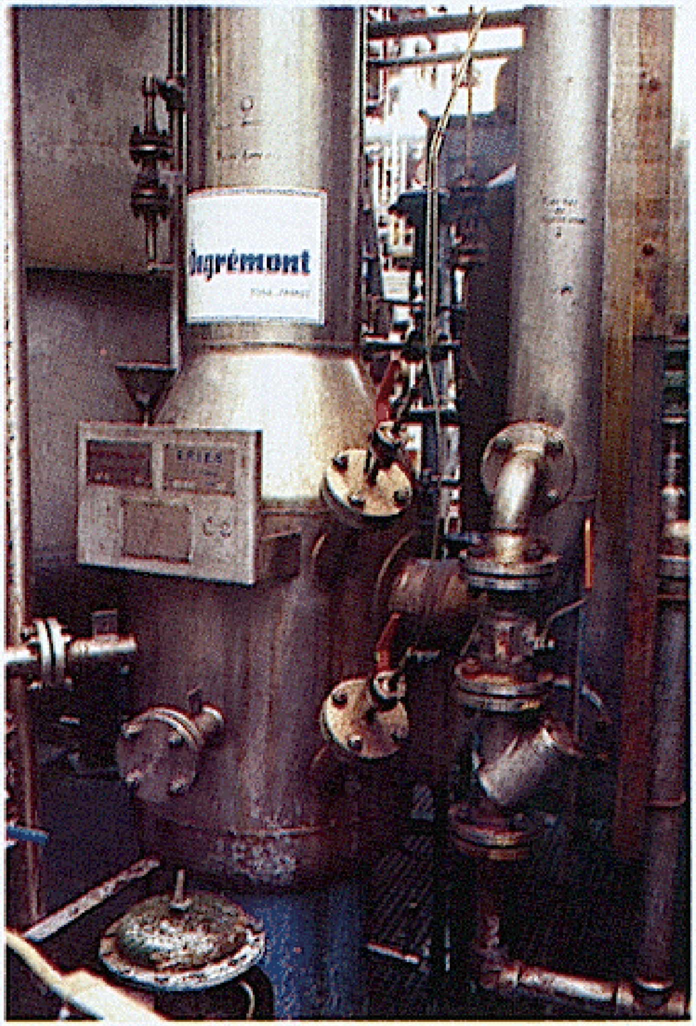


Figure 130. Lindsey refinery (Great Britain). Treatment of spent caustic soda by stripping and solvent extraction.

The liquid phase 1 is a homogeneous mixture. The solvent must not be miscible with one of the two initial compounds. The inert compound and the solvent are usually not miscible.

The liquid/liquid extraction is also governed by the laws of mass transfer and it is necessary to determine features that favour exchange, such as maximum interfacial area, wide concentration difference and a notable transfer (or extraction) coefficient.

There are two main types of industrial equipment employed in the liquid/liquid extraction process:

- contactors with several separate stages in series. At each stage, the functions of dispersion followed by separation of the two phases take place in two successive units: the mixing-settling tank and the hydrocyclone-settling tank,
- differential contactors in which one phase is dispersed into the other on a countercurrent basis. Following this, the phases are separated in the two ends of the vertical column (see Figure 131).

The method of dispersion of the two phases may be by gravity, mechanical stirring, pulsation, etc.

Liquid/liquid extraction is used it! phenol removal from spent caustic soda from refineries using gas oil as a solvent. The efficiency of phenol removal is high (90-95%) when pulsed columns with perforated trays are used.

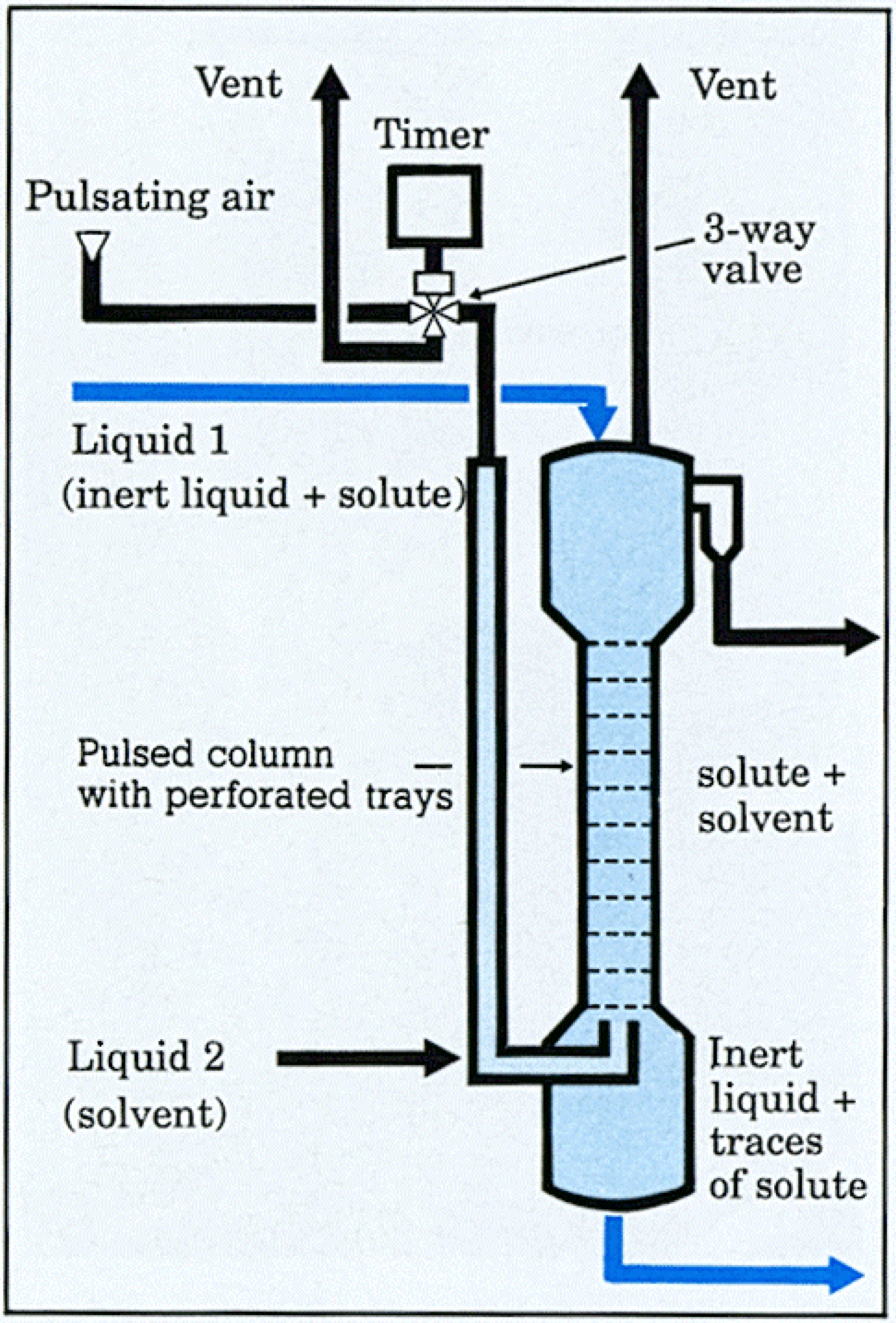


Figure 131. Diagram of a pulsed column.

4

BASIC BIOLOGICAL PROCESSES IN CATER TREATMENT

1. GENERAL

The biological treatment of water involves various types of **fermentation.** Fermentation is the deterioration of certain organic substances and is often accompanied by the release of gases due to the action of the enzymes that are secreted by microorganisms.

1.1.

GROWTH OF A BACTERIAL CULTURE

After being seeded, a bacterial culture continues to grow until the nutrients in the medium are used up, provided that the environmental conditions are favourable. Figure 132 illustrates the variation of **X, the concentration of a bacterial culture,** in terms of mass per unit volume as a function of time t, under constant conditions of temperature, pH, etc. Several phases occur in succession:

. Lag phase

During this acclimatization phase, the cell synthesizes mainly those enzymes that are required for the metabolization of the substrate. This phase is especially important when the water has not previously been seeded with suitable microorganisms. This may be the case in certain industrial effluents. During this phase, there is no cellular reproduction.

$$X=C=X_o$$

Where, X_o is the cellular concentration at time t = 0: the growth rate is therefore zero:

$$\frac{dX}{dt} = 0$$

. Exponential growth phase

This phase occurs when the cellular reproduction rate reaches its maximum and remains constant in the presence

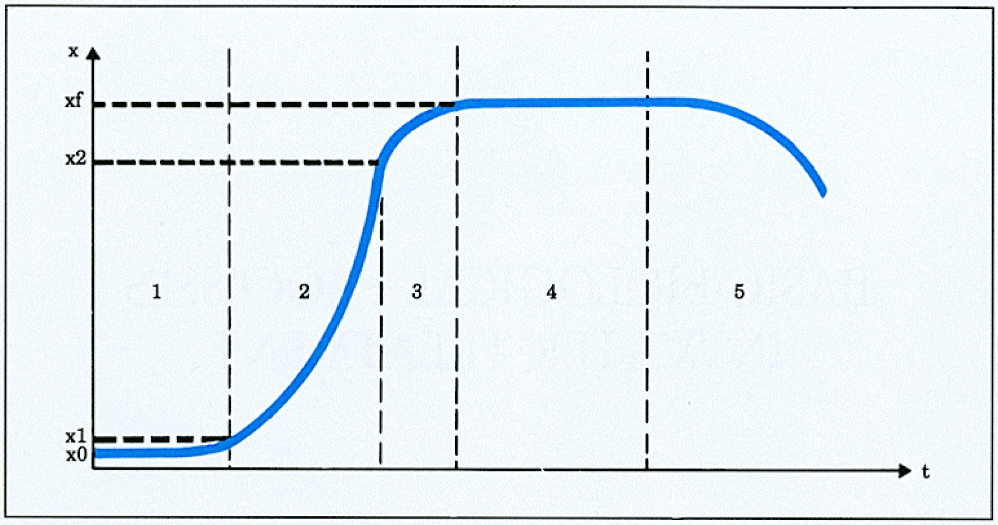


Figure 132. Growth of a bacterial culture.

of a non-limiting concentration of the substrate. This phase is measured by the generation time tg (or doubling time), which corresponds to a doubling of the bacterial population, which thus has its minimum value. During this phase, the growth rate, dX/dt, increases in proportion to X, resulting in the exponential form of the curve. In semi-logarithmic coordinates, the curve takes the form of a straight line with the following equation:

$$\frac{dX}{dt} \cdot \frac{1}{X} = \mu_m$$

where μm is the maximum **growth rate**. Or:

$$\text{Log}\,\frac{X_2}{X_1} = \mu_m\,(t_2 - t_1)$$

where t_g is given for $X_2 = 2X_1$:

$$t_g = \frac{\text{Log}2}{\mu_m} = \frac{0.693}{\mu_m}$$

. Declining growth phase

This phase comes about with the depletion of the culture's medium and the disappearance of one or more elements necessary to the bacterial growth. In some cases, growth is slowed by the accumulation of inhibiting products resulting from bacterial metabolism. X continues to increase, but dX/dt decreases.

. Stationary phase

X reaches its maximum value, X_{max} Growth comes to a halt even if the cells maintain some metabolic activity.

. Endogenous phase

The concentration of living cells decreases because of an increasing mortality rate. The enzymatic autolysis of the cells causes them to die.

These various phases and the equations that govern them are applicable to aerobic and anaerobic media. The values of the various coefficients depend, of course, on the nature of the microorganisms, the substrate, and various factors, such as temperature and pH.

1.2.
BACTERIAL GROWTH MODELS

In most industrial applications, the biomass is in the declining growth phase because the required levels of pollution control result in weak final concentrations of the substrate. Several mathematical models have been proposed to integrate the part of the curve corresponding to the declining growth phase and beyond. However, most perfected models attempt to cover the total growth curve.

Monod's model is the oldest, the best known, and the most widely used. It is an empirical model, very close to the Michaelis-Menten equation for enzymatic reactions. It is expressed as follows:

$$\frac{dX}{dt} = \mu X$$

where $\mu = \mu_m . \left(\frac{S}{K + S}\right)$

where S is the concentration of the solution in the growth-limiting substrate.

K signifies a concentration threshold below which the growth rate becomes closely dependent on the concentration of substrate. This constant corresponds to the value of S for which $\mu = \frac{\mu_{max}}{2}$

K is usually very small, and during the entire exponential growth phase, $\mu = \mu_{max}$

It must be emphasized that in the case of bacterial growth involving other strains of microorganisms, the measured value of g is in fact a resultant g. At any given moment, some bacteria may be in a different growth phase from other bacteria.

Other models are used for specialized studies such as pure cultures and the use of a metabolite.

1.3
THE ACTIVITY OF A BIOMASS

In every fermentation process the mass of microorganisms present is an important factor, but another equally important factor is their activity. The goal is to optimize the product mass of microorganisms x specific activity.

Several methods have been suggested to measure the activity of a biomass. The ATP (adenosine triphosphate) measurement has been all but abandoned by water treatment specialists because the results are difficult to interpret. The measurement of the dehydrogenase activity is hindered by the dispersion of the results, while the measurement of DNA (deoxyribonucleic acid) involves a long and painstaking dosing process.

Respirometric methods are used most often (see Page 367).

1.4.
ELIMINATION OF THE SUBSTRATE

With a given mass of microorganisms, the elimination of substrate S, as a function of time, may occur at different rates.

The concept of reaction order is generally used. A reaction is said to be of zero order if dS/dt is constant, which means that the reaction rate is independent of the substrate concentration. The opposite of this is a relation of the type $dS/dt = K. S^n$, where the reaction is said to be of nth order.

In water treatment, the development of S as a function of time, for a given constant mass of microorganisms, often corresponds to the curve in Figure 133.

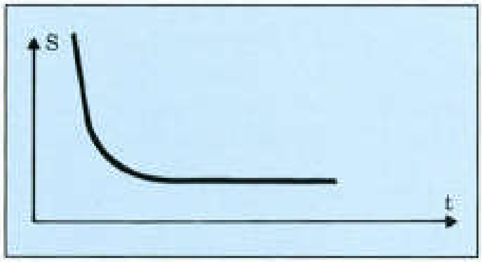


Figure 133. Elimination of substrate.

Initially, the reaction is of zero order. Once the substrate concentration drops below a certain value, the order of the reaction changes, i.e., the rate at which the substrate disappears drops. This means that the final substrate fractions are often difficult to eliminate.

The first phase corresponds to complex biosorption and flocculation of colloidal matter phenomena. Subsequently, the disappearance of substrate is linked to its interaction with the microorganisms.

1.5.
AEROBIC AND ANAEROBIC GROWTH

Biological processes used in water treatment applications simply harness natural phenomena. There are two ways of controlling removal of pollutants from effluents:

- with **aerobic processes** when oxygen is involved in the reactions. These processes occur spontaneously in water that is sufficiently aerated. Organic carbon is transformed into COz and biomass;
- with **anaerobic processes** when the reaction takes place without air, in a reducing medium. After degradation, organic carbon exists in the form of CO_2, CH_4 and biomass. Because of the low redox potential, nitrogen occurs in the shape of NH_3, and sulphur in the form of H_2S or the various types of organic sulphur compounds, such as mercaptans.

It is usually possible to illustrate the degradation of glucose in these two processes:

$$C_6H_{12}O_6 \xrightarrow[\text{in aerobic conditions}]{} 6CO_2 + 6H_2O + 2.72\ \text{kJ.mol}^{-1}\ (650\ \text{cal.mol}^{-1}).$$

$$C_6H_{12}O6 \xrightarrow[\text{in anaerobic conditions}]{} 3CO_2 + 3CH_4 + 0.144\ \text{kJ.mol}^{-1}\ (34.4\ \text{cal.mol}^{-1}).$$

In the synthesis of one gramme of biomass, which requires the same input of energy whichever process is used, the rate of generation of aerobic nuclei is higher than that of anaerobic nuclei, and the degradation process of the carbonaceous matter is more rapid. On the other hand, less sludge is produced in anaerobic conditions.

The term **anoxia** is generally applied only to an environment practically devoid of dissolved oxygen, but in which acid and anaerobic fermentation does not occur.

1.6.
TOXICITY AND INHIBITION

Successful fermentation, whether aerobic or anaerobic, requires rather stringent conditions concerning the medium. The temperature and the pH play particularly important roles. Equally important, the medium must not contain any toxic products or inhibitors that may slow the process or irreversibly halt bacterial activity.

Most heavy metals act as toxins on bacterial flora. This is especially true of copper, chromium, nickel, zinc, mercury and lead. These metals act by attaching themselves to certain enzymatic sites and blocking them, or by denaturing certain enzymes or, lastly, by changing the permeability of the cellular membrane.

Anions such as cyanides, fluorides, arsenates, chromates and dichromates all behave in a similar way. Halogens and certain organic compounds may also denature proteins or other cell components.

Bacteria are not equally sensitive to different toxins. Their sensitivity to a given product also depends on their physiological state. Some strains are even capable of degrading toxins such as cyanide and phenols.

In practice, it is often possible to acclimatize a bacterial growth to the presence of toxins or inhibitors and thus lower the toxicity thresholds. Certain metals attach themselves to bacterial floc in the form of insoluble organometallic compounds without disturbing bacterial growth. It should be noted, however, that excessive levels of these metals in sludge may render the sludge unsuitable for agricultural use.

Above a certain threshold, certain metabolites may themselves inhibit bacterial activity.

1.7. SALIENT FEATURES OF BIOREACTORS

1.7.1. Suspended growth and attached growth

Bacterial growth may be used in many different ways. Traditionally, a distinction is drawn between "suspended growth" and "attached growth" processes.

Suspended growth processes, used solely for treating wastewater, stimulate the growth of a bacterial culture dispersed in floc form in the liquid being treated. The culture is kept in suspension in a stirred tank in which one of the following conditions exists:

- a given concentration of oxygen, in the case of aerobic processes such as activated sludge and aerated or natural lagoon processes;
- the exclusion of oxygen, in the case of anaerobic processes such as contact-clarification, sludge blankets, and anaerobic lagoon processes.

Attached growth processes make use of the ability of most microorgan isms to produce exopolymers, which enable them to become fixed to widely varying supports so as to form a biofilm. Attached growth, like suspended growth, may be used in either aerobic or anaerobic treatment (fine granular media biofilters, trickling filters, biological discs, etc.).

Suspended growth has the basic advantage of being easy to use. However, since the concentration of microorganisms cannot exceed certain limits, suspended growth processes require structures that can hold large volumes of liquid.

Reactors can be smaller when attached growth is used, because higher concentrations of biomass, and at times higher activity levels, can be obtained.

It should be noted that in suspended growth as well as in attached growth there is an excess production of biomass, which must be extracted, treated and disposed of

1.7.2. Dispersion and hydraulic retention time

Another important distinction, especially in suspended growth processes such as those involving activated sludge, must be made between the homogeneous or completely mixed bioreactor and the heterogeneous bioreactor, such as the **plug flow type.** A bioreactor is said to operate as completely mixed when the concentrations (biomass, substrate, oxygen, etc.) and the temperatures are identical throughout the reactor. In plug flow bioreactors, the channels have a high length-to-width ratio and axial concentration gradients exist.

In an ideal plug flow reactor, all the particles entering the reactor at a given moment are thereafter continuously subject to identical hydraulic conditions (velocity and direction). The hydraulic retention time is theoretically the same for all the particles, whereas in a completely mixed reactor the distribution of the retention times for the particles is Gaussian.

These hydraulic factors are important because they may affect the reaction kinetics and may even encourage the growth of particular bacterial species.

Reaction kinetics

Theoretical considerations indicate that, for a unit containing a given volume and when the reaction order is greater than zero, the reactions in a plug flow bioreactor will be more advanced than those in a completely mixed bioreactor, in other words, that plug flow reactors can be smaller than completely mixed units.

Dispersion coefficient

On an industrial scale, there are no bioreactors that are strictly of either the completely mixed or the plug flow type. However, some units are approximately equivalent to one type or the other. In order to measure just where the units are positioned in this respect, a longitudinal dispersion coefficient is used. A value of zero signifies a perfect plug flow, while an infinite value corresponds to a perfect complete mixing.

Hydraulic retention time

Given that:

t_t is the theoretical retention time given by $t_t = V/Q$, where V is the volume of the reactor and Q is the flow,

and t, is the weighted average real retention time, the response curve may be drawn after instantaneous injection of a tracer.

A number of cases may arise:

- $t_t < t_t$ (Figure 134).

This case is an indication of the **dead zones** in which stagnant water plays little or no part in the various reactions. This phenomenon is usually reflected in the curve by a decline.

- $t_t = t_t$.

In this case the complete geometrical volume is traversed by water.

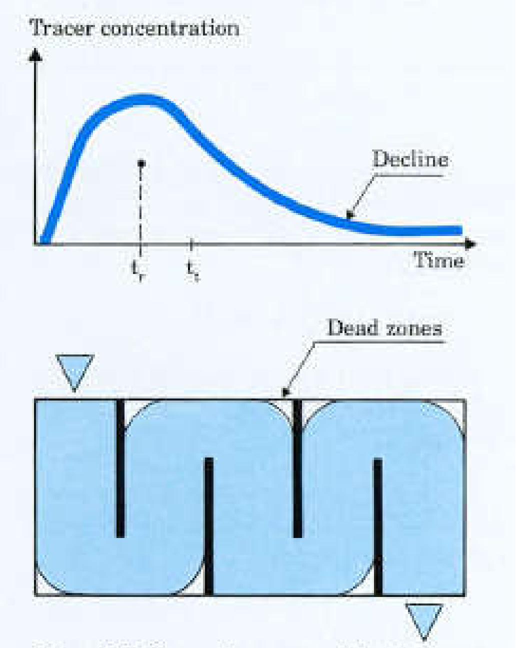


Figure 134. Curve of a reactor with dead zones.

- $t_t = t_t$., (Figure 135)..

This result indicates that there is a **short-circuit** inside a reactor, if t, is the average retention time of water having actually passed through the reactor.

The use of bioreactors in the treatment of water that operate under increasingly intensive conditions requires that all these hydraulic concepts be taken into consideration.

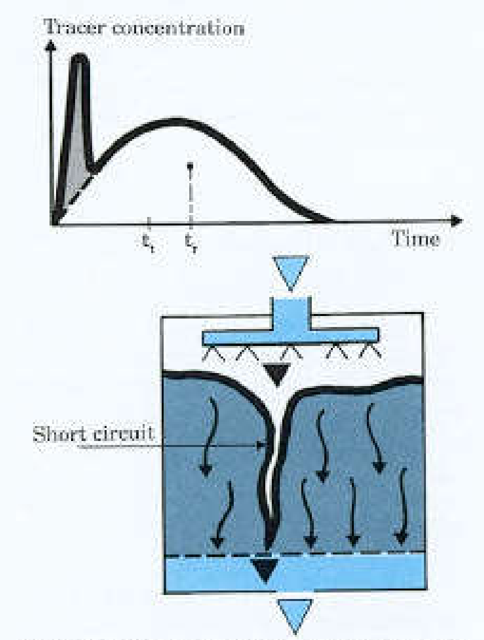


Figure 135. Tracer curve of a reactor with short circuiting.

1.8.
PROPERTIES OF THE SUBSTRATE

A substrate is a group of products that is contained in water and is liable to be used by bacteria for growth. These elements may be classified in the following way:

- major elements: C, H, O and N;
- minor elements: P, K, S and Mg;
- vitamins and hormones;
- trace elements (Co, Fe, Ni, etc.).

In the particularly complex environment of most types of wastewater there are usually sufficient concentrations of the trace elements, vitamins and hormones for proper purification to take place. The same is true for K, S and Mg. On the other hand, there may not be enough phosphorus or even nitrogen, in which case they must be added. These elements may have to be removed, in order to combat eutrophication (see Page 30).

In order to treat an effluent by biological means, it must have properties that are compatible with bacterial growth: suitable pH and temperature, no inhibitors or toxins.

1.8.1. Carbonaceous pollution

(see page 18)

Organic carbon is usually the main pollutant that must be removed. Organic carbon is also the principal constituent of the biomass, a highly simplified formula being $C_5H_7NO_2$. Because there are so many different forms of carbonaceous pollution, it is usually described in terms of global characteristics.

Figure 136 shows changes in BOD versus oxidation time. About twenty-one days at 20°C are needed for complete oxidation, at which point the ultimate BOD, or the BOD_{21}, is obtained.

If all the organic matter in a water was biodegradable, then:

$$COD = BOD_{21}$$

This is the case for glucose, where:

$$\frac{DBO_{21}}{DBO_5} = \frac{DCO}{DBO_5} = 1{,}46$$

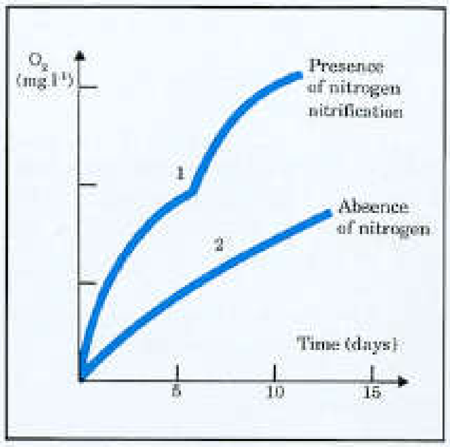


Figure 136. Changes in BOD.

When there is non-biodegradable organic matter, as in the case of domestic wastewater and many types of industrial waste, then:

$$COD > BOD_{21}$$

Examples of non-biodegradable organic substances are cellulose, lignin, tannins, sawdust, etc.

During a biological treatment process, the COD/BOD_5 ratio of the effluent increases substantially.

1.8.2. Nitrogenous pollution

Practically all sources of organic and inorganic nitrogen can be used by various microorganisms. When metabolized, nitrogen produces essentially proteins, nucleic acids and the polymers of cell walls. Nitrogen can be said to represent approximately 12% of the dry weight of a pure biomass. In the case of wastewater treatment, this value usually drops to below 10%.

The following types of nitrogen are found in wastewater:

- **reduced forms,** which correspond to Kjeldahl nitrogen: organic N, $N\text{-}NH_4^+$ (ammonia nitrogen).
- **oxidized forms:** $N\text{-}NO_2$ (nitrous nitrogen), $N\text{-}NO_3^-$ (nitric nitrogen).

The term "total nitrogen" is often used in wastewater treatment to refer to the sum of all reduced and oxidized forms.

1.8.3. Phosphorous pollution

Phosphorus is present mainly in nucleic acids, phospholipids and polymers of bacterial walls. In certain cases, it may be stored in the cell in the form of polymetaphosphate (for biological phosphate removal, see Page 303). A very small fraction of the phosphorus is in the form of diffusible organic phosphorus, such as ATP (adenosine triphosphate).

Phosphorus accounts for 1.5 to 2% of the dry weight of a biomass. It should be noted, however, that this percentage rises with the growth rate and varies inversely with the temperature.

Phosphorus may be present in wastewater either in the form of orthophosphate, polyphosphate or organic phosphorus. Similarly, the term "total phosphorus" is used to refer to the sum of all forms of phosphorus.

1.9.

POLLUTION AND THE RECEIVING MEDIUM: THE IMPORTANCE OF MODELS

The consequences of discharging pollution in a receiving water can be estimated by direct, on-site measurements, but this is usually performed for only a very limited range of hydraulic conditions.

On the other hand, in order to project the influence that future discharges or accidental spills would have, or to set up a programmed reduction of pollution discharges, the use of mathematical models is indispensable. The models currently used are based on:

- the re-oxygenation of the aqueous environment (from the air and by photosynthesis of aquatic plants and algae);
- the oxidation of organic matter and of reduced forms of nitrogen.

The purpose of these models is to determine the changes in the levels of dissolved oxygen and in BOD_5 (or TOC), $N\text{-}NH_4^+$, etc., downstream of the point of discharge.

The formulae proposed are almost entirely based on experience. The reaeration constants in river water depend mainly on the velocity and the depth of the watercourse. Using models of reduced forms of nitrogen remains risky because of the uncertainty in defining the polluted flows (especially those from agricultural operations) as well as the complexity of nitrification phenomena. Substantial difficulties arise when the changes in river sediments are taken into account.

Models have probably been most successful in the field of eutrophication of lakes.

1.10. BIOLOGICAL PERSPECTIVES

Progress in biotechnology is evidenced by the appearance of new techniques in **enzymatic, immunological and genetic** engineering. These new techniques hold great promise for the water treatment sector, even if some of them remain to be perfected or may appear unrealistic because of the complexity of the substrates to be treated.

One interesting method is to use the specific features of the enzyme either to accelerate the degradation of particular substances that are present in high levels or to develop biological sensors or probes. These systems, based on the attachment of enzymes or microorganisms to a membrane, should provide for rapid and selective measuring of pollutants or micropollutants (such as pesticides, etc.). Other techniques will be able to make use of methods of immunity recognition to detect microorganisms even in very low concentration (for the treatment of drinking water).

It is also tempting to use biotechnology to generate microorganisms capable of removing the pollution from effluents with kinetics that are much higher than normal levels, or to degrade substrates that have thus far eluded conventional methods.

However, the production and use of these "mutant" bacteria on an industrial scale also pose some difficult problems:
- competition with natural microorganisms;
- their behaviour in the presence of the large number of substances to be degraded;
- leakage of these microorganisms into the natural environment.

On the other hand, isolating and producing microorganisms taken from the natural environment so as to introduce large numbers into environments where they are lacking, may be a means of accelerating a selection and purification process that would otherwise be too slow.

2. AEROBIC BACTERIAL GROWTH

Aerobic treatment facilities have long been designed empirically by rule of thumb: 150 to 200 litres of aeration tank per population equivalent or 100 litres of trickling filter per population equivalent, etc.

A more rational approach to planning and designing such facilities is now possible thanks to:

- on the one hand, the benefits of microbiological studies, which, by explaining many phenomena, have perfected the original treatment processes for removing not only carbonaceous pollution, but also nitrogenous and phosphorous pollution;
- on the other hand, the development of fermentation technology that makes it possible to determine more precisely the principal parameters of a facility, such as hydraulic circuits, tank capacity, oxygen requirements, sludge production, etc.

2.1

SUSPENDED GROWTH (ACTIVATED SLUDGE)

2.1.1. Definitions

Activated sludge processes essentially involve a phase in which the water to be purified is brought into contact with a bacterial floc in the presence of oxygen **(aeration), followed** by a phase of separation from this **floc (clarification).** In fact, these processes amount to an intensification of the phenomena that occur in the natural environment. The difference lies in the greater concentration of microorganisms which results in a greater oxygen volume demand. Moreover, in order to maintain the bacterial mass in suspension, it must be artificially mixed.

The birth of this process can probably be traced back to Friday, April 3, 1914, when two British researchers, Edward Ardern and William Lockett, presented an account of their work, entitled "Experiments in the Oxidation of Sewage without Filters" to the Industrial Chemical Society of London.

Until the end of World War II, purification facilities were very modest in design. It was not until later that high rate systems using combined tanks (Aero-accelerator, Oxycontact, Oxyrapid) and the °Biosorption or Contact Stabilization" processes, etc. were developed.

Currently, research into more efficient purification processes prompted by the frequent need to remove nitrogen and the relative difficulties involved in operating high rate systems, have reawakened interest in low rate treatment.

An activated sludge facility always includes (Figure 137):

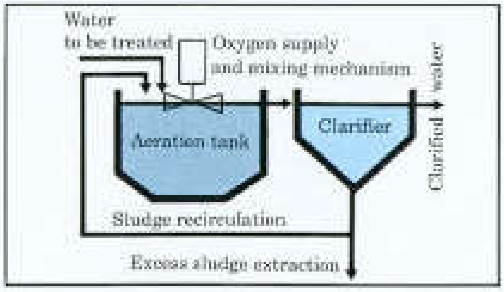


Figure 137. Simplified diagram of an activated sludge system.

- a so-called aeration tank, in which water to be purified comes into contact with the purifying bacterial mass;
- a clarifier, in which the purified water is separated from the bacterial growth;
- a recirculation device for the return of the biological sludge from the clarifier to the aeration tank. This arrangement enables the tank to support the quantity or concentration of microorganisms required to maintain the desired level of purification;
- a device for the extraction and disposal of excess sludge, or surplus bacterial growth, which is permanently synthesized from the substrate;
- a device supplying oxygen to the bacterial mass in the aeration tank;
- a stirring device in the aeration tank that guarantees optimal contact between bacterial cells and the nutrient, prevents deposits and promotes the distribution of oxygen to all the areas where it is needed.

The same unit is very often used for both aeration and stirring.

The sludge suspension in the aeration tank containing the purifying bacterial flora is called **activated sludge.**

The way in which a treatment facility using activated sludge is fed is an important parameter. There are various methods (refer to Page 691).

2.1.2. Basic relations for the removal of carbonaceous pollution

These relations involve the use of typical coefficients that depend on the nature of the substrate and the physio logical state of the biomass (sludge age, see Page 297).

2.1.2.1. Oxygen requirements and excess sludge production

While the biodegradable organic matter is consumed by a mass of microorganisms under aerobic conditions, the following occur:

- on the one hand, the microorganisms consume oxygen to satisfy their energy demand, their reproduction by cellular division (synthesis of living matter) and their endogenous respiration (auto-oxidation of their cellular mass);
- on the other hand, a surplus of living matter and inert matter is generated, which is called **excess sludge.**

It is difficult to determine experimentally the active concentration Xa of activated sludge. However, it is possible to measure the concentration of volatile substances Xv and that of total SS (organic and inorganic), Xt.

To illustrate these various phenomena, glucose may be used as an example of the degradation of a totally biodegradable molecule. In the first stage, additional assimilable nitrogen transforms the glucose into cellular protein, whose formula can be represented as CsH7NOz. In the second stage, this protein is degraded inside the cell itself to provide the energy required to sustain the cell. These two reactions can be expressed by:

- **Synthesis**

$$6\ C_6H_{12}O_6 + 4\ NH_3 + 16\ 0_2 \rightarrow 4\ C_5H_7NO_2 + 16\ CO_2 + 28\ H_2O$$

- Auto-oxidation or **endogenous respiration**

$$4\ C_5H_7NO_2 + 20\ O_2 \rightarrow 20\ CO_2 + 4\ NH_3 + 8\ H_2O$$

These two reactions clearly both occur in a purification plant, but the latter never achieves completion because the requisite retention time of the sludge would demand extremely large volume tanks.

Even though the second reaction is never fully completed, it does occur to a varying degree, depending on the processes used. The higher the degree of completion, the less excess sludge is produced but the more oxygen is consumed.

In the above example, the complete oxidation of 6 molecules of glucose required 36 molecules of oxygen. These 36 molecules correspond to the COD of 6 molecules of glucose, or the ultimate BOD. Of the 36 molecules of oxygen, 16 were used for synthesis and 20 for endogenous respiration.

The fraction of the ultimate BOD used for synthesis, a'_u is defined as:

$$a'_u = \frac{16\ O_2}{36\ O_2} = 0{,}45$$

The fraction of the ultimate BOD used for the complete oxidation of living matter, a., is defined as:

$$a_u = \frac{20\ O_2}{36\ O_2} = 0{,}55$$

The parameter am. may be compared to cellular efficiency and corresponds to the mass of cells formed by the mass of the ultimate BOD removed. In the preceding case:

$$a_{mu} = \frac{4\ C_5H_7NO_2}{36\ O_2} = 0{,}39$$

Thus, when degrading 1 g of the ultimate BOD, 0.39 g of living matter is synthesized.

. **Application to determine oxygen requirements**

There are two sorts of oxygen requirements:

- oxygen required for bacterial synthesis, which is expressed by: a'_u x ultimate BOD removed
- oxygen required for endogenous respiration.

As already mentioned, the entire mass of synthesized bacteria is not oxidized into CO_2 and H_2O. Only a fraction b_u of the synthesized $4C_5H_7NO_2$ is transformed into CO_2 and H_2O. In other words, only a fraction b'_u of the $20O_2$ required for the complete oxidation of the living matter must be furnished:

$$b'_u = \frac{b_u}{4\ C_5H_7NO_2} \cdot 20\ O_2$$

Oxygen requirements for endogenous respiration may be expressed by the formula:

b'u.mass of living matter

Thus, the overall requirements are:

a'u.ultimate BOD removed + b'u.mass of living matter.

For the purpose of calculations, the oxygen requirements are expressed in kg per day.

For greater convenience, the following values are generally used:

- a' referring to BODS and not the ultimate BOD;
- b' referring to the mass of volatile substances (and, at times, the total mass) and not to living matter.

. **Application to determine the production of excess biomass**

The production of excess biological sludge is affected by two factors:

- the production of biomass during synthesis reactions;
- the consumption of a part of the biomass during endogenous respiration reactions.

The biomass produced during synthesis is expressed by: $a_m.BOD_5$ removed.

Endogenous respiration consumes: b.mass of VS.

Thus the balance is: $a_m.BOD_5$ removed - b.mass of VS.

Sludge production is expressed in kg of SS per day. The amount of nonbiodegradable suspended solids contained in the raw influent must be added.

For greater convenience, the coefficient am is expressed in relation to the BOD5, rather than the ultimate BOD, and the coefficient b is expressed in relation to the volatile solids, rather than to the living matter.

In the medium rate biological treatment of municipal wastewater (see below), the following values may be adopted as first approximations:

a' = 0.5 kg per kg of BOD_5
b' = 0.1 1 per kg of VS
a_m = 0.6 kg per kg of BOD_5
b = 0.05 $kg.d^{-1}$ per kg of VS

<u>2.1.2.2. Factors relating- to the operation of a biological reactor</u>

In water treatment, a biological reactor may be defined by three basic parameters: the loading (F/M ratio and loading), the settleability of the sludge, and the sludge age.

. **F/M ratio and BOD or COD loading**

The F/M ratio (or sludge loading) is the ratio of the mass of food (usually expressed in terms of BOD5) entering the reactor per day and the sludge mass contained in the reactor:

$$F/M = \frac{Q.S_o}{X_t.V}$$

where:
Q :the daily flow,
So: the substrate concentration,
X,: the concentration of mixed liquor suspended solids (MISS),
V :the volume of the reactor.

It would be more logical to consider volatile solids X, instead of total suspended solids Xt. In this way, the F/M ratio would become F/M'.

$$F/M' = \frac{X_t}{X_v} \cdot F/M$$

In line with common practice, the F/M ratio will be used to define the sludge loading.

This concept of F/M ratio is important in the case of activated sludge, since it determines:

- the purifying efficiency. Low rates correspond to a high purification efficiency and high rates correspond to lower purification efficiency;
- the production of excess biological sludge. With a low rate the endogenous respiration is greater than with a high rate due to limitation in the substrate; the production of biomass is therefore lower;
- the degree of stabilization of the excess sludge produced. Since forced endogenous respiration leads to a biomass with a high mineral level, low rate procedures are characterized by less fermentable excess sludge;
- the oxygen requirements associated with the removed pollution. Compared to high rate processes, the amount of endogenous respiration with low rate processes results in higher levels of oxygen consumption relative to the pollution removed.

The various types of activated sludge treatment can be classified according to the F/M ratio at which they operate.

F/M ratio kg BOD_5/kg SS.d	**Type of treatment**
F/M < 0.15	Low rate (or extended aer- ation if F/M < 0.07)
0.15 < F/M < 0.4	Medium rate
0.4 < F/M	High rate

Another concept of loading is often used: volume loading. The loading is the food mass (usually referred to in terms of BODO entering the unit per unit reactor volume per day:

$$C_v = \frac{Q\ S_o}{V}$$

usually expressed in kg BOD5/m^3.d.

Sludge age

The sludge age A is the ratio between the mass of sludge present in the reactor and the daily mass of excess sludge extracted from the unit.

The daily production of excess biological sludge is given on Page 295. If Xv refers to the concentration of volatile solids in the aeration tank and V is the volume of the tank, then:

$$A = \frac{X_v.V}{a_m.BOD_5 \text{ removed} - b.X_v.V}$$

If E is the efficiency of BODs removal, the following simplified equation is obtained:

$$A = \frac{1}{a_m.E.F/M' - b}$$

Thus, sludge age is inversely proportional to the F/M ratio. This sludge age is particularly important because it expresses the physiological state of the microorganisms. The respiratory coefficients a' and b' cited earlier are closely correlated to sludge age (Figure 138). Moreover, the sludge age indicates the presence or absence of nitrifying bacteria (see Figure 139).

. **Settleability**

The efficient operation of an activated sludge facility depends on the correct operation of both the aeration tank and the clarifier. For the clarifier to efficiently separate the biomass from the treated water, the biomass must be properly flocculated.

Under certain conditions, the microorganisms agglomerate in flocs. This is **called bioflocculation.**

During the phase of exponential growth, the bacteria remain dispersed throughout the culture. As soon as the declining growth phase begins, they agglomerate in brownish, jagged floccules that are often several millimetres long.

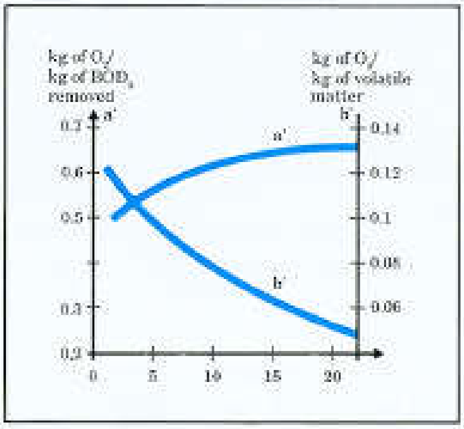


Figure 138. Changes in the a' and b' coefficients, depending on the sludge age.

Seen under a microscope, the flocs frequently appear to be branched like the fingers of a glove, and the bacteria seem to be enveloped in a gelatinous substance. The floc remains in the endogenous metabolic phase. However, by observing the correlations between the sludge age and the changes in the percentage of free organisms not associated with the floc, it is possible to determine that the minimum value lies in a range of four to nine days. After more than nine days, although the settleability remains adequate on the whole, a deflocculation process begins. The flocs become smaller, and increasing numbers of small particles escape (pinhead flocs).

Conversely, in less than four days, the very hydrophilic floc settles poorly and the number of free microorganisms increases very rapidly.

Bioflocculation is a complex phenomenon. For the time being, it has been firmly established that:

- it is controlled by the physiological state of the cells;
- it is not unique to a single species, but is a fairly wide-spread phenomenon among common microflora;
- the basic effect is linked to the excretion of polymers, among which the polysaccharides play a special role.

A simple and practical way of assessing the ability of a sludge to settle is to determine its SVI (see Page 163).

Aeration

Oxygen is introduced into water by bringing the water into intimate contact with air. At the interface, the monomolecular boundary layer is saturated with oxygen as soon as it is formed. At the same time, the gas starts diffusing toward the deeper layers of water.

The quantity of oxygen diffused per unit of time is:

$$\frac{dm}{dt} = K_L a \frac{dC}{dt}$$

KL is known as the **transfer coefficient** (see Page 277).

On the basis of this equation, the **oxygenation capacity** (OX.CAP.) of an aeration system is defined as the quantity of oxygen expressed in g.rri 3 supplied in one hour to pure water with a constant zero oxygen content, at a temperature of 10°C, and at atmospheric pressure of 760 mm mercury.

The following equation allows the value of OX.CAP. to be calculated:

$$\frac{dC}{dt} = 11.25 \frac{1}{t_1 - t_0} \log \frac{C_s - C_o}{C_s - C_t} \sqrt{\frac{k_{10}}{k_t}}$$

where:

C_s : the O_2 concentration at saturation in g.m^{-3}

C_o : the O_2 concentration at the beginning of the experiment, in g.m^{-3}

C_t : the O_2 concentration at time t

11.25 : the saturation concentration of O_2 at 10°C in g.m^{-3}

t_1-t_o : the observation period in hours

dC/dt : the oxygenation capacity in g/m^3.h

k_{10} and k_t: diffusion coefficients at 10°C and t°C

Taking CS - C° = D° and Cs - C, = D, as Oz deficits at the start and at time t, the result is:

$$\text{CAP.OX.} = 11{,}25 \,.\, 2{,}3 \frac{1}{t_1 - t_0} \log \frac{D_o}{D_t} \sqrt{\frac{k_{10}}{k_t}}$$

The relation between D° and DC plotted on logarithmic coordinates gives a straight line as a function of time, the slope of which, tan a, defines the oxygen dissolution rate:

$$\text{CAP.OX.} = 25{,}9 \text{ tg } \alpha \sqrt{\frac{k_{10}}{k_t}}$$

The quantity of oxygen introduced depends on:
- the value of the interfaces between the air and water, and their renewal;
- the oxygen concentration gradient between the air and water;
- the time available for oxygen diffusion.

There are, however, physical and technical limits to the optimal values for these conditions.

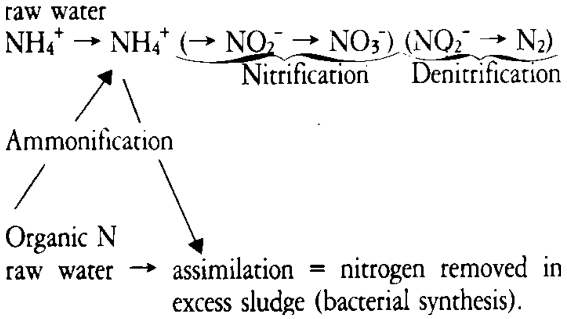
The size of the bubbles is an important parameter. However, they do have a lower limit, as the air bubble escaping from an orifice under water has a diameter much larger than that of the pore. In practice, the bubbles formed by porous aeration devices have a diameter of about one millimetre. Smaller bubbles can only be obtained by air release from air-saturated water (a process used for flotation).

All other factors being equal, the oxygen transfer coefficient KL depends on the nature of the water (clean water, wastewater containing suspended or dissolved solids, the presence of surfaceactive agents), the aeration system used, and the geometry of the reactor.

In general, aeration systems are compared on the basis of their oxygenation capacity per m3 of pure water per hour. The **specific oxygen transfer capacity** of a system can also be expressed in terms of the oxygen supplied per kWh.

2.1.3. Nitrification and denitrification

In municipal wastewater as well as in the many types of industrial wastewater, nitrogen is present mainly in organic and in ammonia forms. In units designed to remove nitrogen, all the reactions can be illustrated in the following diagram:



In the treatment of drinking water, the assimilation phase is insignificant.

Thus, the biological removal of nitrogen involves four main reactions.

2.1.3.1. Ammonification

Ammonification is the transformation of organic nitrogen into ammonia nitrogen. The ammonification rate depends essentially on the concentration of ammonia nitrogen. A Monod-type inhibition constant is used. Thus, if rX is the ammonification rate, then:

$$r_x = \frac{r_x\,(N - NH_4 = 0).K_n}{K_n + N^*}$$

where:
N^*: the ammonia nitrogen concentration
K_n: experimentally determined as equal to 10 $mg.l^{-1}$
r_x ($N\text{-}NH_4 = O$) = 1.5 mg N per g of VS and per h.

In view of the nature of organic nitrogen and plant operation factors and, more particularly, the retention time of the water in the facility, most organic nitrogen will invariably undergo ammonification without problem.

Nitrification 6-e-n-irrification

2.1.3.2. Assimilation

Assimilation is the use of part of the ammonia nitrogen, and possibly the organic nitrogen, for bacterial synthesis. Assimilation can play an important role in removing nitrogen from certain types of industrial wastewater. However, in many cases and particularly in municipal wastewater, assimilation alone is not sufficient to remove nitrogen because the quantities present in the wastewater to be treated are much higher than those that can be assimilated for synthesis.

2.1.3.3. Nitrification

Nitrification is the process in which ammonia nitrogen is oxidized into nitrite and then into nitrate. Nitrification takes place in two stages and is brought about by autotrophic microorganisms. The process involves:

- the oxidation of NH_4^+ to NO_2^- , which is basically the work of bacteria known as **Nitrosomas**
- the oxidation of NO_2^- to $NO3^-$. The bacteria responsible for this second reaction belong mainly to the genus **Nitrobacter.**

The entire simplified reaction may be represented as:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H2O$$

Nitrification occurs only when nitrogen is initially present in its ammonium form. The transformation rate of ammonium into nitrate in an activated sludge process is of the order of 3 mg of $N\text{-}NH_4^+$ oxidized to NO_2^- per g of VS and per h. The value is, therefore, relatively high.

The generation time of bacteria in nitrification is often the factor that determines the design of equipment used for nitrification purposes. For these bacteria, the µm. values are as follows:

- Nitrobacter: $\mu_{max} = 0.03\ h^{-1}$
- Nitrosomonas: $\mu_{max} = 0.08\ h^{-1}$

This order may be inverted under certain conditions, for instance when treating cold drinking water with low ammonium concentration, but the limiting factor is usually the bacteria responsible for the oxidation of ammonium into nitrite.

Because the growth rate of the heterotrophic bacteria responsible for the oxidation of carbonaceous pollution is higher than that of the autotrophic nitrifying bacteria, the sludge age in the selected purification system has a determining effect on nitrification. Under pH conditions of between 7.2 and 8, the minimum sludge age (in days) to start the nitrification in an activated sludge system is related to temperature as follows

$$A_{minimum} = 6.5\ (0.914)^{T-20}$$

where T is the temperature in °C.

Figure 139 shows that the sludge age depends greatly on the temperature, and that nitrification at temperatures below 12 or 13°C leads to the adoption of low rate processes.

It is extremely risky to start the nitrification process at temperature below 8°C. However, if the nitrifying flora can be developed beforehand and introduced at normal temperatures, the nitrification process can continue at very low temperatures, resulting in a reduced oxidation efficiency of ammonia nitrogen.

Nitrification requires additional oxygen. It is necessary to supply 4.6 mg of oxygen per mg of $N(NO_3^-)$ produced; or more precisely, 4.2 mg, taking into account the oxygen released by HCO_3. The nitrifying bacteria tolerate, however, periods of insufficient oxygen relatively well.

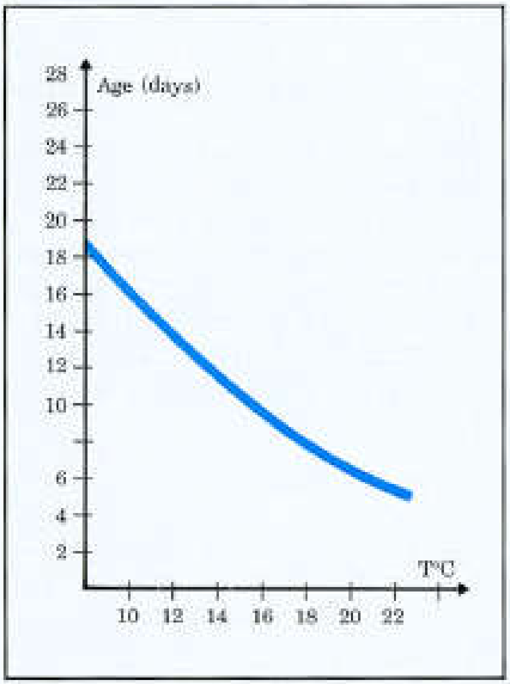


Figure 139. Sludge age required for nitrification.

One point to be emphasized is the destruction of alkalinity. The growth rate of nitrifying bacteria falls substantially when the pH drops below 7.2. The alkalinity of raw wastewater is an important consideration, since the nitrification reaction produces H^+ ions. Calculations and experience show that 7.2 mg of alkalinity expressed as $CaCO_3$ (0.72 Fr. deg.) are required to neutralize the H+ ions that are produced by the oxidation of 1 mg of $N\text{-}NH_4^+$. This explains why, in certain soft water areas, when no correction is made the nitrification process results in a pH that is too low for the complete oxidation of ammonia.

Lastly, nitrifying bacteria are sensitive to many factors in their environment. The presence of certain organic or inorganic compounds may modify or even inhibit the growth of nitrifying bacteria, particularly in certain industrial wastewaters.

2.1.3.4. Denitrification

Denitrification is a process where certain bacteria reduce nitric nitrogen to a lower oxidation state.

These bacteria may be autotrophic, but their activity is weak, which is why heterotrophic bacteria are generally used.

This reduction takes place in the form of several reactions, which may be expressed as follows:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

In the treatment of wastewater, the following reaction is acceptable:

$$NO_3^- + 6H^+ + 5e^- \rightarrow 0,5N_2 + 3H_2O$$

The preferred source of electrons is organic carbon, or the. bacterial mass itself.

Four essential factors influence the denitrification rate: temperature, dissolved oxygen, pH, and the source of organic carbon.

Temperature

The influence of the temperature may be expressed by the following equation:

$$r_T = r_{20°c}.?^{(T-20)}$$

where rX and rzo c are the denitrification rates at temperatures Tx and 20°C expressed in mg of N-N03 reduced per mg of VS and per h. B, which is deter mined experimentally, equals 1.116 for temperatures between 5 and 27°C (see Figure 140).

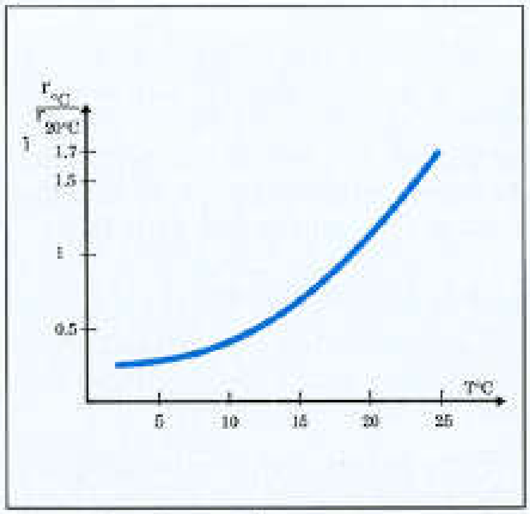


Figure 140. Influence of temperature on the denitrification rate.

Dissolved oxygen

The presence of oxygen inhibits denitrification. Denitrifying bacteria draw their energy from the energy released in the transfer of electrons from organic compounds to O_2, NO_2^- or NO_3^- . If these three elements are available to accept electrons, then' the preferred recipient is clearly the element that yields the greater quantity of energy per unit of oxidized organic matter. Since more energy is yielded with oxygen than with the other elements, electrons are transferred preferentially to oxygen.

In reality, it is difficult to fix concentration limits for O_2, above which denitrification is inhibited, since values depend on how large the floc is and how easily oxygen transfers to the bacteria. These values also depend on the nature and concentration of organic carbon. However, Oz concentrations higher than 0.5 $mg.l^{-1}$ are known to be highly inhibiting. Another approach is to measure the redox potential instead of the dissolved oxygen. Even though the figures observed frequently vary, it seems that denitrification is not satisfactory unless the redox potential is less than 220 mV.

.pH

The optimum pH lies between 7 and 8.2.

Source of carbonaceous substrate

The nature and concentration of the carbonaceous substrate both have an effect. The following table gives the kinetics of nitrate reduction for several substrates expressed in mg of N-NO^{3-} reduced per g of VS and per hour, at a temperature of 20°C. These values of $r_{20°C}$ were obtained with denitrifying activated sludge.

Ethanol	5.1
Acetate	4.9
Propionate	5.1
Methanol	2.5
Butyrate	5.1
Municipal wastewater	3.3
Endogenous respiration	1.5

Denitrification using the organic carbon present in municipal effluent thus achieves wholly acceptable kinetics as compared with the kinetics obtained with easily biodegradable products.

However, in some cases the quantities of organic carbon introduced by an effluent may be insufficient to obtain advanced denitrification. It should be noted that the use of organic carbon released by endogenous respiration results in weak kinetics. In practice, this requires structures that are very large in volume, which explains why this technique is not often implemented.

2.1.4. Biological phosphate removal

Many research projects have studied the possibility of removing phosphates biologically, i.e., without introducing a reagent and practically without producing additional excess sludge. These studies really began in the mid 1960s with the work of Shapiro and Levin. They observed that non-aerated activated sludge released phosphorus and then reabsorbed it as soon as the oxygen concentration increased.

The principle of biological phosphate removal consists in accumulating phosphorus in a biomass. This accumulation may be due either to the chemical precipitation of inorganic phosphorus in the vicinity of bacteria under particular micro-environmental conditions, or to an accumulation of phosphorus by the microorganisms themselves, or to a combination of the two.

2.1.4.1. Extracellular precipitation of inorganic phosphorus

The main causes of the formation of these precipitates would be an increase in the pH or an increase in the concentration of precipitating ions. Several observations confirm the possibility of these phenomena. When a bacterial growth is subjected to anaerobic conditions, its level of extracellular calcium falls, and it discharges phosphorus, potassium, and magnesium: potassium and magnesium ions stabilize intracellular polyphosphate. The release of phosphate ions appears to cause a drop in the calcium concentration, which supports the hypothesis of precipitation.

In the absence of oxygen, changes in pH due to denitrification and the acid fermentation of organic products could cumulate with the effects of increased phosphorus concentration and either accentuate or lessen the consequences.

2.1.4.2. Intracellular accumulation of 303 polyphosphates by microorganisms in activated sludge

In addition to extracellular precipitation, which is highly variable and difficult to assess and control, it has now been determined that bacteria accumulating polyphosphates also play a key role (poly-P).

The phenomenon of polyphosphate storage has often been observed in microbiology, especially in cases where an imbalance in the nutrient medium impedes the synthesis of nucleic acids. The accumulated polyphosphates may serve either as an energy reserve comparable to the phosphate chain in the ATP/ADP system, or as a phosphorus reserve. Nuclear magnetic resonance (NMR) analyses on phosphorus-removing sludge have confirmed the presence of substantial quantities of poly-P, which is invariably found in the form of "volutin" granules.

2.1.4.3. Factors involved in biological phosphate removal

The biological removal of phosphates requires **alternating anaerobic and aerobic sequences.** The aim of alternating these sequences is to modify the enzymatic equilibrium regulating the poly-P synthesis in the anaerobic phase.

The anaerobic phase

Acetate-producing bacteria, facultative anaerobes, use the available organic carbon, existing for example in raw water, to produce acetate. Aeromonas are the main organisms responsible for this anaerobic acidogenesis. It should be noted that the presence of nitrates in this anaerobic phase prevents the production of acetate. This point is explained by the denitrifying capabilities of Aeromonas, which do not use their fermentative metabolism as long as there are nitrates in the medium to act as final electron acceptors.

The acetate produced is reused by the bacteria of the **Acinetobacter/Moraxella** group. These bacteria are strictly aerobic and can only use a limited range of substrates. They consume acetate, ethanol, lactate, citrate and several amino acids, but they cannot use sugars or volatile fatty acids with a molecular weight higher than that of propionic acid.

The acetate used by the Acinetobacter/Moraxella is stored in situ in the form of PHB (polyhydroxyburyrate). The energy required for this storage comes from the hydrolysis of poly-P, which explains the accelerated release of phosphate into the medium. In this process, acidogenesis is the limiting step, which explains why free acetate is not found in anaerobic zones.

. **Aerobic phase**

The Acinetobacter/Moraxella locate the electron acceptors for their metabolism (N03, oxygen). The PHB is then used as organic substrate for their growth and the replenishment of their reserve of poly-P through the reabsorption of interstitial phosphorus. The quantities reabsorbed exceed the amount released during the anaerobic phase. Thus, in a succession of anaerobic-aerobic phases, phosphorus is gradually accumulated in these microorganisms in quantities reaching 10 to 11 % of dry weight. In a phosphorus-removing activated sludge in which other bacteria live, this value could reach 7% of dry weight.

It should be noted that in the aerobic phase, other heterotrophic organisms that do not accumulate poly-P have at their disposal only a fraction of the organic matter, which is, moreover, the least biodegradable.

The different reactions are illustrated in Figure 141.

The common denominator in all these processes using the biological removal of phosphates is thus the alternating of an anaerobic phase, in which the biomass comes into contact with the organic carbon in untreated water, with an aerobic phase in which the previously released phosphorus is reassimilated.

These processes fall into two general categories:

- processes in which no chemical reagent is added; in these systems the phosphorus is "biologically" stored in the sludge and removed with the excess sludge. The efficiency of phosphate removal thus de

pends wholly on the phosphorus content of the sludge and on the production of excess sludge;
- processes in which the phosphate removal is a combined biological and physical-chemical process. The biologically accumulated phosphorus in the sludge is released in a small volume of water. A high concentration of phosphorus is thus obtained in the interstitial liquid, to which chemical reagents are added.

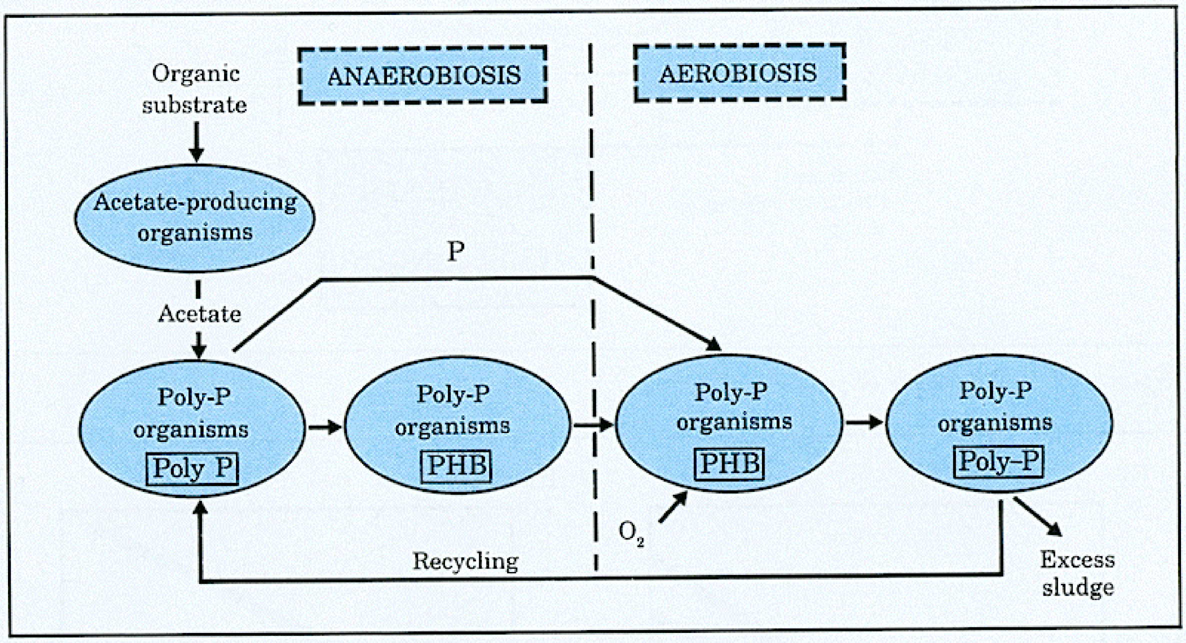


Figure 141. Phenomena involved in biological phosphate removal.

2.1.5. Aerobic stabilization

This process, which is designed to reduce the level of OM in sludge, is also often referred to as "aerobic digestion°. In this method, the extended aeration of the sludge is used to stimulate the growth of aerobic microorganisms beyond the period of cell synthesis and depletion of the substrate until the stage of auto-oxidation is reached. This is the mechanism of endogenous respiration (Figure 142).

The cellular matter (represented as CsH7NOz) is transformed in the following reaction (see Page 294):

$C_5H_7NO_2 + 5O_2 \text{->} 5CO_2 + NH_3 + 2H_2O$

The ammonium may then be oxidized, resulting in the following overall reaction:

$C_5H_7NO_2 + 7O_2 \rightarrow 5CO_2 + NO_3^- + H^+ + 3H_2O$

The pH may then drop substantially if the alkalinity of the wastewater is insufficient.

Aerobic stabilization is used most often with activated sludge, but may also be applied to sludge produced in plain, primary settling, as well as to biofilms in attached growth reactors. Thus, the reduction rates of OM (E%) obtained, vary widely. E% may generally take the form E = p.log t + q, where t is the stabilization time. Figure 143a shows the reduction rate in the case of activated sludge with

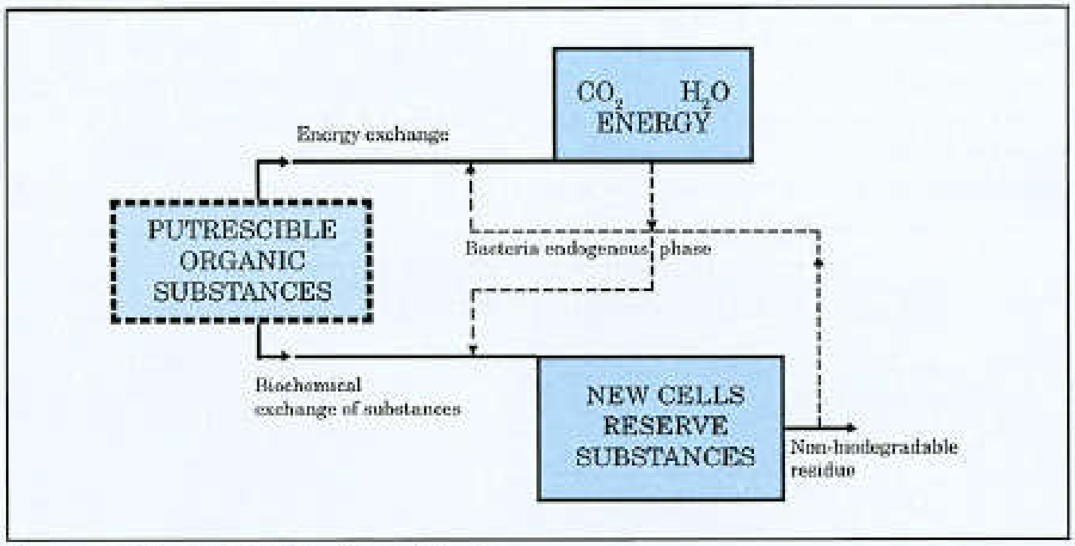


Figure 142. The principle of aerobic stabilization.

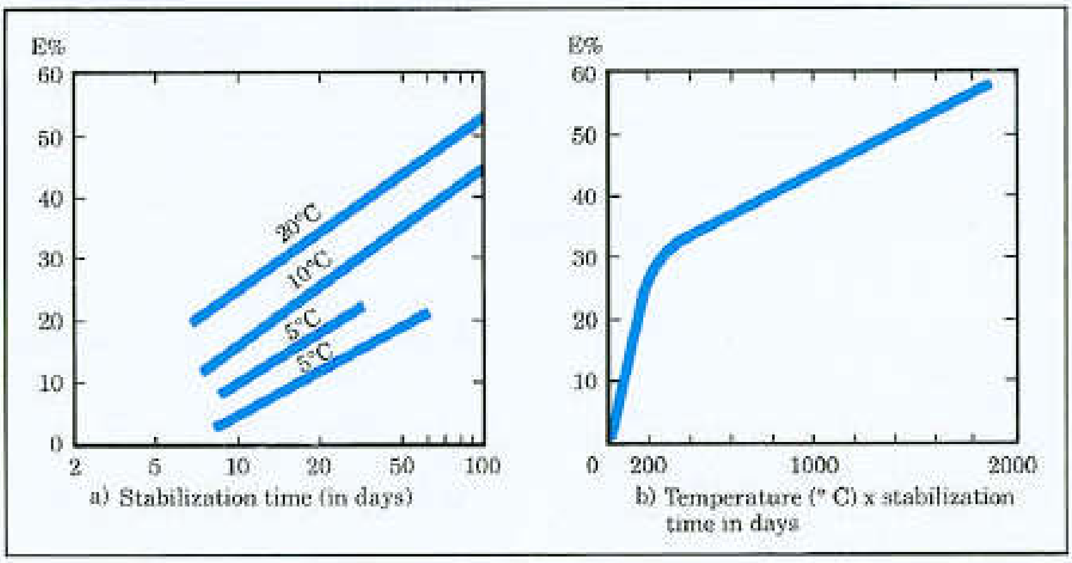


Figure 143. The reduction rate of OM E% in aerobic stabilization.

an age of five days, obtained from nonsettled municipal wastewater.

Oxygen requirements for a stabilization time of 15 days at 15°C vary from 0.1 to 0.15 kg of O_2 per day and per kg of VS, depending on the source of the sludge. This oxygen consumption also depends on the temperature.

Koers and Mavinic consider that the product (temperature °C x stabilization time) can be used to calculate the reduction rate of organic matter for sludges of the same type (see Figure 143 b).

Various quantitative criteria have been proposed to define a sufficiently stabilized sludge:

- the respiration of the sludge: 0.1 kg Oz per kg of OM per day, at 20°C;
- weight loss of less than 10% after 120 h of aeration at 20°C in a medium with an Oz level of 2 mg.l^{-1}.

Another proposed method is to assess the amount of volatile acids formed and the amount of nitrogen ammonified per gramme of OM maintained under anaerobic conditions.

The **term thermophilic aerobic digestion** refers to the stabilization process that, by limiting heat losses, benefits from the exothermic nature of the OM oxidation reaction to heat the sludge to more than 50°C.

2.2.

ATTACHED GROWTH

2.2.1. The biological film

Most microorganisms are able to grow on the surface of a solid when organic compounds, mineral salts and oxygen are available. They are anchored by means of an exopolymer-based gelatinous material produced by the bacteria, inside which the bacteria can, to some extent, move about. The colonization of the solid matter begins in selected areas, whence the biofilm develops continuously until the entire surface of the support is covered with a monocellular layer. From this moment on, growth is carried on by the production of new cells covering the first layer.

The oxygen and nutrients carried in the water to be treated diffuse throughout the biofilm until the deepest cellular accumulations are no longer affected by the oxygen and nutrients.

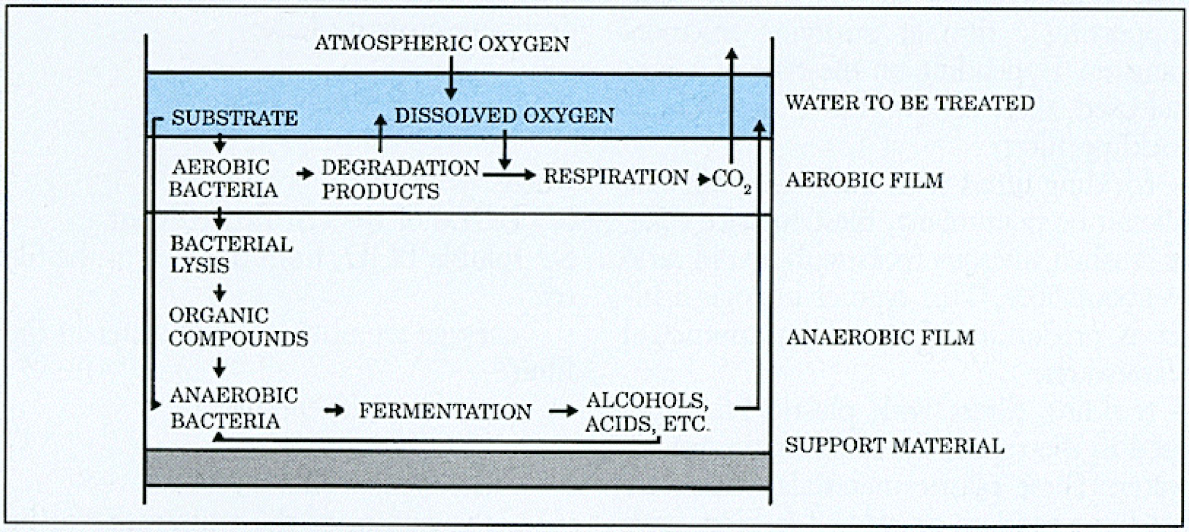


Figure 144. Specific section of a biofilm.

After some time, stratification occurs with an aerobic layer, where the oxygen is diffused, on top of a deeper anaerobic layer in which there is no oxygen. The thickness of these two layers varies according to the type of reactor and support (see Figure 144).

The use of biofilm methods for treating water shows that:

- the rate at which the substrate is used stabilizes at a constant value when the biofilm is deep enough for oxygen to become a limiting factor in the deepest layers. The "active" depth may be about 300 - 400 µm;
- the bacteria attached to a support usually display higher specific activity than those observed in suspended growth.

2.2.2. Trickling filter (bacteria beds)

The operating principle of a trickling filter (sometimes referred to as a biofilter or as a percolating filter) consists in allowing the water to be treated to trickle onto a mass of material with a specific surface area of between 50 and 200 $m^2.m^{-3}$ and supporting a film of purifying microorganisms. Depending on the type of material used, there are two basic categories of trickling filter:

- trickling filters with traditional fill. The fill can be pozzuolana, blast furnace coke, or crushed siliceous rocks with a void ratio of about 50%. This type of biological filter is predominantly used for municipal wastewater;
- trickling filters with plastic fill, often used in the treatment of industrial wastewater. These plastic materials, which are used in a random or ordered fashion, have void ratios above 90%.

If the substrate fails to reach them, the microorganisms in the anaerobic layer die, then undergo autolysis. In this way, their cellular contents become available to other facultative aerobic or anaerobic microorganisms. When all of the substrate reserves are truly exhausted, the lysis of the remaining cells causes the biofilm to become locally detached from the surface. This surface then becomes available for a new colonization. The action of water currents on the surface of the biofilm can bring about or contribute to its detachment (sloughing).

Whatever the material, all trickling filters operate on the same principles.

The filter is aerated, in most cases by natural draught, but occasionally by forced countercurrent ventilation.

2.2.2.1. Basic equations

The **BOD** removed by a trickling filter depends on the nature of the water to be treated, the hydraulic load, the temperature, and the type of fill material.

The mathematical formulation is based on the assumption that the microorganisms in the trickling filter are in the declining growth phase:

$$\frac{\bar{S}_f}{S_o} = \exp.\,(-\,k_1\,t)$$

where:

S_f: BOD_5 of the clarified effluent

S_o: soluble BOD_5 from the feed to the filter

t: average retention time of water in the filter

k_l:a constant depending on:

. water temperature

. the type of fill

. the nature of the wastewater to be treated.

Figure 145. Trickling filters.

The median value of t is expressed as:

$$t = k_2 \cdot \frac{H}{Q^n}$$

where:

H : filter depth
Q : flowper unit of horizontalsurface
k_2 and n: constants

Hence,

$$\frac{S_f}{S_o} = \exp.\left(- k_1 \cdot k_2 \cdot \frac{H}{Q^n}\right)$$

2.2.2.2. Trickling filters with traditional fill

With traditional fill materials and a bed depth of 2 m, purification efficiency is relatively low (66%) when the loading (expressed in kg of BOD_5 per m^3 of material per day) is high. In this case, efficiency can be increased by recirculating the filter effluent back to the filter, thus diluting the feed water.

Empirical equations have been developed for domestic wastewaters. For example, Rankin gives the following equations, based on a maximum hydraulic load (including recirculation) of 1.13 in m^3/m^2 h:

-single-stage trickling filter:

$$S_f = \frac{S_o}{2\,r + 3}$$

- two-stage trickling filter:

$$S_{f1} = 0{,}5\ S_o$$

$$S_{f2} = \frac{S_{f1}}{2\,r + 2}$$

where r = recirculation rate.

Depending on the loading used, a distinction is made between low-rate and high-rate filters, which have the following performance ratings with municipal wastewaters:

Loading	Low rate	High rate
BOD kg /m3.d	0.08 to 0.15	0.7 to 0.8
Hydraulic loading m /m .h	< 0,4	> 0.7

In high rate filters, which normally require recirculation, the hydraulic loading is sufficient to homogenize the bacterial flora at the various levels. Selfcleaning of the material, which then retains only a thin active film, encourages rapid exchanges and relieves the trickling filter of the task of breaking down the cellular material that develops. This process of mineralization (stabilization) occurs in other sections of the facility, such as the anaerobic digester, which means that a clarifier must be used at the filter outlet to collect the settled matter for transfer to the sludge treatment facilities.

In a high rate filter, the activity of predatory agents is limited.

On the other hand, in a low rate filter there is no continuous washing of the sludge, which tends to build up in the contact mass. The action of predatory agents is essential, and this, together with endogenous respiration of the bacteria, limits excessive growth of the film.

Nitrification may take place if the organic carbon load applied is sufficiently low. Figure 146, showing the curve obtained for municipal wastewater settled at 15°C (G. Martin), gives the TKN removal efficiency as a function of the loading in a trickling filter with pozzuolana packing.

Unlike in activated sludge, nitrification is not an "all or nothing" process, because the microorganisms are stratified throughout the entire depth. The top portion contains primarily heterotrophs, while the bottom part is mostly made up of autotrophs. In contrast to activated sludge, the limiting factor is not the sludge age, but the kinetics of nitrification.

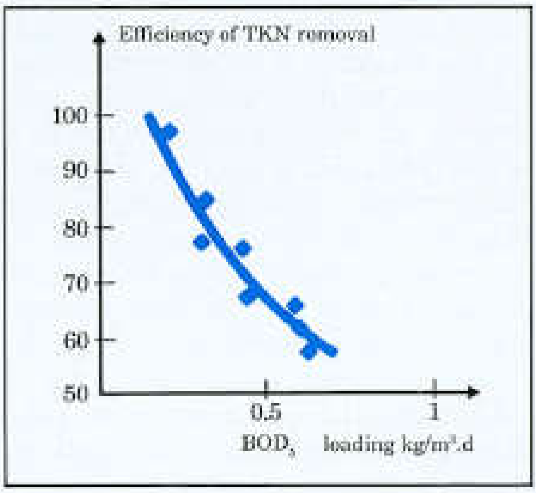


Figure 146. TKN removal in a trickling filter with traditional fill.

Owing to the depth of the zoogloea attached to the support and the fact that oxygenation is often insufficient, trickling filters frequently enable partial denitrification to take place. This denitrification is improved by recycling and it essentially occurs in the upper layers of the trickling filter, where the organic carbon from the raw water is available.

In a low rate filter, the sludge is strongly mineralized and can be discharged into the outlet without final clarification if periodic discharges of sludge into the final effluent are permissible.

Because of the frequent risk of clogging, the large fly population they encourage and their high cost, low rate filters are little used despite their high efficiency (95% for BODS). High rate filters, with recirculation, are more commonly used for removing carbonaceous pollution.

Recirculation

Recirculation has several advantages:
- self-cleaning of the trickling filter,
- seeding of the settled effluent,
- diluting of the high BOD wastewater.

There are several types of recirculation possible (Figure 147).

Method No. 1 is the most frequently used recirculation system. The secondary sludge is continuously recycled. Since the recirculation flow is drawn from the bottom of the clarifier, the surface area of the clarifier can be designed exclusively for a rising velocity corresponding to the flow Q to be treated. On the other hand, the primary settling tank must be designed to take Q(1+r), where r is the recycle rate

The fill materials used for trickling filters must be clean and non-friable. Particle size must be regular and between 40 and 80 mm. The void ratio is about 0.5, which means that, allowing for the biological film, the void left free for aeration is limited to about 0.15. Whatever the traditional material used, the risk of clogging by coarse suspended solids from the raw water requires the construction of a primary settling tank upstream of the filter.

2.2.2.3. Trickling filters with plastic fin

Trickling filters with traditional fill are little used for the treatment of high BOD industrial wastewater flows from sources such as the agrifood industries, because of the risk of clogging and the excessive proliferation of filamentous biological films.

Plastic fill considerably reduces these risks and provides a higher oxygen transfer coefficient. The applications of plastic packing filters are very different from those with traditional fill for the following reasons:

- they may be operated with high BOD$_5$ loadings of between 1 and 5 kg/m^3.d, or even higher;
- since plastic is more expensive than traditional fill, the aim is to use plasticmedia high rate trickling filters. Under these conditions, the BOD$_5$ removal is too low to yield an effluent complying with the standards usually in force, since it fluctuates between 50 and 80% depending on the type of flow treated and the loading chosen. For this reason, treatment by a trickling filter with plastic fill is often followed by a stage of conventional treatment, such as activated sludge.

Random packings seem to become clogged more readily than ordered materials, and their use is generally limited to low pollution flows free of suspended solids, fibres or greases.

They may also be used in nitrifying filters downstream of an activated sludge stage. Thus, the nitrification rate for industrial wastewater is approximately 100 g of N-NH4 per m^3 and per day at 20°C and 50 g at 15°C.

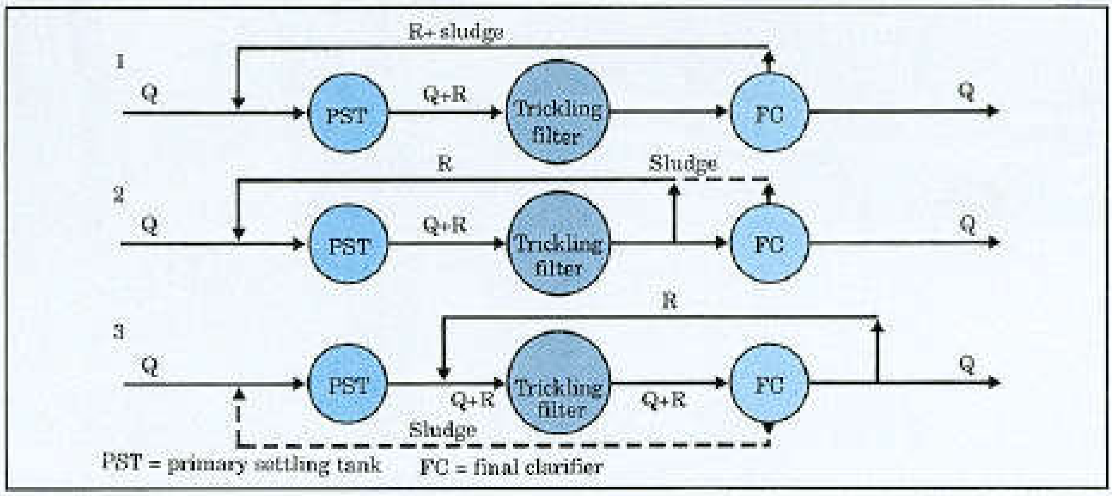


Figure 147. Modes of recirculation in trickling filters.

Figure 148. Enlarged view of an aerobic biological film on a granular support (x 1000).

2.2.3. Granular beds

The activity of a bacterial growth depends in particular on its exchange surface with the substrate and oxygen. In activated sludge this surface is restricted by the flocculated state of the microorganisms. This flocculated state is indispensable for proper separation of sludge and treated water in the final separation tank. The larger the floc, the more slowly the substrate and oxygen are diffused toward the microorganisms inside.

In trickling filters, the developed surface of the support material, related to m^{3} of reactor, remains small and the perfect distribution of water to be treated across the entire surface of the biofilm is difficult on an industrial scale.

When microorganisms are attached to granular supports with an effective size of less than 4 or 5 mm, the supports offer a specific developed surface area, and consequently an exchange surface, that is much larger than the surface offered by other processes. For example, Biolite with an ES of 2.7 mm, provides an exchange surface of 700 m^{2}.m^{-3}. A turbulent bed, using a support with an ES of 375 gym, expanded by 100%, develops a surface exchange area of 6500 m^{2}.m^{-3} of reactor, compared with 100 or 200 m^{2}.m^{-3} in a trickling filter with plastic fill.

Figure 149. Fixed bed reactor (Nitrazur) being washed. Louveciennes plant near Paris (France). Nitrification of groundwater, Maximum flow: 5000 mj.h^{-1}.

It is thus possible to operate at high BOD loadings and still obtain, in a single stage, purification efficiencies that produce municipal wastewater effluent meeting usual discharge standards.

These granular-media bioreactors may be divided into two main groups:

- those which perform biological purification and retain the SS initially present in the raw wastewater as well as the excess sludge produced. These are **fixed granular beds**, also known as **biofilters**;
- those in which the bioreactor performs only biological purification, with SS being removed by a unit situated downstream. In this case, the exchange surface for microorganisms and substrates is optimized by using very fine granular materials that are kept in motion. These units are known as moving granular beds.

Fixed bed reactors may operate in upflow or downflow, according to the direction of the water flow chosen. Depending on the relative directions of the water to be treated and the oxygenating gas, a distinction may also be made between cocurrent and countercurrent reactors. The granular support material is periodically regenerated by washing in the reactor itself (Figure 149). Note that, in theory, the principle of purification applied in fixed granular beds can be extended to include floating granular beds made up of low-density beads.

Moving beds can be:

- fluidized, where oxygen is dissolved in the recirculated effluent. However, controlling the growth of the biological film requires an extraction, washing and material recycling system. The loadings used are limited by oxygenation capacity.

Figure 150. Aerobic reactor with a turbulent granular bed at the Beghin-Say sugar refinery in Thumeries in northern France.

- **turbulent,** where air is directly introduced into the reactor (Figure 150). A settling tank downstream is essential. The purification efficiency is limited.

2.2.4. Other systems

2.2.4.1. Biological discs

This method, which is also known as the Rotating Biological Contactor (RBC), goes back to the 19th century, to the work of Weigrand on the purifying capabilities of water mill wheels.

The biomass is attached to discs that turn around a horizontal axis and are partially bathed in the water to be treated (Figure 151). Rotation brings the biomass alternately in contact with the water to be treated and the oxygen in the air.

An electric motor usually provides the energy for the discs to rotate. Several methods have been designed to aid rotation and oxygenation by blowing additional air into pockets attached to some of the discs. The discs, which are made of polystyrene, PVC, or corrugated polyethylene sheets, are 2 to 3 m in diameter. They are spaced 2 to 3 cm apart and turn at 1 to 2 rpm.

A clarifier, designed for rising velocities of up to 2 m.h^{-1}, retains the excess sludge.

The absence of any stirring in the aeration tank:
- necessitates the presence of a primary settling tank;
- prohibits the recirculation of sludge after the clarifier.

These systems are often made up of several disc stages, the first of which remove organic carbon, and the last of which perform nitrification. Loadings are expressed in g BODS per m^2 of disc surface per day Loadings rarely exceed 25 to 30 g/m^2.d. With considerably lower loadings, nitrification is possible but the system is highly temperature-sensitive.

The advantage of this method is that it consumes little electrical energy (2 to 4 W.m^{-2} of disc), but widespread use has been hindered by:
- the need to stabilize primary and biological sludge;

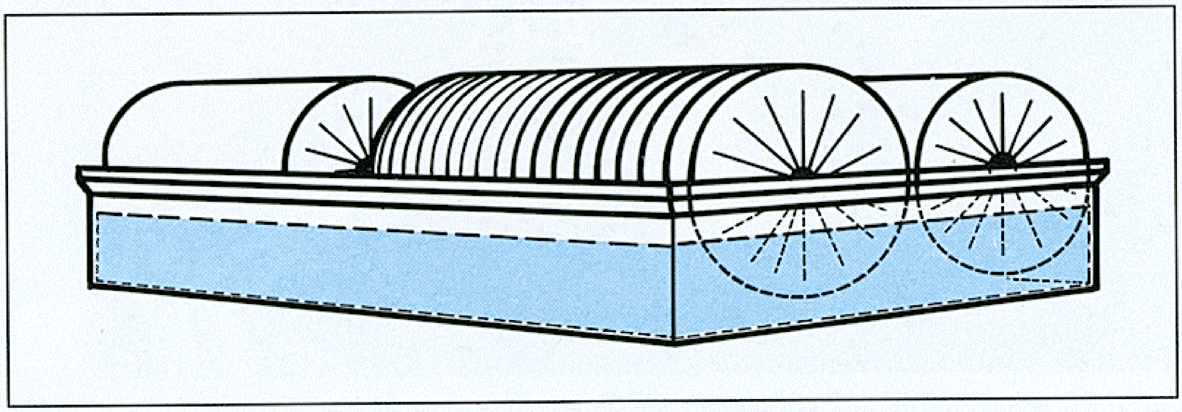


Figure 151. Biological discs.

- the great difficulty in obtaining a treated municipal wastewater effluent with less than 40-45 mg.l^{-1} BOD_5 without making heavy additional investments; - the need to cover the discs to protect them against harsh weather.

2.2.4.2. Submerged contact structures

This method consists in submerging in a tank of activated sludge a fixed or floating structure on which an additional biomass has developed, which is not required to pass through the clarifier. Thus, it is theoretically possible to improve the performance of a biological purification facility without enlarging the clarifier, which may be limited by the solids loading applied (see Page 164).

Another more promising application involves nitrification tanks that are fitted with these contact structures and placed downstream of a conventional facility removing carbonaceous pollution. This system can be compared with a method that is widely used in small facilities in Japan, where a final aeration tank fitted with honeycomb modules is located downstream of the small plant with no final settling tank.

The criteria determining the choice of contact structure are:
- the specific surface area. The growth of the biomass concentration depends directly on the surface area. Processes may be grouped on the basis of this criterion, which determines all the subsequent technological options;
- sensitivity to clogging and the possibilities of cleaning;
- the resistance to wear and tear;
- the material and installation costs.

The processes differ mainly in the type of materials used:

- flat materials.

These processes use plastic fill similar to that used in trickling filters. The BOD loadings applied remain below 2 kg/m^3.d. The increase in the level of sludge is about 20 to 40% as compared to traditional activated sludge;

- filiform materials. The threads employed may be used in two ways:

  * by direct implantation of threads arranged in various ways (loops, clusters, etc.), mainly using the "ring-lace" technique.

  * by using 2 to 3 cm edge cubes made of polyurethane mesh.

The major drawback of this method lies in the especially high risks of clogging and agglomeration, particularly with waters containing fibres, greases, etc.

- floating materials.

3. ANAEROBIC BACTERIAL GROWTH

3.1.
THE BIOCHEMISTRY AND MICROBIOLOGY OF METHANOGENESIS

Anaerobic fermentation is brought about by populations of complex bacteria which, in very specific environmental conditions (redox potential of about-250 mV, and an almost neutral pH), form stable associations. The process is strictly anaerobic and results in the formation of methane.

This process takes place in the natural environment when a high concentration of OM occurs in the anaerobic state: marshlands, lake sediments, digestive tracts, etc.

In a simple example, such as glucose, the general equation for anaerobic digestion may be written as follows:

$$C_6H_{12}O_6 + 0.2NH_3 \rightarrow C_5H_7NO_2 + 2.5CH_4 + 25CO_2 + 0.6H_2O$$

The methane fermentation of OM takes place in ecosystems that ore "cold" C), and (10-15C), mesophilic (30-40°), and even thermophilic (>45°C).

The various forms of degradation of complex organic matter in the anaerobic state may be described in the following manner (Figure 152):

. **Hydrolysis and acidogenesis phase**

This phase is performed by a wide variety of species: mesophilic, thermophilic, obligate or facultative anaerobes.

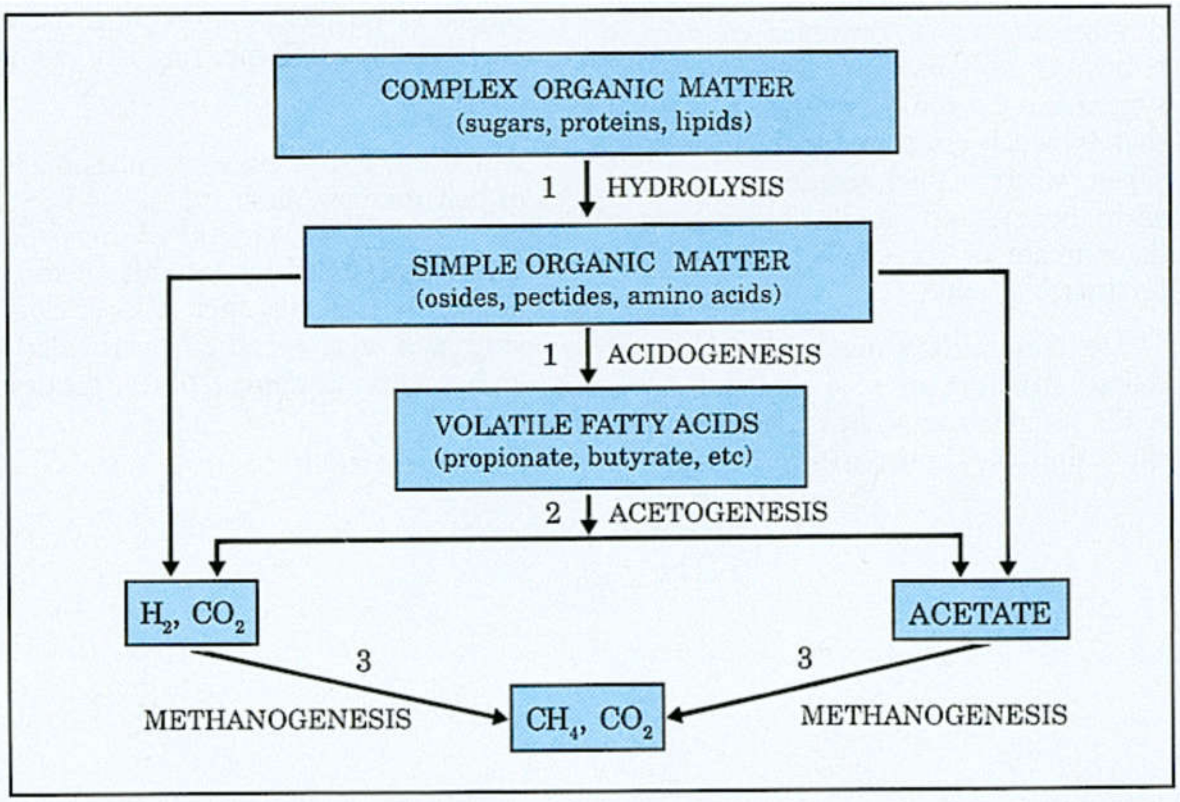


Figure 152. The anaerobic degradation of organic matter.

This first phase results in a mixture of volatile fatty acids, such as acetic, lactic, propionic, butyric, etc., neutral compounds such as ethanol, gaseous products such as CO_2 and H_2, and ammonium.

These microorganisms often have shorter generation times than those in the following phases.

Acetogenesis phase

This singular acetogenesis (acetate production) phase is brought about by bacteria that are obligate producers of hydrogen (or obligate proton reducers). The process uses reduced metabolites from the hydrolysis and fermentation phases (lactate, ethanol, propionate, butyrate). The dehydrogenation of these compounds is a process which, in the absence of microorganisms capable of using hydrogen (or a combination of hydrogen with sulphur for example, to form H_2S), is thermodynamically unfavourable, if not impossible:

$$\text{Lactate} + H_2O \rightleftarrows \text{acetate} + 2H_2 + CO_2 + 4.18\ \text{kJ. mole}^{-1}$$

$$\text{Ethanol} + H_2O \rightleftarrows \text{acetate} + 2H_2 - 9.6\ \text{kJ. mole}^{-1}$$

$$\text{Butyrate} + 2H_2O \rightleftarrows \text{acetate} + 2H_2 - 48.1\ \text{kJ. mole}^{-1}$$

$$\text{Propionate} + 2H_2O \rightleftarrows \text{acetate} + 3H_2 + CO_2 - 76\ \text{kJ. mole}^{-1}$$

However, at very low partial pressures of hydrogen, the reaction becomes thermodynamically possible and its energy variation is sufficient to allow for the synthesis of ATP and bacterial growth.

Thus, this phase is sensitive to the presence of hydrogen. It follows that to break down propionate, which is thermodynamically the most unfavourable agent, the reaction is only possible at a partial hydrogen pressure of less than 10 Pa.

Methanogenesis phase (in the strict sense)

Two general methods of methanogenesis are identifiable. In the first, the H_2/CO_2 couple forms H_2O and CH_4. In the second, which is known as acetatecleaving, acetate is broken down into CO_2 and CH_4. The second method produces about 70% methane.

Other sources of carbon such as methanol, formaldehyde, and methylamines may also be used by methane-producing microorganisms.

3.2.
THE NATURE OF METHANE-PRODUCING BACTERIA

Methane-producing bacteria are obligate anaerobes. They are characterized by the presence of co-enzymes or very specific factors such as **factor F 420**, whose fluorescent properties allow these bacteria to be seen under a microscope equipped with UV. Factor F 430 contains nickel, an element indispensable to the growth of these populations.

The following are the main genera:

Genus	Substrates
Methanobacterium	H_2/CO_2
Methanobrevibacter	H_2/CO_2
Methanococcus	H_2/CO_2
Methanosarcina	H_2/CO_2/acetate
Methanothrix	acetate

The generation time varies widely, depending on the type of substrate, from several hours for hydrogenophilic bacteria to several days for acetate-cleaving bacteria.

The affinity constants with regard to the substrates also vary widely, while very low acetate levels tend to promote the presence of **Methanothrix** in anaerobic ecosystems.

3.3.
FACTORS CHARACTERISTIC OF ANAEROBIC DIGESTION

3.3.1. Biogas

The composition of the gas formed depends on the composition of the substrate and the conditions under which the fermentation units operate (loading, retention time). As a first approximation, the following values may be considered:

CH_4: 55 to 75% H_2: 1 to 5%
CO_2: 25 to 40% N_2: 2 to 7%

Other products may also be present, including H_2S and the thiols from inorganic or organic sulphur present in raw wastewaters, and NH_3 from proteins in the biomass. These components are responsible for the characteristic foul odour of this gas.

The quantity of CH_4 formed also depends on the type of substrate. The following table gives some indications:

Substrate	CH_4 production ($m^3.kg^{-1}$ of substrate)
Sugars	0.42 to 0.47
Proteins	0.45 to 0.55
Greases	Up to 1

In sludge digestion methane production is 0.6 to 0.65 m per kg of VS destroyed.

3.3.2. Sludge production

When treating industrial wastewater, the production of excess biomass ranges from 0.10 to 0.15 kg DS per kg of soluble COD removed. This value is low compared to the values obtained in aerobic treatment where, depending on the rate, production varies between 0.2 and 0.4 kg DS per kg of soluble COD removed. This is one of the advantages of anaerobic processes.

3.4.
IMPLEMENTATION

The process of anaerobic digestion may be implemented in a variety of ways. Certain methods are similar to those used in aerobic fermentation.

The bacterial culture may be developed in free suspension (suspended growth) or attached to a support (attached growth).

The digestion methods with suspended growth are currently more widely used but those using attached growth are the subject of much research.

3.4.1. Suspended growth

One important feature of methane fermentation processes using suspended growth is the difficulty encountered in separating the solid phase from the interstitial liquid. Clarification, if it is desired, is difficult because of the usually very fragile nature of the biological floc, the release of methane gas in the form of microbubbles inside the floc, and the frequently high density of the interstitial liquid. Clarification is necessary in the treatment of wastewaters if the content of microorganisms in the fermenting reactor is to be enriched, thus reducing volume by recycling settled sludge.

This clarification stage requires an extensive settling area. Clarification can be stimulated by cooling the liquor, which slows or blocks gas release (to the detriment of the system's energy efficiency) by prior deaeration, by using the filtering effect of the sludge blanket, or by introducing flocculating agents.

When treating industrial wastewater, normal loadings vary between 2 and 15 kg COD/m^3.d. When treating sludge, it is possible to introduce 2.5 kg VS/m .d in a high rate digester.

. **Sludge granulation**

With suspended growth it is also possible to use certain granulation properties of anaerobic biomass. Strictly speaking, the granules are agglomerations of bacteria measuring up to 8 mm in size. These granules have excellent settling characteristics (0.5 to 3 cm.s^{-1}), which means that the liquid to be treated can pass without entraining a significant number of particles.

The formation of these granules is far from clear. It has been demonstrated that inert micro-particles play a role in initiating the granulation process. The importance of the calcium concentration (greater than 100 mg.l-') in the granule formation phenomena has often been indicated. Starch is another element that promotes this process.

. **Two-stage digestion and sulphate reduction**

Another method used in suspended growth is two-stage digestion. In order to optimize the action of each stage, it is necessary to separate hydrolysis-acidification and acetogenesis-methanogenesis. This separation may be particularly applicable in the following cases:

- when the hydrolysis stage is limiting and a separate optimization process is necessary (pH conditions and temperature). An example of this is waste containing cellulose;
- when there is a risk that the first stage will inhibit the second. Examples of this are:

a) rapid acidification of simple sugars in which the slightest variation in loading results in major pH fluctuation;

b) the risk of sulphate-reduction in S concentrations greater than 200 mg.l^{-1} (H_2S is toxic for the acetogenesis-methanogenesis phase).

3.4.2. Attached growth

In contrast to suspended growth, attached growth cannot be used for sludge for practical operating reasons, such as clogging of the support.

. **The use of plastic support material** (Figure 153)

The support materials used in this case

are similar to those in trickling filters, except that they are submerged. The high void ratio of these materials substantially limits the risk of clogging, while the relatively high developed surface area allows operation at satisfactory loadings, generally greater than 10 kg/m^3.d of COD.

. The use of moving support materials (Figure 153)

Moving supports usually have a particle size of a few hundred microns. They are expanded by an ascending flow of water. A very good substrate-culture exchange and a high concentration of active biomass can be achieved with these reactors. The loadings here may reach 50 kg/m^{3}d of COD or even more for some effluents.

It is necessary to control the growth of the bacterial mass so as to avoid an excessive buoyancy increase of the support material or congestion of the bed.

Methane fermentation is well suited to certain fluidized or expanded bed reactors, but the hydraulic system must be perfectly controlled.

Figure 153. The Anafix fixed bed reactor. The Saint-Hubert dairy. Magnieres factory in eastern France.

Figure 154. Methane fermentation pilot. Anaflux reactor.

4. USING MEMBRANES IN THE TREATMENT OF WASTEWATER

See Chapter 15, Page 851.

5. LARGE SURFACE AREA PROCESSES

Large surface area processes involve purification processes with low concentration of purifying organisms in the biological reactor. These systems do not include recirculation of bacterial liquor or a separate clarification stage. They require a substantial surface area, but installation of the treatment unit is always very simple and requires little electromechanical equipment.

5.1.
VARIOUS TYPES OF LAGOONING

5.1.1. Natural lagooning (aerobic)

Rays of sunlight are the source of energy enabling aquatic food chains (trophic chains) to produce living matter.

Figure 155 shows the principal biological cycles that develop in the lagoon.

Aerobic bacteria, which are oxygenated by the photosynthetic action of vegetables that also take part in the direct synthesis of organic matter, are mainly responsible for the purification of effluents.

Aerobic bacteria include:

- **microphytes,** or microscopic algae, which are mainly green or blue algae (see Page 406) that are difficult to separate;
- **macrophytes,** or macroscopic plants, which include free forms such as duckweed and fixed forms such as reeds.

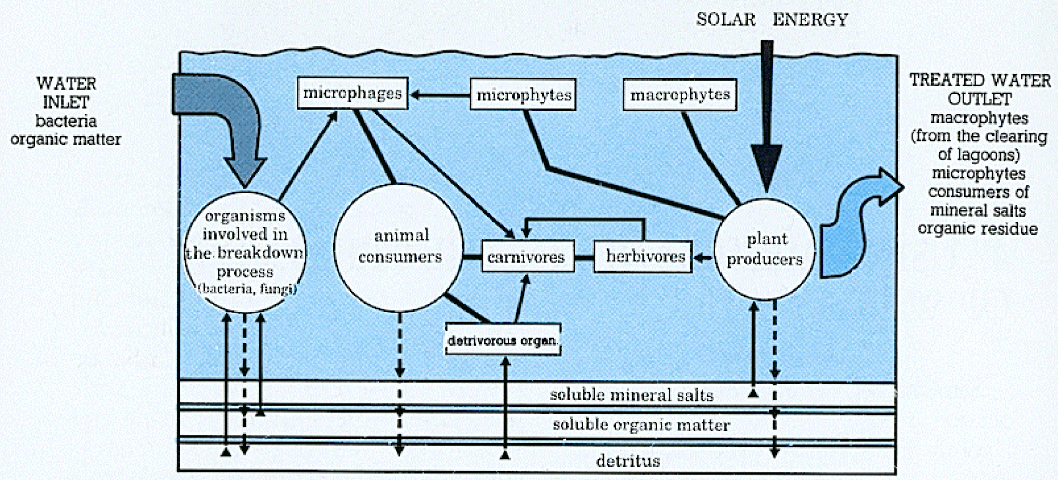


Figure 155. Biological cycles in a lagoon (after CEMAGREF).

Water hyacinths may take root. Superior vegetables act as support and normally promote the proliferation of purifying bacteria and algae.

If macrophytes attached to rhizomes develop after planting, they will exchange nutrients with the soil, the sediment, and the water. A host of predatory fauna of bacteria, phytoplankton, etc. proliferates inside the lagoons: Protozoa, Cladocera, Copepoda. Fish life may be abundant in the areas downstream of the lagoons.

A natural lagoon is a very complex biological structure, where balance is not always easily achieved.

5.1.2. Aerated lagooning

Oxygen is supplied artificially by floating or fixed mechanical aerators or by air injection. Unless it is adequately compartmentalized, the biological reactor is similar to a completely mixed system. The biological equilibria resemble those in the traditional activated sludge process although some algae growth is inevitable.

The microorganism concentration is low and the settling of bacterial floc is poor. Aerated lagoons are often followed by huge settling lagoons, some of which are equipped with facilities to remove the sludge.

The mixing action of aerators in the aerated zones (2 to 5 W per m^3 of lagoon) greatly reduces the formation of deposits as compared with natural lagoons.

5.1.3. Anaerobic lagooning

In these lagoons, the expected purification efficiency depends mainly on the development of methane fermentation. For this reason, this process is only applied to very concentrated effluents and usually as a form of pre-treatment before a second aerobic purification stage.

The risk of pollution is particularly high and these lagoons become ineffective at low temperatures. Therefore, they may be used only in sufficiently remote areas and under favourable climatic conditions. Measures taken to cover the lagoons providing the means of recovering the biogas and improving the aesthetics of the system, have been applied to certain industrial effluents.

In practice, classifying various types of lagoons as either aerobic or anaerobic is somewhat artificial. In particular, the liquid medium of aerobic lagoons is not oxygenated in its entirety.

In the zones upstream of an aerobic lagoon, especially in the case of a natural lagoon that is compartmentalized, the pollution brought by the inflow of raw wastewater produces an oxygen deficiency.

Moreover, in the deeper layers, deposits made of the heavier suspended solids and of residue from biological activity gradually collect. Within the deposits, anaerobic fermentation phenomena occur, organic substances are mineralized and CO_2, CH_4 and possibly H_2S, are released. These deposits are particularly significant in the absence of mixing and where the wastewaters contain a great amount of easily settleable suspended solids.

In any lagoon, the aerobic and anaerobic phenomena are more or less related. If, in an aerobic lagoon, a large part of the liquid mass is deprived of oxygen and is the scene of anaerobic bacterial growth, the lagoon is referred to as **facultative.** In the upper water layers, organic matter is removed through the action of aerobic bacteria and algae, while in the layers lying below the surface, it is removed by anaerobic bacteria and so-called "facultative" bacteria, which are bacteria that are adapted to both environments.

5.2.
PERFORMANCE AND DESIGN

The purpose of lagoons is to remove organic pollution, reduce bacteriological pollution and sometimes to nitrify treated effluent. Temperature is an essential parameter, particularly with regard to bacterial decontamination. There is no simple mathematical model capable of explaining the purification kinetics of the complex biological phenomena occurring in natural lagoons.

5.2.1. Natural lagoons

Natural lagoons are sufficiently shallow to enable an adequate amount of light to penetrate. Microphyte lagoons should be no deeper than 1.2 to 1.5 m. On the other hand, they must be deeper than 0.80 m to avoid the proliferation of macrophytes. If, on the other hand, the desired intent is to facilitate the growth of these macrophytes, as in the case of a polishing lagoon for example, a depth of no more than 0.30 m is recommended. In the temperate climate of France, the lagoon size is based on a daily loading of 50 kg of BOD_5/hectare.day, which corresponds roughly to 10 m^2 per capita and a retention time of 50 to 60 days. This basis is commonly used to convert about 90% of the BOD_5 at a temperature of 10-15°C. The level of suspended solids in the treated effluent remains high and varies considerably (from 50 to 150 $mg.l^{-1}$) depending on the season. This figure rises steeply with increased insolation. The total BOD_5 of a municipal effluent treated by lagooning is therefore usually greater than 50 $mg.l^{-1}$.

In polishing lagoons situated downstream of a conventional activated sludge treatment facility and designed to reduce bacterial contamination (a reduction of 3 to 4 logarithmic units of bacterial concentration expressed in indicator germs), a retention time of about 30 days is usually adequate under typical conditions in France as long as the temperature does not drop below 15-20°C. This temperature is also very important if nitrification is required.

5.2.2. Aerated lagoons

Aerated lagoons may be as deep as 2.5 to 3 m. The maximum acceptable depth depends on the stirring power of the aeration system.

One approach to the necessary retention time is based on the application of Monod's model for a single completely mixed reactor (refer to Page 285). If So and Sf are BODS levels in the raw and treated wastewaters, then:

$$\frac{Sf}{So} = \frac{1}{1 + K_T t}$$

where:
t is the retention time in days,
KT depends on the temperature T in °C according to the relation KT = Kzo x 1.07T-z° if T> 10°C. For municipal wastewater, Kzo is about 0.5.d-1.
The temperature Ti in the lagoon may be calculated by the equation:

$$(T_o - T_l) = \frac{(T_l - T_a)\ FA}{Q}$$

where:
T_o is the temperature in °C of the wastewater to be treated,
T_l is the temperature in °C in the lagoon,
T_a is the temperature in °C of the ambient air,
A is the surface area in m^2 of the lagoon,
Q is the flow in $mj.h^{-1}$,
F is a coefficient that varies from 0.5 to 1.2 in the temperate zones of the northern hemisphere.

In reality, dividing the lagoon into compartments and rational distribution of aerators reaps some of the benefits of having the tanks arranged in series. On the other hand, the dispersed character of the bacterial floc in low concentrations (low sludge age and limited level of stabilization) and the development of algae are detrimental to good separation of suspended solids. In the treatment of municipal wastewater, the SS concentration in the treated effluent may vary between 50 and 250 $mg.l^{-1}$.

Locating a settling lagoon downstream of the aerating lagoon allows these values to be reduced. The soluble BODS of the treated effluent is low and corresponds to a reduction of 80 to 90% for a retention of about 10 days in temperate climatic conditions.

The efficiency of bacterial decontamination depends mainly on the retention time and the absence of preferential paths in the lagoon.

It is therefore clear that aerated lagoons are best suited to the breakdown of organic pollution and that natural lagoons are particularly well suited to reducing the bacterial concentration in an effluent that has already undergone secondary purification, whence the name `stabilizing' or `ripening' lagoons.

5.2.3. Anaerobic lagoons

The retention times are greater than 20 days and often exceed 50. The BOD loadings are about 0.01 $kg/m^3.d$ and the removal efficiency may vary in a wide range of 50 to 80%. The SS level is high.

Deep lagoons (5 to 6 m for example) should theoretically enhance the process.

5.3.
DESIGN AND MAINTENANCE OF LAGOONS

The compartmentalization and operation of lagoons in series tends to improve efficiency. This layout allows for successive facilities corresponding to different ecosystems and/or purifying procedures. However, extensive anaerobic phenomena and foul odours may occur if the raw effluent is concentrated.

A geotechnical study is indispensable before selecting a lagoon process solution. Also the reservoir must be watertight. The banks must be as steep as possible and be protected against wave action (adequate rock support, sufficient freeboard) especially in aerated lagoons.

The operation of the lagoons is made easier if settleable and floating matter is previously removed from the wastewater. The ideal solution for municipal wastewater consists in installing upstream of the lagoon a pretreatment and primary settling facility combined with, for example, an anaerobic digestion plant. However, economic factors generally dictate that the lagoon be supplied with wastewater that has not been previously settled. The upstream zones of lagoons often carry large amounts of sludge deposits that may cause a nuisance.

The systematic cleaning of lagoons is an essential part of operations and it is important that this be taken into account in the study phase. Sludge removal is often accompanied by the clearance of excess aquatic plants, particularly in natural lagoons

5.4. THE USE OF SOIL FOR PURIFICATION

The first method used to purify wastewater was land disposal. Using soil for purification takes advantage of:

- the physical and physical/chemical properties of the soil, including filtration, adsorption, ion exchange, retention capacity;
- the biological properties of the soil, including the action of the microflora and plants.

The purification system is thus made up of both soil and plants. Some of the polluting elements are released into the atmosphere. Some of the carbon is transformed into carbon dioxide by bacterial respiration and by photosynthesis. Other polluting elements are removed by plants. Firstly, C and N, then, P, K, Ca, Mg and finally, to a lower extent, heavy metals.

The three main treatment methods using soil are irrigation, infiltration-percolation and controlled runoff (see Figure 156).

Table 45 gives typical characteristics and performance of these treatment systems.

Irrigation is the most widespread system. Water is supplied through ditches or sprayed. The underground water table must not be located at a depth of less than about 1 m. The soil must be moderately permeable and drainage is frequently recommended. It is clear that the quantities of water employed vary according to the type of plant growth, the nature of the soil, and the climatic conditions. The amount of water applied, including precipitation, must correspond to the natural evaporation rate and plant requirements (evapotranspiration and growth). This figure varies throughout the year. The balance of nutrients must also be taken into account. The organic loads usually applied range between 5 and 20 kg of BOD_5 per hectare per day.

Apart from the occupation of extensive areas of land, the main difficulty in apply ing these irrigation techniques is the limited period of use. For annual crops, land disposal is only possible during 3 to 6 months per year. In grassland, land disposal is not possible during the rainy season or in the months before animals are put out to pasture. Tree plantation (poplars) are more tolerant. A detailed plan of irrigated crop rotation has to be drawn up.

It is preferable that the raw wastewater has at least undergone settling before use (refer to Page 81). The more advanced the pretreatment of the effluent, the more constant and rapid its infiltration rate.

Table 45. Characteristics and performance of the main methods of treating municipal wastewater by soil.

Treatment	**Annual hydraulic loading** m/year	**Daily hydraulic loading** mm/day	**Required pretreatment**	**Treated water mg.l^{-1}**		
				SS	**BOD$_5$**	**TKN**
Irrigation	0.5 to 3	3 to 10	Primary settling	< 5	< 5	3 - 5
Infiltration-percolation	4 to 50	20 to 200	Primary settling	< 5	< 5	10
Controlled runoff	1 to 10	10 to 30	Screening	< 20	< 15	5

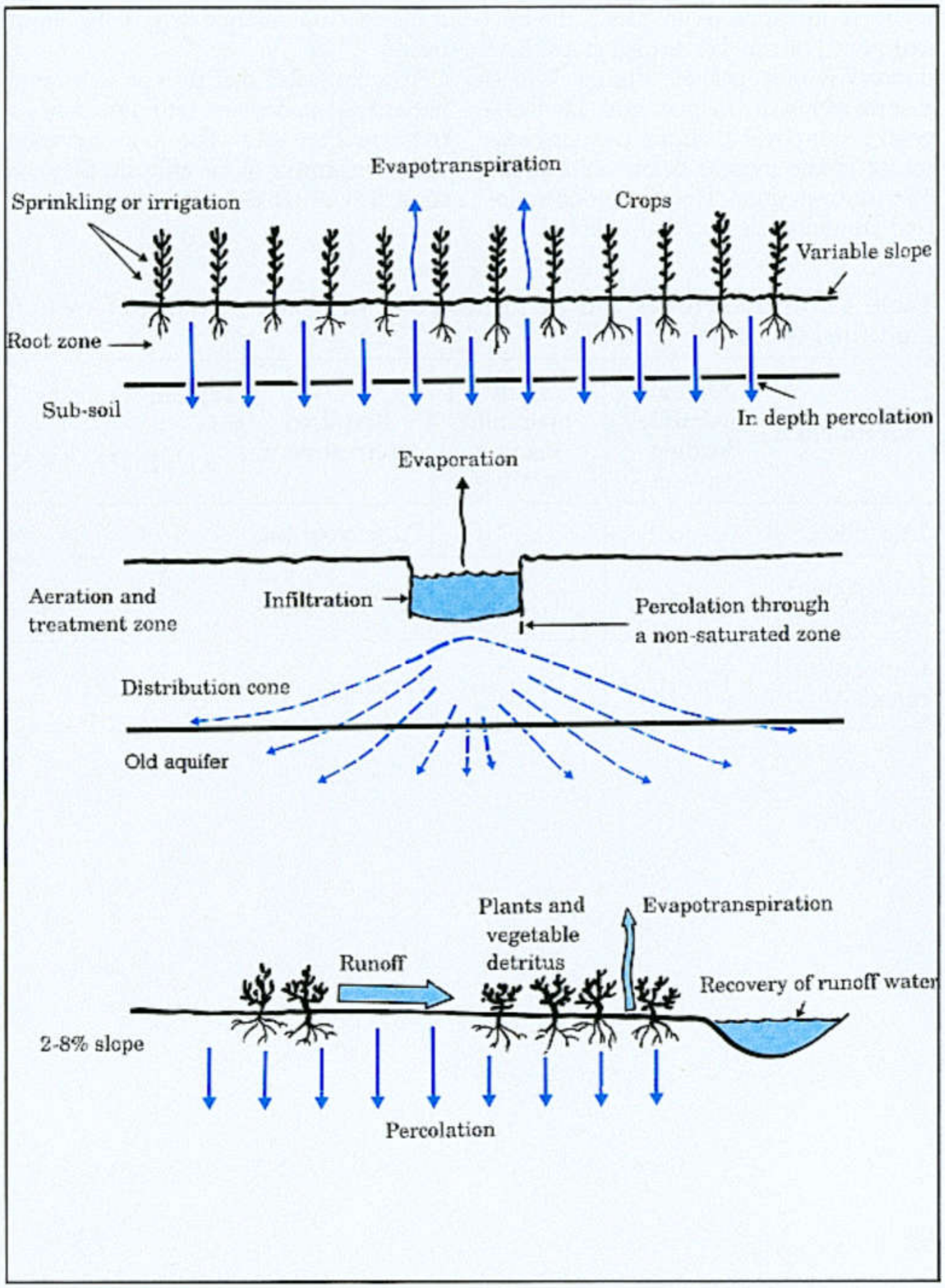


Fig. 156. Soil treatment systems.

5

METHODS AND MEANS OF ANALYSIS

1 GENERAL

Analysis is absolutely necessary to design a water treatment installation project as well as to monitor its operation and to evaluate the quality of the treated water (plant outlet, systems, natural environment).

The relentless progress of analytical techniques makes it possible to improve our knowledge of the constituents of the different types of water and their effects. Quality standards are increasingly rigorous, treatments are increasingly sophisticated and monitoring needs to be all the more precise and reliable.

1.1

PRECISION

The precision of a method includes several criteria.

Accuracy is the difference between true value and the average of the results. It depends on systematic errors (interferences, sampling, calibrating).

Reliability is determined by repeatability (same procedural conditions for the same operator) and reproducibility (different procedural conditions with different operators). The statistical expression of techniques makes it possible to improve our knowledge of the constituents of the different types of water and their effects.

Quality standards are increasingly rigorous, treatments are increasingly sophisticated and monitoring needs to be all the more precise and reliable.

these deviations is provided by the standard deviation.

Sensitivity is determined by the measurable deviation compared to the value to be measured.

Detection limit is the minimum concentration that can be detected with 95% probability. For all spectrometric measurements, the detection limit of an element is the concentration corresponding to twice the signal due to the background noise of the apparatus.

Statistical methods that are more advanced make it possible to intervene in cases of systematic errors, to choose analytical methods, to elaborate sampling policies (locations and frequency), etc.

1.2.

LABORATORY ANALYSES AND ON-SITE ANALYSES

Legislation on water quality is continually developing. The growing number of quality parameters (62 for the EEC, for example) and the low level of certain guide levels (GL) compel laboratories to revise the methods and equipment used. The growing number of verifications the operators and health organizations are imposing on themselves compel the persons in charge to invest in sophisticated analytical equipment (chromatograph, atomic absorption or emission spectrometer, in some cases even mass spectrometer, etc.).

This analytical equipment is obviously not suited to on-site analyses requiring:

- an investigation with simple, sturdy analytical techniques (follow-up of small plants or study for the design of an installation),
- the use of portable, self-contained, compact multisensors with data processing,
- continuous monitoring (warning unit for raw water, "quality" sensors for treated water).

1.3.

COMPUTERIZATION OF THE LABORATORY

Programs currently make it possible to process analysis information and data for administrative and technical purposes.

Automated administrative management of the laboratory

Software can follow a sample from its arrival in the laboratory until the results report is issued. It is possible to verify the coherence of said results in order to automatically confirm the analysis.treatment

Technical management

The results stored can be processed in statistical manner to establish quality assessments, the evolution of parameters with time, correlations between parameters and information (climatology, treatments the water has undergone, reagent dosages), water quality maps in the systems. It is also possible

- to improve treatment lines,
- to choose intermediate treatment points in the system (rechlorination, for example),
- to establish historical, mathematical models to help with deciding in choices of.

2. SAMPLES

The primary objective of sampling is to obtain samples representative of the element that one wishes to analyze (water, material, sludge, deposit, gas, reagent, etc.).

Samples of water must be taken in particularly clean bottles rinsed several times with the water to be examined, unless the bottle, originating from the laboratory, contains a chemical agent: for example, a chlorine removing agent (bacteriology) or preservative acid (metals), etc.

In most physical-chemical analyses of water intended for supply (system water, drilling water, etc.), it is necessary to wait the needed amount of time to obtain a constant water quality. With regard to lake or reservoir water, the choice of sampling sites must take into account the variations in the parameters to be measured in relation to depth, season, winds, rains, etc.

2.1.
SAMPLING MODE

2.1.1. Grab sampling

This is the sampling mode used most often. The bottles are filled without shaking the water upon contact with the air. It is therefore necessary to use a tube adapted to the sampler and immerse it to the bottom of the bottle, to replace the contents of the bottle several times and then to stopper the bottle immediately. Certain analyses (oxygen, carbon dioxide, pH, etc.) require any shaking or contact with air to be avoided. Samples for bacte-

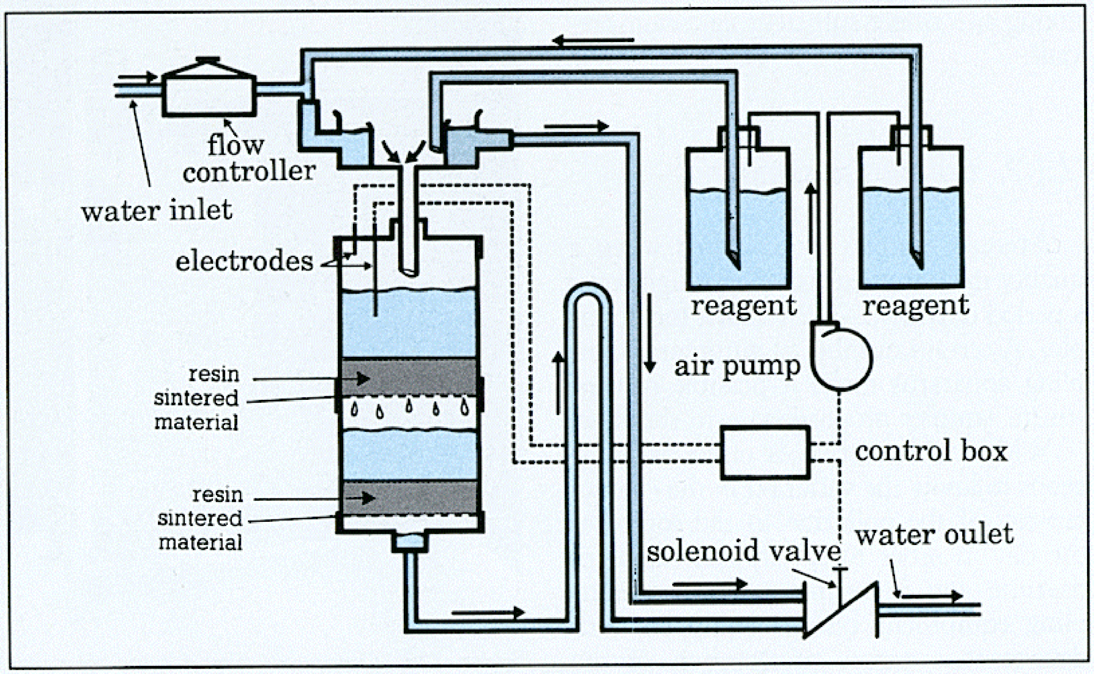


Figure 157. Continuous system of adsorption-extraction on macroporous resins.

riological analyses are conducted in sterile bottles after having sterilized the drawing point (metal tap) by flame and having let the water flow at constant flow for about one minute under the protection of the flame before taking the sample. It is absolutely necessary to record the date, origin and nature of the water on each sample.

For wastewater, daily variations in quantity and quality make grab samples insufficiently representative of the polluting flow. Isolated samples are taken when the presence of unusual or undesirable elements or concentrations is noted. For example:

- toxic residues such as cyanides (by smelling), chromium, copper (by colouration),
- oils and greases,
- concentrated organic residues stemming from dairy farms, slaughterhouses, paper mills, etc.

The heterogeneousness of wastes makes sampling difficult and requires a sample taking site where sufficient agitation prevails.

2.1.2. Composite sampling

Average samples are collected when a quality measurement is being sought over a period of time (2 or 24 hours, for example). A certain number of automatic sampling apparatus make it possible to constitute samples proportionate to the flow.

With wastewater, it is often advantageous to know the variation in the characteristics of the pollution in the course of the day in order to specify the extent of daytime and nighttime pollution. Sampling equipment can be equipped with devices that ensure preservation of the sample at a temperature of +4°C.

2.1.3. Sampling with concentration

A concentration-extraction step is necessary to measure organic micropolluting substances; it can take place in the laboratory, but based on a small volume or, directly at the site, by means of continuous, automatic equipment; in this case, the sample can correspond to the concentration of several hundred litres collected over several days.

Three types of equipment are used:

- water sampler for volatile substances, combined with closed loop stripping,
- continuous adsorption-extraction system on macroporous resins (Figure 157),
- continuous liquid-liquid extractor (Figure 158).

Figure 158. Continuous liquid-liquid extractor (Lyonnaise des Eaux-Dumez licence).

The latter two pieces of apparatus can operate at several pH levels. An extraction cell is less sensitive to the presence of SS than resins; on the other hand, the latter make it possible to recover a greater number of compounds (humic acid, for example). The liquid-liquid extractor also has the advantage of providing more easily quantifiable results and presents fewer blank testing problems.

2.2. PRESERVING SAMPLES FOR THE PURPOSE OF ANALYSIS

Various preservation techniques are used, making it possible to limit the physical-chemical and bacteriological evolution of the water being analyzed. The choice of materials of the bottles should limit losses due to adsorption or, on the contrary, prevent the releasing of substances depending on the elements to be measured. Table 45 indicates the primary preservation modes of the samples in terms of the parameters to be measured.

Table 45. Preservation of samples.

Determination	Flasks	Recommended preservation conditions	Maximum periods of non-evolution
pH	250 ml, Pyrex	Analysis on-site preferably	24 hours
TH, M alk., Cl^-, NO^{2-}, $N0^{3-}$, NH_4^+ , SO_4^{2-}, color, SS, dry solids	2 1, plastic or Pyrex	Refrigeration at 4°C	48 hours
Tasting	1 1, Pyrex	Refrigeration at 4°C	Less than 24 hours
Dissolved oxygen	125 ml, Pyrex	1 ml solution A ($MnSO_4$) 1 ml solution B (KI) (see Winkler method) Refrigeration at 4°C	12 weeks
Detergents, P04 3-	250 ml plastic	1 ml 50% H_2SO_4 Refrigeration at 4°C and darkness	4 weeks
CN-	1 1, Pyrex	2 ml NaOH, pH 10, Refrigeration at 4°C and darkness	24 hours
Al, B	250 ml plastic	5 ml HNO_3	4 weeks
Heavy metals	1 1, plastic	5 ml HNO_3	4 weeks
TOC	125 ml, Pyrex	2 ml H_2SO_4 pH 2, 4°C	1 week

Table 45. Preservation of samples (cont.).

Determination	**Flasks**	**Recommended preservation conditions**	**Maximum periods of non-evolution**
Hydrocarbons	1 1, Pyrex	2 ml H_2SO_4, pH 2, 4°C	24 hours
Phenols	1 1, Pyrex	1.5 ml H_3PO_4 and 10 ml 10% $CUS0_4$ solution	1 week
TKN	1 1, Pyrex	2 ml 50% H_2SO_4 at 4°C in darkness	1 week
PAH and pesticides	2 1, Pyrex	Refrigeration at 4°C in darkness	1 week
Halomethanes	30 ml glass	0.5 g thiosulphate and to be filled up to shoulder level	1 week
Bacteriology	250 ml or 500 ml plastic	Sterile flasks with thiosulphate - Refrigeration at 4°C vital	24 hours
Algology	1 1, Pyrex	40 ml formol - Refrigeration at 4°C and darkness	1 week
COD	1 1, Pyrex	2 ml H_2SO_4,	1 week
BOD	1 1, Pyrex	Refrigeration at 4°C or 2 ml H_2SO_4	6 hours 1 week

3. ANALYSES

3.1.
ON-SITE ANALYSES

Certain parameters can vary while transporting samples to the laboratory and it is always preferable to determine the following in the field: pH, temperature, O_2, CO_2, H_2S, NH_3, oxidationreduction potential, residual oxidizing agents, etc. Measuring these parameters often depends on methods that are less accurate than laboratory methods, but the advantage of immediate measuring can be predominant considering the variations liable to occur during transportation and preservation in the laboratory. Furthermore, these analyses are also necessary in the extended study of raw water or wastewater with a view to establishing a project or optimally improving a treatment installation.

Figure 159. Degrémont case for swimming pools.

3.1.1. Potentiometric methods

These methods usually use selective electrodes that are immersed in water; they make it possible to measure: pH, oxidation-reduction potential, oxygen, turbidiry, resistivity, fluorides, cyanides, etc. Coupling these probes to a central data acquisition unit (microprocessor or microcomputer) makes it possible on site to follow the evolution of the water quality
with time.

3.1.2. Colorimetric methods

These methods are based on "coloured reactions" in which the intensity of the colour obtained is evaluated using comparators that have colour discs, plates or strips serving as gauges.

3.1.3. Volumetric methods

Numerous parameters are determined by volumetry (alkalinity, total hardness, calcium hardness, chlorides, etc,). Small cases containing standard laboratory glassware make it possible to determine these parameters (burettes, Erlenmeyer flasks, graduated cylinders, phials, etc.).

3.2. LABORATORY INVESTIGATIONS

3.2.1. Concentration of samples

Methods of concentration by extraction are basically used to analyze organic micropolluting substances. Four techniques can be mentioned:

- liquid-liquid extraction and concentration of the solvent. Dichloromethane is often chosen to later determine pesticides and PAHs,
- extraction of volatile compounds by the technique of closed loop stripping (CLSA),
- extraction of volatile and semi-volatile compounds by the technique of simultaneous distillation-extraction (SDE),
- cryometry.

3.2.2. Taste test

To better evaluate the tastes of treated water, tasting techniques are used increasingly often in research as well as in monitoring. Two of them can be mentioned:

- determining the **taste threshold** (AFNOR T 90 035). Water is diluted with tasteless water. Tasting is carried out starting with the greatest dilution levels and until the taste becomes perceptible. The threshold corresponds to that dilution rate, which should be perceived by most of the operators (a team of at least three),
- determining the **"flavor" profile.** This method provides more information than the preceding one. A panel of trained, experienced tasters (four operators minimum) establishes a summary of the odors, tastes and sensations noted, each on a 0 to 12 scale of intensity. Their origins must be identified among a list of descriptive characteristics.

3.2.3. Gravimetry

Its principle is based on measuring a mass that is equal or directly proportional to the element sought. Measuring the SS after solids-liquid separation is an example of the applications. Determining the SO_4^{2-} ions can be carried out by $BaSO_4$ precipitation. These methods are obviously limited by the accuracy of the scales.

3.2.4. Volumetry

By definition, this involves measuring the volume of a standard solution proportional to the element sought. The reactions used can be:

Acid-base equilibrium

When determining the P alk. and the M alk., for example, the standard acid used is sulphuric acid. Colored indicators have been chosen according to the pH of their color change.

Precipitation

The example of the precipitation of silver chloride by a standard solution of silver nitrate can be mentioned. The end point of the reaction is made obvious by the red color of the silver chromate precipitate, a salt that is more soluble than silver chloride.

Oxidation-reduction

In cases of permanganate value and COD measurements, the oxidizing agents, i.e., permanganate and potassium bichromate, are introduced in excess com pared to the reducing organic substances under analysis. A standard reducing agent (Mohr's salt, for example) makes it possible to measure the remaining oxidizing agent. The end point of the reaction is once again indicated by a change in color.

Complexometric titration

The hardness is determined by chelating the Ca" and Mg" ions with a standard EDTA chelating solution. The end point of the reaction is also colorimetric.

3.2.5. Nephelometry

This principle is applied to measure turbidity (Figure 160). The particles contained in a given type of water more or less scatter light. If an observer is placed at a 90° angle to the incident beam, he receives a quantity of light based on the particles present. Certain pieces of equipment compare the scattered light with the light transmitted in order to take substances that only slightly scatter light into account. The turbidity levels obtained are compared to gauges (AFNOR, ASTM and ISO have chosen formazine), and expressed in NTU (Nephelometric turbidity unit, equivalent to JTU – Jackson or FTU - Formazine).

This measurement requires precautions: avoid air bubbles, make dilutions for high turbidity levels. Comparative turbidity measurements must be carried out on the same apparatus.

3.2.6. Amperometry

Oxidizing agents such as chloride, chlorine dioxide or ozone can be measured by amperometry. A depolarization current between two electrodes is proportional to the concentration of the oxidizing agent. This property allows continuous measurements in the water systems. In the laboratory, for reasons of precision, a reducing agent (phenylarsine oxide) is introduced, lowering the current to a characteristic end-of-reaction level; this method is, in fact, a type of volumetric method the end of reaction of which is indicated by amperometry.

3.2.7. Electrometry

The potential difference measured between an ion-selective electrode and a ref

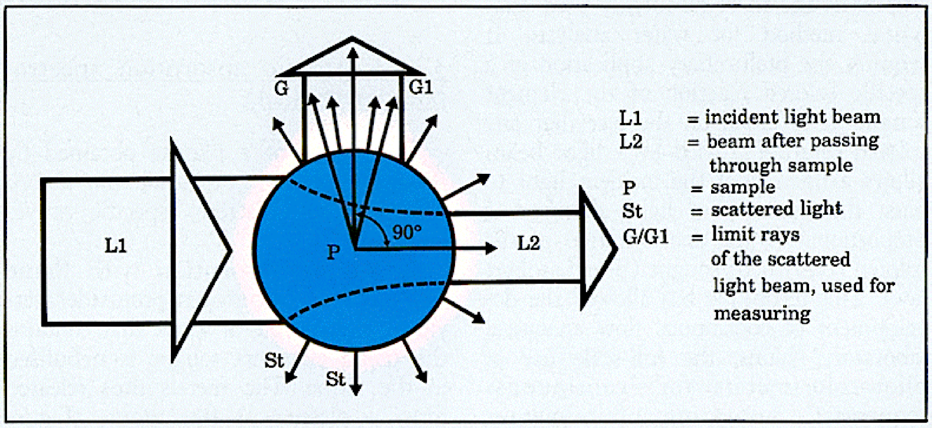


Figure 160. Principle of a turbidimeter

Figure 160. Principle of a turbidimeter

erence electrode is a logarithmic function (Nernst equation) of the activity of the element sought. The pH electrode, a glass membrane electrode, is still the best selective electrode model.

Electrometry is also used for measuring the oxidation-reduction potential.

Electrometric measuring makes it possible, thanks to a set of selective electrodes and an electrometer (high-performance pH meter), to measure about fifteen ions.

In some cases, using indicator electrodes in potentiometric measurements provides very precise results.

Electrodes for measuring free F and CN^- ions are the most commonly used.

Selective electrodes are also extremely useful for analyzing elements in the field but they imply maintaining the temperature of the water under constant analysis and imposing a given ionic strength on the medium.

3.2.8. Spectrophotometry

3.2.8.1. Molecular absorption spectrophotometry

This is the most frequently used analytical method for water analysis. It requires the preliminary application of a specific colored reaction of the element sought. It is based on the fact that any colored solution crossed by a light beam allows a fraction of the incident light to pass; the quantity of light absorbed is proportional to the concentration of the colored constituent sought (Beer-Lambert law). This technique has allowed the development of continuous flow analytical laboratory chains, the full-scale use of photocolorimeters for "continuous sequential" measuring of numerous parameters (silica, ammonium, etc.).

3.2.8.2. UV and IR spectro hotometry

With regard to water, these techniques are used particularly to quantify OM families.

Measuring **UV absorption at 254 nm** is a characteristic index of substances having one or two double bonds.

The same measure at other wavelengths completes the examination (humic acids, for example).

Measuring the **TOC** (NF T 90102) involves the mineralization of the organic carbon by chemical and UV oxidation (Figure 161) or by combustion and detection of the CO_2 by IR. The detection limit of the method is 0.2 mgl^{-1} and the accuracy is 10%.

The **CH_2** index makes it possible to measure pollution by hydrocarbons; generally a technique is used that is based on the absorption of the -CH, $-CH^2$, $-CH_3$ bonds in the infrared region included between the number of waves 2,800 and 3,000 cm^{-1}. There are several procedural methods for which the fields of application can be uncertain and the interpretation can be difficult.

3.2.8.3. Atomic absorption spectro-photometry (AA)

The atoms of a plasma obtained by thermal or electric excitation can absorb radiations of discrete, specific wavelengths.

In **atomic absorption with flame (air/acetylene** or nitrogen protoxide/acetylene), the sample of water that contains the metal elements sought is nebulized in the flame. The metals thus released form a plasma of free atoms (Figure 162).

In the case of **flameless vaporization,** obtained by electric means, the volumes used are smaller. The vaporization device consists of a tube of graphite that is heated to a temperature of between 1500 and 2800°C. Its objective is to produce an atomic vapor from the water sample.

3.2.8.4. Flame emission spectrophotometry

Vaporizing a water solution containing metals in a flame is characterized by decomposition and dissociation into atomic state of the metal traces. The atoms of the metals are thus thermally excited by the flame, and their return to

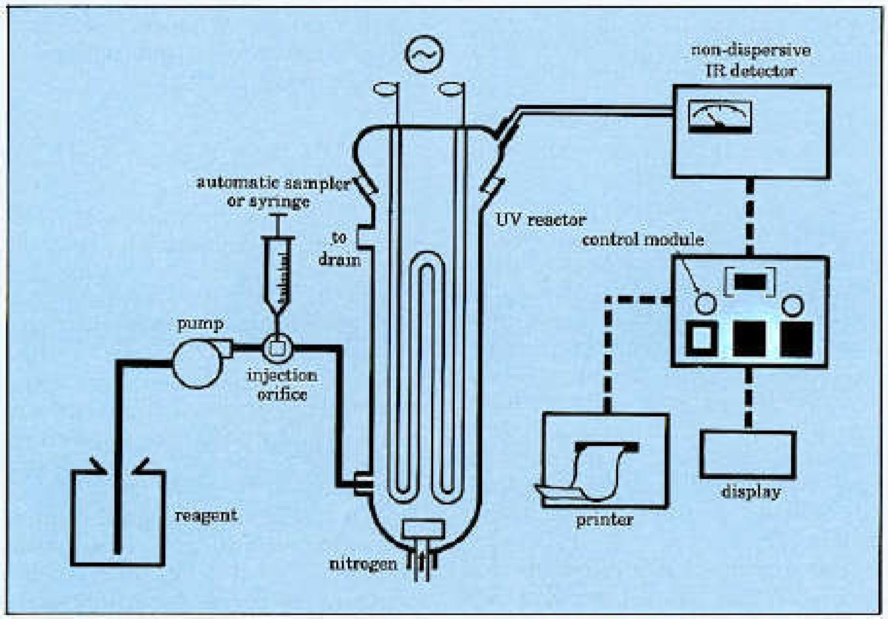


Figure 161. Principle of TOC measurement.

Figure 161. Principle of TOC measurement.

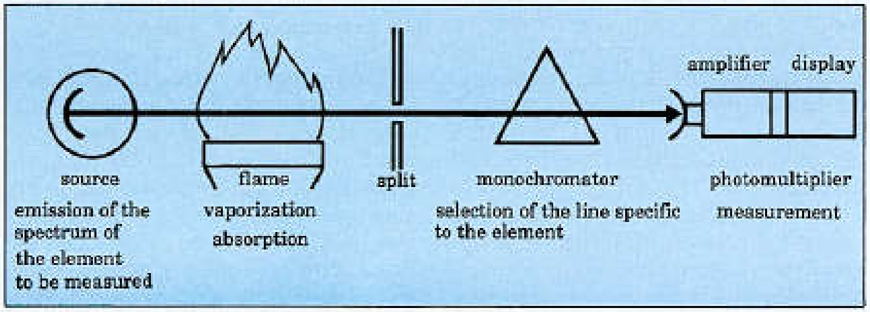


Figure 162. Principle of AA spectrometry.

Figure 162. Principle of AA spectrometry

the fundamental state is accompanied by the emission of radiation the wavelength of which is specific to the element sought and the intensity of which is directly proportional to the concentration. This technique is appropriate for direct determination of alkaline elements: Na, K, Li.

3.2.8.5. Inductive coupling plasma spectrophotomet , (ry ICP)

Inductive coupling plasma spectroscopy is a technique that uses the atomic emission phenomena for which the source of atoms is an argon plasma. At high temperature a mixture of atoms and particles forms in the midst of the argon, charged according to a balance $Ar \rightleftarrows Ar^+ + e^-$.

The plasma is produced by inductive means using a high frequency generator.

Its temperature varies between 6,000 and 8,000°C. The elements to be measured are introduced into the plasma and transformed into atomic vapor and sometimes ionic vapor by excitation when they collide with the elements constituting the plasma.

This technique has a broader field of application than flameless atomic absorption but it has a lower detection power.

The high temperature of the plasma makes it possible to limit the interference of matrices and because of this, ICP can be widely used for seeking heavy metals in the MWW sludge the matrices of which are very rich in organic elements and require a mineralization stage in an acid medium.

All spectrophotometers include a system of light dispersion to choose the appropriate wavelength as well as a photomultiplier to measure the intensity received.

3.2.9. Fluorescence

Fluorescence is a luminescence phenomenon: molecules emit radiation in all directions thanks to the energy received from an incident light. Fluorescence is the property of the aromatic cyclic compounds.

It is measured by spectrofluorometers with UV incident light and reading at a 90° angle in UV and visible light.

3.2.10. Chromatography

To identify and determine **OM**, chromatographic techniques are generally used.

In gas chromatography (GC), the capillary column technique is used because of its unequalled resolving power, the availability of universal detectors and its easy coupling with mass spectrometry (MS).

A gas or liquid chromatograph includes three parts: an injector, a separation column and a detector. After having introduced the sample through the injector by means of a microsyringe, the molecules are separated in the column according to a temperature gradient.

When they leave the chromatographic column, the separated compounds individually pass into a detector whose function is to give a signal (in peak form) the intensity of which is proportional to the quantity of compound injected, making it possible to provide a quantitative analysis by calibration. Universal detectors present an average sensitivity to most organic compounds, while "selective" detectors give a much more intense response to certain chemical families.

The universal detector par excellence is the flame ionization detector (FID). Selective detectors are the electron capture detector (ECD) sensitive to halogenated compounds, the thermionic detector for nitrogen and phosphorus compounds, the photoionization detector (PID) for aromatic compounds.

High pressure liquid chromatography (HPLC) normally uses aqueous or organic solvents as mobile phase. The utilization techniques are more varied than in gas chromatography. Reversed phase chromatography, which uses a polar liquid phase for elution of a column containing a nonpolar phase, makes it possible to determine the PAHs. Ion exchange chromatography makes it possible to separate a large number of cations and anions.

Steric exclusion chromatography separates, on a porous gel, compounds according to their size and makes it possible to determine their apparent molecular weight; fractions of different molecular weights are thus available for further analyses.

3.2.11. Polarography

Polarography is based on measuring current-voltage curves. Between two electrodes (one generally a dropping mercury electrode and the other a reference electrode), current intensity is recorded according to a continuous variation in potential. The difference in intensity between two plateaus is proportional to the oxidized or reduced element. One of the main applications is the analysis of the metal cations and of their specific nature (degree of oxidation, chelating). Other polarographic techniques improve sensitivity.

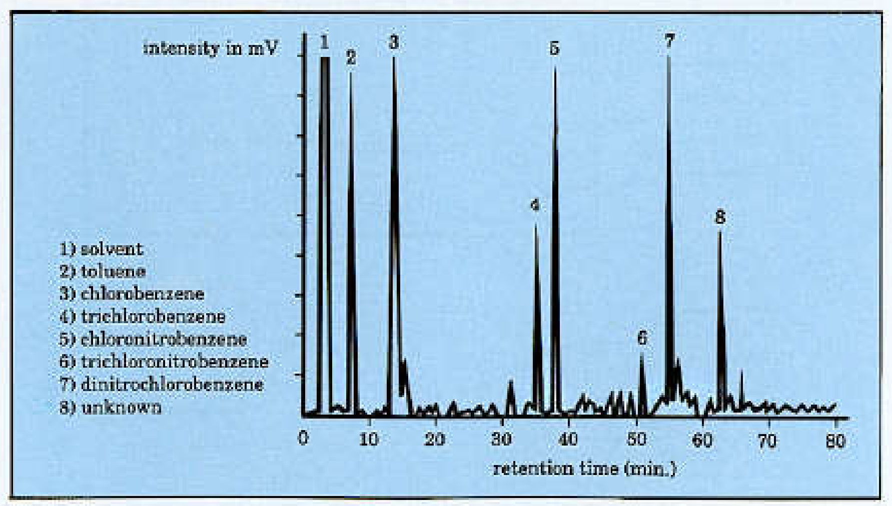


Figure 163. Chromatogram of a polluted surface water.

Figure 163. Chromatogram of a polluted surface water.

3.2.12. Mass spectrometry (MS)

The use of a GC-MS combination makes it possible to measure the different families of compounds that can be chromatographed in gas phase using a single extraction solvent (e.g., dichloromethane) and a single chromatographic separation.

The compounds emerging from the chromatograph are fragmented by a bombardment of electrons. The whole of the ions detected (mass/charge) constitutes the characteristic spectrum of the molecule. The computer comes to the technician's rescue to exploit the spectra. This detector is the most effective because it makes it possible to identify molecules even in case of poor separation on the column, hence the advantage of mass spectrometry compared to selective detectors (Figure 164).

3.2.13. Measuring radioactivity

To monitor distribution water, determinations are generally made without prior chemical separation:
- total a, activity,
- total ß activity,
- ? spectrometry.

In more complex cases, detailed radioanalyses are carried out after chemical separation. To monitor water, only the ß and y activities are generally taken into account to follow the evolution of the radioactivity; nevertheless, the radioactivity of water is always low and for this reason, not many types of equipment make correct countings. The most widely used types of detectors are:
- gas counter using ionization (GeigerMüller counter, proportional counter),
- scintillation or semiconductor detector, sensitive to radiation.

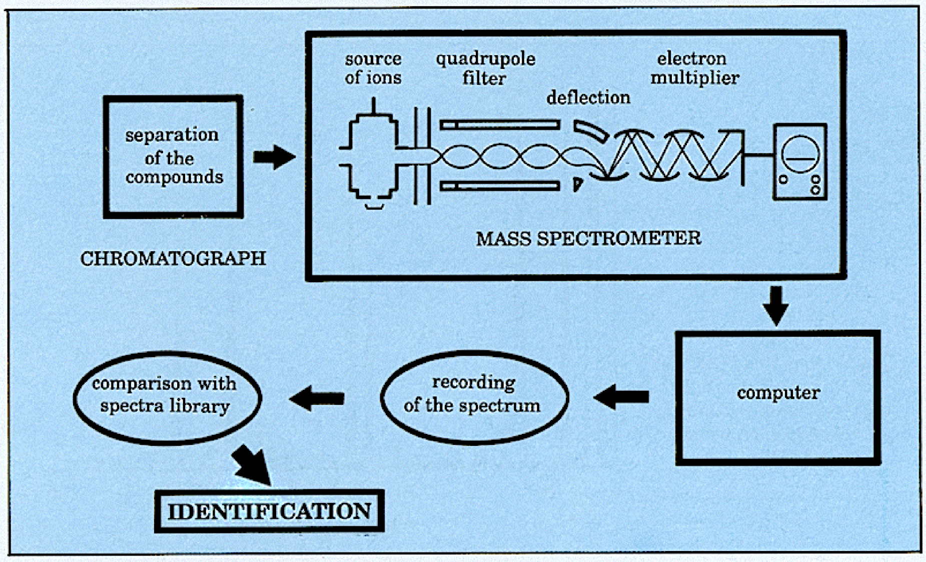


Figure 164. Principle of utilization of mass spectrometry.

Figure 164. Principle of utilization of mass spectrometry.

3.2.14. Combination of techniques

Many analytical determinations use several techniques. GC-MS combination is an example: separation followed by detection.

The overall methods of OM determination are also divided into two parts: reaction and detection.

	Reaction	**Detection**
COD	Reflux boiling oxidation	Volumetry by oxidation-reduction
TOC	Combustion Chemical oxidation + UV	IR absorption for $C0_2$
BOD	Biochemical oxidation	Volumetry of O_2 or selective electrode Manometry

3.3. MICROBIOLOGICAL ANALYSES

3.3.1. Bacteriology

Feces are the primary potential source of pathogenic bacteria in water. These bacteria are only emitted by a small proportion of the population and represent a very limited percentage of the bacterial mass brought in by feces. In order to have a simple, sensitive method, only indicator germs of fecal contamination are generally sought: total coliforms, thermoduric coliforms (also known as fecal coliforms), fecal streptococci, sulphite-reducing, anaerobic, sporulated germs.

In the case of a more complete examination, the following are sought more specifically: Salmonella, Shigella, Legionnella, Giardia, Vibrio cholerae.

In wastewater, total coliforms are counted above all, but also the thermoduric coliforms and fecal streptococci

In water for consumption, counting of the mesophilic bacteria revivable at 20 and 37°C is strongly recommended. The fluctuations of these populations are a good index of the quality of the water and the state of the system (deposits, stagnation zone, assimilable carbon, etc.).

Counting methods use appropriate culture media and metabolic reactions to reveal the colonies sought. In case of a positive result for the specific isolation media, a verification test is always necessary.

Quick, even less precise counting of the bacterial colonies is an objective to attain in order to provide more advanced automation of disinfection treatments. The principles of the sensors studied vary.

3.3.2. Virology

The most widely used method consists in counting the enteroviruses.

A preliminary concentration is absolutely necessary. The most widely used techniques are membrane filtration or ultrafiltration, methods of adsorption-elution on different supports (cellulose nitrate, glass microfiber cartridge, glass powder), and organic flocculation methods.

Most of the viruses usually sought in the water can be isolated on different cellular systems. The most widely used are BGM (buffalo green monkey) type kidney continuous lineage cells or human cancer cells (Hela cells). The probability of isolating a virus increases with the number of cellular systems used. The use of at least two different systems is thus recommended.

The concentrated samples taken are inoculated into the in-vitro cultures, and the appearance of a cytopathogenic effect, revealed by microscopic observation, indi cares viral multiplication and the presence of viruses in the inoculum.

3.3.3. Algology

Algae can be counted by optical or electron microscopy. The species are differentiated by the nature of the pigments they synthesize, their morphology or their mode of reproduction (see page 402).

The samples are generally fixed by adding formol (3 to 5 ml of 40% solution for 100 ml of sample). If the water is low in algae, the sample must first be concentrated either by centrifugation (5,000 rpm) or by sedimentation (1 week in a 11 cylinder). Optical counting is then carried out.

One can also evaluate the total algae load of water by measuring chlorophyll pigments, namely chlorophylls a, b and c.

3.4.
SYNOPSIS OF THE ANALYSES

Table 46 provides general information on the most widely used analytical techniques of the different parameters of drinking water, industrial water and wastewater. Classification of the parameters follows that of the European legislation on supply water. The table is to be used in conjunction with the following remarks:

-other techniques": analytical techniques that are different from those recommended by the AFNOR standards; they can include ASTM standards

- ion exchange chromatography (IC) and inductive coupling plasma spectrophotometry (ICP) have extremely broad areas of use and are only mentioned for their most suited applications,

- (*) analyses used as frequently on wastewater,
- colorimetry: visible absorption spectrophotometry,

- AA: atomic absorption spectrophotometry,

- GC: gas chromatography,
- HPLC: high pressure liquid chromatography.

Table 46. Synopsis of the main analytical methods

PARAMETERS	**AFNOR STANDARDS**			**ASTM**	**OTHER**
	NF T Series Number	**Analytical technique**	**Detection limit**	**STANDARDS Series D**	**TECHNIQUES**
Organoleptic parameters					
(*) Color	90.034	Colorimetry	2.5 mg.l^{-1} Co-Pr		Colored disk Measure not applicable to certain wastewater
(*) Turbidity	90.053	Nephelometry	0.1 NTU	1880-81	Secchi disk
Odor-taste	90.035	Sensory analysis	Tasteless	1296-86	
Physical-chemical parameters					
(*) pH	90.006	Colored indicator		1293-84	
	90.008	Selective electrode			
(*) Oxidation-reduction potential rH				1498-81	Selective electrode
(*) Conductivity µS.cm^{-1}) or resistivity	90.031	Conductimetry		1125-82	
(*) Chlorides	90.014	Volumetry (precipitation)	5 mg.l^{-1}	512-81	Coulometry IC
(*) Sulphates	90.009	Gravimetry (precipitation)		516-82	Nephelometry IC
Silica	90.007	Colorimetry	5µg.l^{-1}	859-80	ICP
(*) Calcium	90.016	Complexometry (EDTA)	200 µg.l^{-1}	511-84	ICP
	90.005	AA			Colorimetry
(*) Magnesium	90.005	AA	50 µg.l^{-1}	511-84	ICP
(*) Sodium	90.019	Flame emission	10 µg.l^{-1}	1428-82	IC
	90.020	AA			
(*) Potassium	90.019	Flame emission	50 µg.l^{-1}	1428-82	
	90.020	AA			
(*) Aluminium				857-79	Colorimetry AA, ICP
Total hardness	90.003	Complexometry (EDTA)		1126-86	Colorimetry
(*) M alk.- P alk.	90.036	Alkalimetry		1067-82	
(*) Dry solids	90.029	Gravimetry (evaporation)		1888-78	Calculation by conductivity
(*) Dissolved oxygen	90.106	Volumetry (oxidation-reduttion) or selective electrode		888-81	

PARAMETERS	**AFNOR STANDARDS**			**ASTM STANDARDS Series D**	**OTHER TECHNIQUES**
	NF T Series Number	**Analytical technique**	**Detection limit**		
Free carbon dioxide	90.011	Acidimetry		513-82	Carbonate balance calculation
Undesirable substances					
(*) SS	90.105	Filtration or centrifugation and gravimetry	0.5 mg.l^{-1}	1888-78	
(*) Nitrates	90.012	Colorimetry	1 mg.l^{-1} N03^{-}	992-71	Selective electrode IC UV absorbance
(*) Nitrites	90.013	Colorimetry	5 µg.l^{-1} $N0_2^-$		
(*) Ammonium	90.015	Colorimetry or alkalimetry	5 µg.l^{-1} NH_4^+	1426-79	Selective electrode
(*) TKN	90.110	Mineralization and alkalimetry	0.5 mg.l^{-1} N	3590-84	
PV	90.050	Oxidation-reduction in hot medium	0.4 mg.l^{-1} O_2		4 h in cold medium
(*) TOC	90.102	Oxidation IR absorption	0.2 mg.l^{-1}	2579-85	
(*) H_2S				4658-87	Distillation-volumetry Selective electrode Colorimetry Potentiometry
Substances extractable by chloroform (SEC)					Extraction Gravimetry
(*) Total hydrocarbons (CH_2 index)	90.114	Extraction and IR absorption	50 µg.l^{-1}		UV Fluorescence
(*) Phenol index	90.109	Colorimetry	10 µg.l^{-1} phenol	1783-80	GC
Boron	90.041	Colorimetry		3082-79	ICP
(*) Anionic detergents	90.039	Extraction and colorimetry	50 µg.1^{-1} LAS	2330-82	AA
Haloforms					GC
Iron	90.017	Colorimetry or AA	10 µ.1^{-1} 10 µg.l^{-1}	1068-84	ICP
Manganese	90.024 90.112	Colometry or AA	20 µg.l^{-1} 10 µg.l^{-1}	858-86	ICP

PARAMETERS	**AFNOR STANDARDS**			**ASTM STANDARDS Series D**	**OTHER TECHNIQUES**
	NF T Series Number	**Analytical technique**	**Detection limit**		
(*) Copper	90.022 90.112	Colorimetry or AA	5 µg.l^{-1} 1 µg.1^{-1}	1688-84	ICP Polarography
(*) Zinc	90.112	AA	1 µg.1^{-1}	1691-84	ICP Polarography
(*) Phosphorus	90.023	Colorimetry of orthophosphate and hydrolyzable phosphates	10 µg.l^{-1}	515-82	ICP
(*) Fluorides	90.004	Selective electrode	50 µg.l^{-1}	1179-80	Colorimetry
Cobalt	90.112	AA	1 µg.l^{-1}		
Residual chlorine	90.037 90.038	Colorimetry or oxidation-reduction	0.03 mg.l^{-1}	1253-86	Amperometry Volumetry
Residual ozone					Colorimetry
Residual CIOi					Amperometry Volumetry
Barium	90.118	AA	5 µg.1^{-1}	4382-84	ICP
Silver	90.112	AA	5 µg.1^{-1}	3866-82	
Toxic substances					
Arsenic	90.026	Colorimetry	1 µg.l^{-1}	2972-84	AA
Beryllium				3645-84	
Cadmium	90.112	AA	0.1 µg.1^{-1}	3557-84	
(*) Cyanides	90.107 90.108	Colorimetry	10 µg.l^{-1}	2036-82	Electrometry
(*) Chromium	90.112	AA	1 µg.l^{-1}	1687-86	Colorimetry ICP (CrVI)
Mercury	90.113 90.131	AA	0.03 µg.1^{-1}	3223-86	
(*) Nickel	90.112	AA	1 µg.l^{-1}	1886-84	ICP
(*) Lead	90.112 90.028	AA or colorimetry	1 µg.l^{-1}	3559-85	Polarography ICP
Antimony				3697-83	AA
Selenium	90.025	Colorimetry	5µg.1^{-1}	3859-84	AA
Vanadium				3373-84	ICP
Pesticides	90.120	GC	10 ng.l^{-1}	3086-85 3478-83	

PARAMETERS	**AFNOR STANDARDS**			**ASTM STANDARDS**	**OTHER TECHNIQUES**
	NF T Series Number	**Analytical technique**	**Detection limit**	**Series D**	
PCB				3534-85	GC
PAH	90.115	HPLC		4657-87	
Microbiological parameters					
(*) Total coliforms	90.413 90.414	Seeding in liquid medium or membrane filtration			
(*) Thermoduric coliforms	90.413 90.414	Seeding in liquid medium or membrane filtration		3508-76	
(*) Fecal streptococci	90.416	Membrane filtration			
(") Sulphite-reducing clostridia	90.415 90.417	Incorporation in gelose or membrane filtration			
Total germs	90.401 90.402	Incorporation on gelose - Incubation at 37 and 20°C		F488-79 4455-85	Epifluorescence
Chlorophyll	90.116 90.117	HPLC Colorimetry		3731	
(*) Specific wastewater parameters					
COD	90.101	Volumetry (oxidation-reduction)	30 $mg.l^{-1}$ O_2	1252-83	
BOD	90.103	Volumetry (oxidation-reduction) Selective electrode	3 $mg.l^{-1}$ O_2		Selective electrode
Inhibitory toxicity to daphnia	90.301	Growth test			
Total hydrocarbons (refinery effluents)	90.202	Flocculation-filtration Extraction-gravimetry		4281-83	Fluorescent chromatography
	90.203	Extraction and IR absorption		3921-85 3328-78	
Phenols that can be removed by steam stripping	90.204	Extraction and colorimetry			

4. DRINKING WATER AND PROCESS WATER

To design a water treatment plant, knowledge, even in-depth knowledge, of physical-chemical analysis is necessary, yet it is not sufficient. According to the final use (drinking water or process water), it is often indispensable to carry out certain tests to choose the process and evaluate its effectiveness. These tests must be carried out on site or shortly after the sample is taken.

4.1.TREATABILITY TESTS

4.1.1. Study of natural settling and sedimentation

in the case of water with a high SS content (exceeding 2 $g.l^{-1}$) it is often necessary to apply a preliminary roughing stage. Tests determine passage velocity, possible addition of reagents, volume of the sludge to be drawn off and its concentration.

The laboratory flocculator is then used, in the same way as with a coagulationflocculation study (see below), with or without adding inorganic or organic reagents. Settling in cylinder is monitored according to time (SS of the settled water and percentage of sludge).

4.1.2. Study of coagulation and flocculation of water

The object of this study is to determine the nature and the dosages of reagents that make it possible to treat water in the best conditions:

- coagulants and flocculants,
- adjustment of the pH,
- adsorbent.

It is often useful to also add oxidizing agents (chlorine, ozone, chlorine dioxide). The amount of electrolyte needed can be determined either by electrophoresis or by flocculation tests.

4.1.2.1. Electrophoresis

This technique consists in observing the movement of the colloids placed in an electric field. The apparatus used for this calculation (zeta meter) includes a monitoring box, an electrophoretic cell, a lighting device, and a binocular microscope that makes it possible to examine particles with dimensions of about a micron. The moving speed of the colloids is measured manually or automatically. Calculations are first carried out on the raw water, then with increasing amounts of coagulant. The zeta potential of the colloidal particles can be calculated from the velocity and the temperature (see page 133).

This makes it possible to draw a curve representing the evolution of the potential (expressed in millivolts) according to the amount of electrolyte (Figure 165). In the case of water corresponding to curve 1 (basically colloidal turbidity), it is sufficient to adopt dose A of reagent, making it possible to attain a potential of -3 to -4 millivolts. On the other hand, for water corresponding to curve 2 with considerable presence of algae or of OM, it is necessary to adopt a dose B nullifying the zeta potential.

Transporting the water from the place of sampling to the laboratory does not greatly affect the result of the electrophoretic study.

4.1.2.2. Flocculation tests

In addition to determining the dose of coagulant, these tests make it possible to visualize the flocculation and to know its effects on settled water as well as on sludge. They must be carried out at a temperature near the one that the water

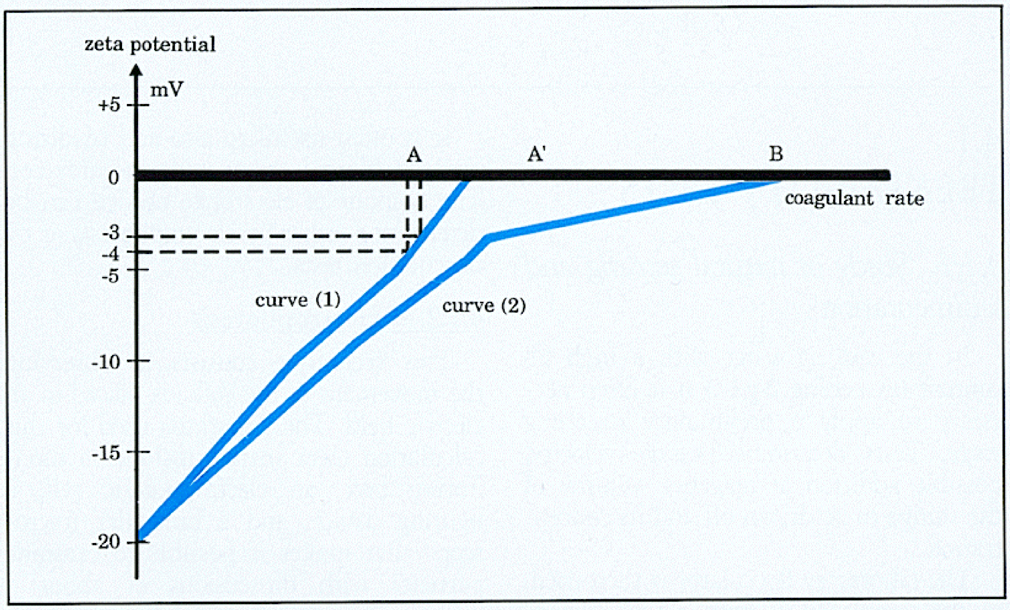
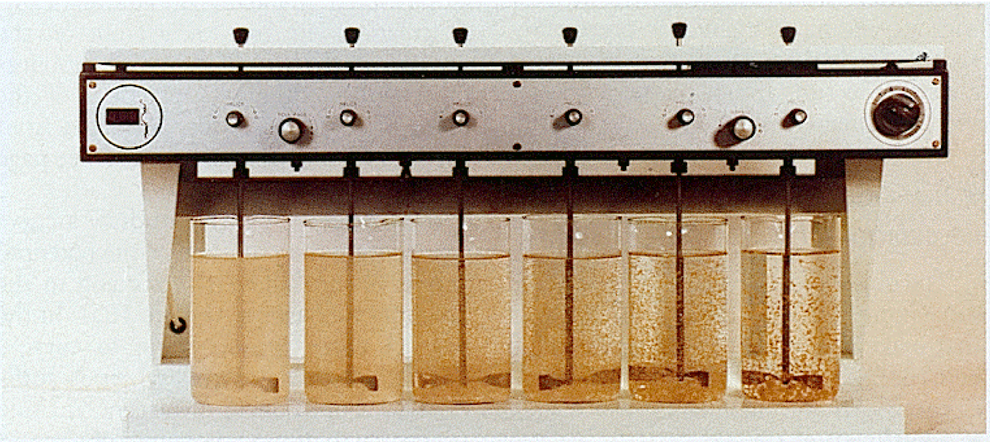


Figure 165. Determining the treatment rate by the method of zeta potential.



Electrically controlled flocculator, variable speed drive and time switch.

Electrically controlled flocculator, variable speed drive and time switch.

will actually have in the course of its fullscale treatment.

First of all, a single reagent is experimented at different dosages; if the result is insufficient, a new test is run repeating the treatment that produced the best result in the first test and experimenting with another treatment at the same time. If several reagents are used, it is important to take the order and the sequence of their introduction into account.

A flocculator making it possible to simultaneously shake the liquid contained in a series of beakers must be used for the results to be comparable. The rotation speed must be identical in all beakers; the optimal value is near 40 revolutions per minute for a 1 x 5 cm blade turning in a 1 liter beaker.

This test is carried out for 20 minutes. Note down the following information:

- **Dosage of reagents and sequence.**
- **Appearance of the flocculation** expressed by a mark:

  0 : no floc,
  2 : barely visible floc, small dots,
  4 : small floc,
  6 : floc of average size,
  8 : good floc,
  10: very large floc.
- **pH after flocculation**. For the best results obtained, these indications are completed with the following information:

- color and turbidity of the settled water,
- percentage of sludge after settling,
- flocculent settling velocity,
- cohesion coefficient or settling velocity of the sludge,
- settled water's permanganate value,
- measurements specific to the treatment under study: Fe, Mn, TOC, specific pollutants, etc.

4.1.2.3. Study of settling

The electrophoretic study and the flocculation test are not enough to transpose the results to a full-scale level, as the most important thing is to know at what speed the clarifier can be operated. It is thus advantageous to also study settling.

Two.cases can occur:

- **relatively limited flocculation:** if the flocculated water is allowed to rest, each of the particles deposits as if it were alone, some at high velocity and others at lower velocity. The liquid gradually clears and a deposit forms at the bottom of the beaker; this is known as flocculent settling,
- **abundant flocculation:** settling involves the whole of the flocculated particles, causing a clear liquid above a sludge layer at the upper part of the beaker; this is known as hindered settling which, practically speaking, only occurs when liquids that are very rich in flocculable substances are treated.

The measurements to be carried out are different in either case.

- **Measuring the cohesion of the sludge**

If one adds an increasing quantity of sludge to the water from a previous test, it will be noticed that the settling velocity increases. This occurs until the liquid has been loaded with a sufficient quantity of sludge to obtain hindered settling. This observation is at the basis of industrial use of "solids contact" clarifiers.

It can be observed that a sludge layer submitted to an upward water current expands and occupies an apparent volume roughly proportional to the velocity of the water, according to a ratio that characterizes the cohesion of the sludge. A 250 ml cylinder (see Figure 167) is used in which one places the sludge collected from different beakers in the course of the flocculation test with each beaker having received the same amounts of reagents. This is allowed to rest for ten minutes. Then the excess sludge introduced is siphoned off so as to only leave an apparent volume of about 50 ml in the cylinder.

A small funnel is then introduced into the cylinder; this funnel is extended by a tube the end of which is located about 10 mm from the bottom of the cylinder.

Then, water is poured in the cylinder through the funnel, which must be pushed lightly into the cylinder in order to keep the air bubbles from being drawn along; this water must imperatively be the water settled in the course of the flocculation test so that **no variation in pH or temperature** is introduced. This water must be introduced in a discontinuous manner by small quantities, with the excess liquid running off by overflow from the top part of the cylinder.

The effect of this is to expand the sludge, and one calculates the upward velocities of the water which correspond to different states of expansion of the sludge.

The measured time T (in seconds) corresponds to the introduction of 100 ml of water for apparent volumes V ml of the sludge equal to 100, 125, 150, 175 and 200 ml.

To calculate the velocity v, if A is the height in mm of the cylinder corresponding to 100 ml (distance between the 100 and

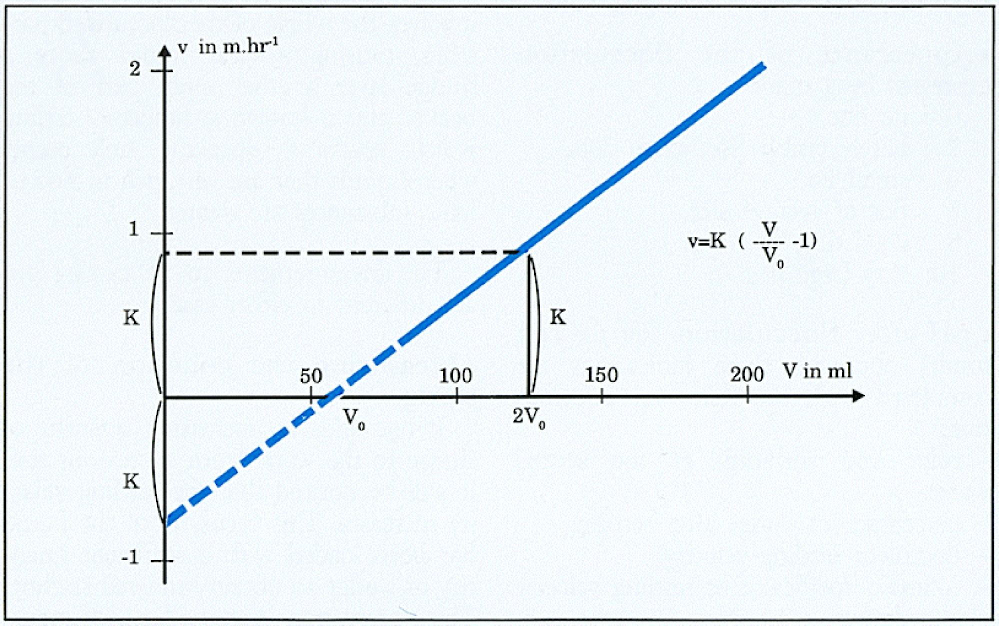


Figure 166. Measuring the cohesion coefficient of the sludge.

200 ml marks on the 250 ml cylinder), v is equal to 3.6 A/T m;hr^{-1}

The results are represented graphically plotting v on y-axis and V on x-axis (Figure 166).

It will be noted that the curve representing the variations in velocity according to the volume of the expanding sludge is a straight line:

$$v = K\left(\frac{V}{V_0} - 1\right)$$

v: upward velocity in the cylinder necessary to obtain the volume V,

V: apparent volume of the sludge in expansion,

V_o: volume of the settled sludge corresponding to a zero velocity and measured on the graph.

The **coefficient "K"** is the characteristic of the cohesion of the sludge; it is known as sludge cohesion coefficient. It depends on the temperature which must therefore be carefully noted down. For quickly settled consistent sludge, the value of the coefficient K can reach 0.8 to 1.2.

On the other hand, for sludge composed of a flocculate that is fragile, light and rich in water, the value of the coefficient K might not exceed 0.3. Measuring this coefficient thus constitutes a valuable piece of information to find out how precipitates behave in a "solids contact" clarifier and to determine the influence of a flocculant aid.

There is a priori no relation between the size of a floc and its cohesion.

Measuring the hindered settling velocity

When the flocculation test directly produces hindered settling, it is quite naturally pointless and even harmful to enrich the liquid with sludge; consequently, there is no reason to consider the use of a "solids contact" clarifier.

The contraction velocity of the sludge mass is measured straightaway as it results from the flocculation test and as it will occur in natural manner in a fullscale clarifier.

The same procedure is used as with measuring the coefficient K, but work is done with a concentration equal to that of the sludge obtained by flocculating 1 liter of water under examination.

The 250 ml cylinder is filled with flocculated liquid; the sludge is allowed to settle for 5 to 10 minutes so that the floc forms again; water is then introduced in a discontinuous manner through the funnel so as to gradually place the sludge in expansion until its initial 250 ml apparent volume is restored.

The velocity established indicates the upward velocity that could be theoretically allowed in a full-scale clarifier. It corresponds to the velocity of the linear portion of Kynch curve (see page 162).

Following this operation, it is advantageous to let the sludge settle down naturally in the cylinder while recording the apparent volumes in comparison with the initial volume occupied by the sludge layer as a function of time (from 0 to 2 hrs). This makes it possible to know the volumes of sludge that need to be withdrawn and, consequently, to calculate certain components of the clarifier such as sludge collecting pits, scraper blades, etc.

Figure 167 summarizes the operations:

- height of the cylinder corresponding to 100 ml .... A mm
- volume of water introduced in 1 minute to maintain the upper level of sludge at the level of the liquid placed in the cylinder (250 ml) ....B ml
- theoretical sedimentation velocity ....VS $m.h^{-1}$

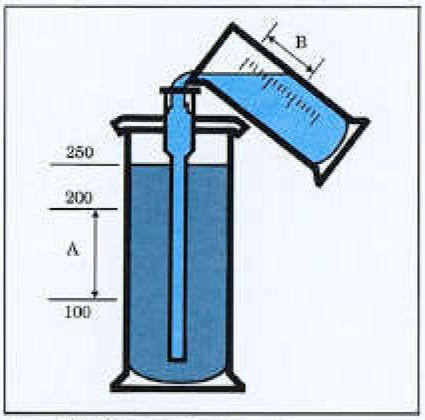


Figure 167. The velocity V_s equals $\frac{0.6\ AB}{1000}$ $m.hr^{-1}$.

4.1.2.4. Flotation test

Using a pressurized water vessel, increasing volumes of pressurized water are introduced into different beakers where the optimal flocculation of the water to be treated was carried out previously. The following characteristics are recorded:

- % of pressurized water,
- rising velocity of the bubbles,
- rising velocity of the floc,
- appearance of the floc,
- thickness of the cake,
- measures in the floated water: turbidiry, colour, OM, etc.,
- resistance and aptitude of the sludge to scraping.

4.1.3. Lime softening test

As a rule, the coagulant is ferric chloride, but one can also try aluminium sulphate with or without an aid. In this case, the aluminium is dosed after filtration through paper (aluminium is clearly soluble in an alkaline medium).

A first test is run without coagulant to determine the dose of lime, while at the same time introducing 10 g of $CaCO_3$ in powder form (50 µm) per litre. Shake for 5 minutes, let settle and filter through slow filtering paper. Titrate the filtered water:

	Dose of lime in $mg.l^{-1}$				
	100	125	→	350	375
P alk.					
M alk					
total hardness					
calcium hardness					

Then, with the amount of lime that produced either a P alk. 0.5 Fr. deg. greater than half the M alk., or a minimal degree of hardness, a new flocculation test is run but with increasing doses of coagulant.

In the case of silica removal, another reagent (magnesia) can be used, and the silica is measured in the filtered water. In the case of softening, sodium carbonate must be used.

4.1.4. Determining the oxidizing agent demand

4.1.4.1. Chlorine absorption test

A series of bottles is used all having the same capacity and made of glass of identical composition.

Introduce the same volume of water to be examined into each of the bottles and increasing dosages of chlorine from the first bottle to the last bottle. After a contact time generally corresponding to the retention time of the water in the installation, at constant temperature and away from the light, the chlorine remaining in the water of each bottle is measured (for some studies, it is recommended to carry out this study after different contact times: 1, 2, 5 ... 24 hours).

One can thus establish the curve representing the residual chlorine vs the chlorine introduced (see Figure 119, page 253).

Analysis of total chlorine and of free chlorine is always recommended, especially if the absorption curve shows no breakpoint, in order to determine chlorine demand according to a residual chosen for a certain contact time. Moreover, certain specific measurements can be carried out according to increasing chlorine dosages: formation of haloforms, color, organic matter, influence on the flocculation, taste thresholds.

- **Quick method of determining the breakpoint**

This is used carrying out a single measurement, introducing a largely excessive dose of chlorine into the raw water (A in Figure 119 of page 253); after contact, measuring the residual chlorine (Aa) makes it possible to determine approximately the value of the breakpoint:

$$Om = OA - Aa$$

- **Network test - Chlorine absorption kinetics curve**

For a chosen level of chlorine, the concentrations of free chlorine and total chlorine are measured as a function of time (see page 254 - Figure 120). The curve sections to examine, most specifically, correspond to the "immediate demand" (less than one hour) and to consumptions after a long contact time (long networks). This test can provide indications on the usefulness of chlorination at different points in the network.

4.1.4.2. Chlorine dioxide absorption test

To find out the chlorine dioxide demand of water, the same procedure is used as for the chlorine demand: the curve of the disinfectant residual is drawn according to the amounts introduced. In the presence of ammonia, the curve shows

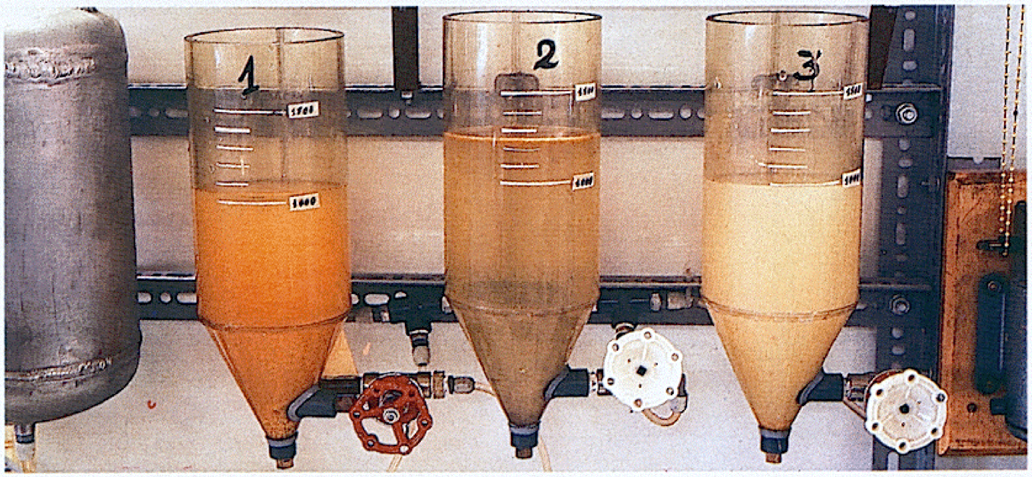


Figure 168. Laboratory flotation test apparatus (Flottatest).

no breakpoint (since the dioxide does not react with the ammonium ion). A concentrated solution of chlorine dioxide is prepared from sodium chlorite in the presence of an excess of hydrochloric acid.

The concentration of the stock solution is about 15 $g.l^{-1}$ ClO_2. The standard solution is generally prepared at 0.5 $g.l^{-1}$. This concentration must be verified as well as the absence or presence of chlorite.

4.1.4.3. Ozone absorption test

In the laboratory or on site, the ozone demand of a given water is determined using a special flask (Figure 169).

The ozonated air is injected in A using a graduated syringe. Opening the tap B makes it possible to displace a volume of water identical to the volume of ozonated air. After closing the tap B, the bottle is shaken manually for a period corresponding to the contact time of the water in the ozonation column. The residual ozone is measured by titration with diethylphenylenediamine (DPD) after adding potassium iodide.

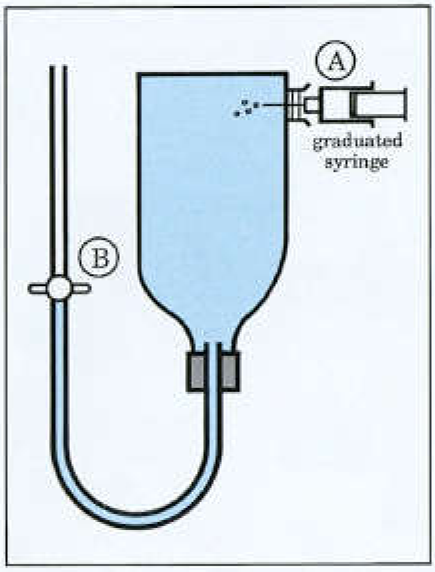


Figure 169. Ozone demand: experimental equipment.

The rate of ozone introduced is determined by the following formula:

Level of ozone $mg.l^{-1}$

$$\frac{C_{O3} \cdot V}{V - v}$$

with:

C_{O3}: concentration of ozone in the air in $mg.l^{-1}$, V : volume of the flask (l),

v : volume of ozonated air (l).

The corresponding residual ozone concentrations are recorded graphically as a function of the different rates of ozone introduced. This generally produces a straight line (cf. Figure 170) the important points of which are the following:

Point A, intersection of the extended straight line with the x-axis, represents the rate of ozone that must be introduced to meet the water's chemical ozone demand and to produce a residual of ozone.

Point B of the straight line corresponds to the level of ozone that must be introduced to meet the ozone demand and to obtain a residual of 0.4 $mg.l^{-1}$ after the chosen contact time.

4.1.5. Deaeration-aeration test

It is sometimes useful to expel the free C02 by trickling the water in contact with air. To appraise the efficiency of the operation, proceed as follows:

- use two 1 l beakers. Transfer the water from one to the other, letting the water fall from a height of 20 cm and at a flow of about 1 l in 10 sec.,
- measure the free CO_2 and note the pH as a function of the number of transfers and until the pH hardly varies.

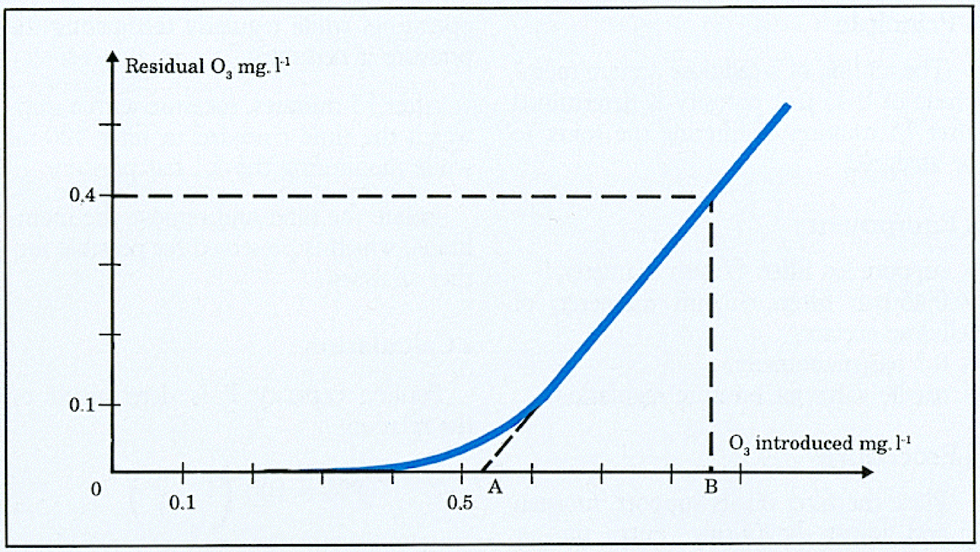


Figure 170. Ozone demand: absorption curve.

4.1.6 Physical-chemical iron removal test

Iron removal by oxidation with air is not always possible, particularly for waters rich in OM. To determine. this, a test must be carried out. This must be performed on site, immediately after the samples are taken:

- aerate quickly by transferring the water 20 times from one beaker to another,
- filter through blue strip Durieux paper or through 0.45 µm membrane,
- monitor the concentration of residual iron, the change of pH, the dissolved oxygen and carbon dioxide.

If the concentration of residual iron is not less than 0.1 mg.l^{-1}, more complete tests must be carried out, on a pilot installation if possible, making use of other oxidizing agents and/or various coagulants and flocculants (alginates, for example).

4.2.

MEASURING OVERALL PARAMETERS

In the field of water treatment there exist some indices that are characteristic of the water or the operation of an installation or are used for selecting treatment procedures Three such indices are described below

4.2.1. Fouling index (FI)

When the criterion of turbidity is no longer sensitive enough, the presence of particles can be determined by the fouling of a filter (Figure 171). This measurement is applicable to membrane filtration processes.

- **Principle**

The fouling of a cellulose acetate membrane of 0.45 µm porosity is determined after 15 minutes of filtering the water to be analyzed.

- **Equipment**

- support for filter 47 mm diameter,
- 0.45 µm filter, 47 mm diameter, of cellulose acetate,
- 0.5 bar manometer,
- needle valve for pressure regulation.

- **Procedure**

Place the filter on its support, moisten it and adjust the O-ring. Purge the air from the circuit and attach the support in such a way that the membrane is exactly 360 vertical. Adjust the pressure to 2.1 bar (30 psi) and measure with a stopwatch the time to needed to filter a further 500 ml of water (this period must be greater than 10 seconds). Repeat the process if the pressure varies ± 5% during measuring. Leave the filter in place and operating, while regularly readjusting the pressure if necessary.

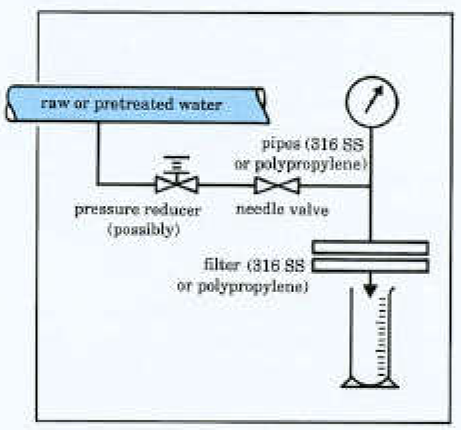


Figure 171. Principle of the FI measuring device.

After 15 minutes, measure with a stopwatch the time t needed to filter 500 ml while monitoring the 2.1 bar pressure.

Isolate the filter and remove the membrane, which is preserved for possible further analyses.

- **Calculation**

Fouling capacity P is determined by the relation:

$$P\% = 100\left(1 - \frac{t_0}{t}\right)$$

If this percentage is greater than 80% in 15 minutes, the same test must be repeated for 10, 5 or even 3 minutes.

The fouling index is calculated from P% and the time T in minutes between the two measurements:

$$FI = \frac{P\%}{T}$$

Example: at 2.1 bar
t_o = 28 seconds,
t = 44 seconds (after 15 min., i.e. T = 15).

$$P\% = 100\left(1 - \frac{28}{44}\right) = 36{,}4\,\%$$

$$FI_{15} = \frac{36{,}4}{15} = 2{,}4$$

4.2.2. Particle count

Particle count is a criterion used increasingly widely (injection water, ultrapure eater, filtration through membranes and cartridges, etc.).

The analytical equipment is becoming increasingly efficient: counting, particle size distribution curve, measuring ranges. Nevertheless, measurement remains tricky: transporting the sample, choosing measurement ranges, possible dilution. Equipment proposed in the field of water treatment is usually based on optical principles of scattering, absorption, diffraction (light or laser).

4.2.3. Marble test

To determine the aggressivity or scaling power of water, a chemical test can be carried out in addition to calculating the carbonate balance (see page 262).

Fill a 125 ml bottle with the water sample, adding 1 to 2 grammes of finely crushed marble previously washed several times with distilled water then with the water under test. The bottle must be filled completely without any air bubbles.

Shake slowly for 24 hours and measure pH, M alk. and hardness of the water after filtration.

Comparing these values with the pH, M alk. and hardness of the water before contact with the marble makes it possible to determine the aggressive or scaling tendency of this water.

4.3. THE ANALYSIS OF VERY LOW TDS WATER

The guarantees required for the condensates of nuclear power stations and particularly for ultrapure water involve all domains: inorganic, organic, particulate, bacteriological, etc. Equipment must be of increasingly high performance. Practically speaking, only continuous analyses have any real significance.

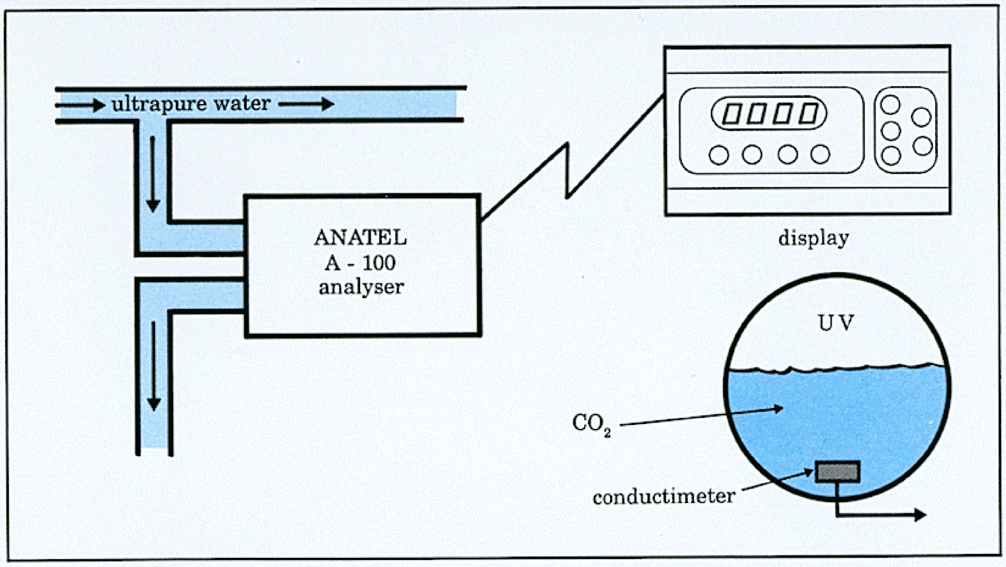


Figure 172. Operating principle of the TOC-meter for ultrapure water.

Any transport may affect the accuracy of the results. The main parameters to take into account are as follows:

- **Resistivity**

This measurement must be carried out in a flow cell able to detect 25 MO.cm.

- **Salts and metals**

The concentration limits sought can be below µg.l^{-1}, for sodium and heavy metals, among others. Certain selective electrodes and ion exchange chromatography featuring an eluent suppressor column with prior concentration, can meet these requirements.

- **TOC**

Equipment measuring a lowering of resistivity, after mineralization of the organic matter, is the best adapted (announced detection limit of 20 µg.l^{-1}).

- **particle count**

If the sampling circuit is very short, the results of measurements taken on site and without dilution are correct and reproducible.

- **Fouling indices**

These are very low. The results are only significant if measurements are carried out continuously by a PLC.

- **Bacteriology**

Analysis by point sampling provides typical results. The technique of membrane filtration is appropriate because it makes it possible to filter volumes considerably larger than those required for examining suitability for drinking.

5. WASTEWATER

5.1. SPECIFIC ANALYSES

5.1.1. Biochemical oxygen demand (BOD)

The biochemical oxygen demand is usually measured at the end of five days. This is the BOD_5; it corresponds to the assimilation and synthesis phases. It can be useful to know the ultimate BOD, at the end of twenty days, including the auto-oxidation phase (endogenous metabolism).

- **Dilution method** (NF T 90.103)

Suitable dilutions of the water to be examined are prepared with a seeded pure water which is periodically checked to verify that it does not absorb significant quantities of oxygen itself. Seeding will not be necessary in the presence of municipal wastewater. The best results are obtained when the loss of oxygen in the course of the test is between 35 and 60% of the initial content. The dilutions used depend on the pollution. To determine these, one can use the COD value, since the BOD_5 is generally lower than the COD and the COD/BOD_5 ratio is usually between 1.5 and 3. Assuming that a water stabilized at 20°C contains about 8 $mg.l^{-1}$ of oxygen, the following can be stated:

$$\text{dilution factor} = \frac{\text{expected } BOD_5}{4}$$

At least three different dilutions are prepared so as to completely bracket the expected value. The dilutions are kept in the dark for five days at 20°C. The dilution water used must remain at this temperature and be in perfect equilibrium with the atmosphere, something that can be achieved easily by keeping the reserve of this pure water in the regulated incubator in the thermostat-controlled bath used for incubating diluted samples.

To avoid positive interferences on the result in case of nitrification, nitrifying organisms must be eliminated by acidifying the sample. The dilution water must be seeded before going back to the procedural mode.

It is obvious that since measuring the BOD_5 is a measurement of a biological nature, the presence of microorganisms capable of degrading the polluting matter must be ensured. A microbial culture can be prepared from a compost through which the water under test has been allowed to percolate, or from sludge taken downstream from the discharge point into the river.

- **Manometric methods**

Equipment based on manometric methods makes it possible to follow the progress, in a closed receptacle and as a function of time, of the disappearance of oxygen in the atmosphere of the receptacle.

To decide on the choice of a treatment process, it is often advantageous to know:
- the total BOD_5 of the raw water sample,
- the dissolved BOD_5 after filtration through membrane,
- the BOD_{5AD} (after settling) which encompasses the colloidal and dissolved BOD; in France, this settling is often carried out in two hours.

The uncertainty in determining the BODs can be considerable, particularly on certain raw IWW if the seeding is not suitably adapted. On raw MWW, the imprecision does not exceed 10 to 15%; on MWW after extensive biological purification, however, it can reach 50%.

5.1.2. Chemical oxygen demand (COD)

The standardized method (NF T 90.101) for wastewater uses potassium dichromate in a hot sulphuric acid medium, a powerful oxidizing agent the consumption of which makes it possible to define the **COD**. The precision of this measurement is in the 10% range for values located above 50 mg.l^{-1} of O_2. Other methods are adapted to lower COD levels.

The COD represents everything that can be oxidized, particularly certain oxidizable mineral salts (sulphides, sulphites, etc.), and most organic compounds. Only certain nitrogen compounds and hydrocarbons escape this powerful oxidizing agent.

The accuracy of the COD test is not satisfactory for chloride concentrations exceeding 2 g.l^{-1}.

Permanganate value under cold (4 hours) or hot (10 min. boiling) conditions can also constitute a good field method for monitoring the quality of water at a treatment works (especially treated water).

Measuring the **TOC** is now more and more widely used (see page 340); the oxidation of the organic matter is generally more complete than when measuring the COD.

It is often advantageous to measure the three criteria TOC, COD and BOD_5 and to know the COD/TOC and COD/BOD_5 ratios which can be indicative of particular types of pollution (industrial wastewaters).

5.1.3. Suspended solids (SS)

Membrane filtration methods seem simple but the analytical methods must be scrupulously adhered to. The operational procedure must always be the same for the results to be comparable. Error sources are numerous: type of membrane, value of pressure, vacuum or acceleration (method using centrifugation), volume of the test samples, washing procedure after separation and, particularly, subsequent precipitation between sampling and analysis (hydroxides, carbonates, phosphates, gypsum, etc.).

5.1.4. Volume of settleable matter

The analysis is carried out on samples passed through a 5 mm sieve to remove large debris. Substances that deposit in a liquid at rest during a period commonly set at two hours are known as settleable matter. The graduates are conical or cylindroconical in shape, making it possible to evaluate a settled volume. This measurement is only representative on relatively highly loaded water.

5.1.5. Hydrocarbons

The analytical methods to determine hydrocarbons as a whole are quite numerous and their results can be very different. Numerous parameters are important: the solvent, extraction conditions, gravimetry or IR absorption, calculation of IR absorbance levels (method of calibration, wavelengths used). The methods applied must always be specified and the operational procedures must be scrupulously adhered to. The results according to the standards NF T 90.114, 90.202 and 90.203 can thus differ considerably.

The oils and fats present in MWW or food industry wastes are generally measured by the methods described in 6.4.

5.1.6. Nitrogen

To follow the evolution of nitrogen compounds throughout a treatment, the different forms must be known:
- ammonia nitrogen,
- nitrous nitrogen making it possible to detect any biological inhibition,
- Kjeldahl nitrogen (TKN) or organic and ammonia nitrogen. This category does not include the oxidized compounds of nitrogen: nitrites, nitrates and certain nitrated organic compounds. Measuring low values of TKN is a delicate procedure.

It should be pointed out that in France, nitrogen as a whole in all its forms is often called total nitrogen (TN).

All analyses must be carried out after inhibiting the biological reactions when taking the sample.

5.1.7. Phosphorus

Analysis makes it possible to distinguish three different forms of phosphorus:
- orthophosphates,
- polyphosphates (acid hydrolysis),
- organophosphates (acid hydrolysis with oxidation).

Inductive coupling plasma spectrometry makes it possible to determine the total phosphorus directly.

5.1.8. Sulphur

Sulphides can be determined by iodometry after fixing the sulphides, by potentiometry using a silver electrode, or by colorimetry for low levels. Determining other reducing forms in IWW is always more delicate (thiosulphates, dithionates, sulphites, sulphocyanides, etc.). Selective methods using precipitation or chelation should be avoided. Ion exchange chromatography can be used in certain conditions.

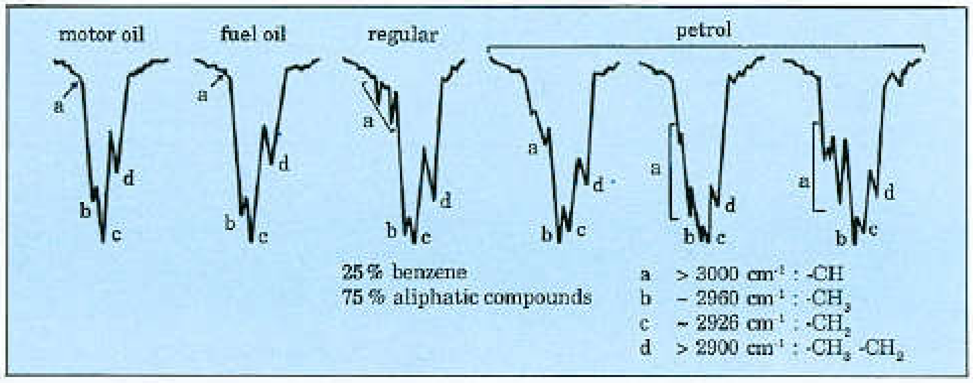


Figure 173. Infrared spectra for different petroleum products (conditions of CH_2 index determination).

For following up methane fermentation of certain IWX1s, sulphates must also be taken into account.

5.1.9. Methylene blue test

The principle of this test, used less and less, is to follow the discoloration of a methylene blue solution through time and to evaluate the putrescibiliry of the sample.

Its interpretation is often much debated. It must be used with great caution, because it can provide erroneous indications, particularly for IWW which can contain reducing substances, and for low BOD effluents from purification plants (BOD_5 less than 15 $mg.l^{-1}$), rich in oxidized salts which themselves are susceptible_ceptible to anaerobic reduction.

5.1.10. M alkalinity

This parameter must be monitored during nitrification (acidification) or denitrification (alkalinization) processes.

5.1.11. Heavy metals

Heavy metals must be monitored after prior mineralization of the sample (atomic absorption spectrophotometry). The most important heavy metals are: cadmium, mercury, lead, hexavalent chromium, copper and nickel. They are mainly monitored in:

- surface treatment wastes, before discharge into the receiving watercourse or sewer,
- wastes before biological purification.

It may also be necessary to know the content of certain trace elements that promote methane fermentation (e.g., nickel).

5.1.12. Toxicity

The concept of toxicity is complex: it includes the action of a great number of elements in quite varied forms (chelated, ionized, oxidized, etc.). It is evaluated by a biological test.

The test using daphnia (NF T 90.301) can be cited as the most widely used. In the wastewater, the short-term inhibition of the growth of Daphnia magna (Crustacea, Cladocera) is determined. Daphnia magna are designated by the common name daphnia. The results are expressed in **equitox defined** as follows: waste contains one equitox per m^3 if, in the test conditions, it causes a 50% reduction of daphnia growth in 24 h.

5.1.13. SVI (Moh1man index)

(See page 163.)

5.2.
TREATABILITY TESTS

5.2.1. Oxygen consumption measurements

The measurements used to evaluate BOD_5 or toxicity are applied, where necessary, by adding sludge or seeded media.

Measuring in reactor

An oxidized sample is shaken in a stopped bottle; oxygen consumption is followed or lowed up by a specific probe.

- **Manometric measuring by Warburg respirometer**

The Warburg respirometer is less a monitoring apparatus than an apparatus for studying the respiratory activity of activated sludge (Figure 21), using a low volume sample (a few ml).

Its principle lies in the fact that at constant volume and temperature, any variation in gas quantity can be measured by the variation in its pressure. The oxygen exchange can be easily measured by absorbing the carbon dioxide in a potassium hydroxide solution. The respirometer can be used to test the toxic effects of certain products and particularly to determine the respiratory coefficients a', b', and the sludge production coefficients am and b (see page 294).

Warburg respirometers have a certain number of disadvantages, however, because their oxygenation capacity is difficult to control and the procedures require several stops which can mask certain phenomena when the polluting matter can be assimilated very quickly.

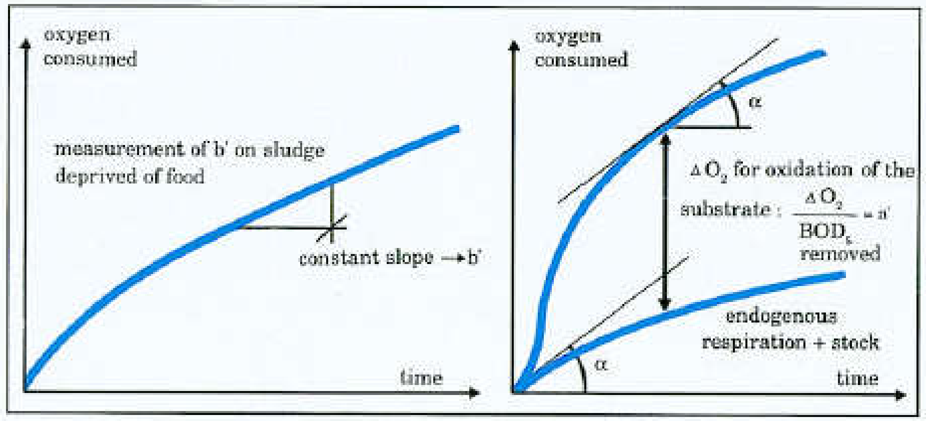


Figure 174. Principles of the Warburg determination of respiratory coefficients.

5.2.2. Nitrification test

Wastewater seeded with nitrifying sludge or specific strains is aerated and shaken in a bottle. Determination of the nitrogen forms $N0_3$, $N0_2$ and NH_4^+ is carried out every day. The evolution curves of the nitrogen species makes it possible to evaluate treatability and oxidation kinetics. These tests are applied mainly to IWW.

5.2.3. Denitrification test

This test makes it possible to evaluate the kinetics of denitrification, either of IWW or of MWW nitrified with or without the addition of assimilable carbon.

Figure 175 makes it possible to visualize the test procedure. The bottles used are sealed by a septum allowing injections and sampling by syringe without modifying the anoxic nature of the medium (initial flushing with nitrogen).

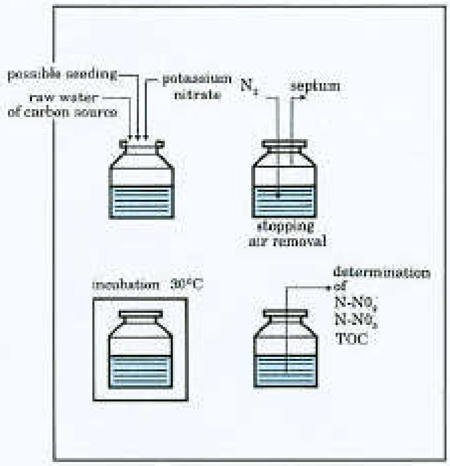


Figure 175. Principle of a denitrification test.

5.2.4. Test bench

- **Aerobic medium**

Continuous or batch operation reactors are used, in which the air is generally introduced in excess. The overall parameters COD, BOD are monitored with respect to time. Continuous monitoring of pH, redox potential, oxygen, TOC, etc. can be used.

Figure 176 represents a laboratory apparatus that constitutes a genuine miniature treatment plant with aeration and clarification zones. The activated sludge, after aeration, passes into the lower part of the clarifying cylinder and is recycled by an air lift after having been separated from the treated water. This is an apparatus operating in the complete mixing mode, which simplifies the mathematical relations that can be established based on the operating parameters observed.

The air lift can be replaced by a peristaltic pump in order to monitor the recycle flow precisely and make the aeration independent from the pumping of return sludge.

To adapt an activated sludge to a difficult IWW, one usually starts with a sludge taken from a municipal treatment

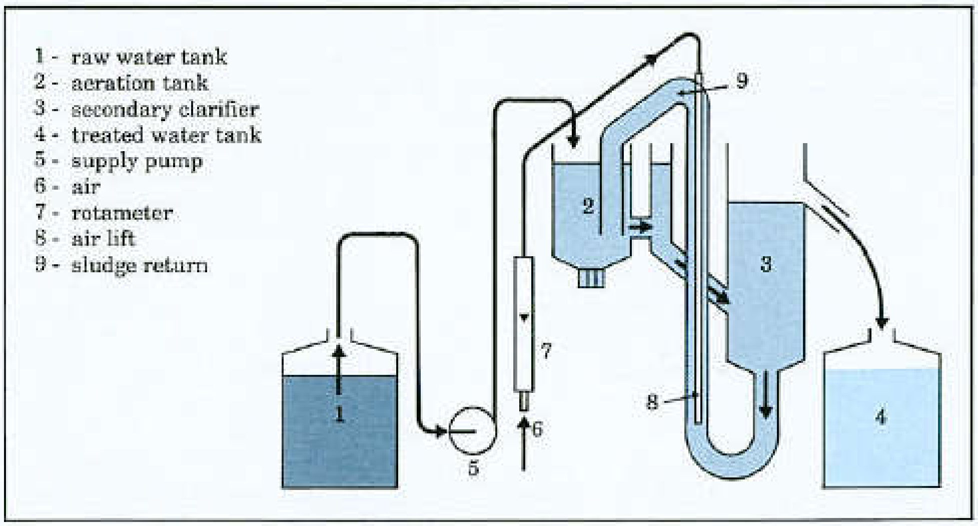


Figure 176. Combined pilot apparatus for laboratory studies.

plant and feeds the pilot with a mixture of municipal wastewater and the water to be tested. In about ten days, the IWW proportion is gradually increased in steps of one to two days. If 100% IWW is reached, it can be concluded that it is treatable; if not, one can determine to what proportion it needs to be diluted with an MWW for it to remain a valid food for microorganisms. Of course this test must be carried out on a medium that is naturally balanced in assimilable carbon, nitrogen and phosphorus.

- **Anaerobic medium**

Discontinuous fermentations in batches are carried out in small reactors (Figure 177), seeded by sludge from municipal sludge digesters presenting a wide bacterial population. The initial operations are carried out under nitrogen bubbling, then the bottle is hermetically sealed. The batches are maintained at 37°C in a shaking incubator. Samples of gas and waste are taken at regular intervals to monitor the formation of methane and the reduction of the COD. Complementary analyses can be carried out (composition of the gas, VFAs on the supernatant) so as to display the limiting stages or the inhibition of the degradation reactions.

Figure 177. Laboratory anaerobic reactor.

6. SLUDGE

6.1.

SUSPENDED SOLIDS (SS) IN THE LIQUID SLUDGE

When the sludge is not very concentrated, the dry weight should not include the quantity of dissolved substances of the interstitial water of the sludge. Two methods are proposed:

6.1.1. Centrifugation

A laboratory centrifuge equipped with graduated 100 ml tubes is used. Each tube is filled with 80 ml of sludge and centrifuged at 4,000-5,000 rpm for 10 minutes. At the end of the operation, the supernatant is removed and all the sludge sediments are carefully recovered and allowed to dry in an oven at 105°C until a constant weight is obtained (generally for at least 12 hours).

NOTE: prior flocculation of the sludge by a few $mg.l^{-1}$ of polyelectrolyte (in situ flocculation in the tube) makes it possible to obtain homogenous sediments that are easy to recover without substance loss. Let **M** (g) be the weight of dry residue obtained and V (ml) the volume of centrifuged sludge (V = 160 or 320 ml).

$$\text{SS concentration} = \frac{M \text{ x } 1{,}000}{V}\ g.l^{-1}$$

6.1.2. Filtration

This method is reserved for sludge that is not very concentrated (5 to 20 $g.l^{-1}$, for example).

A paper filter (ashless type extra rapid filter, 150 dia., Durieux for example) is weighed precisely and the sludge (25 to 100 ml depending on the concentration) is filtered through a glass funnel. This process can be quite lengthy in some cases where the sludge is not easily filterable. The filter is then dried in an oven at 105°C until attaining a constant weight.

$$\frac{M - F}{V} \text{ x } 1{,}000\ g.l^{-1}$$

where:

M: dry weight of the filter paper and the cake

F: weight of the filter paper alone

V: volume of filtered sludge

6.2.

DRY SOLIDS (DS)

The dry solids content includes both the **suspended solids and dissolved salts.** It is the residue on evaporation which is also used to determine the degree of dryness of the sludge (expressed in %).

6.2.1. DS at 105°C

The dry solids content is expressed in g.1 1. The measuring method consists in placing a sludge sample (25 to 100 ml, according to the concentration of sludge) in the oven at 105°C until a constant weight is obtained.

M_1 is the weight of the moist sample and M_2 the weight after drying.

$$DS = \frac{M_2 \times 100}{M_1} \%$$

6.2.2. DS at 175 to 185°C

Drying at 175 to 185°C, compared to drying at 105°C, makes it possible to evaluate the water-of-crystallization content of salts, the content of water bound to hydroxides and certain volatile substances.

6.2.3. DS at 550°C and volatile solids (VS)

The residue is brought to 550°C for. two hours in a muffle furnace, heated beforehand, and monitored by thermostat. Silica crucibles with 10 to 20 g of finely ground dry sludge are generally used.

The quantity of volatile solids volatilized at 550°C must not be **confused with the organic matter content,** for several reasons:

- a portion of the inorganic substances and salts can decompose between 105°C and 550°C,
- a portion of the OM (namely certain organocalcic or organometallic complexes) might not volatilize at 550°C but rather at about 650 to 700°C,
- in the case of lime conditioned sludge, the $C0_2$ produced by the combustion of the OM is faced by the lime to yield $CaC0_3$ which only decomposes at over 550°C.

Nevertheless, for most sludge, determining the VS is an approximate evaluation of the organic matter. The VS rate is generally expressed in % of DS

6.2.4. DS at 900°C

The VS between 550 and 900°C are essentially composed of the $C0_2$ resulting from the decomposition of carbonates contained in the initial sludge.

6.3.
RAPID METHOD FOR DETERMINING THE M ALK. AND THE VOLATILE ACIDS (VFA) LEVEL IN LIQUID SLUDGE

These calculations are important for the proper operation of the anaerobic digester.

25 ml of sludge are measured as precisely as possible. This sludge is centrifuged first at 5000 rpm for 10 min. The supernatant is collected in a 400 ml beaker. Recover the sediment with 50 ml of distilled water taking care not to lose the solid portion.

Centrifuge again at 5000 rpm for 10 min and use the beaker to collect the supernatant. Recover the sediment again using distilled water.

The whole of the supernatants collected contains the soluble bicarbonates and volatile acids.

6.3.1. Measuring the M alk.

The liquid collected in the beaker is stirred magnetically. The electrodes of a pH meter are dipped in the liquid and the initial pH is recorded.

Using a burette calibrated in 1/10 ml, add 0.1 N H_2SO_4, down to pH 4, i.e., V ml:

$$\text{M alk.} = \frac{V \times 0.1 \times 1000}{25}$$
$$= V \times 4, \text{ in meq.l}^{-1}$$

or:

M alk. = V X 4 X 0.05, in $g.l^{-1}$ of $CaCO_3$

6.3.2. Measuring the VFAs

0.1 N H_2SO_4 is then added to reach a pH 3.5. The liquid is then boiled at pH 3.5 for precisely 3 min, and allowed to cool. Put the cooled liquid under the electrodes of the pH meter and while shaking add, with a burette calibrated in 1/10 ml, 0.1 N NaOH to pH 4; let V_2 be the volume obtained.

Continue to add NaOH up to pH 7; let V_3 be the new volume.

$$\text{Volatide acids} = \frac{(V_3 - V_2) \times 0.1 \times 1000}{25}$$
$$= (V_3 - V_2) \times 4, \text{ in meq.l}^{-1}$$

Volatile acids = $(V_3 - V_2) \times 4 \times 0.06$, in $g.l^{-1}$ of acetic acid.

6.4.
LEVEL OF GREASES AND OILS

Numerous methods are proposed to measure the hydrocarbons, fats and oils that are often in the form of emulsions or saponified.

The greases and oils are separated by filtration after acidification and addition of a sodium chloride solution. The deposit recovered is then extracted using a Soxhlet extractor (solvent to be chosen: freon, hexane, trichloroethylene, chloroform, etc.). A final gravimetric determination is carried out after distillation of the solvent.

The standard NF T 90.114 can be used but it is adapted mainly to soluble hydrocarbons in small quantity.

6.5.
FILTERABILITY TEST

6.5.1. Filterability test under vacuum using a Buchner funnel

Measuring specific resistance of sludge under 0.5 bar vacuum.

This calculation makes it possible to approximately evaluate the capacity of a full-scale vacuum filter. It also makes it possible to set the optimal dosages of reagents for filter presses, but in this case the compressibility factor must be taken into account.

Figure 178 describes the equipment needed for the test.

Operational procedure

Fill the Buchner funnel with sludge to be filtered (conditioned beforehand); 100 ml of sludge is generally sufficient to obtain a final cake of 8-10 mm thickness.

Set up the vacuum and quickly achieve the vacuum required, 0.5 bar (approx. 40 cm Hg), making sure that it remains constant throughout the test.

As soon as the vacuum is attained, start the stopwatch and record the volume of filtrate already collected: volume Vo corresponding to the time t = 0 that will

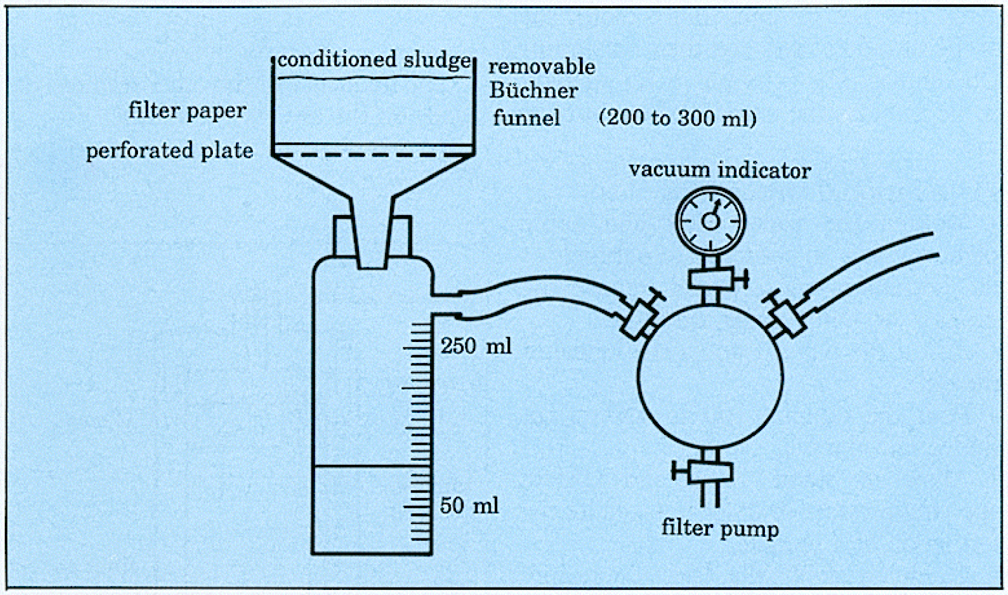


Figure 178. Filterability test under 0.5 bar vacuum.

have to be subtracted from the volumes collected later. Record the volumes of filtrate collected in the course of the test for different filtration times: every 10, 15, 20, 30 or 60 seconds, according to the filtration rate.

The test is conducted until the cake is dewatered (loss of vacuum due to the cracking of the cake).

- **Calculation of the specific resistance to filtration**

The volumes of the filtrates V_0, V_1, V_2, V_3, etc., corresponding to the times T_0, T_i, T_2, T_3, etc., are recorded.

Record on a graph the points that have VX as abscissa and as ordinate:

$$\frac{T_x}{V_x - V_o}$$

Theoretically, these points form a straight line (except at the beginning of filtration and during dewatering). The slope of the linear portion of the curve obtained represents coefficient a (see Chapter 3, par. 5.1.2). **The specific resistance** under 0.5 bar (49 x 103 Pa) is given by the relationship:

$$r_{0.5} = \frac{2\ a\ PS^2}{\eta C}$$

a: in $s.m^{-6}$
P: in Pascal (i.e., 49 x 10^3 Pa)
S: in m^2 in Pa.s. (at 20°C, near 1.1 x 10^{-3} Pa.s.)
C: in $kg.m^{-3}$ j
r: in $m.kg^{-1}$

NOTE: C, residue on evaporation at 105°C divided by the volume of sludge, is an approximation of W (weight of SS deposited per unit filtrate volume).

6.5.2. Filterability rest under pressure (see Figure 179)

A cell under pressure is used not only to determine specific resistance but also to determine the compressibility coefficient of the filtration cakes and their maximum DS content. The principle of the method is the same as the one described on page. 372.

- **Operational procedure**

- Moisten the paper filter and apply slight pressure to ensure watertightness of the bottom of the cell and remove the excess water retained by the filter.
- Adjust the cylinder under the funnel of the cell.
- Pour the sample (100 to 150 ml) of sludge into the cell,
- Allow to stand 15 seconds before applying pressure in order to facilitate the formation of a precoat.
- Gradually apply the selected pressure (0.5 to 15 bar); using a piston is not recommended for pressures of less than 2 bar.
- Let the filtrate flow and record its volume V_0 (roughly 10% of the sludge volume to be filtered).
- Start the stopwatch and record the volume V of the filtrate as a function of time. Draw the curve:

$$\frac{T}{V_x - V_o} = f(V_x).$$

The frequency of the other readings depends on the flow of the filtrate

- To calculate resistance, refer to page 372.

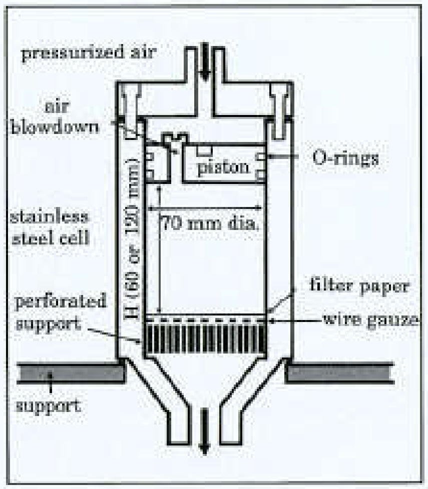


Figure 179. Test cell for the filterability under pressure.

6.6.
DETERMINING COMPRESSIBILITY COEFFICIENT

Measure specific resistance r to filtration under several pressures P and draw the curve log r = flog P). Verify the linearity and measure its slope which equals the compressibility coefficient.

The equipment used is the same as that of the preceding test.

In order to obtain maximum precision, it is desirable to use pressures that are reg

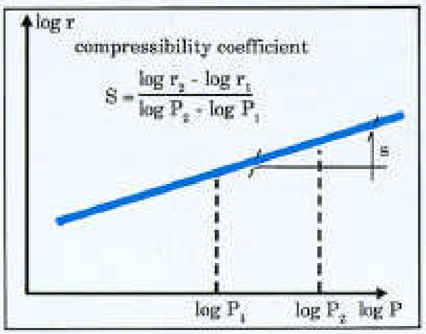


Figure 180. Determination of the compressibility coefficient.

ularly spaced. The following values are recommended:
P = 49 kPa - 147 kPa - 441 kPa and 1323 kPa (or maximum pressure allowed by the laboratory equipment).

The compressibility coefficient is expressed in the form of a dimensionless number.

6.7.
DETERMINING DRYNESS LIMIT

The equipment is identical to that used on page 374.

The piston is, in this case, absolutely necessary. Its purpose is to transmit the pressure received in the cell uniformly to the sludge and to keep the cake from cracking.

The operational mode is the same as that used on page 374, but after having poured the sludge sample into the cell, the following operations must be carried out:

- depress the piston, with blowdown screw removed, until it touches the sludge lightly,
- replace the blowdown screw and tighten it,
- then go back to the operational mode of the test and continue measuring specific resistance until the vertical asymptotic part of the curve $\frac{t}{V} = f(V)$ is obtained. In practice, filtering should be stopped when the slope of the tangent at the point in question is 5 times greater than the slope of the initial straight portion. Determine the DS content of the cake at the chosen pressure (at 105°C ± 2°C, until a constant weight is obtained).

6.8. THERMOGRAVIMETRY

(See page 125.)

6.9.
CST (CAPILLARY SUCTION TIME) TEST

- **Principle**

A sludge sample (conditioned or not) is submitted to a filtration force caused by the capillary action of an absorbent paper filter.

- **Equipment** (Figure 181)

The equipment is made up of two elements: an actual filtration block and an automatic clock.

The filtration medium is a thick paper filter (generally Whatman No. 17 or equivalent), sandwiched between two rectangular, transparent plastic blocks. A hollow cylinder then presses against the filter paper and is used as sludge reservoir. The upper block is held away from the filter paper resting on five contacts, IA, 113, 2, 3 and 4. 1A and 1B are probes embedded in an initial circle concentric to the sludge cylinder. Probe 2 is situated on a second concentric circle. Electric connections are made between these three probes and the time trigger. Contacts 3 and 4 are only for adjusting the upper block and the filter paper.

- **Procedure**

1. - Fill the reservoir (10 or 18 mm dia. according to the filterability of the sludge) with a representative sample of the sludge.

If a monitoring test is involved, repeat the test at least twice in view of the small volume of sludge used.

If a flocculation study is involved, respect the repetitive conditioning methods.

2. - As soon as the cylinder is filled, the filtrate gradually expands more or less quickly out of the cylinder under the effect of the capillary suction of the filter paper. The speed at which the filtrate "halo" expands concentrically to the surface occupied by the sludge depends on the quality of the paper but mainly on the filterability of the sludge. When the liquid filtrate front reaches 1A and 113, the increase in conductivity between these two probes causes the clock to start. When the filtrate reaches probe 2, a similar change in conductivity between it and 1A stops the clock.

The apparatus thus automatically determines the time the filtrate halo takes to go from a diameter of 32 mm to 45 mm. The reference times are from 5 to 10 seconds according to the equipment.

- **Interpretation**

The lower the CST, the more filterable the sludge. This test, which is quite rapid, makes it possible to compare the effectiveness of a mineral or thermal conditioning (formation of very fine flocs).

In the standard conditions of use, and for a given sludge (low variation in concentration), the CST can be correlated with the specific resistance to filtration. This is thus a quick, sufficient indication of sludge filterability, that is particularly well suited to operating checks in filter press or vacuum filter facilities.

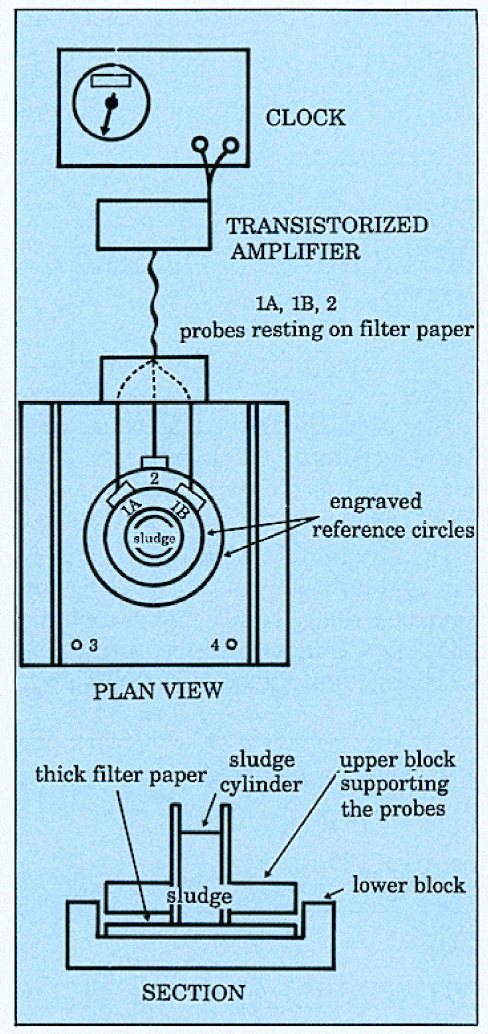


Figure 181. Device for measuring the CST.

If the CST is used to check the quality of flocculation with a polyelectrolyte, the results are hardly exploitable when there are highly differing flocs several millimetres in diameter. This is the case for the flocculation needed for the operation of belt filters, and a simple drainage test is then preferable

.

6.10.
HEAVY METALS

With a view to land disposal, the heavy metal content levels must be monitored. After extended mineralization of the sludge in acid medium, the metals can be measured by ICP spectrophotometry.

7. EXAMINATION OF GRANULAR AND POWDERED MATERIALS

7.1. CHARACTERISTICS OF THE MATERIALS

The nature of the granular materials used in treating water has become widely varied (sand, anthracite, expanded clay, activated carbon, limestone, resins, etc.).

Preparation of the sample

For all granular media, one must remember that the weight of the sample taken must be representative of the product supplied. In the same way, the test sample determined by the analyst must also be representative of the sample.

7.1.1. Particle size of filtration media

The recommendations of the French standard NF X 11.507 are referred to for granulometric analyses under the best conditions.

Weigh 100 g of material (50 g in the case of a granular activated carbon) after drying for 4 hrs at 120°C.

Sift this matter consecutively on the standardized AFNOR sieves
No. X 11.501 (table 47) and record the weight retained on each sieve.

Based on these results, calculate the weight of matter that has gone through each sieve (total of matter retained or not on all sieves smaller than the one under consideration) and express it as a percentage of the weight of material used for the analysis.

Draw the curve representing these percentages in terms of the mesh size of each sieve (cf. Figure 182).

For this purpose, use preferably semilog paper.

- **Effective size (ES)**

This is the size corresponding to the percentage 10.

- **Uniformity coefficient**

Read the size corresponding to .the percentage 60 on the graph.

The uniformity coefficient is the ratio

$$UC = \frac{\text{mesh size of } 60\%}{\text{mesh size of } 10\%}$$

It is preferable for it to be lower than 1.6. Coefficients of up to 1.8 are acceptable.

Comments: Table 47 shows the correspondence of the sieves used in the English standards, the American standards, etc.

For substances with particular shapes (rod-shaped, for example), the equivalent diameter of the granular substance giving a comparable head loss is often defined.

7.1.2. Friability

The friability of a substance is calculated by assessing the quantity of material that can be used after grinding, i.e., having the same effective size as the initial sample.

- **Operational procedure**

The friability test is carried out on 35 ml of precisely weighed material. The

Table 47. Standardized nominal mesh sizes of wire gauze.

ISO/GREAT BRITAIN			FRANCE/GERMANY			USA		
ISO 565 - 1983 / BSI 410 - 1986			F X 11.501 - 1970 / DIN 4188 - 1977			ASTM El 1-87 - 1987		
Main series	Additional series		Main series	Additional Series		Design ationgn		
µm	1° µm	2° µm	µm	1° µm	2° µm	mm	Inches	Mesh
125			125			125	5	5 in.
	112				112			
		106				106	4.24	4.24 in.
	100		100			100	4	4 in.
90				90		90	3.5	3 1/2 in.
	80		80					
		75				75	3	3 in.
	71				71			
63			63			63	2.5	2 1/2 in.
	56				56			
		53				53	2.12	2.12 in.
	50		50			50	2	2 in.
45				45		45	1.75	1 3/4 in.
	40		40					
		37.5				37.5	1.5	1 1/2 in.
	35.5				35.5			
31.5			31.5			31.5	1.25	1 1/4 in.
	28				28			
		26.5				26.5	1.06	1.06 in.
	25		25			25	1	1 in.
22.4				22.4		22.4	0.875	7/8 in.
	20		20					
		19				19	0.750	3/4 in.
	18				18			
16			16			16	0.625	5/8 in.
	14				14			
		13.2				13.2	0.53	0.53 in.
	12.5		12.5			12.5	0.500	1/2 in.
11.2				11.2		11.2	0.438	7/16 in.
	10		10					
		9.50				9.5	0.375	3/8 in.
	9				9			
8			8			8	0.312	5/16 in.
	7.10				7.10			
		6.70				6.70	0.265	0.265 in.
	6.30		6.30			6.30	0.250	1/4 in.
5.60				5.60		5.60	0.223	3 1/2 in.
	5		5					
		4.75				4.75	0.187	4 in.
	4.5				4.50			
4			4			4	0.157	5 in.
	3.55				3.55			
		3.35				3.35	0.132	6 in.
	3.15		3.15					
2.80				2.80		2.80	0.11	7 in.
	2.5		2.50					
		2.35				2.36	0.0937	8 in.
	2.24				2.24			
2			2			2	0.0787	10 in.
	1.80				1.80			
		1.70				1.70	0.0661	12 in.
	1.60		1.60					
1.40				1.40		1.40	0.0555	14 in.
	1.25		1.25					
		1.18				1.18	0.0469	16 in.
	1.12				1.12			
1			1			1	0.0394	18 in.
	0.90				0.90			

ISO/GREAT BRITAIN			FRANCE/GERMANY			USA		
ISO 565 - 1983 / BSI 410 - 1986			**F X 11.501 - 1970 / DIN 4188 - 1977**			**ASTM Ell-87 - 1987**		
Main series	**Additional series**		**Main series**	**Additional series**		**Designation**		
µm	1° µm	2° µm	µm	1° µm	2° µm	mm	Inches	Mesh
		850				850	0.0331	20
	800		800					
710				710		710	0.0278	25
	630		630					
		G00				600	0.0234	30
	560				560			
500			500			500	0.0197	35
	450				450			
		425				425	0.0165	40
	400		400					
355				355		355	0.0139	45
	315		315					
		300				300	0.0117	50
	280				280			
250			250			250	0.0098	60
	224				224			
		212				212	0.0083	70
	200		200					
180				180		180	0.0070	80
	160		160					
		150				150	0.0059	100
	140				140			
125			125			125	0.0049	120
	112				112			
		106				106	0.0041	140
	100		100					
90				90		90	0.0035	170
	80		80					
		75				75	0.0029	200
	71				71			
63			63			63	0.0025	230
	56				56			
		53				53	0.0021	270
	50		50					
45				45		45	0.0017	325
	40		40					
		38				38	0.0015	400
	36				36			
32			32			32	0.0012	450
	28				28			
25			25			25	0.0010	500
	22				22			
20			20			20	0.0008	635
16								
12.5								
10								
8								
6.3								
5								

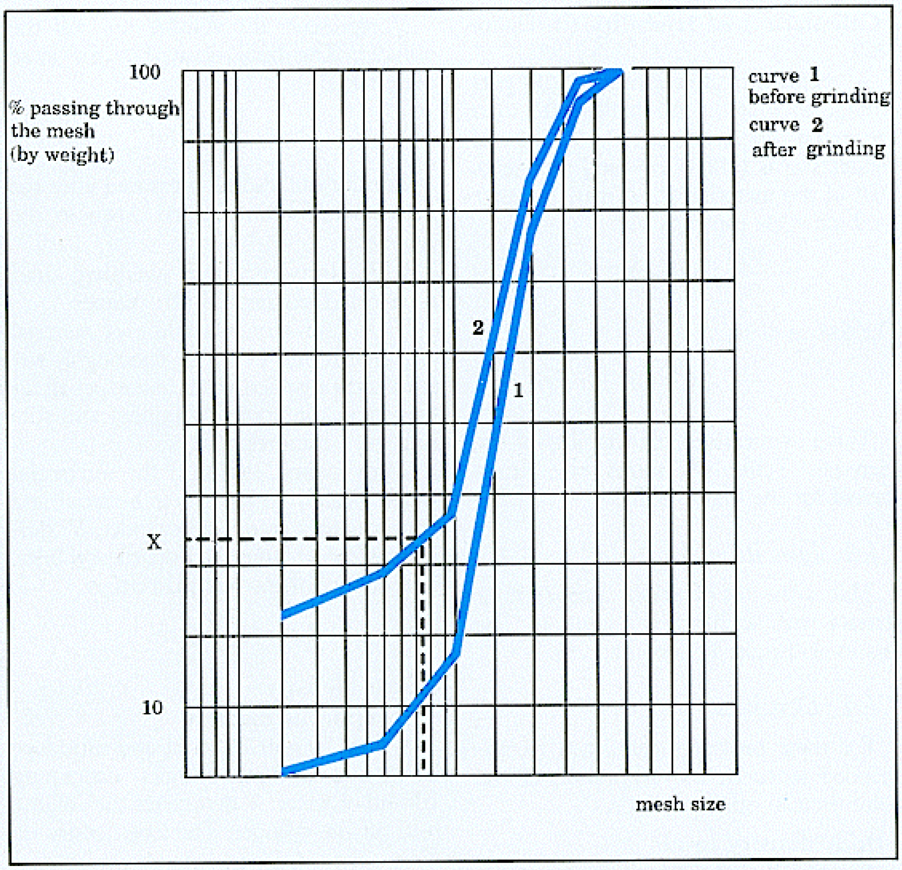


Figure 182. Use of particle size distribution curves (for the assessment of friability).

material is introduced into a metallic cylinder with an inner diameter of 40 mm and a useful height of 100 mm. This cylinder is secured radially to a wheel 34 cm in diameter. The wheel is rotated around a central spindle at a speed of 25 rpm. Inside the cylinder, 18 steel balls 12 mm in diameter are also introduced.

Friability must be measured on the same sample of filtering material in three consecutive measurements. In an initial measurement, the grain size of the material tested is determined. Then, after having collected all material from each sieve, two measurements are carried out: one after 15 minutes of operation (750 strokes, i.e., 375 revolutions) and the other after 30 minutes (1,500 strokes, i.e., 750 revolutions). After each experiment, the particle size distribution curve of the material is established.

- **Calculation of friability** (cf. Figure 182)

X represents, after crushing, the percentage of material of smaller size than the initial "effective size"; the fraction of greater size is (100 - X)% and represents 90% of the material which is usable after crushing. One can thus use:

$$\frac{100}{90}(100 - X)$$

The loss in % is:

$$\frac{10}{9}\ (X - 10)$$

This loss measures the friability of the material. Table 48 shows the limits thereof for the main media.

7.1.3. Loss in acid

This is the loss of weight after 24 hour contact with a 20% HCl solution. The loss in acid must be less than 2%.

7.1.4. Densities

For these measurements, it is recommended to check the calibration of the volumes read off the cylinders

- **Bulk density in air**

Weigh 100 g of material, pour it into a graduated cylinder.

V represents the volume read off the cylinder.The bulk density of the loose material is:

$$\rho a = \frac{100}{V}\ g.ml^{-1}$$

Density can also be measured after the material has been tamped down in the cylinder.

- **Bulk density after washing and natural draining of the water**

Take approximately 100 g of material and pour it into a beaker. Thoroughly wet it with the distilled water and expel all air present in the grains by boiling and stirring for ,5 minutes.

After cooling, drain off the interstitial water. Weigh 100 g of wet material and pour it into a graduated cylinder. V' designates the volume read off the cylinder. The density of the wet material is:

$$\rho' a = \frac{100}{V'}\ g.ml^{-1}$$

- **True density**

- Nonporous material

Weigh 50 g of material and introduce it into a 250 ml cylinder containing 100 ml of water. V designates the volume read off the cylinder. The true density is:

$$\rho = \frac{50}{V - 100}\ mg.l^{-1}$$

Table 48. Friability limits.

Material	Sand, Biolite, anthracite ,		Activated carbon	
Normal range of use	15 min. 750 strokes	30 min. 1500 strokes	15 min. 750 strokes	30 min. 1500 strokes
Very good	6-1076	15-20%	6-25%	30-50%
Good	10-157c	20-25%		
Poor	15-20%	25-35%		
To be rejected absolutely	> 20%	> 35%	> 3596	> 60%

- Porous material

Weigh 50 g of material and introduce it into the 250 ml ground neck cylinder equipped with a vacuum tap, containing 100 ml of water. Connect the cylinder to a vacuum pump and maintain a partial vacuum of 800 mbar for 15 min.

After breaking the vacuum, with V designating the volume read off the cylinder, true density is:

$$\rho = \frac{50}{V - 100} \text{ g.ml}^{-1}$$

7.1.5. Moisture content

This measurement applies to both granular and powdered materials (PAC, for example).

Weigh precisely 50 g (approx.) of filtering material (or 5 g of powdered material); let Pi be this weight. Place the sample in an oven at 120°C for 4 h. After cooling in a desiccator, weigh the material again; let P_2 be the weight obtained.

The moisture content H is expressed as follows:

$$H = \frac{P_1 - P_2}{P_1} \times 100 \text{ in \% of the weight.}$$

7.2. STUDY OF THE ADSORPTIVE CAPACITY OF A CARBON

7.2.1. Particle size of a powdered activated carbon (PAC)

Dry the carbon for 4 hours at 120°C. Weigh precisely 10 g (approx.) of carbon to be placed on the initial sieve (125 µm). After wetting it, wash the carbon remaining on the sieve with water under pressure. Washing is done while verifying in a white enamel bowl that no further carbon goes through the sieve. Then put the sieve in the oven for 4 h at 120°C for drying. Weigh the material that remains on the sieve. By subtracting this figure from the original weight, calculate the quantity of carbon that has gone through the sieve. Express the ratio in percent.

Proceed in the same way with smaller mesh sieves (90 - 63 - 45 µm).

7.2.2. Adsorption isothermal curve

The adsorptive capacity of an activated carbon can be estimated using a Freundlich lich adsorption isotherm with regard to a given pollutant.

Freundlich equation establishes the ratio between the pollutant weight retained per unit of carbon weight (X/m) and concentration (C_e) of the pollutant under study at equilibrium with the carbon.

$$\frac{X}{m} \quad K\, C_e^n$$

where K and n are two coefficients defined by the experiment.

Starting from the isothermal curves, the following can be defined:

- a normal adsorption capacity of a carbon which makes it possible to estimate the maximum pollutant weight retained per unit of carbon weight for an equilibrium concentration of pollutant equal to the initial concentration of pollutant introduced,
- an adsorption index of a pollutant defined as the pollutant weight retained

per unit weight for a pollutant concentration equal to a tenth of the initial pollutant concentration. This index makes it possible to estimate the adsorption capacity of the carbon for average conditions close to the normal use of carbon,

- an index defining the treatment rate necessary for a pollutant to go from one concentration to another.

The user must be attentive to the operational conditions used by the various suppliers to define these parameters.

7.2.2.1. Establishing an isothermal curve

- Take 6 No. 1.2 litre glass bottles.
- Introduce 1 litre of water containing the pollutant the removal of which is to be studied.
- If a naturally polluted water is studied, the water is introduced as is.
- If a synthetic water is studied, generally a 1 mg weight of pollutant under testing is introduced into each bottle.
- Grind the carbon under study to a powder in a mortar and sift dry on a 40 gm sieve. Keep the particles which pass through the sieve.
- Dry the carbon for 4 h at 120°C in a crucible.
- Increasing dosages of carbon, precisely weighed, are introduced into the bottles containing the polluted water under analysis:

Bottle No.	1	2	3	4	5	6
Dosage ($mg.l^{-1}$)	0	10	20	30	40	50

After one hour of moderate stirring (30 to 40 rpm) at constant temperature, each sample is filtered on a 0.45 µm cellulose acetate membrane. Remove the first 100 millilitres and determine the pollutant remaining on the rest of the filtrate. For each carbon dosage, one thus obtains the equilibrium concentration of the pollutant in the water after contact.

Draw the isothermal curve in log-log coordinates plotting the concentration equilibrium expressed in $mg.l^{-1}$ on the x-axis and the pollutant weight (mg) retained per gramme of carbon on the y-axis (Figure 183).

7.2.2.2. Kinetic study

In the case of granular carbon contact can be made without grinding the carbon, by continuing to shake for a substantial period of time (several weeks). Measuring the equilibrium concentration after different contact times makes it possible to model the adsorption of the pollutant under study.

7.2.3. Ash residue of the carbon

Weigh precisely 1 g (approx.) of dry carbon and introduce it into a calcining crucible; let Pi be the initial weight.

Calcine the carbon at 625°C (± 25°C). Make sure the calcination is complete. After cooling, weigh the ash; let P2 this weight.

The ash content C is expressed as follows:

$$C = \frac{P_2}{P_1} \times 100 \text{ en } \%$$

7.2.4. Iodine index

The iodine index represents the number of milligrammes of iodine absorbed per gramme of carbon for a residual iodine concentration in the filtrate of 0.02 N. The adsorption capacity of a carbon depends on the concentration of the medium to be adsorbed with which it is in contact. Therefore, the concentration of the filtrate must be known so that a correction factor can be applied in order to comply with the definition.

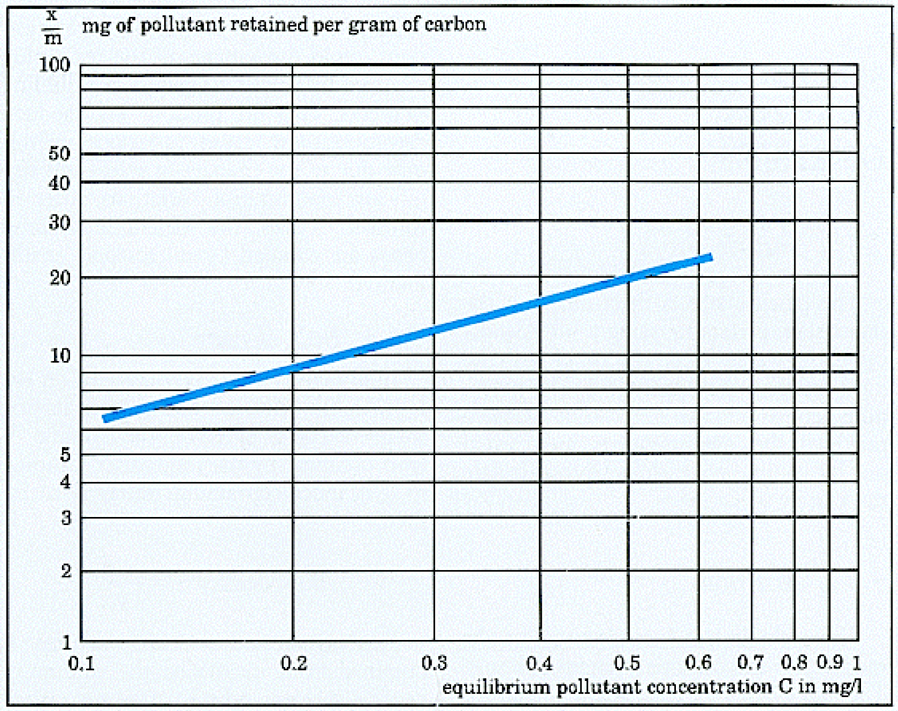


Figure 183. Typical activated carbon isothermal adsorption curve ($\frac{X}{m} = C^n$)

7.2.5. Dechlorinating capacity

The dechlorinating capacity of a carbon is characterized by the depth of carbon needed to remove half the chlorine present for a percolation velocity of 20 m.h^{-1}.

Remove all the air the carbon is liable to contain by boiling it in distilled water. Place the moist carbon away from the air in a tube (22 mm in diameter) until an exactly 10 cm high column is obtained.

Prepare a solution of chlorinated water containing 10 mg.l^{-1} of active chlorine using a solution of sodium hypochlorite, at pH 7.5.

Pass this chlorinated water through the carbon column at the velocity of 20 m.h^{-1}. After 30 minutes operation, accurately titrate the chlorinated water at the inlet to the column (a = mg.l^{-1}) and at the outlet of the column (b = mg.l^{-1}).

With h representing the layer depth in cm, calculate the length of half-dechlorination G:

$$G = \frac{0{,}301.h}{\log \frac{a}{b}} \text{ cm}$$

This test can be reproduced with the same operational conditions for other oxidizers such as chloramines, chlorine dioxide, etc.

7.3.
SPECIFIC ANALYSES OF RESINS

7.3.1. Particle size

The particle size is determined in the moist state preferably using a sifter working under water. 50 or 100 ml of resin are introduced on the upper sieve. The procedure defined on page 378 can be followed provided the measurements are carried out by volume on each sieve to calculate the percentages.

7.3.2. Attrition

These checks are intended to test the mechanical and osmotic strength of resins. They apply mainly to resins intended for continuous process facilities (CIE type). The methods are numerous and diversified; the one described below, using a Degrémont apparatus, is the most representative of the stresses imposed on the resin in the continuous ion exchange systems.

A resin sample is placed in a tube, only occupying a part of its volume. The tube is closed at both ends by a plastic sieve allowing liquids but not the resin to pass through. The test consists in successively passing, at very high speed and for short periods, highly concentrated reagents making it possible to have many exhaustion and regeneration cycles.

These reagents (acid and caustic soda) are injected from bottom to top and each injection phase is separated from the following one by water rinsing from top to bottom; thus there are, during the injections, rapid movements of the resin plug followed by collisions against the filtering elements, rises in pressure and sudden decompressions, rapid variations in volume due to the changes in states and significant concentration variations. After 30 complete cycles the deteriorated resin beads are counted by microscopic examination.

7.3.3. Bulk density

Bulk density must be measured on the resin in its delivered form. After having weighed 100 g of resin, the volume V (ml) occupied by the resin, after tamping in a cylinder containing water, is measured:

Furthermore, the actual density is obtained from measuring the volume of water displaced under a partial vacuum of 800 mbar making it possible to eliminate the air trapped in the pores.

7.3.4. Capacities

7.3.4.1. Cations - Measuring total capacity

- **For weak acid canon resins.**

A resin sample, regenerated with hydrochloric acid until saturation, then rinsed, is put into contact with a known quantity of caustic soda. Then the excess caustic soda is titrated and the volume of resin is measured accurately. The caustic soda consumed compared to this volume gives the total capacity.

- **For strong acid canon resins.**

A resin sample is regenerated with hydrochloric acid until saturation, then rinsed. Then an NaCI solution is passed through until effluent shows neutral to pH indicator paper. The displaced acidity is titrated in the waste and the resin volume is measured accurately. The acidity released compared to this volume gives the total capacity sometimes called in this case strong (or salt-splitting) capacity.

7.3.4.2. Anions - Measuring strong (salt-splitting capacity and total capacity

For weak base and strong base anion resins

A resin sample is regenerated with caustic soda until saturation, then rinsed. Then an NaCI solution is passed through until the effluent shows neutral to pH paper. The displaced alkalinity is titrated in the effluent; compared to the resin volume, it gives the strong capacity. The same resin sample is then placed into contact with a known quantity of HCI. The excess acid is then titrated; the fraction consumed represents the weak capacity of the resin. The total capacity is obtained by finding the sum of the strong and weak functions thus measured.

7.3.5. Contamination of resins

- **Organic matter:** a volume of resin is put into contact with a known volume of an NaCI solution (100 $g.l^{-1}$)~ and an NaOH solution (20 $g.l^{-1}$) for 12 hours. This solution's permanganate value is then determined; compared to the resin volume, it gives the quantity of organic matter eluted, expressed in weight of oxygen per liter of resin.

- **Iron**: a known volume of resin is put into contact with a known volume of hydrochloric acid maintained at a temperature of 80 to 90°C for 30 minutes. The determination of iron content in the waste makes it possible to calculate the weight of iron eluted per liter of resin.

- **Silica:** a known volume of resin is put into contact with a known volume of caustic soda maintained at a temperature of 80°C. The determination of silica content in the waste makes it possible to calculate the weight of silica eluted per liter of resin.

6
AQUATIC ORGANISMS

Figure 184,

1 GENERAL

Life originated in water and a large number of vital phenomena still occur both in the original marine environment as well as in lakes, rivers, ponds, reservoirs, etc.

Many of these phenomena are useful. For example, the mass of organic com pounds generated by photosynthesis or by human activities are remineralized, through the action of bacteria and other microorganisms, in the self-purification process.

In fact, biological treatment and purification of water are examples of man's "domestication" of aquatic microorganisms.

However, waterborne life may be harmful to the aquatic environment and to man if it is present in excess (accelerated eutrophication). In the natural environment, microorganisms may generate compounds which are difficult to remove and which give the water a strong earthy, muddy or mouldy taste. They may also interact with pipe walls, giving rise to red and cloudy water (iron bacteria). Finally, by their very nature, they may pose a threat to public health (pathogenic microorganisms).

This chapter deals with the biology of fresh water by first summarizing the classifications generally used for these organisms and then by providing several key identification features which should assist the reader in referring to more specialized texts for a precise definition.

2. PRINCIPLES OF CLASSIFICATION OF LIVING CREATURES

There are three kingdoms: bacteria, animals and plants, the first having its place at the lower end of the other two. Viruses, large molecules of nucleic acid (combined with proteins), may be considered to mark the border between life and inert matter. They form a separate world which is quite distinct from the "cellular" life represented by the three kingdoms mentioned above.

A simplified table (see pages 392 to 395) is given for each kingdom, containing only certain subdivisions (phylum, class, order, family and genus) and including only those groups which live in aquatic environments. For the purpose of illustration only, a few isolated examples are given at the level of order, family and genus: greater detail can be found in the sub-chapters on bacteriology and the study of plankton.

2.1.
THE BACTERIAL KINGDOM

This is composed of microscopic unicellular organisms, living either separately or in colonies. It is distinguished from the other two kingdoms by numerous characteristics; in particular, bacteria are Procaryotae (having no nuclear membrane), a characteristic which they share with the Cyanophyceae (see later: Procaryotae Protista).

Nevertheless, bacteria have affinities with both of the higher kingdoms. The classification of bacteria given here (Prévot, 1961), is divided into four phyla: alongside true bacteria (Eubacteria), the three other phyla show certain analogies with fungi (Mycobacteria), with algae (Algobacteria) and with unicellular or protozoan animals (Protozoobacteria).

2.2.
THE PLANT KINGDOM

This classification begins with Myxomycetes(higher fungi). They are followed by numerous phyla of algae, from which, going through the Bryophyta (mosses) and the Pteridophyta (vascular cryptogams), the mycetes (lower fungi) and the Eumycetes higher plants are reached

THE BACTERIAL KINGDOM

Phylum	Class	Order	Family	Genus (examples) *
Eubacteria	Asporulales	Micrococcales	Neisseriaceae	Neisseria
			Micrococcaceae	**Streptococcus,** Staphylococcus
		Bacteriales	Pseudomonadaceae	**Pseudomonas,** Serratia
			Enterobacteriaceae	**Escherichia, Salmonella,** Shigella
			Parvobacteriaceae	Pasteurella, Brucella
			Ristellaceae	Ristella
			Protobacteriaceae	**Nitrobacter, Nitrosomonas, Thiobacillus**
			Bacteriaceae	Bacterium, Lactobacillus
		Spirillales	Vibrionaceae	**Vibrio,** Cellvibrio
			Spirillaceae	Spirillum
	Sporulales	Bacillales	Bacillaceae	**Bacillus** (B. subtilis)
			Innominaceae	Innominatus
		Clostridiales	Endosporaceae	Endosporus
			Clostridiaceae	**Clostridium** (Cl. perfringens)
		Plectridiales	Terminosporaceae	Terminosporus
			Plectridiaceae	Plectridium
		Sporovibrionales	Sporovibrionaceae	**Sporovibrio** (or **Desulfovibrio)**
Mycobacteria	Actinomycetales	Actinobacteriales	Sphaerophoraceae	Sphaerophorus
			Actinomycetaceae	**Actinomyces,** Nocardia
			Streptomycetaceae	**Streptomyces,** Micromonospora
		Mycobacteriales	Mycobacteriaceae	Mycobacterium
	Myxobacterales	Myxococcales	Myxococcaceae	Myxococcus
		Angiobacteriales	Archangiaceae	Archangium
			Sorangiaceae	Sorangium
			Polyangiaceae	Polyangium, Chondromyces
		Asporangiales	Cytophagaceae	Cytophaga, Flexibacter
	Azotobacterales	Azotobacterales	Azotobacteriaceae	Azotobacter
Algobacteria	Siderobacteriales	Chlamydobacteriales	Chlamydobacteriaceae	**Sphaerotilus, Leptothrix**
			Crenothricaceae	**Crenothrix,** Clonothrix
			Siderocapsaceae	Siderocapsa, Sideromonas, Ferrobacillus
		Caulobacterales	Caulobacteriaceae	Caulobacter
			Gallionellaceae	**Gallionella**
	Thiobacteriales	Rhodothiobacteriales	Thiorhodaceae	Thiocystis, Chromatium
			Thiobacteriaceae	Thiobacterium, Thiospira
			Athiorhodaceae	Rhodopseudomonas
		Chlorobacteriales	Chlorobacteriaceae	Chlorobium, Pelodictyon
			Chlorochromatiaceae	Chlorochromatium
		Leucothiobacteriales or Beggiatoales	Beggiatoaceae	**Beggiatoa, Thiotrix**
			Achromatiaceae	Achromatium
Protozoobacteria	Spirochaetales	Spirochaetales	Spirochaetaceae	Spirochaeta
			Treponemaceae	Treponema, Leptospira

* The genera most frequently found in the literature on water treatment, in bold type.

THE VEGETABLE KINGDOM

Phylum or sub-phylum	Class (examples)	Order (examples)	Family (examples)	Genus (examples)
– *Thallophyta* (cellular cryptogams) :				
– Myxomycetes	Myxogastromycetidae	Physarales	Didymiaceae	Didymium
– Eumycetes	Phycomycetes	Leptomitales	Leptomitaceae	Leptomitus
	Zygomycetes	Mucorales	Mucoraceae	Mucor
	Ascomycetes	Aspergillales	Aspergillaceae	Aspergillus
	Basidiomycetes	Agaricales	Amanitaceae	Amanita
– Chlorophyta (green algae)	Chlorophyceae	Volvocales	Chlamydomonadaceae	Chlamydomonas
		Chlorococcales	Hydrodictyaceae	Pediastrum
		Ulothrichales	Ulothrichaceae	Hormidium
		Chaetophorales	Chaetophoraceae	Draparnaldia
		Conjugales	Zygnemataceae	Spirogyra
– Euglenophyta	Euglenophyceae	Euglenales	Euglenaceae	Euglena
– Chrysophyta (yellow algae)	Bacillariophyceae or Diatoms	Centrales		Cyclotella
		Pennales	Araphideae	Synedra
			Monoraphideae	Rhoicosphenia
			Biraphideae	Navicula
	Chrysophyceae	Ochromonadales	Synuraceae	Synura
	Xanthophyceae or Heterokontae	Heterotrichales	Heterotrichaceae	Tribonema
		Heterosiphonales		Vaucheria
– Cyanophyta (blue algae)	Myxophyceae	Chroococcales	Chroococcaceae	Microcystis
		Hormogonales	Oscillatoriaceae	Oscillatoria
– Rhodophyta (red algae)	Rhodophyceae	Bangiales		Bangia
		Florideae		Batrachospermum
– Pyrrhophyta	Cryptophyceae	Cryptomonadales		Cryptomonas
	Dinophyceae (or Peridiniaceae)	Peridiniales		Peridinium
		Dinocapsales		Gleodinium
– Phaeophyta (brown algae)	Phaeophyceae	Fucales		Fucus
– *Bryophyta* (Muscineae)	Hepaticae	Jungermanniales		Riccia
	Musci	Sphagnales		Sphagnum
– *Pteridophyta* (vascular cryptogams)	Filicineae			Ferns
– *Spermatophyta* or *Phanerogamia:*				
– Gymnospermae	Coniferophytae	Abietales	Pinaceae	Fir
– Angiospermae	Monocotyledonae	Naiadales	Potamogetonaceae	Potamogeton
		Graminales	Gramineae	Cereals
		Cyperales	Juncaceae	Rush
			Cyperaceae	Sedge
		Spadiciflorae	Lemnaceae	Lemna, Wolffia
		Pandanales	Typhaceae	Typha
	Dicotyledoneae	Ranales	– Ceratophyllaceae	Ceratophyllum
			– Nymphaeaceae	Nuphar, Nymphaea
		Rosales	Papilionaceae	Pea, bean
		Fagales	Fagaceae	Oak, beech

2.3
THE ANIMAL KINGDOM

The simplest organisms are unicellular animals (Protozoa), which include numerous parasitical forms (among the flagellates, only the Polymastigina and the Diplomonadina include free living forms: the Sporozoa are all parasites).

The plankton and fauna in activated sludge include large numbers of Protozoa which play a very significant role.

The Porifera form the transition between Protozoa and Metazoa, the primitive sponge being made up of a colony of differentiated protozoans. Then, moving up towards the higher animals, important planktonic phyla are encountered, particularly among the worms, the Vermidae (Rotifera) and the Arthropoda (crustaceans and insect larvae).

The system of classification proposed here cannot be considered as universal, since variations exist.

THE ANIMAL KINGDOM Sub-Kingdom **I: Protozoa**

Phylum	Class (examples)	Order (examples)	Genus (examples)
Rhizopoda	Amoebina		Amoeba
	Foraminifera		Polystomella
	Radiolaria		
	Heliozoa		Actinophrys
Flagellata	Zooflagellates	Herpetomonadina	Trypanosoma
		Polymastigina	Trichomonas
		Diplomonadina	Giardia
		Hypermastigina	
Sporozoa	Telesporidia	Gregarinida	
		Coccidae	
		Haemosporidia	Plasmodium
	Cnidosporidia		
Protociliata		Opalinidae	
Infusoria	Ciliata	Holotricha	Paramecium, Coleps
		Heterotricha	Stentor
		Peritricha	Vorticella
		Hypotricha	Euplotes, Aspidisca
	Suctoria (Acineta)		Podophrya Acineta

THE ANIMAL KINGDOM Sub-Kingdom **II: Metazoa**

Phylum	Class (examples)	Sub-Class (examples)	Order (examples)	Genus (examples)
Porifera	Calcareous sponges			
	Siliceous sponges	Demospongiae	Tetractinellida	Spongilla
Coelenterata	Hydrozoa		Hydroida	Hydra
	Scyphozoa		Medusae	Craspedacusta
	Anthozoa	Zoantharia	Madreporaria	Corals
Echinodermata	Echinoidea			Sea urchins
Platyhelminthae (flat worms)	Turbellaria	Neoophores	Tricladida	Planaria
	Trematoda		Digenea	Fluke, bilharzia
	Cestoidea	Eucestoda	Cyclophyllidea	Tapeworm
Nemertea	Nemerteans	Armata	Hoplonemertea	Prostoma
Nemathelminthes (round worms)	Gasterotricha		Chaetonotoidea	Chaetonotus
		Aphasmidia	Trichinoidea	Threadworm
	Nematoda	Phasmidia	Tylenchoidea	Anguillula
			Ascaridoidea	Ascaris
	Acanthocephala			Pomphorhynchus
	Nematomorpha		Gordiodea	Gordionus
Rotifera	Bdelloidea		Bdelloidea	Philodina
			Ploimidea	Keratella
	Monogononta		Flosculariacea	Hexarthra
Echiuroidea	Gephyrea		Echiuroinea	Bonellia
Annelida (ringed worms)	Polychaeta		Errantia	Nereis
			Oligochaeta	Tubifex, nais
	Clitellata		Hirudinidae	Leech
Lophophores	Bryozoa	Ectoprocta	Phylactolaemata	Cristatella
	Brachiopoda	Articulata		
Mollusca	Amphineura			Chiton
	Scaphopoda			
	Gastropoda	Euthyneura	Pulmonata	Planorbis
	Lamellibranchia		Eulamellibranchia	Dreissensia (mussel)
	Cephalopoda	Dibranchia	Octopoda	Octopus
			Decapoda	Cuttlefisch
Arthropoda	Crustacea	Entomostraca	Ostracoda	Cypris
			Copepoda	Cyclops
			Cladocera	Daphnia, Bosmina
		Malacostraca	Isopoda	Asellus, wood louse
			Amphipoda	Gammarus
			Decapoda	Astacus (crayfish)
	Tardigradata		Eutardigrada	Macrobiotus
	Myriapoda	Diplopoda	Chilognatha	Julus
	Arachnida		Acarina	Hydrachna
	Insecta	Pterygota	Diptera	Chironomus
Stomochordata	Hemichordata			
Chordata – Urochorda	Ascidiacea			
– Acrania				Branchiostoma
– Vertebrata	Cyclostomata			Lamprey
	Chondrichthyes	Elasmobranchii	Selachii	Shark
	Osteichthyes	Neopterygii	Teleostei	Trout
	Batrachia		Caudata	Proteus
			Salientia	Frog
	Reptilia		Testudinata	Tortoise
	Birds		Anatidae	Duck
	Mammals	Eutheria	Primates	Man

3. IDENTIFICATION OF AQUATIC MICROORGANISMS

For practical purposes, these of identification are grouped according to the role played by the microorganisms in rudiments relation to water, firstly as a product for human consumption and secondly as a product to be purified.

3.1

MICROORGANISMS TO BE CONSIDERED IN PRODUCTION, DISTRIBUTION AND CONSUMPTION

3.1.1. Pathogenic microorganisms

A wide range of pathogenic microorganisms may be found in the water destined, after treatment, to become drinking water. Numerous different techniques must therefore be used to identify and remove them. These organisms can be classified in the following large groups: bacteria, viruses, fungi, amoebae, worms, insects.

Bacteria

Bacteria are said to be pathogenic when they are capable of proliferating within a multicellular organism, thus causing more or less serious health problems. This pathogenic character is particular to certain types of bacteria, although some which are generally non-virulent may become pathogenic if the environmental conditions are favourable or if they accidentally invade a biological tract in which they are not usually found (as for example in the case of colon bacilli in the bloodstream).

After isolation, bacteria are generally identified by revivification on specific media by means of chemical reagents and/or sero-agglutinating reactions which show up all the biochemical characteristics of the bacterial cytoplasm and membrane as well as their virulence (figures 185 and 18G).

When testing the bacterial quality of water to ensure the absence of all pathogenic agents, an indirect method is generally used, involving verification of the absence of bacteria indicating fecal contamination (see page 345).

However, since Pasteur, specific media and reactions have been developed to determine the type and the virulence of all pathogenic bacteria. Generally, the techniques used for water derive from those used in hospitals. The main additional difficulty inherent in aquatic environments is the degree of dilution of the bacteria and the state of stress that their stay in the water sometimes brings about. Special concentration methods (filtering membranes) and revivification techniques (incubation at several temperature levels) are therefore used to isolate them.

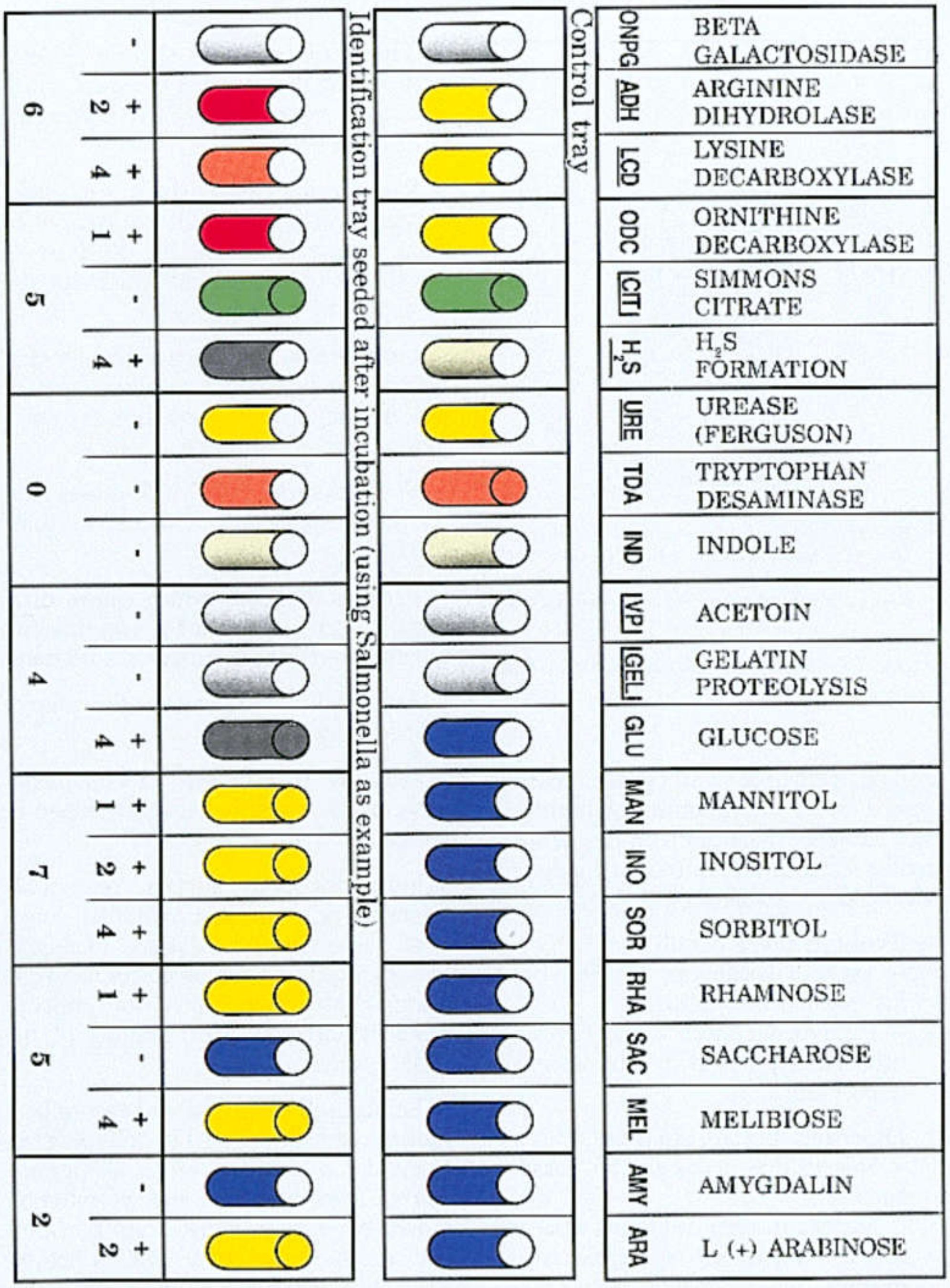
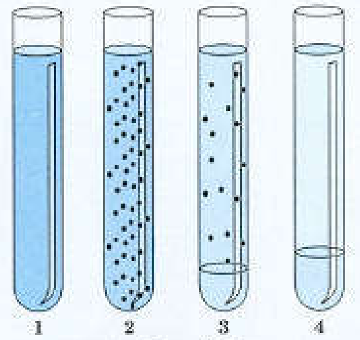


Figure 185. Example of an identification tray revealing the enzymatic characteristics of the bacterium (using the micro-method API 20E)



1 Control tube
2 - 3 Agglutination
4 Settling

Bacterial agglutination causes the formation of a bacterial floc which settles. The bacteria tested can thus be identified as they correspond to the specific serum used.

Figure 186. Example of sero-agglutination (illustrations).

The principal pathogenic bacteria passed into the environment by healthy or sick carriers, which can then be transmitted by water to non-immunised individuals, include the following:

- Typhoid fever bacilli:

- Typhoid bacillus or Berth's bacillus: Salmonella typhus,
- Paratyphoid bacilli A and B: Salmonella paratyphi and S. schottmuelleri, respectively.

- Dysentery bacilli, such as:

- Shigella dysenteriae and Sh. paradysenteriae,
- Shigella flexneri or Flexner's bacillus (pseudodysenteric). Gastrointestinal diseases, which include salmonellosis and shigellosis, are not all well defined. There are many benign cases.

- The cholera vibrio (Vibrio cholerae or V. comma) discovered by Koch, which is in the form of small, curved, flagellate and motile rods.

- **Pasteurella tularensis** which causes tularemia, a disease normally transferred from person to person by the bites of blood sucking insects, but which can also be spread by water.

- Campylobacter which, although once believed to be mainly an animal pathogen, is today a cause of enteritis as important as that of Salmonella.

- Proteus morganii, which causes fetid diarrhea, especially in children in summer.

- Proteus vulgaris which causes diarrhea, intestinal catarrh (resembling typhoid fever) and a variety of infections.

- Escherichia coli, which is the cause of colibacillosis.

- **Bacillus pyocyaneus** (Pseudomonas aeruginosa), which is frequently found in sewage.

- **Staphylococcus aureus**, responsible for many skin and gastrointestinal infections (abscesses, furunculosis, food poisoning) which is often tested for in swimming pool water when its presence generally indicates poor cleaning of the surface water.

- **Legionnella,** which was shown to be a human pathogen in 1976 following an epidemic in a group of retired legionnaires. There are two types of infection caused by these bacteria: acute pneumonia or a more benign form (Pontiac fever). These bacteria multiply in hot water (showers, air conditioners) and contamination is generally airborne.

- Leptospira (or Spirochaeta) icterohemorragiae, the cause of spirochetal jaundice, which is very widespread throughout the world. Many carriers exist, in particular the rat. Sewer workers sometimes contract this disease.

Alongside these well-known pathogens, whose clinical effects have been carefully studied, there exist a number of opportunist bacteria which may become virulent, particularly in organisms with a weakened immune system, for example, bacteria of the Yersinia and Aeromonas groups.

These bacteria, unlike the other pathogens mentioned above, are unfortunately well adapted to the aquatic environment. They are

capable of multiplying at temperatures close to 0°C and in a dilute organic substrate, conditions very close to those likely to be found in a water distribution system.

Viruses (figure 187)

Viruses are minute pathogenic agents, visible only by electron microscope and capable of multiplying only inside a living cell. A virus consists of a nucleic acid and a protein, components which can be separated chemically and even crystallised. The union of these two components reconstitutes the virus with all its biological properties. When a living cell has been attacked by a virus, it is soon totally transformed into a granular mass of new viruses ready to infect new cells.

The following viruses can be found in water:

- Enterovirus:
- poliomyelitis virus which attacks the nerve centres,
- Echovirus (derived from Entericpresent Cytopathogenic Human Orphan virus) causing generally mild intestinal sickness (diarrhea in children); certain serological types can cause lymphocytic meningitis (reversible),
- Coxsackie A & B which can cause lymphocytic meningitis, myalgia and myocardosis as well as infantile gastroenteritis.

- **The infectious hepatitis viruses:** only type A is transmissible by water (type B is transmissible by blood transfusions). The disease is endemic in some hot regions.

- **The Ad enoviruses** which attack the upper respiratory passages and the eyes but which are also present in the intestine.

- **The Rotaviruses,** responsible for diarrhea symptoms, frequently severe in young children. They are believed to be responsible for 20 to 70% of cases of infantile diarrhea.

- **Influenza** which can sometimes be transmitted in swimming pools since this virus, although rarely found in the intestine, is very abundant in nasal mucus.

- **The Reo viruses** which are still little understood.

- **The Papillomavirus** which is responsible for the verrucas contracted in swimming pools.

In fact, the role of water in the transmission of some viral diseases is the subject of much debate. Moreover, in the rare cases where it has been possible to prove that a viral epidemic was caused by the water supply, the water has always been massively contaminated by sewage. It thewould appear that a risk of epidemic exists only in extreme conditions, though knowledge of minimum infecting doses is still poor.

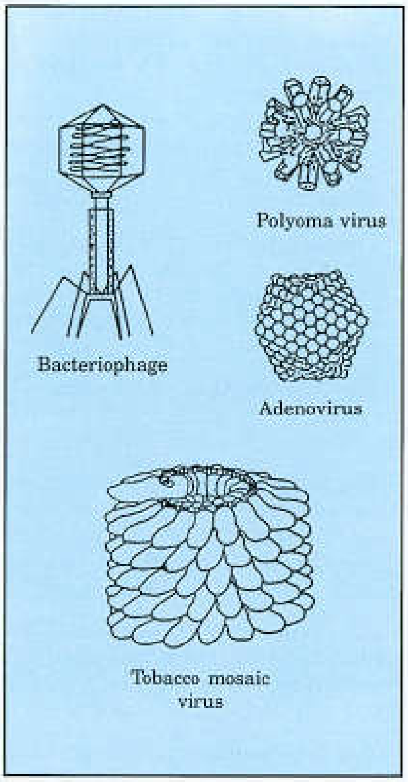


Figure 187. Forms of certain viruses.

If present in water, viruses are generally found in very small quantities. The water to be analysed must therefore be concentrated (see page 346).

Fungi

A microscopic fungus, Histoplasma capsulatum, sometimes infests mains piping and causes histoplasmosis.

Other than this exceptional case, no other waterborne epidemic is known to have been caused by fungi.

.Amoebae

Amoebae are able to survive for over a month in water in the form of cysts. However, they can be removed by ozone treatment with a residual presence of 0.4 $mg.l^{-1}$ after 4 min of contact. Two waterborne species are pathogenic to man: Entamoeba histolytica which causes serious, sometimes fatal, dysentery (Chicago epidemic in 1934); Naegleria gruberi which causes meningitis transmitted through water, especially in swimming pools.

These organisms' resistance to disinfection, which is greater than that of most bacteria, complicates their eradication, but can provide a valuable indication of the effectiveness of disinfection.

Protozoa

Giardia lamblia is responsible for numerous cases of waterborne gastroenteritis throughout the world (4 to 22% in the U.S.A.). The large spread of infection is due to the abundance of healthy carriers. Its resistance to disinfection is particularly high when it is in the cyst state. It can be successfully removed by flocculation treatment using optimised dosages, followed by rapid filtration through sand.

. Worms

Water may serve as the vehicle for many parasitic worms affecting man and animals. These worms and their eggs are not destroyed by disinfection using normal dosages but they are usually large enough to ensure that efficient filtration will practically eliminate the risks of contamination. These worms generally develop in a succession of different hosts:

- **Taenia solium** (tapeworm): spherical egg measuring 35 µm, encysts in pigs,

- **Taenia saginata** (tapeworm): oval egg 25 x 35 µm, encysts in cattle,

- **Taenia echinococcus:** adult stage in dogs, encysts in sheep (hydatid cyst); egg 25 x 35 µm,

- **Bothriocephalus latus**: adult stage in man. The oval egg, 45 x 70 hum, develops in water, releasing an embryo which infects a copepod. When this latter is swallowed by a fish, the embryo becomes a larva (8 to 30 mm long) and lodges in the muscles of the fish,

- **Distoma hepatica**: a flat worm, adult stage in man and sheep. The ovoid egg, 70 to 130 µm, develops in water and produces a ciliated embryo which infects a water snail, inside which it transforms into a cercaria. This swims away to attach itself to a water plant before infecting a sheep again. The adult form fixes itself in the liver,

- **Distoma lanceolata**: similar to the above, the intermediate host being a planorbis snail,

- **Bilharzia:** a trematode worm, whose generic name is Schistosoma and which is the cause of a serious disease called bilharziosis or schistosomiasis, widespread in the hotter parts of the world. There are two forms of the disease and three species of this parasitic worm:
    - vesical schistosomiasis, due to S. haematobium (Egypt, tropical Africa, Madagascar)
    - intestinal schistosomiasis, caused by S. mansoni (Egypt, tropical Africa, Madagascar, South America) or by S. japonicum (Far East).

The adult lives in the blood vessels of man. The egg is ovoid (50 x 150 gym) with a 25 gm spike. It is excreted in the urine, develops in water to produce a ciliated embryo (miracidium) which infects a snail which lives in still waters. There it turns into a cercaria (larva with a forked tail) which returns to the water and invades a new human host through the skin (or the mucous membranes of the mouth if the water is swallowed). The cercaria has a life span of two days.

This epidemic is fought by destroying the molluscs which act as intermediate host, using either chemical methods (molluscicides), biological means or changing the habitat of the molluscs.

In drinking water the cercariae can be removed by filtration through fine sand (0.35 mm maximum). However, total destruction of the cercariae requires effective prechlorination and final disinfection (chlorine or ozone) using suitable dosages and contact times,

- **Ascaris lumbricoides:** occurs frequently in the small intestine of man and pigs. Ovoid egg 50 x 75 µm. It develops in water or wet soil to form an embryo 0.3 mm long which is transmitted directly to man,

- **Oxyuris vermicularis:** often found in children. Oval egg with one slightly flattened side 20 x 50 elm. Does not seem to live long in water,

- **Eustrongylus gigas:** infects the urinary tract. The elliptical egg (40 x 60 gym), paler at each end, is expelled in the urine. The embryo, 0.25 mm long, infects a fish as an intermediate host,

- **Ancylostoma duodenale** (hookworm): a small worm, 6 to 20 mm in length, that lives in the intestine, pierces the mucous membranes and causes persistent hemorrhages and diarrhea (ancylostomiasis or hookworm disease). The egg, 30 x 60 gm, develops in water. It requires a minimum temperature of 22°C. The 0.2 mm embryo produces a larva capable of penetrating the skin to infect a new victim,

- **Filaria medinensis** (Dracunculus, Guinea worm, Medina worm). A viviparous worm. The 0.5 to 1 mm embryo infects a copepod to form a larva. If the copepod is swallowed with water, the larva develops in man. The worm burrows through the intestinal wall and forms subcutaneous abscesses (dracunculosis). The adult worm is 0.5 to 0.8 m long and 1 mm in diameter. Transmission is also possible by direct passage of the larva through the skin,
- **Filaria sanguinis hominis:** this worm lives in the vessels in the lower part of the body, particularly in the bladder, causing hematuria. Contamination occurs via a mosquito which acts as an intermediate host,
- **Anguillula intestinalis:** a worm of 2 to 3 mm in length which lives in the duodenum. The egg develops in water to form a worm (Anguilla stercoralis) which lays eggs in the water, the larvae from which can reinfect man if they are swallowed or pass through the skin.

- Insects

The main aquatic insects constituting a danger to health are mosquitoes, whose larvae can live only in water. They transmit a number of diseases.

Malaria, or marsh fever, is transmitted by the Anopheles mosquito (A. maculi-pennis, funestus or gambiae), the agent of the disease being Laveran's hematozoon.

Yellow fever (Typhus amaril) is carried by Aedes aegypti. The genus Culex can also be the vector of certain diseases (viral encephalitis, filariasis).

3.1.2. Saprophytic microorganisms whose natural habitat is fresh water

Alongside the microorganisms described above, which live as parasites at the expense of higher organisms, warm blooded animals in particular, there exists a whole group of organisms adapted to aquatic life. These creatures are the flora and fauna of water. They play a beneficial role in the balance of nature as detrivorous organisms. However their proliferation in nitrogen- and phosphorus-rich water can lead to problems for the water users: allergic reactions in bathers, unpleasant tastes and smells which are difficult to remove during drinking water treatment.

The aquatic biotopes form a complex equilibrium in which the consumers of organisms and organic molecules (heterotrophs) and the producers of organic matter (autotrophs) exist side by side. Algae and aquatic plants are able to build up vast quantities of organic matter using simple elements (C, N, P) by photosynthesis or chemosynthesis.

3.1.2.1. Chemoautrophic bacteria

(see page 29)

3.1.2.2. Algae

These may be floating (plankton) or attached to a support (periphyton). They not only synthesise their own matter but also release chemical mediators (metabolites) into the aquatic environment which, when algae are abundant, cause problems in drinking water (halomethane precursors with strong and varying tastes) (see table 49).

Table 49. Algae-generated tastes and odours
Table taken from "Identification and Treatment of Tastes and Odours in Drinking Water" - J. Mallevialle, Suffer IH, 1987.

Algae class	Odour description		Tote description	Tactile sensation
	Moderate quantities of algae	Large quantities of algae		
Cyanophyceae				
Anabaena	grassy, musty, nasturtium	rotten, septic, medicinal	-	-
Anabaenopsis	-	grassy		
Aphanizomenon	grassy, musty, nasturtium	rotten, septic, medicinal	sweet	dry
Cilindrospermum	grassy	septic	-	-
Gloeotrichia	-	grassy	-	-
Gomphosphaeria	grassy	grassy	sweet	-
Microcystis or Anacystis	grassy, musty	rotten, septic, medicinal	sweet	-
Nostoc	musty	rotten, septic medicinal	-	-
Oscillatoria	grassy	musty, spicy	-	-
Rivularia	grassy	musty	-	-
Chlorophyceae				
Actinastrum	-	grassy, musty	-	-
Ankistrodesmus	-	grassy, musty	-	-
Chara	garlic, musky	musty, garlic	-	-
Chlamydomonas	musty, grassy	fishy, septic medicinal	sweet	soft, oily
Chlorella	-	musty	-	-
Cladophora	-	septic	-	-
Closterium	-	grassy	-	-

Table 49. (contd.)

Algae class	**Odour description**		**Taste description**	**Tactile sensation**
	Moderate quantities of algae	Large quantities of algae		
Cosmarium	-	grassy	-	-
Dictyosphaerium	grassy, nasturtium	fishy	-	-
Eudorina	-	fishy	-	-
Gloeocystis	-	rotten, medicinal	-	-
Gonium	-	fishy	-	-
Hydrodictyon	-	rotten, septic	-	-
Nitella	grassy	grassy, rotten	bitter	-
Pandorina	-	fishy	-	-
Pediatrum	-	grassy	-	-
Scenedesmus	-	grassy	-	-
Spirogyra	-	grassy	-	-
Staurastrum	-	grassy	-	-
Tribonema	-	fishy	-	-
Ulothrix	-	grassy	-	-
Volvox	fishy	fishy	-	-
Bacillariophyceae (Diatoms)				
Asterionella	spicy, geranium	fishy	-	-
Cyclotella	grassy, spicy, geranium	fishy	-	-
Diatoma	-	aromatic	-	-
Fragilaria	grassy, spicy, geranium	musty	-	-
Melosira	grassy, spicy, geranium	musty	-	soft, oily

Table 49. (contd.)

Algae class	Odour description		Tote description	Tactile sensation
	Moderate quantities of algae	Large quantities of algae		
Meridion	-	spicy	-	-
Pleurosigma	-	fishy	-	-
Stephanodiscus	grassy, spicy geranium	fishy	-	soft, oily
Synedra	grassy	musty, fishy	-	soft, oily
Tabellaria	grassy, spicy, geranium	fishy	-	soft, oily
Chrysophyceae				
Dinobryon	violets, fishy	fishy	-	soft, oily
Mallomonas	violets	fishy	-	-
Synura	cucumber, rotten, medicinal, muskmelon	fishy	bitter	dry, metallic, soft
Uroglenopsis	cucumber	fishy	-	soft, oily
Euglenophyceae				
Euglena	-	fishy	sweet	-
Dinophyceae				
Ceratium	fishy	rotten, septic, medicinal	bitter	-
Glenodinium	-	fishy	-	soft, oily
Peridinium	cucumber	fishy	-	-
Cryptophyceae				
Cryptomonas	violets	violets, fishy	sweet	-

Identification of planktonic algae (or phytoplankton)

The classification of algae is based primarily on their pigments (large phyla) and then on the morphology, the stored substances, the flagellae. Algae comprise a vast range of organisms representing more than 2000 genera, many of which are composed of many dozen species.

The identification of algae is a highly specialised task, requiring long experience and the use of many references.

The following illustrations are not sufficient in themselves for the identification of an individual species but simply give an indication of the genus or group (see figures 188, 189, 190).

3.1.2.3. Zooplankton

Fresh water zooplankton comprises relatively few genera and species; they are rarely represented by a large number of individuals in streams and rivers although the opposite is true in lakes and ponds. They include mainly Crustacea, Rotifera and Protozoa (see figures 191, 192, 193). Planktonic animals are transparent. They swim fairly actively and possess appendages which enable them to support themselves in the water. They sink to varying depths according to the degree of turbulence on the water surface. Daily vertical migrations also take place due to phototropism. Their size is highly variable. Some phyla only include microscopic individuals (Protozoa, Rotifera), whereas others include individuals of several millimetres in length (Crustacea). They feed on algae, bacteria, organic detritus or on each other. Their multiplication is influenced by seasonal changes affecting the growth of phytoplankton, which in turn is influenced by the zooplankton. Indeed, algae proliferation has been observed in rivers and reservoirs following the destruction of algae-consuming zooplankton using toxic chemicals.

In addition to the three main groups given above, there are other organisms whose larvae are planktonic while the adults live attached to a support. Some may form themselves into groups which are large enough to block pipes carrying untreated water (as in the case of the mollusk Dreissensia polymorpha) or to hinder filtration processes (Mollusca, Porifera, Bryozoa). The eggs, cysts or larvae can pass through filters and develop later (worms, nematodes).

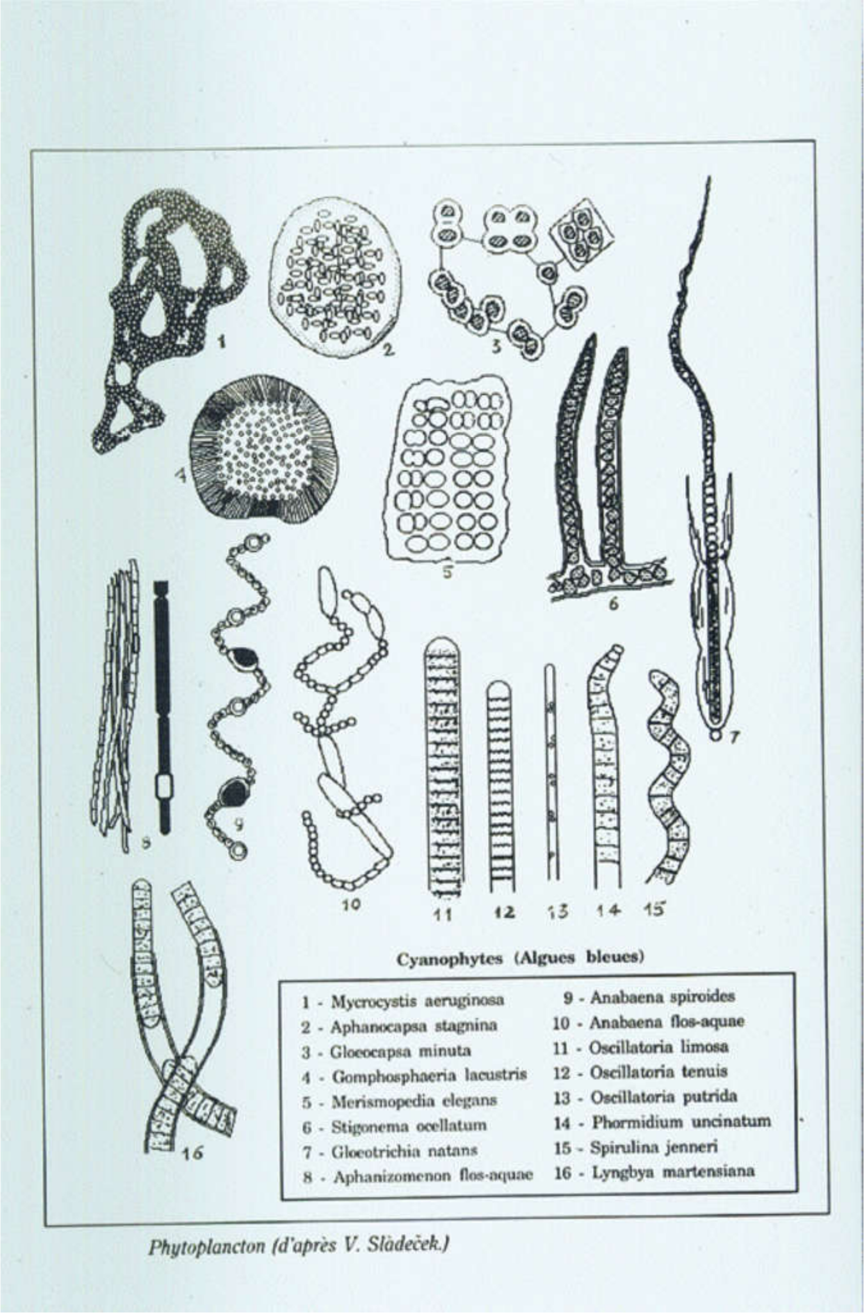
3.2.
MICROORGANISMS ASSOCIATED WITH PURIFICATION

3.2.1. Purifying bacteria

Activated sludge consists essentially of bacteria and protozoans with, in certain cases, fungi, rotifers and nematodes.

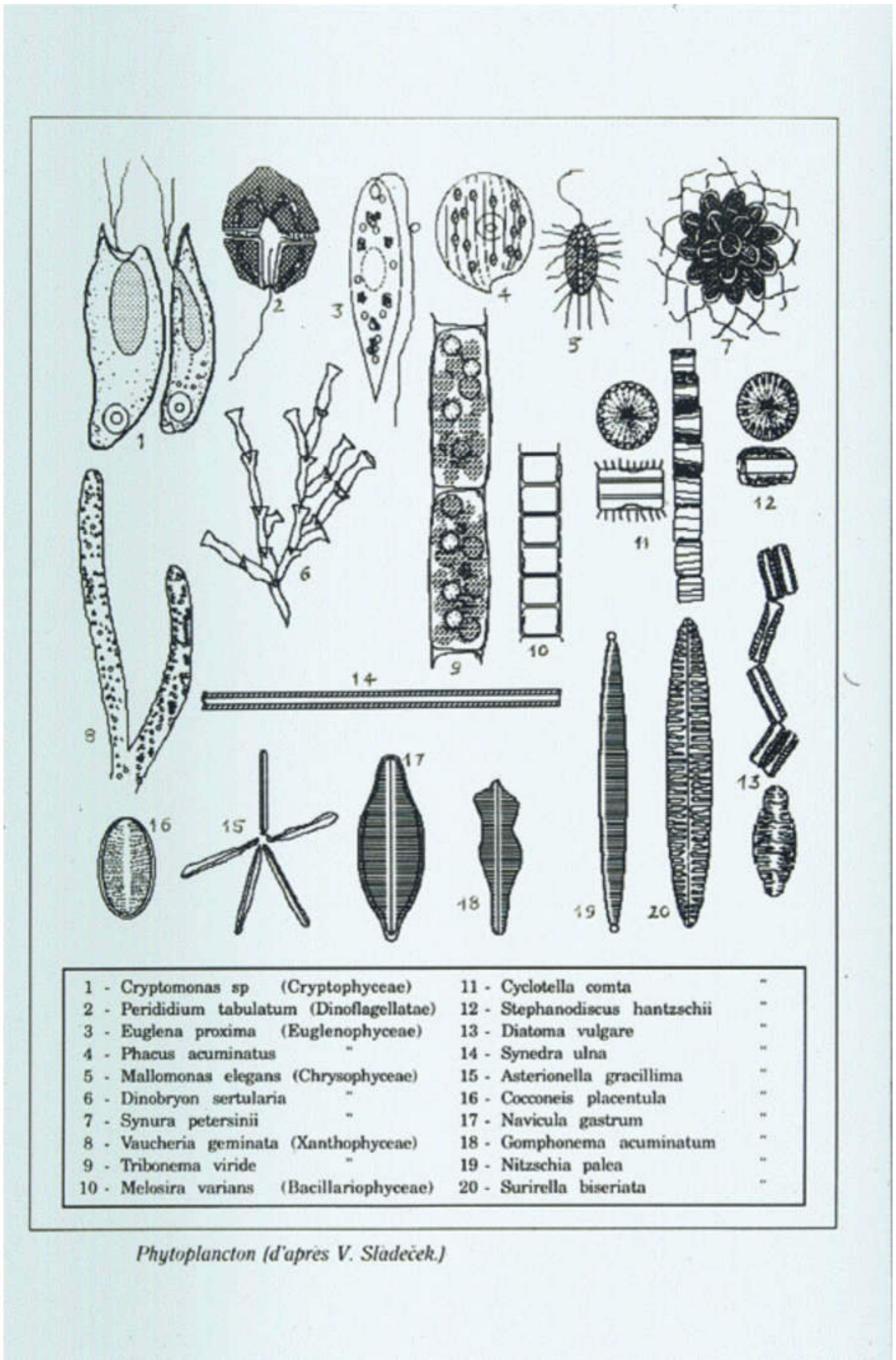
Bacteria form the largest group and are principally responsible for pollution removal and floc formation.

Numerous species of bacteria may be involved in activated sludge formation. The dominant genus present depends on the type of organic compounds comprising the pollution and the environmental



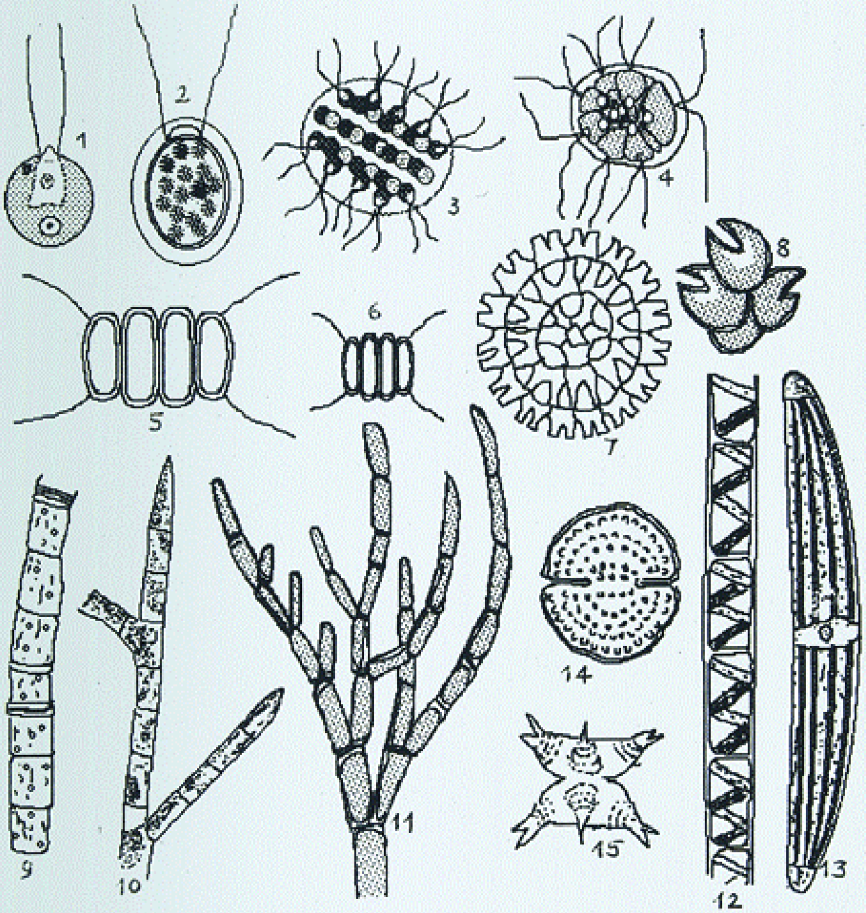
Phytoplancton (d'après V. Sládeček.)

Figure 188. Phytoplankton faker V. Slide&k).



Phytoplancton (d'après V. Sládeček.)

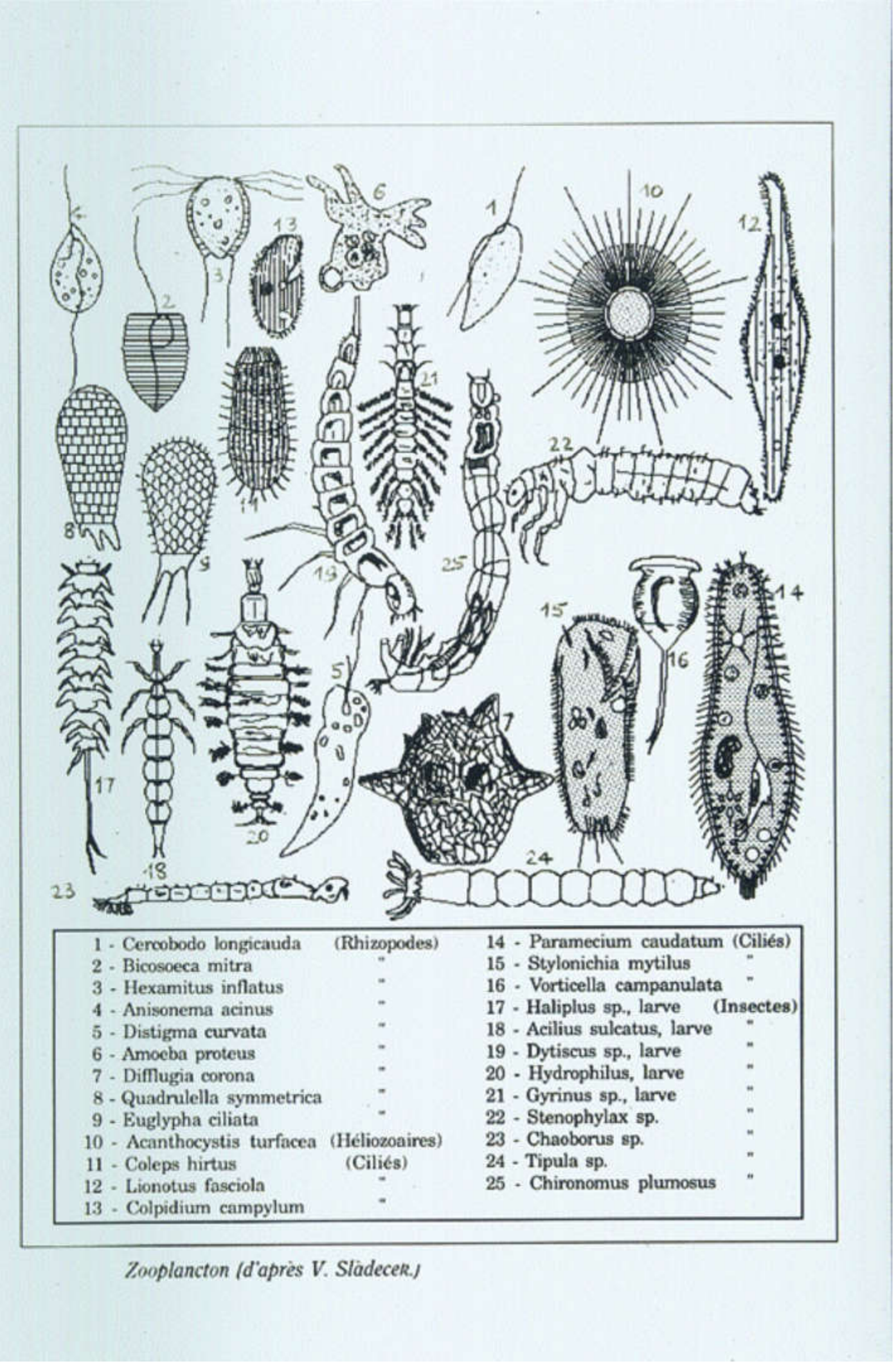
Figure 189. Phycoplankton (after V. Sladecek).



1 - Chlamydomonas simplex (Chlorophyceae)
2 - Gloeomonas ovalis "
3 - Eudorina elegans "
4 - Pandorina morum "
5 - Scenedesmus quadricauda "
6 - Scenedesmus abundans "
7 - Pediastrum biradiatum "
8 - Kirchneriella lumaris "
9 - Oedogonium capillare "
10 - Stigeoclonium sp. "
11 - Cladophora glomerata "
12 - Spirogyra quinina "
13 - Closterium acerosum "
14 - Cosmarium formosulum "
15 - Staurastrum commutatum "

Phytoplancton (d'après V. Slàdeček.)

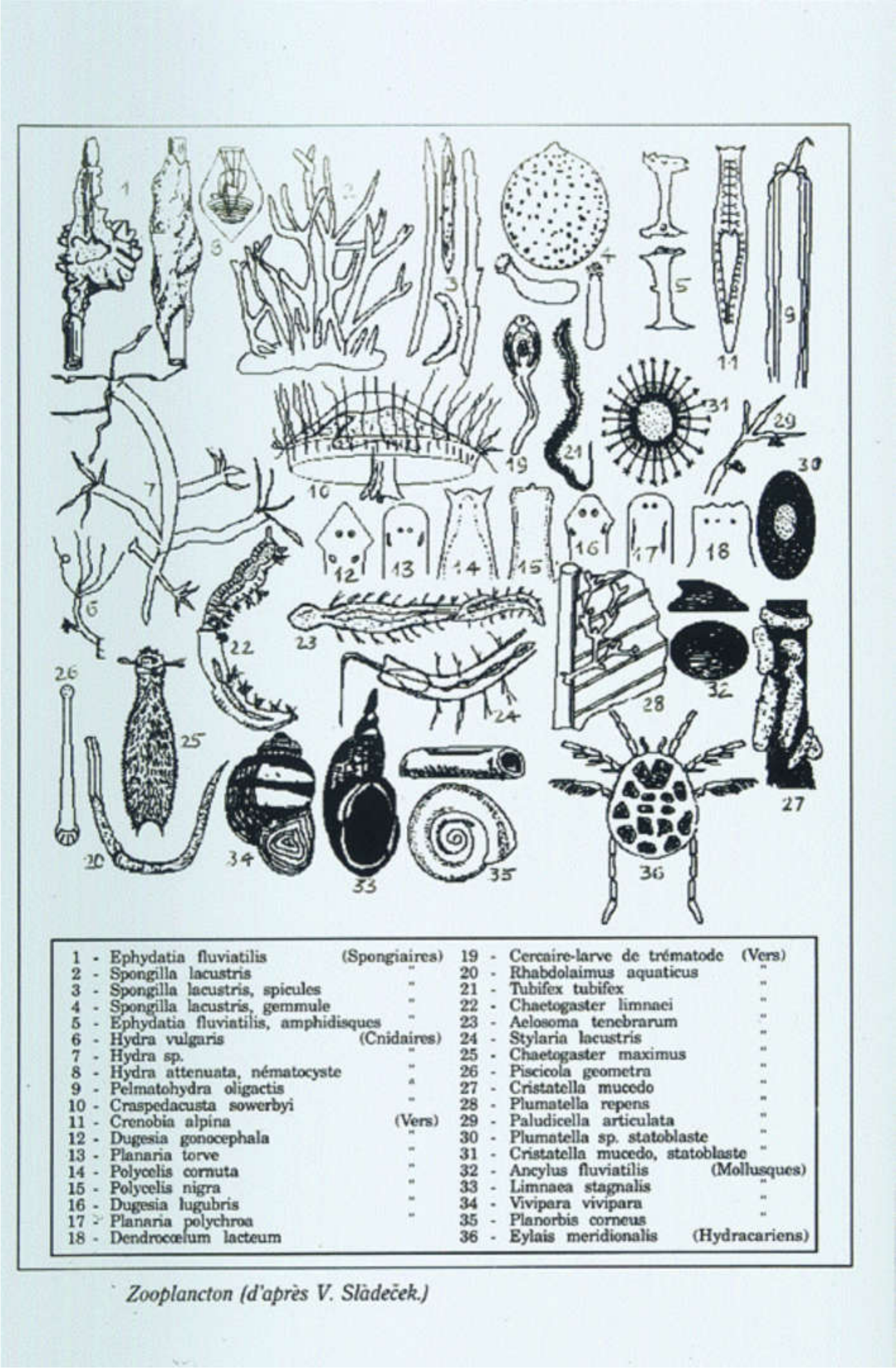
Figure 190. Phytoplankton (after V. Sladecek).



1 - Cercobodo longicauda (Rhizopodes)
2 - Bicosoeca mitra "
3 - Hexamitus inflatus "
4 - Anisonema acinus "
5 - Distigma curvata "
6 - Amoeba proteus "
7 - Difflugia corona "
8 - Quadrulella symmetrica "
9 - Euglypha ciliata "
10 - Acanthocystis turfacea (Héliozoaires)
11 - Coleps hirtus (Ciliés)
12 - Lionotus fasciola "
13 - Colpidium campylum "
14 - Paramecium caudatum (Ciliés)
15 - Stylonichia mytilus "
16 - Vorticella campanulata "
17 - Haliplus sp., larve (Insectes)
18 - Acilius sulcatus, larve "
19 - Dytiscus sp., larve "
20 - Hydrophilus, larve "
21 - Gyrinus sp., larve "
22 - Stenophylax sp. "
23 - Chaoborus sp. "
24 - Tipula sp. "
25 - Chironomus plumosus "

Zooplancton (d'après V. Slàdecer.)

Figure 191. Zooplankton faker V. Sladecek).



No.	Name	Group
1	Ephydatia fluviatilis	(Spongiaires)
2	Spongilla lacustris	"
3	Spongilla lacustris, spicules	"
4	Spongilla lacustris, gemmule	"
5	Ephydatia fluviatilis, amphidisques	"
6	Hydra vulgaris	(Cnidaires)
7	Hydra sp.	"
8	Hydra attenuata, nématocyste	"
9	Pelmatohydra oligactis	"
10	Craspedacusta sowerbyi	"
11	Crenobia alpina	(Vers)
12	Dugesia gonocephala	"
13	Planaria torve	"
14	Polycelis cornuta	"
15	Polycelis nigra	"
16	Dugesia lugubris	"
17	Planaria polychroa	
18	Dendrocœlum lacteum	
19	Cercaire-larve de trématode	(Vers)
20	Rhabdolaimus aquaticus	"
21	Tubifex tubifex	"
22	Chaetogaster limnaei	"
23	Aelosoma tenebrarum	"
24	Stylaria lacustris	"
25	Chaetogaster maximus	"
26	Piscicola geometra	"
27	Cristatella mucedo	"
28	Plumatella repens	"
29	Paludicella articulata	"
30	Plumatella sp. statoblaste	"
31	Cristatella mucedo, statoblaste	"
32	Ancylus fluviatilis	(Mollusques)
33	Limnaea stagnalis	"
34	Vivipara vivipara	"
35	Planorbis corneus	"
36	Eylais meridionalis	(Hydracariens)

Zooplancton (d'après V. Slàdeček.)

Figure 192. Zooplankton (after V. Sladecek).

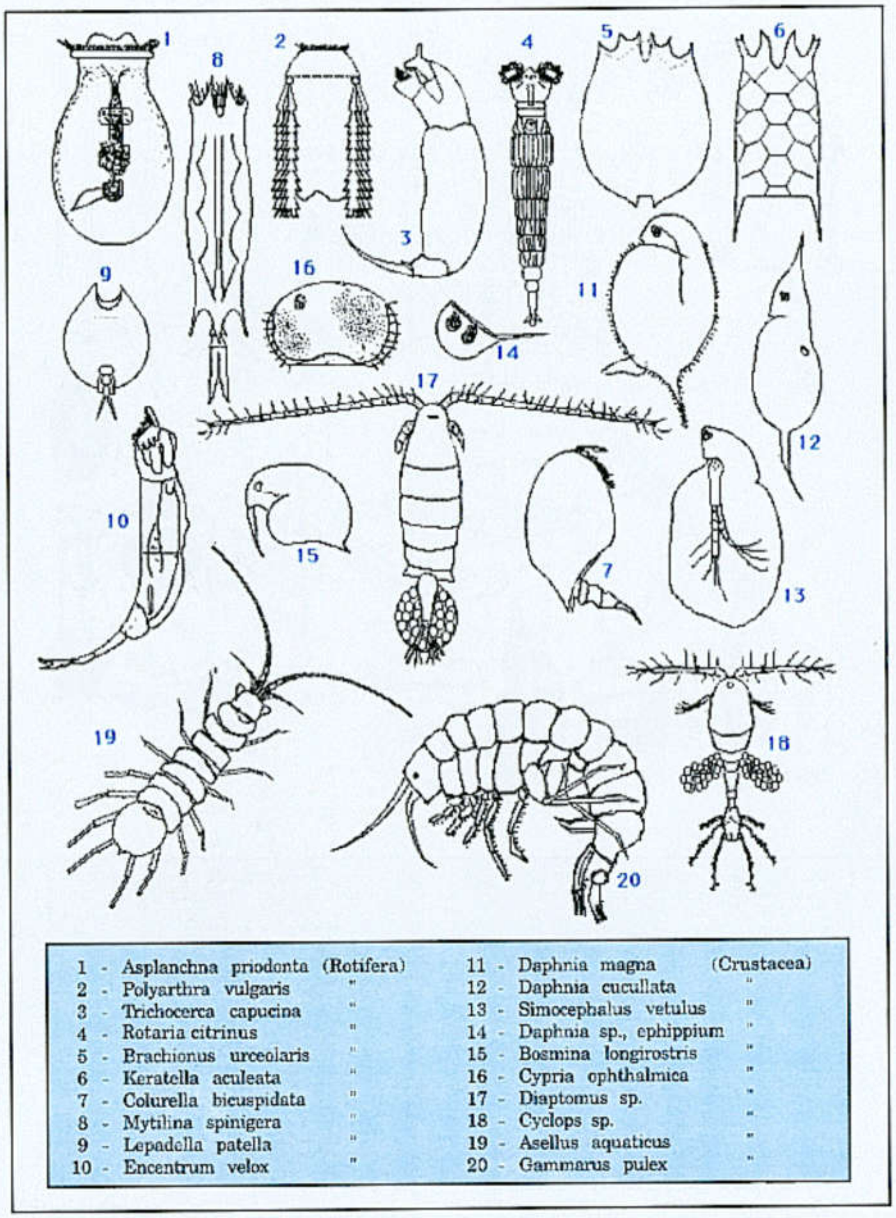


Figure 193. Zooplankton (after V. Slàdeček).

conditions (pH, temperature, dissolved oxygen, etc.).

Thus a protein-rich effluent will promote the development of the genera Alcaligenes, Bacillus or Flavobacterium; a waste water rich in carbohydrates or hydrocarbons will lead to the predominance of the genus Pseudomonas. The presence of reducing sulphur results in the development of the genera Thiothrix, Microthrix, etc.

It was long thought that activated sludge floc was composed of colonies of a particular bacterium called Zoogloea ramigera. It was later proved however, that many kinds of bacteria can be present in the floc and that, while Zoogloea ramigera certainly plays a role, it is only a partial one.

3.2.2. Microflora

Benthic algae develop at the edges of installations and cells are carried away in the sludge and in the nitrifying fibres by abrasion of the biofilm. For example, diatom frustules may be observed under the microscope. However, they do not play a role in purification by activated sludge whereas they do in lagooning.

3.2.3. Microfauna

Beside bacteria, the most important group is that of Protozoa. As they are particularly sensitive to environmental variations, they are valuable indicators for the plant operator, since the predominance of one species or another enables him to assess the adaptation of the activated sludge to the nature of the substrate, the degree of oxygenation, the presence of toxins, etc. Rotifers are indicators of a particularly stable biological system.

As an example, a list is given below of the main animal microorganisms in activated sludge.

- **Rhizopoda or Amoebae (figure** 194) Hyaline protoplasmic masses, which are either unprotected or enclosed in a shell or theca, move about by putting out pseudopoda which are extensions of the protoplasm. Very resistant to anaeorobic conditions, obligate bacteriophages.

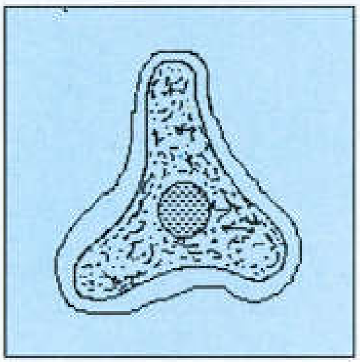


Figure 194. Amoeba.

Thecamoebae are abundant in extended aeration (figure 195).

Figure 195. Thecamoeba.

Free amoebae:

- small species (< 10 µm) are abundant at plant start-up. They are also found in inefficiently operated systems (anaero-

biosis or poisoning of the microfauna),
- large species (> 10 gm) are characteristic of low and medium rate activated sludge and of attached biomass

- **Zooflagellates** (figure 196)

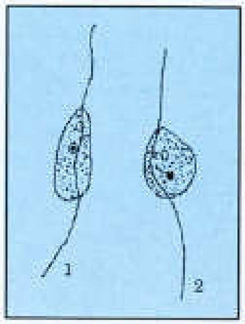


Figure 196.
1 - Bodo mutabilis.
2 - Bodo globosus.

Very mobile organisms propelled by one or several fine and very long flagella. Generally saprophagous, some species can survive in a poorly oxygenated environment. However, certain species (Hexamita) are characteristic of anaerobic environments and are therefore valuable indicators of the dissolved oxygen content. Generally speaking, flagellates react rapidly to the oxygen level and are therefore good indicators.

The zooflagellates are sometimes the only developed population in sludge adapted to certain industrial waters containing phenols or products of organic synthesis. They are the first developed species to appear in young sludge.

- **Aspidisca (figure** 197)

A euciliate of the order Hypotricha and the family Aspidiscidae.

A small ciliate which looks like a crustacean, moves rapidly on the floc surface using its frontal and anal cirri; "browser" of thick flocs. This ciliate is widespread in older, well-balanced activated sludges treating waters of all origins. It is an obligate bacteriophage.

Euplotes: a ciliate similar to Aspidisca, twice as large and found in the same conditions.

Figure 197. Aspidisca.

- Epistylis (figure 198)

A euciliate of the order Peritriche and the family Epistylidae.

An attached ciliate that forms dense clusters. Characteristic of aging and fairly well oxygenated activated sludge. Often replaces Vorticella when municipal wastewater contains a substantial proportion of various industrial wastes (phenols, etc.); obligate bacteriophage.

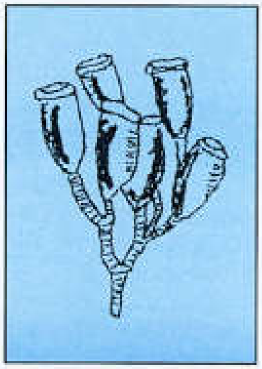


Figure 198. Epistylis digitalis.

- **Opercularia** (figure 199)

A euciliate of the order Peritricha, family Episrylidae.

An attached ciliate in loose clusters with a highly variable number of individuals. Obligate bacteriophage.

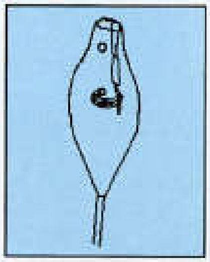


Figure 199. Opercularia coarctata.

Figure 199. Opercularia coaraata.

- Vorticella (figure 200)

A euciliate of the order Peritricha, family Vorticellidae.

An attached ciliate, obligate bacteriophage, with an unbranched stalk. Two types occur frequently: the species V. microstoma (with a small mouth) and a group of species with large mouths. The first is associated with high rates, the latter with medium ones. This frequentlyfound predator is characteristic of well-oxygenated, mature sludge in good condition, in plants working under medium or high rate conditions.

Vorticella are practically absent in low rate installations since these conditions favour their predators.

When the colony is expanding, the free-swimming colonisation form, or telotroch, is abundant.

- **Acineta** (figure 201)

A euciliate of the order Tentaculiferida, family Acinetidae.

Organisms fined on floc, less common than the Vorticella, predators of free microorganisms, bacteria and Protozoa. Other genus of the same group: Podophrya.

Figure 200. Vorticella.

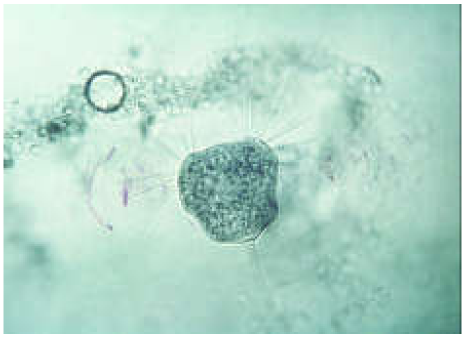


Figure 201. Acineta.

- **Trachelophyllum** (figure 202)

A euciliate of the order Holotrichida, family Holophryidae.

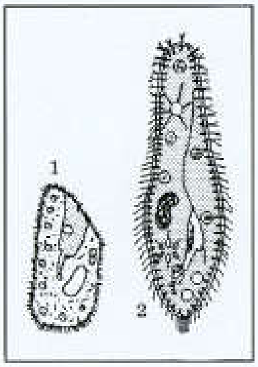
A ciliate which swims and crawls over the floc surface. This genus is often found in sludge which is in full development, just before the attached ciliates appear, in plants operating under normal loading conditions. Requires a good level of oxygenation (more than 1 mg^{-1} of dissolved oxygen).

- **Paramecium** (figure 203)

A euciliate of the order Holotrichida, family Paramecidae.

This is the typical ciliate with a clearly defined buccal cavity surrounded by a peristome with a distinctive fringe of cilia; two fairly distinct nuclei and two contractile vacuoles.

Figure 202. Trachelophyllum.



1 - Paramecium putrinum.
2 - Paramecium caudatum.
Figure 203.

This free-swimming organism is a fairly resistant form which dominates in poorly oxygenated sludge treating municipal wastewater or wastewater from the food industry.

Other less common species have similar ecological characteristics: e.g., Colpidium.

- **Rotifera (figure** 204 and figure 193). Multi-cellular organisms characterised by a head with a corona of cilia and a transparent body, revealing some of its organs, such as the cerebral ganglion and the masticatory organ or mastax. The trunk or abdomen is composed of a large stomach, supplied by the oesophagus, and the genitals. The abdomen terminates in a tail by the anus. Depending on the form of the mastax, they are either obligate bacteriophages or protozoophages. Usually the former live on the floc whilst the latter, which are better swimmers, develop in the interstitial liquid.

Fairly sensitive to toxins and to loading variations, they develop in aging, wellflocculated and well-oxygenated sludge. They are therefore characteristic of extented aeration.

Figure 204. Rotifer.

- **Nematoda (figure** 205)

Multicellular worm-like organisms enclosed in a cuticle and possessing a well differentiated digestive tract as well as genital organs.

These organisms are characteristic of old sludge or sludge in the course of mineralisation. They are frequently found in sludge undergoing aerobic digestion and also in the thick films on trickling filters. More resistant than Rotifera, they are often the indicators of threshold conditions for aerobic life.

Figure 205. Nematode.

7. SEA WATER

7.1. CORROSIVITY AND SCALE FORMATION

The substantial corrosivity of sea water varies in accordance with oxygen content and temperature. Cold water from the depths of the northern seas are more corrosive than warm surface waters from tropical regions. The corrosiviry of sea water cannot be characterized by the Ryznar index.

In permanently submerged areas of calm waters, the overall corrosion of steel, which depends on the speed of the oxygen transfer through marine organisms and the oxide film, is approximately 100 to 200 microns per year. In the flow conditions experienced in tanks and piping, pitting occurs at a rate of between 400 and 700 microns per year, thus prohibiting the use of bare steel.

It is equally important to note the scale-forming properties of sea water at temperatures of more than 60°C on limestone or other non-metallic materials. Rapid corrosion and the formation of scales may both occur when sea water comes into contact with ferrous and nonferrous metal materials. The greater the levels of heterogeneity of the metals, the more severe the process of electrochemical corrosion.

7.2. PROTECTION AGAINST SCALE FORMATION

The formation of scales at temperatures below 90°C is due mainly to calcium bicarbonate. At temperatures greater than 90°C and above certain levels of concentration, calcium sulphate and magnesium oxide also tend to precipitate.

The former problem can be solved by: - acidifying the sea water to bring down the M alk.;

- sequestration by polyphosphates which are only effective at temperatures below 70°C (cooling systems);
- the combined dispersing action of polyacrylates.

The latter problem mainly applies to evaporators and can be solved by the partial removal of calcium and the addition of blends of phosphonic and polyacrylic acids, which respectively have a sequestering and a dispersing effect (Kemazur) and remain stable up to temperatures of 130°C (hot spots).

7.3. PROTECTION AGAINST CORROSION

7.3.1. Constructive measures

- Piping should be made of concrete or steel covered with epoxy pitch, ebonite, or bituminous products.
- The feeders and manifolds of heat exchangers should be coated with a plastic material (Rilsan or Secaphene).
- Shell-and-tube heat exchangers should be made of Admiralty quality brass, or

76.22 brass, which is less sensitive to dezincification, or titanium.

7.3.2. Dynamic measures

Cathodic protection

- Reactive anodes made of Mg or Al are sometimes used in sea water, whose resistivity is low. Protection provided by these anodes is weak and of limited effect.

- The application of an external electromotive force can be used to protect screens and strainer drums and long sections of piping.

Chemical processes

- Brass tube bundles can be protected by injecting ferrous sulphate (refer to Chapter 25, Paragraph 6.9.1.).
- Phosphate-zinc inhibitors can be injected into the feed water entering steel tubes.

Removal of dissolved oxygen

- Vacuum deaeration or gas stripping (refer to Chapter 16) can be used to remove the dissolved oxygen from waters injected into oil deposits.
- Chemical reduction by catalyzed sodium bisulphite (refer to page 260).

7.4.
PROTECTION AGAINST ORGANIC FOULING

Fouling is a major source of corrosion beneath deposits and can considerably impair heat transfer capacity

7.4.1 Three causes

- Organic mucus of bacteria and algae.
- Fixation of soft organisms such as ascidians or sea anemones.
- Incrustation of colonies of hard organisms (crustaceans, mussels, oysters, Balanus), which are difficult to destroy and can cause pitting beneath deposits by differential cell phenomenon.

In systems made of copper alloys, where liquids flow slowly, the dissolving copper is enough to forestall any fouling.

Generation of algae can be better controlled than that of crustaceans thanks to the chlorination process.

7.4.2. Effects of chlorination

Using chlorine against fouling can be an additional source of corrosivity that varies greatly from metal to metal and according to the ions present in the sea water. Chlorine can, however, be used to prevent corrosion beneath deposits.

The action of chlorine in sea water is first and foremost related to the presence of 68 mg.l^{-1} of Br^{-}. Any additional chlorine displaces the bromine in one of two reactions:

$$HOCl + Br^- \rightarrow HO\,Br + Cl^-$$

$$O\,Cl^- + Br^- \rightleftarrows O\,Br^- + Cl^-$$

In view of the pH of sea water (8.3 to7.6), the hypobromous acid HBrO is the main factor behind the bactericidal action and the oxidation of organic matter, which may take several minutes.

Nevertheless, additional chlorine increases the redox potential of oxygenated sea water to critical values when the sea water contains more than 0.3 - 1 $mg.l^{-1}$ of residual free chlorine.

In this case, austenitic steels with high pitting potentials should be used, such as 316 Ti, or even better, Z2 CNDU 17.16, whose pitting potentials remain greater than the redox potential of chlorinated waters.

7.5. COPPER-NICKEL ALLOYS

The behaviour of copper-nickel alloys may be affected by the presence in the water of NH_4 and H_2S.

. **Ammonium**

Above NH_4 levels of a few mg.l-1, corrosion occurring beneath crevices can be countered by adding traces of Fe 21 or by chlorination to 0.5 $mg.l^{-1}$, which transforms the NH4 into N.

. **H_2S**

The oxidation of traces of sulphide by dissolved oxygen is too slow. These sulphides cause corrosion beneath crevices that can be prevented by low-dosage chlorination (0.25 $mg.l^{-1}$). The sulphides are rapidly oxidized and the high corrosiviry of the waters is reduced. In more general terms, the choice of alloys is affected by the circulation velocities in question.

2. FORMATION OF PROTECTIVE LAYERS AND PASSIVATION

Corrosion can be combatted by the spontaneous or induced formation of protective layers. These layers are said to be natural when they result from interaction between the components of the water and

On the other hand, external agents, such as inhibitors or electric current, can be used to induce the formation of an artificial protective layer by a process of inhibition or controlled passivation vation.

2.1.

SPONTANEOUS FORMATION OF PROTECTIVE LAYERS

This general inhibition process, which uses the OH^- ions present, occurs at neutral or alkaline pH values (refer to Page 262).

If no oxygen is present, the solubility of Fe^{2+} and pH value in the vicinity of the boundary layer can be greatly different from those encountered in the water, particularly when the water is stagnant or only slightly agitated.

The OH^- ions combine with the released Fe^{2+} ions to form ferrous hydroxide $Fe(OH)_2$, which forms a more or less regular layer of precipitate on the anodic or cathodic areas. But this layer is fragile and liable to profound transformations that severely impair its protective qualities.

2.1.1. Tillmans film

If massive diffusion of oxygen occurs in the cathodic areas, the nonprotective ferrous hydroxide is oxidized to ferric hydroxide, which cocrystallizes with $CaCO_3$, if the water contains sufficient quantities of calcium bicarbonates. This process occurs in a pH range stretching from 7 to 8.5 and results in the formation of a natural protective layer, known as the Tillmans film. This film is used to protect many water distribution networks. In reality, three conditions are required for the film to form:

- dissolved oxygen must be present in doses of at least 4 to 5 $mg.l^{-1}$;
- the free CO_2 content must correspond to the carbonate balance;
- the calcium bicarbonate alkalinity of the raw water must be great enough to exceed the solubility product of calcium carbonate at the cathodes (about 7 to 11 Fr. deg.).

The probability of this protective film forming can be calculated with the **Ryznar stability index,** which is frequently used to condition cooling systems, and was established in the course of experiments on oxygenated water with bicarbonate alkalinity. The index can be used to empirically establish the tendency of oxygenated water to corrode or form scales. The index is defined as follows:

$$I_R = 2pH_s - pH$$

where:
PH_S = the theoretical saturation PH calculated using the Langelier diagram on Page 265.
PH = pH measured at 25°C.

The table below applies to all temperatures from 0 to 60°C and shows the equivalence between the different values of the index, which are always positive, and the behaviour of the water.

Ryznar index	**Tendency**
4 to 5	heavy scaling
5 to 6	light scaling
6 to 7	equilibrium
7 to 7.5	slightly corrosive
7.5 to 8.5	very corrosive

2.1.2. Magnetite film

At temperatures above 100°C, ferrous hydroxide tends to form magnetite, Fe_3O_4, which is an intermediary oxidation product.

$$3Fe(OH)_2 - Fe_30_4 + H_2 + 2H_20$$

This reaction starts at 100°C and is completed by 200°C.

Magnetite forms a highly resistant layer, which is not liable to re-dissolve at neutral or even slightly acidic pH values.

In very pure waters that are free of oxygen:
- below 200-250°C, the lower the temperature, the greater the need to keep the pH high (LP boilers);

- above 200-250°C, the pH measured at 25°C should be sustained above, neutral.

2.2.
PROTECTION AGAINST CORROSION

Excluding the two notable exceptions mentioned above, steel is active in virtually all waters and is liable to corrode at varying rates.

The Pourbaix diagram shows the different zones of corrosion, passivation and immunity of steel (Figure 210). Passivation corresponds to the covering of metal with a protective film that does not corrode unless destroyed by a secondary reaction. Films are from 20 to 200 A thick for mild steels, or 10 to 25 Å thick on chromium steels.

There are numerous ways of preventing corrosion:
- passivating the surfaces by maintaining a suitably alkaline and oxidizing medium; - adding inhibitors to the water;
- increasing the pH, i.e., neutralizing and alkalinizing beyond pH 10.5 (LP boiler water and other applications);
- lowering the electrode potential to less than -0.58 V; this form of cathodic protection is used to safeguard underground pipelines and hardware used in seawater;
- physical isolation with coverings.

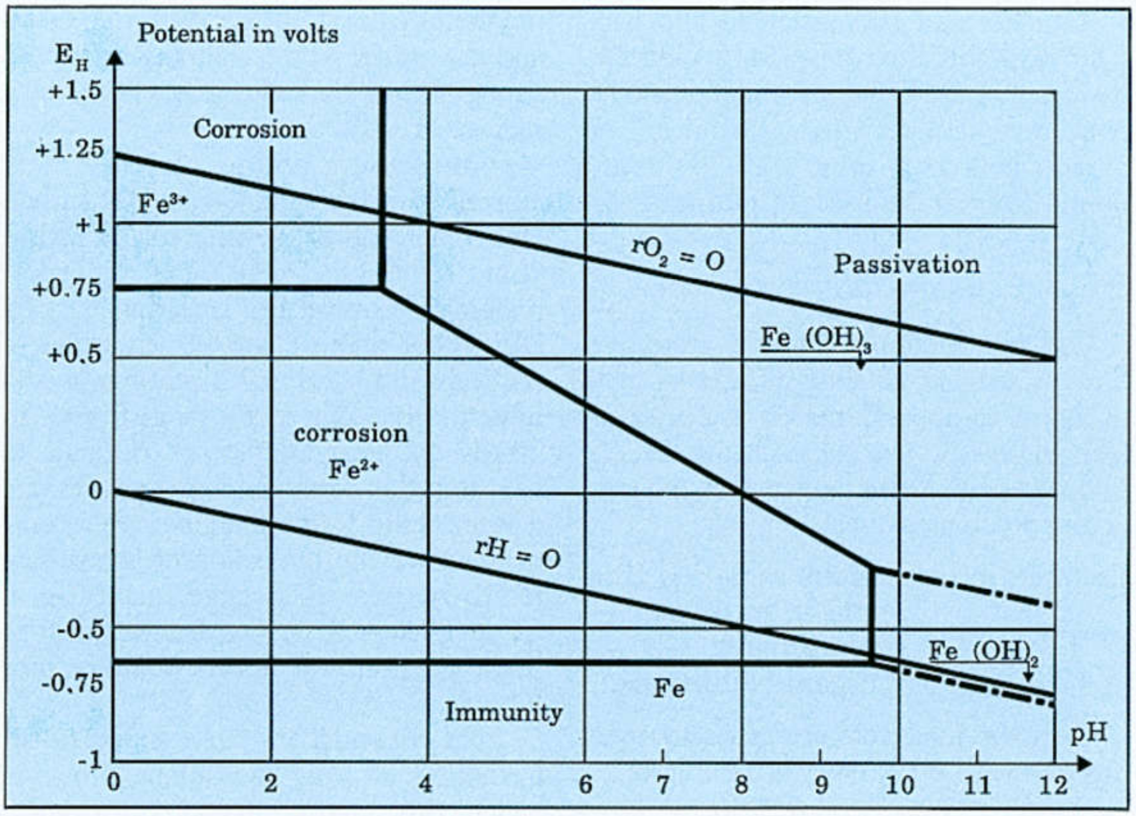


Figure 210. Pourbaix diagram.

2.3.
CORROSION INHIBITORS

Chemicals that are added to water in order to prevent it from corroding metals are also referred to as passivators.

Corrosion inhibitors do not act on the chemical components of the water, but generally form a thin protective film that prevents the water and metal from coming into contact, thus preventing corrosion.

Protective layers are never totally insoluble. Once they have been formed, they can be prevented from re-dissolving by feeding maintenance products.

Inhibitors can be classified according to the way they work, even if the same products can be used in several different processes.

2.3.1. Anodic inhibitors

Anodic inhibitors form protective films on anodic surfaces by stepping the electrochemical reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

Examples include: **chromates** **silicates**
nitrites **borates**
phosphates **benzoates**
molybdates

Tannates and hydrazine can also partially work this effect (refer to Chapter 25, paragraph 1.2). When used alone, anodic protection requires high quantities of product in doses of up to 1 g.l-1, as insufficient doses run the risk of pitting.

2.3.2. Cathodic inhibitors

Cathodic inhibitors form a protective film on cathodic alkaline surfaces by producing a compound that is insoluble at high pH levels. The electrochemical reaction occurring in the presence of oxygen is thus inhibited.

Examples include: **metal salts, and zinc**
salts in particular,
phosphates
organic inhibitors.

Cathodic inhibitors are generally used together with other types of inhibitor.

2.3.3. Mixed anodic/cathodic inhibitors

When the corrosion anodes and cathodes are simultaneously inhibited, the synergism between the ions associated in the formulations offers greater protection against corrosion than the sum of their individual actions. Product dosages can thus be greatly reduced to just a few dozen mg.l^{-1} in oxygenated waters.

Examples include: **chromates - zinc**
polyphosphates - zinc
phosphonates - zinc
polyphosphates - silicates.

2.3.4. Organic inhibitors

These compound products, which feature polar groups, work by forming a monomolecular film between the metal and the water. These compounds have a strong affinity for solid surfaces on which they can be adsorbed.

- **film-forming amines**. In these fatty amines, which contain 4 to 18 carbon atoms, one end of the molecule is hydrophilic, while the other end is hydrophobic. The molecules are arranged parallel to one another and perpendicular to the walls, thus forming a continuous and impermeable film. Doses range from 2 to 20 g.m^{-3}. These amines are difficult to use and the corresponding analyses are delicate. Film-forming amines are recommended for the protection of condensate return circuits when large quantities of CO_2 are released, i.e., when the consumption of neutralizing amines would be prohibitive.

The networks are rarely suited to the formation of truly continuous films, in which this process should be avoided, since all corrosion phenomena would be concentrated on the anodic surfaces, thus provoking serious pitting;

- **azole derivatives** work by chemisorption with a charge transfer between the organic molecule and the atoms of the metal requiring protection. Inhibiting azole derivatives used specifically to protect cuprous metals include **mercaptobenzothiazoles, benzotriazoles, and tolyltriazoles** (more resistant to chlorination).

2.3.5. Protecting non-ferrous metals: copper and aluminium

Inhibiting copper is an important step towards preventing corrosion of the actual cuprous alloys and reducing galvanic losses caused by copper particles and other metals - aluminium and steel in particular). The most widely used specific inhibitors are the **azole derivatives** mentioned above.

Aluminium is particularly sensitive to electrolytic corrosion. The most common corrosion inhibitors are silicates, phosphates, organo-azoles (organic inhibitors), molybdates or nitrates, used in conjunction with other inhibitors.

2.3.6. Inhibitors for composite systems - Industrial solutions

The action of corrosion inhibitors frequently needs to be stabilized, reinforced, or enhanced by other chemicals, such as buffering salts, catalysts, dispersants, or azole derivatives. Corrosion inhibitors are usually delivered in this multi-purpose form. Degrémont has developed its own specific "Complexes" and "Kemazur" formulations that can be used to solve problems occurring in boilers and cooling systems (Chapter 25, par. 1.2).

But protection is not provided by means of corrosion inhibitors alone. There are several other parameters capable of greatly influencing the process, including the way surfaces are prepared, the startup phase and on-going control, the pH, and any pollution (SS, OM, hydrocarbons, etc.).

Skilled conditioning experts must be able to identify the right combination of these different methods.

2.4.
CATHODIC PROTECTION

This form of protection renders metal structure fully cathodic thus preventing corrosion provided that the potential is sufficiently negative so that the surface requiring protection is completely polarized and remains in the passivity range. Cathodic protection can be used:

- in the presence of different electrolytes (concentration cells in more or less salty waters, or more or less humid earth);
- or when several metals are in contact with the same electrolyte.

The criterion generally used to measure cathodic protection corresponds to the values of potential applied (as measured at the copper-$CuSO_4$ electrode), which range from -0.85 to -1.0 V. The current density depends on the metal surface requiring protection:

- 60 $mA.m^{-2}$ for bare mechanical screens immersed in seawater;
- 5 $mA.m^{-2}$ for epoxy-covered mechanical screens;
- 0.1 $mA.m^{-2}$ for Epikote pitch-coated ducts in humid and slightly conducting earth.

There are two ways of providing cathodic protection:

- **Reactive or sacrificial anodes** made of magnesium, zinc, or aluminium, which are all more electronegative than steel, and generate internal galvanic currents.

Sacrificial anodes (refer to table below) can be used with geometrically simple immersed structures or when me chanical considerations prevent the other method from being applied (certain scraper-type settling tanks).

- **Application of an external electromotive force** and generation of an external electric current. The earth connection acts as the anode and is made of resistant material, such as ferrosilicon or platinumplated titanium. Common current densities are respectively 0.1 A.dm^{-2} and 10 A.dm^{-2} of electrode surface area.

Differences in potential of between 5 and 10 V are applied in fresh water, or between 1.5 and 2 V in sea water.

Reactive anodes

Anode	Electrode potential V	Consump-tion by mass kg/A.year	Medium
Mg	- 1.7	10	Brackish water
Al	- 0.8	4	Sea water
Zn	- 1	10	Sea water

3. SECONDARY PARAMETERS OF CORROSION

Corrosion conditions depend mainly on the carbonate balance and oxygen levels. However, other factors do affect the corrosion process by influencing the form and the rate of corrosion. These factors include the presence of dissolved salts - mainly chlorides -temperature, the cleanness of the water, and the presence of microorganisms.

3.1.
THE EFFECTS OF MINERALIZATION

Iron corrodes very slowly in the presence of oxygen in very pure demineralized water. But the slightest amount of dissolved salts provokes corrosion by various means:

The overall mineralization of water increases its conductivity and reduces resistance to the corrosion current. Traces of chlorides or sulphates in doses of less than 1 $mg.l^{-1}$ are capable of provoking corrosion.

Cl^-, F^-, Br, $S0_4^{2-}$ and $N0_3$ ions all stimulate corrosion. When these ions are present, the overvoltages drop and the steel requires less energy to dissolve. The adsorption of these anions on the anodic areas would make it easier for the iron to migrate towards the interface. Migration would be far more pronounced with halogenides than with ions with higher atomic weight and/or valence.

On the other hand, OH^-, $Cr0_4^{2-}$ and $Si0_3^{2-}$ ions tend to enhance the formation of protective layers.

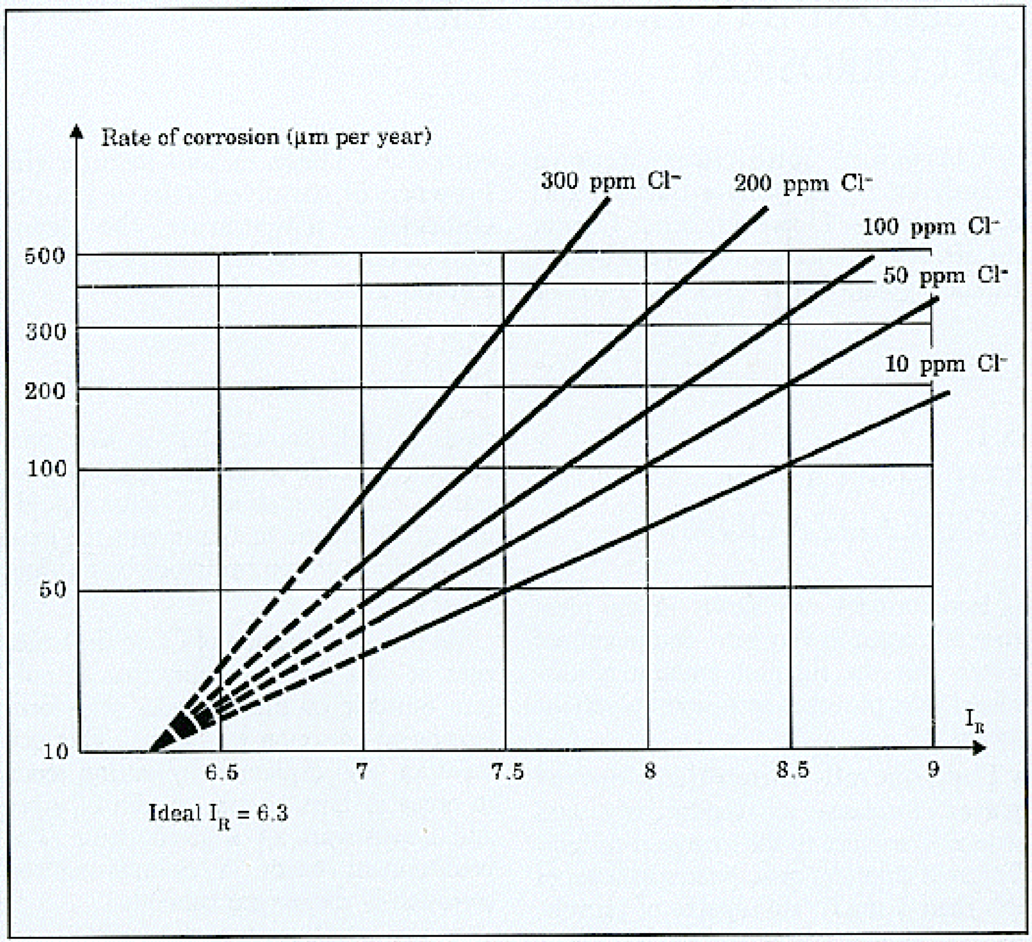
The effect of chlorides on stainless steels is well known, but is also pronounced on mild steels. The high concentration of very mobile Cl^- ions and H^+ ions in the anodic zones prevents the local precipitation of iron hydroxide by forming HCl.

As the concentration of Cl^- in the water rises, so does the probability that an infinite number of micro-anodes will form leading to corrosion by pitting. This observation also explains why pitting tends to occur in lines on the bottom of pipes and downstream of a given point. The predominant factor in chloride-induced corrosion is the oxygen content.

When no oxygen is present, a chloridecontaining water may be only mildly corrosive if prevailing conditions inhibit carbonic aggressivity, which is often the case in sea water.

When oxygen is present, even in small doses, the process of differential cell phenomenon quickly increases corrosivity as the chloride content rises, even in waters in a state of carbonate balance.

The experimental graph shown in Figure 211 relates the rate of corrosion in oxygenated waters to the concentration of chlorides and the Ryznar index at 20°C.



Water analysis:

- M alk. 15 Fr.deg. – Temperature 20°C
- SO_4^{2-} in equivalent concentration of Cl^-
- Na^+ in equivalent concentration of $Ca^{++} + Mg^{++}$

Figure 211. Rate of corrosion of mild steel versus concentration of chlorides and the Ryznar index I_R (graph by P. Mouchet).

.The effects of sulphates are felt in three ways:

-directly, through the increase in conductivity;

- indirectly, through participation in the cycle of sulphate-reducing bacteria and the development of bacterial corrosion;
- through a specific process that is damaging mg to concrete (refer to Page 453).

Cu^{2+} ions in doses of less than 1 $mg.l^{-1}$ can cause a sharp acceleration in corrosion by electrodeposition of copper.

3.2.
THE EFFECT OF TEMPERATURE ON OXYGENATED WATERS

. **Below 60°C**

Heating water in closed recipients makes the water unstable, causes scaling, then establishes the carbonate balance, and simultaneously causes the corrosiviry of the water against steel to rise. A certain degree of protection is sometimes provided by the deposit of CaC03. When heated water that has been stabilized by the CaC03 deposit cools down to its original temperature, it becomes aggressive and is no longer in equilibrium. Indeed the water becomes more corrosive and the absence of any precipitation enables the corrosion to develop.

In an industrial system, which is not dosed, two processes occur:

- Chemical effects: the processes are the same as in an enclosed recipient, except that the equilibrium can be shifted by escaping COz, which enhances scaleforming properties.

- **Electrochemical effects:** the possible coexistence of hot zones (where the pH is low) and cold zones (where the pH is higher) dictates the local concentration levels of H+, which vary in opposing directions, and creates irregular surface patterns featuring hot anodic zones and cold cathodic zones.

A temperature difference of 20°C can thus give rise to differences in potential of 55 mV. At high points, the formation of pockets of carbon dioxide and films of low-salinity condensation water provokes the formation of anodic zones.

. **Above 60°C**

Above 60°C, most of the oxygen is released thus forming differential cell couples, which are added to the existing couples and substantially increase the 433 potential. Corrosion then increases considerably.

Consequently, the protection of hot water systems in buildings is considerably more difficult than the protection of industrial systems, where the temperature differences are usually between four and six times smaller and the average temperature is below 45°C (except hot points).

3.3.
THE EFFECT OF MICROORGANISMS

Biological corrosion is usually a secondary phenomenon and involves several bacterial families. This type of corrosion can be characterized by the formation of closely-knit tubercle concretions that can form serious obstructions, with possible underlying pitting. The concretions are made of accumulations of fibrous iron bacteria sheathed with ferric oxide that is partially dehydrated, and contain calcium carbonate. This tubercle-shaped laminated mass is often hollow. The core contains a mass of liquid, often very black, which oxidizes very quickly when exposed to air.

Adding strong acid can detect the presence of iron sulphide (release of H_2S) and prove the existence of sulphate-reducing bacteria.

Iron bacteria

Iron bacteria of the Leptothrix, Crenothrix or Gallionella types live in aerobic media and draw their synthetic energy from the consumption of ferrous iron, which is oxidized into ferric iron (refer to Page 29). The bacteria accelerate this slow-moving oxidation process by secreting enzymes, thereby impoverishing the oxygen content of the medium and depolarizing the anodes.

Bacteria oxidizing the nascent hydrogen

These bacteria are of the autotrophic Hydrogenomonas strain and draw their synthetic energy from the oxidation of the cathodic hydrogen.

$$Fe \rightarrow Fe^{2+} + 2e^-$$

These bacteria tend to depolarize the cathode, thus enhancing the corrosion process.

Sulphate-reducing bacteria

These facultative anaerobic bacteria may occur in the pipes of a cooling system. These bacteria are autotrophic and enhance the formation of hydrogen sulphide by reducing the sulphates with the hydrogen drawn from the cathodic zones (refer to Page 28).

The sulphides released by the reduction of the sulphates precipitate the ferrous ions in the form of black iron sulphide. In actual fact, several reactions occur:

- the cathode is depolarized by the reducing bacteria;

$$SO_4^{2-} + M^{2+} + 8H^+ \rightarrow S^{2-} + M^{2+} + 4H_2O$$

where M^{2+} represents an alkaline or an alkaline-earth metal that balances the sulphate ion,

- different corrosion products are formed, including:

$$S^{2-} + Fe^{2+} \rightarrow FeS$$

$$3Fe^{2+} + 60H^- \rightarrow 3Fe(OH)2$$

causing the overall reaction:

$$4Fe^{2+} + SO_4^{2-} + 2H^+ + 2H_2O \rightarrow$$
$$3Fe(OH)_2 + FeS$$

Note that in waters with a low content, biological corrosion always follows electrochemical corrosion, which is accelerated by the consumption of hydrogen ions.

Favourable conditions for biological corrosion:

- anaerobic medium;
- pH between 5. 5 and 8.5;
- presence of mineral (SO_4^{2-} PO_4^{2-}, and Fe^{2+}) and organic substances;
- optimal development temperature between 30 and 40°C.

The consumption of oxygen on the surface of the tubercles reduces the diffusion of oxygen to the interior of the tubercle, which passes into a rising state of anaerobiosis, thus favouring the development of reducing bacteria. The formation of sulphides not only provokes the precipitation of iron sulphide, but also the reduction of the ferric hydroxide.

$2 Fe(OH)_3 + 3H^2S \rightarrow 2FeS + S + 6H_2O$

The **volume of the inside of the tubercle contracts** as a result of the transformation of the sheathed ferric hydroxide into more dense iron sulphide.

Oxidizing bacteria (Thiobacillus oxidans)

Inversely, in oxygenated system water (refer to Page 28), these oxidizing bacteria can generate a sulphuric acidification process and sustain the bacterial corrosion.

Nitrifying bacteria

These bacteria may give rise to acidifying nitrification in the presence of NH_4 in wastewater (refer to Page 27).

3.4.

EFFECTS OF THE CONDITION OF THE SURFACE AND THE CLEANNESS OF THE WATER

The presence of deposits in an old and soiled system or that result from the transfer of poorly filtered water can give rise to corrosion for two reasons:

- creation of non-oxygenated zones beneath the deposits that may create anodic areas;
- areas encouraging the development of various bacterial stocks and different depassivating reducing reactions.

Stainless steels are particularly sensitive to this phenomenon.

3.5.

EFFECTS OF THE CIRCULATION VELOCITY

This parameter is extremely important in the development of complex physical and electrochemical processes. There are three possible types of damage:

- cavitation due to local pressure located on either side of the vapour pressure of the water that releases bubbles of vapour then destroys them by implosion at very high pressures, leading to irregular cavernous corrosion of the metal;
- **erosion-abrasion** due to the kinetic energy of the particles of sand or other materials contained in the water that continuously destroy the protective layer and cause even and regular abrasion of the metal. According to Homig, the process is both mechanical and electrochemical;
- **erosion-corrosion** due only to interference with the formation of the continuous layer as a function of the diffusion of oxygen, which in turn depends on the velocity at which the water flows. The process is purely electrochemical.

3.6.

THE EFFECTS OF THE pH IN OXYGENATED WATER

The solubility of Fe^{2+} drops substantially when the pH level rises. As a result, an insulating film of ferrous hydroxide (and other hydroxides already mentioned) is formed, leading to a marked increase in the surface area of anodic zones and a reduction in the anodic zones to occasional surface areas. The smaller the surface area of the anodic zones, the greater the density of the electric corrosion current. The closer the pH value is to 10, the greater the danger of pitting corrosion in the **presence of oxygen.** Beyond 10, the corrosion process slows down and stops at pH 10.5 in most waters (see Figure 212). This is why many cases of local corrosion have been observed in softened waters with a pH of between 9 and 10, but whose alkalinity level is inadequate to sustain the Tillmans film.

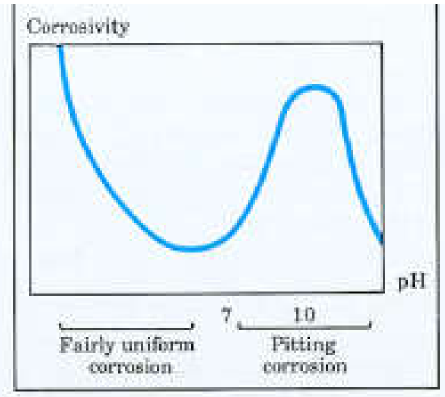


Figure 212. Effects of the pH on the rate of corrosion of iron in oxygenated water.

Figure 213. Coupon corroded by a softened water

3.7. THE EFFECTS OF OXIDIZING AGENTS

3. 7. I. Dissolved oxygen

The effect of dissolved oxygen on the electrode potential has already been discussed, but its role as a corrosion double agent is also worth noting:

- in rising concentrations from 1 to 46 $mg.l^{-1}$, the increase in the corrosiviry of mineralized water is virtually linear. When saturation is reached, a balance is established and a mixed protective film is formed if the alkaline level and calcium content are high enough;
- similarly, in fresh but relatively neutral waters and concentrations of less than 1 $mg.l^{-1}$, steel may enter a passive state.

Ozone is a fleeting compound that cannot have any direct effect in the distribution system. However, oversaturation of oxygen may combine with the ozone thus enhancing occasional degassing and causing local differential cell corrosion.

3.7.2. Oxidizing agents

Depending on the concentration, the presence of powerful oxidizing agents such as chlorine and NaC10 can considerably increase the redox potential of oxygenated waters. Stainless steels are the most sensitive, and grades with increased corrosion pit potential may be necessary. Experience has shown that in sea water at less than 30°C with free Cl_2 doses of less than 1 to 2 $mg.l^{-1}$, there is no worsening of corrosion pitting, which may become serious at doses of 5 $mg.l^{-1}$.

4. CORROSION OF STAINLESS STEEL

4.1. DEFINITIONS

Stainless steel is generally used to refer to iron-chromium alloys with a chromium content in excess of 11.5%. Stainless steels are classified in one of four categories according to their crystalline structures. Three of them - ferritic, austenitic, and austeno-ferritic - are used in hydraulic systems and water treatment systems.

Ferritic steels: these steels have bodycentred cubic crystalline structures and contain between 16 and 30% of chromium. High-chromium steels are resistant to oxidation at high temperatures, particularly in the presence of H2S. Resistance to pitting is further increased by stabilizing with titanium, which traps the sulphur. Ferritic steels with very high chromium contents (28%), also referred to as superferritic, are also highly resistant.

Austenitic steels: these steels have the same crystalline structure. They contain more than 16% chromium and 6% nickel, which is an element that encourages austenitic crystallization. After high-chromium ferritic steels, austenitic steels offer the best resistance to corrosion. Qualities vary in accordance with the carbon, chromium, and nickel contents.

Austeno-ferritic steels: increasing the chromium content favours the ferritic structure (alphagenous element) and reduces the nickel content. The austenitic structure (gammagenous element) causes a certain amount of ferrite to appear in the structure of these steels.

Austeno-ferritic steels are distinguished by mechanical properties that are superior to those of austenitic steels and strong resistance to intergranular and stress corrosion.

Table 51. The main stainless steels.

Designation according to French standards	Z6CN 18-09	**Z2CN** 18-10	Z6CND 17-12	Z2CND 17-13	ZICNDU 25-20	Z5CNDU 21-08
Structure	austenatic	aosrenutic	austerutic	austenutic	austenitic	austeno-femnc
Composition (%)						
Carbon	< 0.08	< 0.03	< 0.08	< 0.03	< 0.02	< 0.08
Chromium	18 to 19	18 to 19	17	17	19 to 22	20 to 22
Nickel	9	9 to 10	11 to 12	12 to 13	26 to 27	6 to 9
Molybdenum			> 2	> 2.5	4 to 4.8	2 to 3
Copper					1 to 2	1 to 2
Chromium equivalent in R6	18	18	25.75	27.4	35	35
U.S. designation	AISI 304	AIR 304 L	AISI 316			
German designation	X5CtNi 18-09	X2CrNi 18-09	X5CrNiMo 18-12	X2CrNiMo 18-12		
Commercial designation:						
Ugine	NS 21 AS	NS 22 S	NSM 21	NSM 22 S		
Creusot-Loire					Uranus B6	Uranus 50

Note: Richer grades do exist (Hastelloy, Incoloy, or Monel) but are only used in special cases.

4.2.
CORROSION OF STAINLESS STEEL IN AQUEOUS SOLUTIONS - PASSIVITY

When suitably alloyed with chromium, iron becomes passive in many media. The rust-proof quality of the alloy depends on the stability of passivation, which corresponds to the formation of a thin layer of chromium oxide on the surface of the metal. Any accidental break in this film will result in the occurrence of corrosion phenomena, apart from in oxidizing media, where the film re-forms on its own (stable passivity). Adding more nickel increases resistance to corrosion in media that are only slightly oxidizing or not oxidizing at all. Molybdenum improves resistance to corrosion in the presence of reducing acids or halogenides (chlorides, bromides, iodides). It is important to note that stainless steel is likely to corrode in highly oxidizing media, such as nitric acid containing hexavalent chromium (socalled **transpassivity).**

The range of passivity of stainless steel can be broadened by adding certain elements. By way of example, adding copper can improve resistance to corrosion by sulphuric acid.

4.3.
DIFFERENT FORMS OF CORROSION OF STAINLESS STEEL

4.3.1. General corrosion

just like any other metal, under certain conditions stainless steel can be corroded in a regular manner all over its surface in media that are not sufficiently oxidizing. The protective layer on the surface of the metal may even disappear altogether, which gives rise to overall corrosion (unstable passivity). The condition of the metal surface also affects the nature of passivity. Maximum resistance is achieved when the surface is free of contamination by ferrous particles or by incrustations of various origins.

4.3.2. Specific cases of corrosion

Three types of specific corrosion may occur on stainless steel:

- **corrosion by pitting and crevice corrosion** may occur in neutral or chloride-laden media;
- **stress corrosion,** which applies to hot water.

Intergranular corrosion in the vicinity of weld beads (local chromium depletion), which was specific to austenitic steels and ferritic steels, has been practically done away with by three precautions:

- lowering the steel's carbon content (<0.03%) in austenitic steels in order to reduce the formation of chromium carbide;
- more frequent is the use of ferritic or austenitic steels stabilized with titanium (type Z8 CT 17);
- overhardening of austenitic steels after welding.

Table 52. Parameters affecting the corrosion of stainless steels

Solution	**Neutral and chloride-laden**		**Acidic and chloride-free**
Type of corrosion	Local		General
	Pitting	Crevices	
Main cause of depassivation	Dissolved Oz and pitting potential of steel too low	Macro-surface irregularities, anfractuosiry. Inadequate circulation	Solution not oxidizing enough

4.3.2.1. Pitting

In neutral or chloride-laden media, highly dispersed local pitting may occur, which is hardly visible but highly perforating. Pitting depends more on the metal-water potential, which itself depends on the type of metal, the temperature of the water, the pH and the concentration of Cl^- ions, than on the condition of the surface. Free chlorine above 0.5 $mg.l^{-1}$ causes the pitting potential to rise rapidly.

The metal should be selected such that its specific pitting potential be greater than the actual metal-water potential at a given Cl^- concentration.

Molybdenum steels with high chromium content and low carbon content usually resist well to pitting. A Z2 CND 17-13 type steel is resistant to pitting in neutral, clean, and cold sea water. Exceptionally, richer alloys, such as uranus, may be used (temperature above 20°C).

4.3.2.2. Crevice corrosion

Crevice corrosion is more frequent and, unlike pitting, occurs in specific zones on the metal surface where either manufacturing irregularities or deposits are present. Such zones constitute an anfractuosity or a dead zone where circulation of

ions or materials is low. The occurrence of corrosion corresponds to the slow but severe acidification of the water by Cl^- ions.

In oxygenated waters that are virtually neutral but contain chloride ions, the hydrolysis of primary corrosion products leads to the formation of hydrochloric acid, which, beyond a given level, initiates the process of crevice corrosion.

Crevice corrosion can be distinguished by a period of incubation that may last several months, but, once underway, corrosion may be both rapid and severe..

Figure 214. Corrosion of a stainless steel flange beneath a faulty seal.

If the corrosion products are removed during the incubation phase by stirring the water, the process is halted and has to start from scratch again

Resistance to crevice corrosion can be assessed using the depassivation pH value, which must be as low as possible. Austenitic steels are more resistant. Additional titanium and molybdenum can prolong the incubation time and increase the chances of interrupting the corrosion process. However, once the incubation period is over and the process has started, it usually develops as quickly in steels with high nickel and molybdenum levels as in steels containing lesser amounts of those elements.

The resistance of a steel to these two types of corrosion and local depassivation can be assessed by its content of equivalent Cr (refer to Table 51)

$$Cr + 3.3Mo + 16N$$

4.3.2.3. Stress corrosion (cracks)

Stress corrosion cracking may appear in austenitic steels subject to residual stress caused by welding, stamping, or the operating conditions.

Cracking occurs in the presence of chlorides. Above 60°C austenitic steels must be replaced with ferritic or austeno-ferritic steels.

4.4.
USE OF STAINLESS STEEL

A number of fundamental guidelines should be observed when using stainless steel.

When designing equipment:

- **all** dead zones must be avoided by ensuring correct liquid flow. Means must be provided of purging unavoidable dead zones;
- the surface area-volume ratio must be as low as possible;
- sharp connections should be avoided;
- severe shaping should be avoided as it may lead to a concentration of martensite due to hard-drawing;
- overlapping assemblies should be welded on both sides;
- mild steel supports should be attached to stainless steel structures by means of an intermediary stainless steel plate, thereby avoiding the dilution of the mild steel elements in the structural steel when welding;
- circulation velocities should be high.

In construction work:

- contact with ferrous metals should be prohibited;
- welding processes should be used that do not affect the resistance of the structure to corrosion (reduced welding energy);
- all parts should be degreased and decontaminated - removal of ferrous inclusions -after shaping or machining;
- welds should be carefully cleaned;
- decontamination should be thorough and natural passivation should be completed by contact with a nitric solution.

4.5.
SELECTING A STAINLESS STEEL

The criterion applied to choose a stainless steel is usually, if not always, its ability to resist corrosion. It is difficult to list a set of precise rules. However, a number of guidelines can be forwarded:
- austenitic steels with very low carbon content or stabilized steels should be used for welded assemblies;
- resistance to corrosion by chlorides can be improved by upping the Mo and Cr contents;
- remember that a stainless steel can also be replaced with a carbon steel - in heat exchangers, where the system water must be conditioned accordingly - or with carefully chosen and specially prepared coverings -recipients holding reagents;
- with chloride-laden waters, the depassivation pH of the steel must be lower than that of the water.

4.6.
HYDRAULIC TESTS

In water treatment systems and installations used in the chemicals industry, many cases of stainless steel corrosion that are initiated during the hydraulic tests may cause pitting immediately or shortly after service entry for two reasons:
- failure to wash systems when flooded leading to differential cell phenomena under the deposits;
- use of more or less chloride-laden waters that are concentrated by evaporation, particularly in any anfractuosities.

Preventive conditioning of waters with three to five parts of $NaNO_3$ to one part of Cl^-, with possible pH correction by $NaHCO_3$, has proved successful.

5. CAST IRON

The corrosion of cast iron by water is different from that of steel mainly due to the presence of carbon particles in form of fine flakes (grey cast iron) or nodules (ductile cast iron). These inclusions form cathodic areas that come together in a carbonaceous framework that sustains the presence of oxidation products in fairly hard and oxygenated waters (particularly in the case of grey cast iron).

In deoxygenated or sulphurous waters, on the other hand, the corrosion process, which is known as **graphitization,** can be amplified by the entrainment of these same products.

The relative uniformity of corrosion, the thickness of the cast parts, and the absence of any macro-irregularities, such as welds, mean that the service life of cast iron is quite satisfactory in naturally occurring or oxygenated alkaline waters below 70°C. Cast iron is used for a number of specific applications, such as pumps or valves.

Water distribution systems need very long term protection. The **interiors** of tubes, which used to be protected by simple bituminous lacquer type coverings, are now preserved by cement mortar-based coverings that can be adapted to wastewaters containing sulphides. Approved plastic-based coverings can also be used.

External protection against corrosion is offered by bituminous coverings measuring about one hundred microns in thickness. Such coverings may be reinforced by pulverized zinc or cathodic protection by imposed potential in aggressive soils (depending on the analysis of the corrosivity of the soil).

The use of **ductile cast iron** tubes has spread widely in view of their high mechanical strength. Although they are not as thick as grey cast iron tubes and the initial rate of corrosion is higher, they offer the same service life performance.

6. CORROSION OF NON-FERROUS METALS

The most frequent problems apply to water distribution systems, and domestic hot water (DHW) systems in particular. The notions discussed hereafter can be extended to include industrial waters whose composition may be less favourable (pH, salinity, NH_4, etc.)

Before addressing the behavioural aspects of different metals, alloys and otherwise, it is important to raise four general points concerning usage:

- the all too frequent coexistence of different materials, which is a source of fast corrosion by macrocouples, is to be avoided, particularly in aggressive waters, whether mineralized or not. In any case, the noble metal (Cu) must be located downstream of less noble metals;
- excessively high temperatures give rise to serious corrosion by deaeration and differential cell phenomenon upon contact with water, especially when there are no deaeration blowdowns. This problem can be avoided by keeping the water below 60°C;
- the stagnation of aggressive water with acidic tendencies depletes the water's oxygen content and can result in the destruction of the passivating layer and the release of metal ions (Pb) in solution;
- drinking water is usually compatible with these metals.

6.1.
ALUMINIUM

Aluminium has a high negative electrical charge and is therefore, in theory, very corrodible. With a potential of -1.67 V, aluminium is in fact passivated by oxidation in moist air and the formation of a fine protective layer of aluminium oxide. This passivation can be artificially induced by anodic oxidation.

Aluminium is sometimes used in sea water, provided that no deposits of impurities form cathodic areas, and that metals of the very highest industrial quality or a perfectly suitable alloy be used (Al + Mg + Mn + CO.

Although slightly acidic waters are acceptable, contact with alkaline waters is strictly forbidden.

6.2.
COPPER

Copper is naturally passivated in oxygenated waters by the formation of a fine layer of oxide made of Cu_2O. Three main types of corrosion are likely to occur on copper.

6.2.1. Type I pitting

This is the most frequent type of corrosion and occurs on annealed tubes in cold waters (below 40°C) that are moderately or highly mineralized. This type of corrosion is distinguished by the appearance of regular pitting covered with a dome of green oxide.

This type of corrosion is affected by two factors:
- the quality of the water, its pH, the residual oxygen content, and the bicarbonate content;
- the presence on the tube surface of films containing carbon and, to a lesser degree, harmful oxides such as CuO. This factor is tending to disappear as new standards are applied that limit the quantity of carbon per unit of surface area.

6.2.2. Type II pitting

This type of pitting is far less frequent and occurs in slightly mineralized waters at temperatures greater than 60°C. The pitting is less visible on the inside of the tubes and is covered with a film that is usually copper sulphate based.

6 2.3. Corrosion-erosion

This type of corrosion is usually due to excessive flow velocities that are generated by specific pipeline geometry (bends, bottlenecks, etc.) although, in rarer cases, it may be caused by abrasive particles. Corrosion-erosion results in the formation of horse shoe-shaped craters (Figure 215).

6 2.4. Other types of corrosion

Other types of corrosion may be encountered:
- in oxygenated waters containing ammonium (industrial waters), serious uniform corrosion may occur due to the solubilization of the protective layer;
- galvanic corrosion may occur between a protruding and badly made weld joint and the tube interior, or differential cell corrosion may exist beneath a deposit of silicon dioxide or iron oxide.

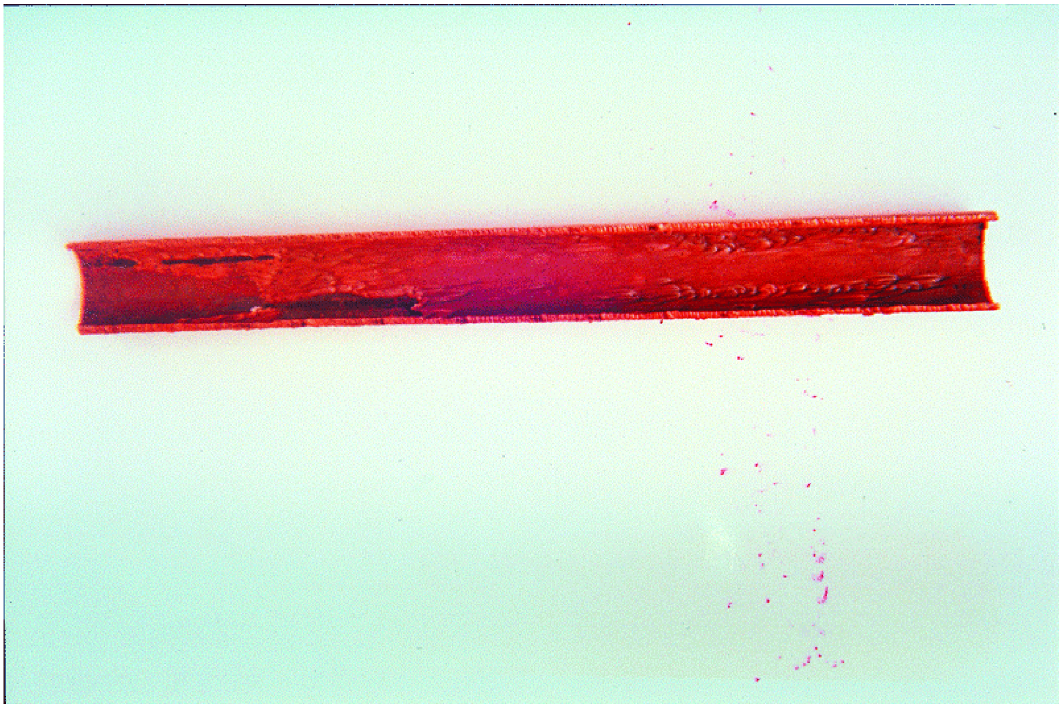


Figure 215. Corrosion-erosion of a copper tube.

6.3.
LEAD

In view of the relatively high solubility of lead oxide PbO and lead hydroxide $Pb(OH)_2$, oxygenated waters are highly corrosive and dangerous, unless the bicarbonate alkalinity levels of the waters are also high (M alk. greater than 12 Fr. deg.) and the concentration of free C02 is low (slightly alkaline pH value). In this case lead hydroxycarbonate will form, which is far less soluble than the hydroxide and of fers protection if precipitated with calcium carbonate. Nevertheless lead piping is not recommended for together the conveyance of drinking water and, is prohibited from use with fresh waters

6.4.
GALVANIZED STEEL

This section only looks at coverings produced by hot galvanization by dipping in a bath of zinc heated to 450°C or by the continuous Sendzimir process.

In these processes, a layer of zinc (η) of variable thickness is securely attached to the steel. The external surface is oxidized to form zinc hydroxide, oxide, or hydroxycarbonate, depending on the temperature and the alkalinity of the water. Unlike the films formed on other metals, this film is a poor conductor and does not change the potential of the zinc metal and does not make it more noble. The action of the film is closer to that of a covering than that of a passivating layer. If there are any breaks in the covering and areas of exposed steel, then the film plays the role of a sacrificial anode.

Attacks on the zinc are restrained and the diffusion of oxygen is slowed down. The high rate of corrosion in fresh water with a low M alk. level drops substantially to become very slow in waters with high calcium bicarbonate alkalinity.

When sufficiently concentrated, chlorides can increase the risk of corrosion by pitting. In domestic hot water (DHW) distribution systems, a maximum Cl^- content of 100 $mg.l^{-1}$ is recommended.

When the film is destroyed in aggressive waters, the highly electronegative zinc (-0.76 V) undergoes accelerated corrosion that finishes by attacking the iron and forming rust.

- **Effects of temperature.** The rate of corrosion increases quickly in line with the temperature, peaking at around 70°C and returning to initial levels at 100°C. At 60°C all the zinc hydroxide would be transformed into oxide, which is less adherent and more porous.

Accelerated or perforating corrosion of non-galvanized areas may then occur. The hypothesis that the polarity of the cell is reversed is rejected in favour of a drop in the intensity of the cathodic protection current, which would no longer be adequate.

- **Effects of copper.** The introduction of Cu^{2+} ions in solution (exogenous copper from the upstream system) means that the layer of zinc oxide conducts electric current and the iron is subject to rapid corrosion.

Galvanization of iron only slows down the corrosion process in a durable manner in cold and non-aggressive waters. It is important to remember that the protection offered by galvanization in aggressive waters, and in sea water in particular, is only temporary.

Table 53 lists recommended forms of protection for domestic hot water systems.

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Table 53. Distribution of domestic hot water. Recommendations for protection against corrosion.

	Galvanized steel	Copper
Maximum water velocity	< 1.5 m.s^{-1} in columns < 2 m.s^{-1} in galleries	
Temperature	$< 55 - 60$°C	
TH	> 10 Fr. deg.	> 5 Fr. deg.
Water quality	slightly scale-forming	no NH_4
Cl^- content	< 100 mg.l^{-1}	
Construction		Element must always be located downstream of heterogeneous systems
Deaeration	High point blowdowns	

*(In continuous flow, velocity must be kept at much lower values.)

6.5.
BRASS

Brass is a copper-zinc alloy that is used in the following forms:

Fittings	
Screw turning	Cu Zn 37 Pb 3 Cu Zn 4 Pb 3
Stamping	Cu Zn 39 Pb 2
Foundry	Cu Zn 40
Shell-and-tube heat exchangers	
Admiralty brass	Cu Zn 30 As Cu Zn 29 As 1

Dezincification, or the dissolving of zinc and release of residual Cu, occasionally occurs in highly saline and soft waters and renders the metal porous and brittle.

Brasses now exist that are protected against dezincification (Cu Zn 35 Pb 2 As) and can be used to avoid this very rare phenomenon.

In highly chloride-laden waters or sea water, exchanger tubes can be made of Admiralty quality brass (Cu Zn 29) or titanium.

7
THE EFFECTS OF WATER ON MATERIALS

When water is being conveyed or used for any purpose, it may degrade in one of many ways the material with which it comes into contact. The most frequent effect is corrosion of metals, and of steel in particular. Other forms of damage are possible, such as the dissolving of calcareous materials or the degradation of concrete.

1. THE ELECTROCHEMICAL CORROSION OF IRON

Pure water will always attack iron, because the two bodies do not share any common conditions of thermodynamic stability. The kinetics of this electrochemical process are greatly affected by the presence of oxygen. If oxygen is absent, then corrosion is due to the action of hydrogen.

1.1.
THE ELECTROCHEMICAL PROCESS

When immersed in an electrolyte solution, any metal tends to release positively charged ions, whilst remaining negatively charged itself. An electrode is formed, whose potential is expressed in absolute terms by Nernst relation (refer to Page 206).

The potential is said to be normal when considered with regard to a normal solution of the ion in question, and is expressed by Eo . The resulting general relation defines the potential of a metal electrode at 25°C:

$$E = E_0^{\circ} + \frac{0{,}058}{n} \log c$$

n: valency of the metal ion
c: activity of the metal ion in the solution

Table 38 in Chapter 3 (page 207) shows the theoretical classification of metals according to their potential. Noble metals have a positive potential, whereas non-noble metals have a negative potential. Real measured potentials may differ as the process preceding the dissolving of the metal may be countered by other processes occurring on more noble parts of the same metal.

A difference in potential is created in the medium and the ensuing electric current sustains the reaction whereby the metal electrode is dissolved, or corroded.

The process is greatly affected by the presence of oxygen.

1.2.
CORROSION IN THE ABSENCE OF OXYGEN OR CORROSION BY HYDROGEN

The antagonistic process is of the gaseous hydrogen electrode type, in which gaseous hydrogen is formed from the H^+ ions in the water (see Figure 206).

This process, which **captures electrons,** is liable to sustain the preceding reaction, which dissolves the metal and generates electrons. Often mistakenly thought to be chemical, corrosion by hydrogen is in fact essentially electrochemical and involves two poles: one is positively charged and the other is negatively charged. An electric current flows between the two poles, which are arbitrarily referred to as the cathode and anode.

At the anode, metal dissolving or oxidation occurs, whereas the cathode is protected against corrosion. The potential of the hydrogen cathode can be established:
- on a metal that is more noble than the anodic metal;
- on an irregularity of the metal's crystalline structure, as cold rolled or work hardened sections act as anodes with regard to the metal itself;
- on deposits of foreign bodies (oxide, soiling).

Corrosion will continue indefinitely as long as there is a plentiful supply of H^+ ions at high pH, or the medium is not saturated in Fe^{2+} ions, which form a protective layer of ferrous hydroxide precipitate that, in theory, halts the corrosion process.

However, the electrolyte flow tends to entrain the precipitate and corrosion can theoretically only come to a halt in stagnant waters.

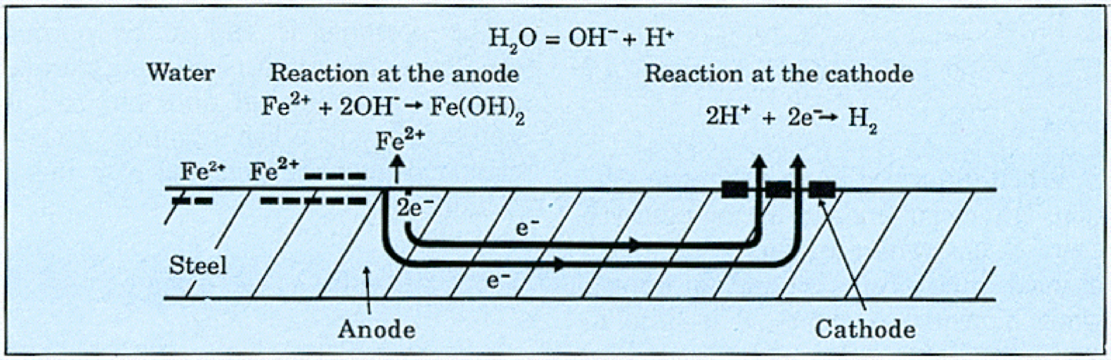


Figure 206. Corrosion by hydrogen in the absence of oxygen.

As more iron is being dissolved, E_{Fe} increases, while E_H decreases as H_2 is released. The phenomenon should stop when the two potentials become equal: $-0.44 + 0.029 \log (Fe^{2+}) = -0.058\,pH$

i.e.,

$$\log (Fe^{2+}) = 15.1 - 2\,pH$$

There are no common conditions of stability shared by iron and water below a pH value of 10.5, at which the solubility of iron is 10^{-6} mol.kg $^{-1}$ and corrosion remains negligible. The lower the pH and the concentration of Fe^{2+} ions, the greater the level of corrosion. In the absence of oxygen, this process leads to the corrosion of metal.

In morphological terms, corrosion by hydrogen is characterized by regular corrosion of metals due to the presence of an infinite number of coexistent anodes and cathodes, that may even feature alternating poles. This so-called acidic corrosion is in fact less dangerous under neutral conditions, as the concentration of H^+ ions is too low to sustain the cathodic reaction, and a protective layer may form.

The Nernst curve shown in Figure 207 can be used to work out the equilibrium potential of each electrode versus the pH value.

The horizontal lines represent the potential of the iron electrode, irrespective of pH, at different concentrations of Fe^{2+} ions in the water. The concentration of Fe^{2+} is limited by the solubility of that ion, which tends to precipitate in the form of ferrous hydroxide $Fe(OH)_2$.

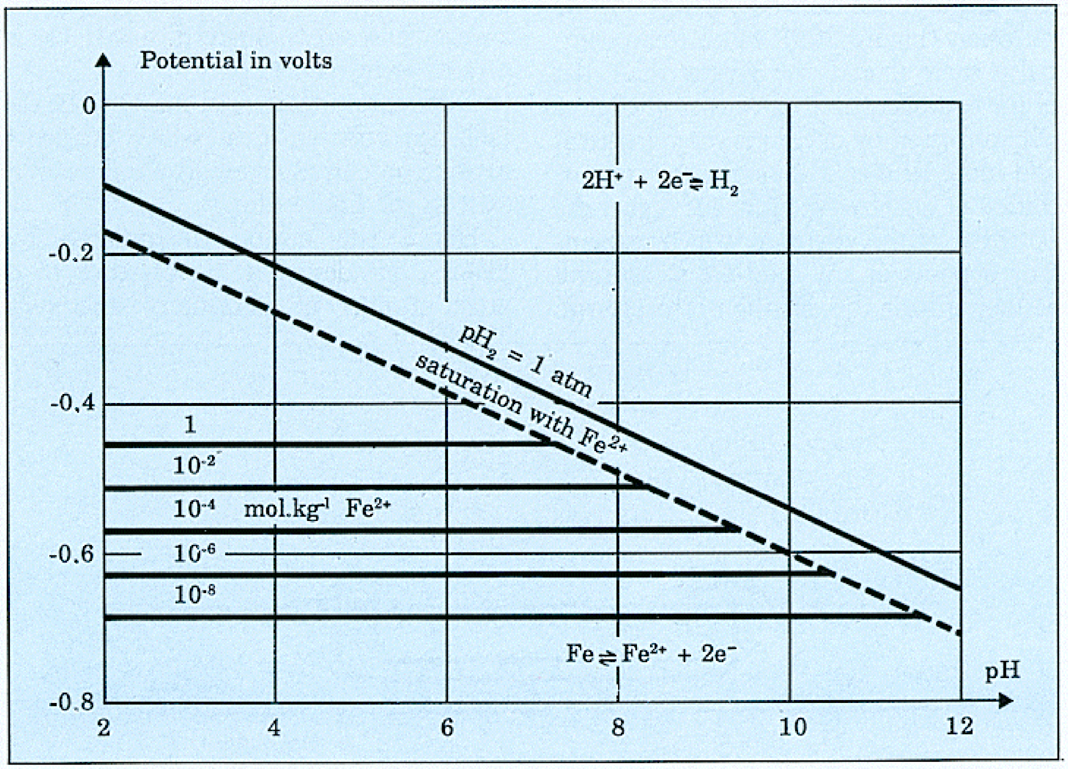


Figure 207. Iron-water equilibrium potential in the absence of oxygen.

1.3
CORROSION BY OXYGEN

1.3.1. Electrochemical processes

In oxygenated water, the role of the complementary electrode is played by the oxygen itself.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

This electrode is likely to absorb electrons, thus behaving like a cathode (Figure 208).

In this instance, the equilibrium potential depends on:

- the concentration of OH-ions, thus the pH value;
- the Partial oxygen pressure,

$E' = Eo^0 - RT/F \text{ In } (OH^-) + RT/4F \ln pO_2$

When this potential is greater than that of the metal electrode, it sustains the corrosion (Figure 209). Since this potential is more than 1 volt greater than that of the hydrogen electrode, it becomes clear why corrosion by oxygen is more frequent and more serious. The higher the concentration of dissolved oxygen, the higher the potential of the electrode, which explains why deposits of any kind are so harmful as they impair the diffusion of oxygen to underlying surfaces and develop an anodic zone.

The release of OH- ions at the oxygen cathode causes the water pH to rise, at least in the immediate vicinity of the metal surface. Further, the Fe^{2+} ions are oxidized to Fe^{3+}. Because ferrous oxide $Fe(OH)3$ is only slightly soluble, the products of corrosion accumulate around the anode rather than being entrained by the water and leaving the surface clean, as is the case with corrosion in the absence of oxygen. These products form "pimples", which further inhibit the diffusion of oxygen and explain why corrosion by oxygen can give rise to pitting.

1.3.2. Differential cell corrosion

The above findings indicate that areas of metal free of dissolved oxygen - hollow threads, breaks, cracks - form the anodic areas, whilst areas where dissolved Oz is present form the cathodes.

Differences in potential may also be established between areas where gradients in the concentration of dissolved oxygen exist in the liquid film.

Hence the notion, formulated by Evans, that describes the presence of a huge number of elementary microcells

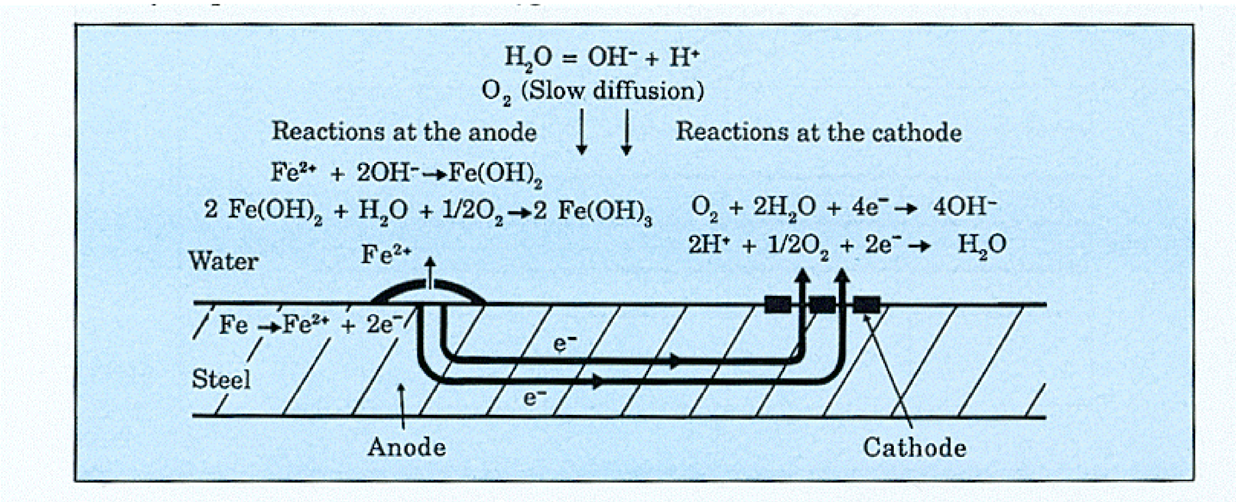


Figure 208. Corrosion in an oxygenated medium.

constituted by **differential cell phenomenon** and can be generally applied to all irregularities in metals due to type, construction, soiling, or simply differences in temperature.

Differential cell corrosion depends on the **solubility** of the oxygen and, in particular on the **speed of diffusion**. Low diffusion speeds enhance corrosion.

The speed at which oxygen is diffused depends on temperature, the water circulation velocity, and the state of the surface. Speed of diffusion is very important to the self-protection process.

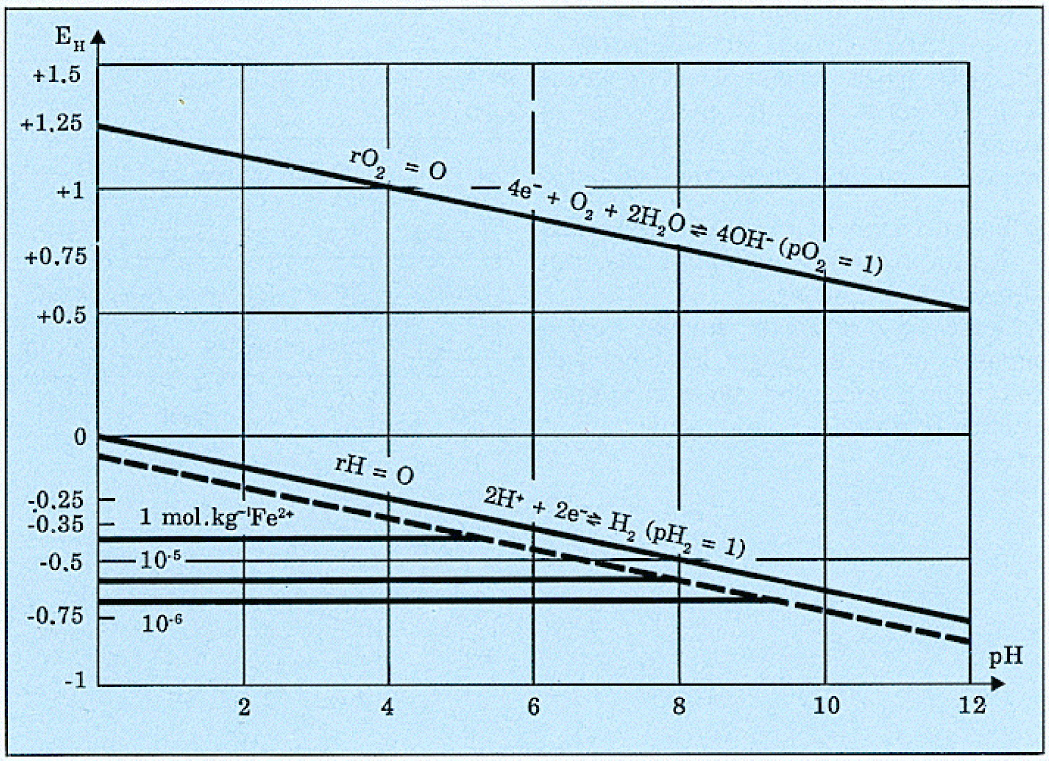


Figure 209. Equilibrium potentials of hydrogen and oxygen electrodes.

1.4.

CONTROLLING AND MEASURING CORROSION

There are three types of measuring device:

Measurement of the corrosion current: corrosion meter.

Corrosion meters are designed to apply a slight difference in potential across two metal electrodes submerged under water (linear polarization), to measure the resulting intensity, and to estimate the rate of corrosion. Corrosion meters are difficult to calibrate and the significance of their readings is relative. A rise in the corrosion current indicates that some form of interference has occurred. Corrosion meters are well suited to inspection purposes.

Measuring using coupons

Coupons of metal are immersed in the water in the system and periodically removed and weighed. The weight loss of the metal versus the unit of surface area is a direct expression of the mean scope of corrosion. Table 50 indicates the equivalences of the most frequently used units.

Examination of network materials

-Removable reference nipples that can be examined regularly.

- Tube sections can be removed from a network or an exchanger for laboratory tests. The number and choice of samples is often restricted.

Table 50. Assessment of corrosion in mild steel (equivalence table for different units).

Rate of corrosion	gm/year	mdd*	mpy*
µm/year	1	0.2	0.04
mdd*	5	1	0.2
mpy*	25	5	1

* mpy: thousandth of an inch per year - mdd: mg/dm^2.day.

Quality of protection			
Excellent	≤ 50	≤ 10	≤ 2
Good	50 to 125	10 to 25	2 to 5
Average	125 to 250	25 to 50	5 to 10
Poor	≥ 250	≥ 50	≥ 10

8. DEGRADATION OF CONCRETE

Concrete is a material made of various aggregates and cement that can be used to cover reinforcing steel.

In theory, the steel reinforcement can only be corroded once the covering has been damaged as a result of the positive electrical charge of the iron in reinforced concrete. The potential of the iron in the concrete, which has a pH of about 11.6, is approximately +100 mV in relation to the hydrogen electrode. Measures to prevent degradation must therefore concentrate firstly on the concrete, except in the case of prestressed concrete in which high stress levels expose fine reinforcements to fatigue by stress and chemical corrosion by infiltrations of water. The degradation of concrete has two phases: the first is mechanical, and the second is chemical.

8.1.
MECHANICAL FACTORS

Mechanical causes can be put in three categories:

- excessive permeability: very high levels of density with cement dosages of some 300 to 400 $kg.m^{-3}$ are a minimum requirement in the presence of aggressive waters;
- presence of crevices and cracks due to inadequacies in the concrete that can be corrected by increasing the ductility of the concrete with a water/cement ratio of less than 0.45 or by introducing a plasticizer;
- erosion due to water flow velocities in the pipes greater than 4 $m.s^{-1}$ or excessively high thermal gradients.

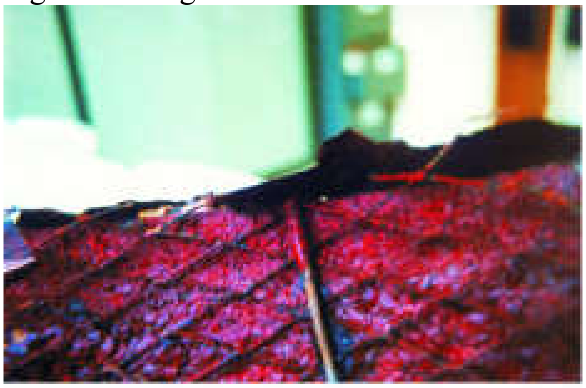


Figure 216. Example of serious external corrosion of concrete piping.

8.2.
CHEMICAL FACTORS

The chemical causes are linked to the composition of the cements and the corrosiviry of the water with which they come into contact.

The cements are made mainly of silica, lime, aluminium oxide, and to a lesser extent, iron, magnesium oxide, and alkalis. Cements are highly basic media with substantial reserves of soluble salts.

When cement sets, Portland cement in particular, large quantities of bound lime are released in the form of $Ca(OH)_2$, with the formation of tricalcium aluminate CA.

Depending on the composition of the cements and the chemical nature of the water, either the free lime or the aluminium oxide may undergo the solubilization process. The table below shows the main components of different types of cement.

Chemical degradation may be the result of a number of factors:

- carbonic attack;
- attack by strong acidity;
- effects of ammonium;
- effects of sulphates;
- attack by strong alkalinity;
- bacterial corrosion with formation of H_2S.

.	**Portland**	**High alumina cements**	**Supersulphated cements**	**Clinker slag** cements
5102	20-25%	5-16%		
A1203	2- 896	30%		
Ca0	60-65%	33-40%	50%	40-4596'
S03	< 4%	< 2.596'	> 5%	< 5%

8.2.1. Carbonic attack

Corrosion by attack by carbon dioxide occurs in fresh waters or whenever the level of excess CO_2 exceeds 15 $mg.l^{-1}$. But the high reserves of lime inside the pores in the concrete result in the precipitation of a deposit of $CaCO_3$ and other salts, which temporarily slow down the rate of destruction of the concrete by these waters. The destruction remains at acceptable levels when the calcium bicarbonate alkalinity of the water is greater than 5 or 6° M alk. and the pH is above 6.5, i.e., in the vicinity of the carbonate balance.

8.2.2. Attack by strong acidity

This form of attack is particularly serious since the resultant calcium salts are more soluble. Increasing corrosivity occurs in the presence of phosphoric, sulphuric, nitric, and hydrochloric acids. Organic acids are also harmful, particularly in effluents from dairies or fruit juice production plants.

In the face of moderate levels of acidity, resistance to corrosion can be improved by reducing the water/cement ratio and/or by resorting to alumina cements, which are very difficult to use. These solutions apply to pH values above 2 and require a number of precautions.

However, in general terms, the danger of structures cracking can only be totally eliminated by applying a suitable covering. Legislation covering the discharge of wastewater often recommends that the pH of the water in contact with the walls be maintained between 4.5 (or 5.5) and 9.5.

8.2.3. Effects of ammonium

Ammonium contained in wastewater can contribute to the destruction of concrete in two ways:

- by developing acidifying nitrification reactions, which can only take place in aerobic media, such as cooling towers

- by releasing the ammonia displaced by the lime. This ammonia then speeds up the solubilization of the lime and damages the cement

Magnesium salts may also provoke the same process with the formation of brucite. Excessive concentrations of NH_4 and Mg should therefore be avoided, especially when sulphates are also present.

8.2.4. Effects of sulphates

The effects of sulphates are highly complex and involve the transformation of calcium sulphate into Candlot salt or ettringite:

- sulphation of the free lime in the cement by the dissolved sulphates in the water:

$$Ca(OH)_2 + .NazSO_4 + 2H_20 \rightarrow CaS0_4.2H_2O + 2NaOH$$

- transformation of the aluminates in the cement into highly expansive ettringite (factor 2 to 2.5):

$$3CaO.Al_2O_3.12H_20 + 3CaSO_4.2H_2O + 13H_2O \rightarrow 3CaO.A1_2O_3.3C_6O_4.27H_2O$$

When magnesia is present, these two phenomena may be accompanied by the decomposition of the alkaline silicates in the cement.

French recommendation AFNOR P. 18.011 defines the categories of aggressivity of saline waters on conventional concretes and the underlying guidelines for protective measures (refer to Table 54).

In extremely aggressive waters the application of special coverings is recommended, while aggressive waters may require cements made of slag with a high hydraulicity index if no other chemical parameters of the water are to be taken into account.

Examples:

- clinker slag cement, with 80% granulated slag;
- blast furnace cement with 60-75% slag.

Different types of cement also exist with low C_3A contents for use in sea water.

8.2.5. Attack by strong alkalinity (NaOH, KOH, Na_2CO_3)

Strong alkalinity is harmful to all cements due to the danger that certain alumina-based components of the cements will be solubilized. If no covering is provided, waters with a pH value greater than 12 should never come into contact with high-alumina cements.

8.2.6. Bacterial corrosion with formation of H_2S

This type of corrosion occurs in systems conveying municipal wastewater. The way the corrosion process works in anaerobic media has already been described. Whereas in cooling systems this process sustains and amplifies existing chemical corrosion, in domestic wastewater or very dirty water, this corrosion is usually initiated by the anaerobic fermentation of deposited materials. The process occurs in two phases:

- formation and release of H_2S;
- oxidation of H_2S in water and formation of H_2SO_4.

These reactions speed up as soon as the pH drops below 6 and are further accelerated by hot waters.

In sewers, attacks take place above the water surface as the water condenses and gas is released. The formation of H_2S be partly or totally avoided by preliminary settling or inputting oxygen or oxidizing can agents.

Table 54. Aggressivity of solutions and soils
(Extract from AFNOR recommendation P.18.011)

Degree of aggressivity	**Al**	**AZ**	**A3**	**Aa**
Environment	**Slightly aggressive**	**Moderately aggressive**	**Highly aggressive**	**Extremely aggressive**
Aggressive agents	Concentration in mg.l-1			
Aggressive CO_2	15 to 30	30 to 60	60 to 100	> 100
SO_4^{2-}	250 to 600	600 to 1 500 (1)	1 500 to 3 000	> 6 000
Mg^{2+}	100 to 300	300 to 1 500	1 500 to 3 000	> 3 000
NH^{4+}	15 to 30	30 to 60	60 to 100	> 100
pH	6.5 to 55	5.5 to 4.5	4.5 to 4	< 4

(1) The limit for sea water is fixed at 3 000 $mg.l^{-1}$.

9. AGEING OF PLASTICS

Just like steels and concretes, plastics are also subject to degradation over time. Many factors contribute to the ageing process and the actual service life of the material depends on the particular property under consideration and the conditions of use..

It is difficult to assess the service life since materials are often required to achieve levels of mechanical and chemical strength that may be affected by numerous additives or fillers (plasticizers, pigments, antioxygen agents, or even impurities).

Over and above the mechanical factors, the potential damage likely to occur in water treatment applications are as follows:

- chemical or biological destruction of the material in reactive liquid media;
- discharge of organic substances in the systems: drinking water and ultrapure water in particular;
- changes due to sunlight prior to flooding - works in tropical regions, lengthy storage periods, etc.

9.1. PHYSICAL AGEING

Physical ageing is due to the penetration of solvents or water (swelling), loss of plasticizer, stress due to surfactants or thermal shocks.

9.2. CHEMICAL AGEING

The different forms of chemical ageing involve depolymerization or chain breaks:

- thermoxidative ageing in air at moderate temperatures;
- chemical ageing in liquid media (re agents);
- biochemical ageing (deterioration by microorganisms or fungi);
- hydrolytic ageing by the slow reaction between certain polymers and the water (acrylic esters).

9.3. WEATHERING

Weathering in the open air is due to direct exposure to sunlight and rain. The main causes are photothermic:

- photo-oxidation is induced by solar UV radiation and is often linked to certain additives (dyes, pigments, minerals). Materials can be photostabilized in numerous ways, including the creation of internal opaque screens (TiO_2, ZnO

and particularly carbon black) or by external screens offering protection against radiation;
- increase in the temperature and rain (hydrolysis) are synergetic factors;
- ozone, which breaks double bonds, also has a harmful effect on polydiene rubbers, polystyrenes, or ABS.

9.4.
GENERAL APPLICATIONS

These different hypotheses imply lengthy methods to gain full understanding of new materials. As far as water treatment applications are concerned, numerous examples of applications of tried and tested materials are available:
-ABS and PVF materials in ultrapure water systems;
- PVC or clean pipe PVC materials in drinking water or bottling systems;
- HDPE in drinking water systems;
- polyester resins for anti-acid coverings;
- PTFE coverings or furan resins for use with aromatic hydrocarbons up to 120°C;
- polypropylene in hot treatments up to 100°C.

When conveying concentrated wastewater or liquid reagents, refer to information on the use of materials or suitable coverings. The presence of accidental pollutants may have a harmful effect in certain applications.

Manufacturers may also offer underground conduits with service lives of up to 50 years, in the case of HDPE materials for example.

8

FORMULAE DIGEST

The Water Treatment Handbook was originally compiled to provide both water treatment engineers and technicians with basic data and practical information most frequently required on-site.

Water treatment engineering calls for increasingly specialized and diversified knowledge, yet there is still a definite need for a digest of basic information and simple numeric or graphic data most frequently used by technicians, particularly when working on rushed projects or during start-up operations. The Formulae Digest sets out to meet this need, although it is difficult to set clear limits to its contents, which should remain concise: for example, the definition of elementary geometric volumes could be useful for determining the capacity of a reagent storage tank; reiterating certain essential regulatory provisions regarding wastewater discharge could be of use to the site manager who may not be familiar with certain regulations, etc.

To some readers, this digest will no doubt seem incomplete, while others will feel it contains too many universally known basic facts. The Digest aims to be of help to the largest possible number of Handbook users. It is simply a "tool kit", for each to use according to their particular requirements.

1. UNITS OF MEASUREMENT

1.1.
SYSTEMS OF UNITS

Systems of units derived from the metric system have gradually been replaced by a single system termed the International System of Units (SI), presented in the first part of this sub-chapter. The cgs (centimetre-gramme-second) system, in which most units correspond to decimal multiples or sub-multiples of the International System, still has advantages in certain fields.

As many countries still persist in using British or US systems of units, the second part of this chapter lists the equivalent values of the British/US and SI systems of units.

1.1.1. The International System of Units (SI)

This system, gradually accepted and improved by the efforts of the General Conferences on Weights and Measures (GCWM) and the International Committee on Weights and Measures (ICWM), comprises base units, derived units, and supplementary units. Its application involves decimal multiples and sub-multiples, with the corresponding prefixes. Besides the units listed below, it admits units called "common units defined in terms of SI units" and "temporarily accepted" units. In principle, it discourages the use of cgs and other units.

The International System tables below relate to units which, for various purposes, affect water treatment. The first of these tables are taken from documents published by the AFNOR (French Standards Committee) and particularly from the International System summary table in accordance with documentation item No. NF X 02-004.

Note:
Extracts from the AFNOR standards included in this document have been reproduced with the authorization of the French Standards Committee AFNOR - Association Française de Normalisation (address: Tour Europe, Cedex 7, 92080 Paris La Defense, France) - which should be addressed if complete documents are required, as only original versions of standards in their most recent editions can be considered valid.

1.1.2. General principles

Unit symbols: writing rules

Unit symbols are only used after a number expressed in figures.. They are printed in straight characters, are invariable in the plural, written without final period and placed after complete numeric values, leaving a space between the numeric value and the symbol.

They are written in small letters; however, the first letter is a capital when the name of the unit is derived from a proper noun.

There should be no more than one fraction line on the same line to represent a composite unit that is the quotient of two units, unless parentheses are used to avoid any ambiguity.

. Base units

Quantity	Unit name	Unit symbol
. length	metre	m
. mass	kilogramme	kg
. time	second	s
.electric current intensity	ampere	A
. absolute temperature	kelvin	K
. amount of substance	mole	mol
.luminous intensity	candela	cd

NOTE: Celsius temperature t is related to absolute temperature T by the equivalence t = T 273.15.

The difference between two temperatures can be expressed either in kelvins or in degrees Celsius. In this case, 1°C = 1 K.

Supplementary units (These can be used as base units.)

Quantity	Unit name	Unit symbol
plane angle	radian	rad
solid angle	steradian	sr

. Multiples and sub-multiples

Power	Prefix	Symbol
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10	deca	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	µ
10^{-9}	nano	n
10^{-12}	Pico	p
10^{-15}	femto	f
10^{-18}	atto	a

1.1.3. Definition of base units and supplementary units

. Base units

Metre: the metre is the length equal to 1,650,763.73 times the wavelength, in a vacuum, of the radiation corresponding to the transition between levels 2 p_{10} and 5 d5 of an atom of krypton-86.

Kilogramme: the kilogramme is the unit of mass; it is equal to the mass of the international prototype kilogramme.

Second: the second is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of an atom of cesium-133.

Ampere: the ampere is the intensity of a constant electric current which, maintained in two parallel, rectilinear conductors of infinite length and negligible circular cross-section, placed at a distance of 1 metre from each other in a vacuum would produce a force equal to 2 x 10-i newtons per metre of length between these conductors.

Kelvin: the kelvin is a unit of absolute temperature equal to 1/273.15 of the absolute temperature of the triple point of water.

Mole: the mole is the amount of substance of a system containing as many elementary units as there are atoms in 0.012 kilogramme of carbon-12. When using the mole, the elementary units must be specified and may be atoms, molecules, ions, electrons, or other partides or specified groups of such particles.

Candela: the candela is the luminous intensity, in perpendicular direction, of a surface of 1/600,000 square metres of a black body at the temperature of solidification of platinum, under a pressure of 101,325 newtons per square metre.

Supplementary units

Radian: the radian is the plane angle comprised between two radii that intercept, on the circumference of a circle, an arc of equal length to that of the radius.

Steradian: the steradian is the solid angle which, having its apex in the centre of a sphere, delimits, on the surface of this sphere, an area equal to the square of the sphere's radius.

1.1.4. Base units and derived units for common quantities

Quantity	**Unit**		Expression in other *(SI)* units	Expression in base units (BU) or supplementary **units** (SU)	Units used with the Sl or temporarily accepted (T)		
	Name	Symbol			Name	Symbol	Value in units
Space and time							
length	metre	m		(BU)	angstrom (T) naut. mile (T)	*A*	*1A* = 10^{-10} m 1 mile=1,852 m
Surface area	Square metre	m^2		m^2	are (T) hectare (T)	a ha	1 are = 100 m^2 1 ha = 10^4 m^2
Volume	cubic metre	m^3		m^3	hire	1	1 1 = 1 dm^3
Plane angle	radian	tad		(SU)	Degree minute second		1° _ (Π/180 tad) 1' = (1/60)° 1" = (1/60)'
Solid angle	steradian	sr		(SU)			
Time	second	s		(BU)	minute hour	min h	1 min = 60 s 1 h = 60 min
			day	d	l d = 24 h		
Angular Velocity	radian per second	rad.s t		*s*t.rad			
Velocity	Metre per second	m.s $^{-1}$		m.s^{-1}	knot (T)	kn	1 kn = 1,852 m/h
Acceleration	metre per square second	m.s $^{-2}$		m s^{-2}			
Frequency	hertz	Hz		s^{-1}			
Mechanics							
Mass	kilogramme	kg		(BU)	tome (metric ton)	t	1 t = l0^3 kg
Density	kilogramme per cubic metre	kg.m 3		M-3 _kg			
Mass flow rate	kilogramme per second	kg.s-l		kg.s-l			
Volume flow rate .	cubic metre per second	$m^3.s^{-1}$		m^3s^{-1}			
Momentum	kilogramme metre per second	kg.m.s^{-1}		m.kg.s $^{-1}$			
Kinetic moment	kilogramme metre squared per second	kg.m^{2}s^{-1}		m^{2}kg.s^{-1}			
Moment of inertia	kilogramme metre squared	kg.m^2		m ^{2}.kg			
Force	Newton	N	kg.m.s^{-1}	m.kg.s^{-1}			
Moment of a force	newton metre	N.m		m ^{2}.kg s^{-1}	bar (T)	bar	1 bar = 10^3 Pa
Pressure, stress	Pascal	Pa	N.m'	in1kg.s-'	normal atmosphere (T)	arm	1 atm = 101,325 Pa
Absolute viscosity	Pascal-second	Pa.s	$m^{-1}kg.s^{-2}$				
Kinematic viscosity	square metre per second	m ^{2} .s^{-1}	m ^{2}.s $^{-1}$				
Surface tension	newton per metre	N .*m* $^{-1}$					
Energy, work, quantity of heat	joule	*J*	N.m	m'kg.s'			
Power	watt	W	*Js'*	m^{2}kgs^{-3}			

Quantity	Unit		Expression in other SI units	Expression in base units (BU) or in supplementary units (SU)
	Name	Symbol		
Thermodynamics				
Thermodynamic temperature	kelvin	K	(BU)	
Linear expansion coefficient	kelvin to the power of minus 1	K^{-1}		
Thermal conductivity	watt per metre-kelvin	W/(m.K)		$m.kg.s^{-3}.K^{-1}$
Specific heat	joule per kilogramme-kelvin	J/(kg.K)		$m^2.s^{-2}.K^{-1}$
Entropy	joule per kelvin	$J.K^{-1}$		$m^2.kg.s^{-2}.K^{-1}$
Internal energy, enthalpy	joule	J		$m^2.kg.s^{-2}$
Optics				
Luminous intensity	candela	cd		(BU)
Luminous flux	lumen	lm		cd.sr
Illumination	lux	lx	$lm.m^{-2}$	$m^{-2}.cd.sr$
Electricity, magnetism				
Electric current intensity	ampere	A		(BU)
Quantity of electricity	coulomb	C	A.s	s.A
Potential, potential difference, voltage	volt	V	$W.A^{-1}$	$m^2.kg.s^{-3}.A^{-1}$
Electric field strength	volt per metre	$V.m^{-1}$		$m.kg.s^{-3}.A^{-1}$
Electric capacitance	farad	F	$C.V^{-1}$	$m^{-2}.kg^{-1}.s^4.A^2$
	ampere per metre	$A.m^{-1}$		$m^{-1}.A$
Magnetic flux	weber	Wb	V.s	$m^2.kg.s^{-2}.A^{-1}$
Magnetic flux density	tesla	T	$Wb.m^{-2}$	$kg.s^{-2}.A^{-1}$
Inductance, permeance	henry	H	Wb/A	$m^2.kg.s^{-2}.A^{-2}$
Resistance, impedance, reactance	ohm	Ω	V/A	$m^2.kg^{-1}.s^3.A^{-2}$
Conductance	siemens	S	A/V	$m^2.kg^{-1}.s^3.A^{-2}$
Resistivity	ohm-metre	Ω.m		$m^3.kg.s^{-3}.A^{-2}$
Conductivity	siemens per metre	S/m		$m^{-3}.kg^{-1}.A^{-2}$
Physical chemistry, molecular physics				
Amount of substance	mole	mol		(BU)
Gramme-molecular weight	kilogramme per mole	$kg.mol^{-1}$		$kg.mol^{-1}$
Molar volume	cubic metre per mole	$m^3.mol^{-1}$		$m^3.mol^{-1}$
Concentration	kilogramme per cubic metre	$kg.m^{-3}$		$m^{-3}.kg$
Molar concentration	mole per cubic metre	$mol.m^{-3}$		$m^{-3}.mol$
Molality	mole per kg			

1.1.5. Units not recommended or to be avoided

Quantity	Symbol SI unit	cgs units	Other units (to be avoided)
Volume	m^3		stere (st); 1 st = 1 m^3
Mass	kg		carat; 1 carat = 200 mg
Force	N	dyne 1 dyne = 10^{-5} N	kgf 1 kgf = 9.81 N
Moment of a force	N.m		m.kgf 1 m.kgf = 9.81 N.m
Pressure	Pa	barye 1 barye = 10^{-1} Pa	kgf/cm, metre of water column mm of Hg
Absolute viscosity	Pa.s	poise (P) 1 P = 10^{-1} Pa.s	poiseuille (Pl) 1 Pl = 1 Pa.s
Kinematic viscosity	$m^2.s^{-1}$	stokes (St) 1 St = $10^{-4} m^2.s^{-1}$	
Energy, work, quantity of heat	J	1 erg = 10^{-7} J	kgf.m 1 kgf.m = 9.81 J calorie (cal) 1 cal = 4.187 J kilocalorie (kcal) = millithermie (mth) 1 kcal = 4187 J
Power	W	$erg.s^{-1}$ 1 $erg.s^{-1}$ = 10^{-7} W	$kgf.m.s^{-1}$ 1 $kgf.m.s^{-1}$ = 9.81 W
Magnetic flux	Wb	maxwell 1 Mx = 10^{-5} Wb	
Magnetic flux density	T	gauss 1 gs = 10^{-4} T	
Conductance	S		mho: 1 mho = 1 S

1.2. SI UNITS AND BRITISH/AMERICAN SYSTEMS OF UNITS -CONVERSION FACTORS

1.2.1. Units of length

Symbol			
in or "	Inch	=	0.0254 m
ft or '	Foot = 12 in	=	0.3048 m
yd	Yard = 3 ft	=	0.9144 m
mile	Statute mile = 1,760 yd	=	1.609 km
m	Metre	≈	1.0936 yd
		≈	39.37 in
		≈	3.281 ft
		≈	$3'3\frac{3}{8}''$
km	Kilometre	≈	0.6215 mile

1.2.2. Units of area

Symbol				
in^2	Square inch	=	6.4516	cm^2
ft^2	Square foot (144 in^2)	≈	9.2903	dm^2
yd^2	Square yard (9 ft^2)	≈	0.83613	m^2
mile^2	Square mile (640 acres)	≈	2.5900	km^2
	Acre (4 roods) (4,840 yd^2)	≈	0.40469	ha
cm^2	Square centimetre	≈	0.1550	in^2
m^2	Square metre	≈	10.764	ft^2
dam^2, a	Square decametre or are	≈	119.6	yd^2
hm^2, ha	Square hectometre or hectare	≈	2.471	acres
km^2	Square kilometre	≈	0.3861	mile^2

1.2.3. Units of volume and capacity

Symbol				
in^3	Cubic inch	≈	16.3871	cm^3
ft^3	Cubic foot	≈	28.317	dm^3
yd^3	Cubic yard	≈	0.7646	m^3
UK pt	British pint (4 gills)	≈	0.5683	l
UK qt	British quart (2 UK pt)	≈	1.1365	l
UK gal	Imperial gallon (8 UK pt)	≈	4.5461	l
US pt	US liquid pint (4 gills)	≈	0.4732	l
US qt	US liquid quart (2 US liq pt)	≈	0.9464	l
US gal	US gallon (4 US liq pt)	≈	3.7854	l
bbl	US barrel (petroleum) = 42 US gal	≈	158.987	l
bu	US bushel (4 pecks)	≈	35.2391	l
	US shipping ton = 40 ft^3	≈	1.13267	m^3
	Registered ton = 100 ft^3	≈	2.83168	m^3
	Acre foot	≈	1233.5	m^3
cm^3, ml	Cubic centimetre or millilitre	≈	0.0611	in^3
dm^3, l	Cubic decimetre or litre*	≈	0.0353	ft^3
	* 1 litre = exactly 1 dm^3 and no longer, according to the former definition, the volume of 1 kg of water at 4°C equal to 1.000 028 dm^3.	≈	1.760	UK pt
		≈	0.220	UK gal
		≈	2.113	US pt
		≈	0.264	US gal
m^3, st	Cubic metre or stere	≈	35.30	ft^3
		≈	1.3079	yd^3
		≈	220	UK gal
		≈	264	US gal
		≈	6.293	US bbl
		≈	28.37	US bu

1.2.4. Units of linear velocity

Symbol				
in.s^{-1}	Inch per second	=	91.44	m.h^{-1}
ft.s^{-1}	Foot per second	=	1.09728	km.h^{-1}
yd.s^{-1}	Yard per second	=	0.9144	m.s^{-1}
mile.h^{-1}	Mile per hour (statute)	≈	1.609	km.h^{-1}
m.s^{-1}	Metre per second	≈	3.280	ft.s^{-1}
m.h^{-1}	Metre per hour	≈	3.280	ft.h^{-1}
km.h^{-1}	Kilometre per hour	≈	0.622	mile.h^{-1}

1.2.5. Units of filtration rate

Symbol				
US gal/ft^2.min	US gal/min.sq ft (US gpm/sq ft)	≈	2.445	m.h^{-1}
UK gal/ft^2.min	UK gal/min.sq ft (UK gpm/sq ft)	≈	2.936	m.h^{-1}
ft.min^{-1}	cu ft/min.sq ft (ft^3/ft^2.min)	≈	18.29	m.h^{-1}
m.h^{-1}	Linear velocity of 1 m per hour Cubic metre per hour and per square metre	≈	0.0547	ft.min^{-1}
		≈	0.409	US gpm/sq ft
		≈	0.341	UK gpm/sq ft

1.2.6. Units of mass

Symbol			
gr	Grain	64.799	mg
oz	Ounce	28.350	g
lb	Pound = 16 oz = 7,000 gr	453.592	g
st	British stone (14 lb)	6.350	kg
qr	Quarter (British) (28 lb)	12.701	kg
cwt	Hundred-weight (British) (112 lb)	50.802	kg
UK ton	Long ton (British) (2,240 lb)	1.016	t
sh. cwt	Hundred-weight (USA) (100 lb)	45.359	kg
sh. ton	Short ton (USA) (2,000 lb)	0.907	t
kg	Kilogramme	35.274	oz
		2.205	lb
t	Tonne	19.684	cwt
		22.046	sh. cwt
		1.1205	sh. ton
		0.9842	UK ton

1.2.7. Units of force

Symbol			
pdl	Poundal (foot-pound/s^2)	0.0138	daN
lbf	Pound-force	0.448	daN
tonf	Ton-force (British) (2,240 lbf)	996.402	daN
	Ton-force (US) (2,000 lbf)	889.644	daN

1.2.8. Units of pressure

Symbol			
lbf.in^{-2}	Pound-force per square inch	6,894.76	Pa
or psi		0.0689476	bar
		or hpz or daN.cm^{-2}	
lbf.ft^{-2}	Pound-force per square foot	47.87	Pa
tonf.in^{-2}	Ton-force per square inch (British)	154.44	bar
	Ton-force per square inch (US)	137.90	bar
in H_2O	Inch of water	2.49	mbar
in Hg	Inch of mercury	33.86	mbar
Pa	Pascal (= 1 N.m^{-2})	0.0209	lbf.ft^{-2}
bar	Bar (= 1 hpz)	14.504	lbf.in^{-2}
	Atmosphere	14.696	lbf.in^{-2}

1.2.9. Units of viscosity

Symbol			
pdl s.ft^{-2}	• Absolute viscosity		
	Poundal second per square foot		
	(Pound per foot second)	$\simeq$ 1.4882	Pa.s
in^2.s^{-1}	• Kinematic viscosity		
	Inch squared per second	$\simeq$ 6.452 x 10^{-4}	m^2.s^{-1}

1.2.10. Units of density and concentration

Symbol			
lb.in^{-3}	Pound per cubic inch	27.6799	g.cm^{-3}
lb.ft^{-3}	Pound per cubic foot	16.0185	kg.m^{-3}
gr.UK gal^{-1}	Grain per imp. gallon	14.25	mg.l^{-1}
gr.US gal^{-1}	Grain per US gallon	17.12	mg.l^{-1}
lb.UK gal^{-1}	Pound per imp. gallon	99.77	g.l^{-1}
lb.US gal^{-1}	Pound per US gallon	119.3	g.l^{-1}
gr.in^{-3}	Grain per cubic inch	10.076	g.l^{-1}

Symbol			
$gr.ft^{-3}$	Grain per cubic foot..............	2.296	$mg.l^{-1}$
$g.cm^{-3}$	Gramme per cm^3 = 1 $kg.dm^{-3}$	0.036127	$lb.in^{-3}$
$kg.dm^{-3}$	Kilogramme per dm^3 = 1 $g.cm^{-3}$....	62.427	$lb.ft^{-3}$
$mg.l^{-1}$	Milligramme per litre.............	0.0703	gr.UK gal^{-1}
$g.m^{-3}$	Gramme per m^3.................	0.584	gr.US gal^{-1}
		0.4356	$gr.ft^{-3}$

1.2.11. Units of energy - work - heat

Symbol			
ft pdl	Foot poundal....................	0.04214	J
ft lbf	Foot pound-force.................	1.356	J
hph	Horsepower-hour.................	2.685×10^6	J
		0.746	kWh
		0.641	th
Btu	British thermal unit..............	1,055.06	J
		0.293	Wh
		0.252	mth
	Therm (= 10^5 Btu)..............	105,500	kJ
		25,200	kcal
J	Joule (= 10^7 erg = 0.239 cal)......	23.72	ft pdl
		0.737	ft lbf
kJ	Kilojoule (= 1/3.6 Wh)...........	0.3725×10^{-3}	hph
		0.948	Btu
Wh	Watt-hour (= 3,600 J = 0.860 mth)	3.41	Btu
kWh	Kilowatt-hour (= 3,600 kJ)........	1.34	hph
cal	Calorie (= 4.187 J)		
kcal	Kilocalorie (= 1.163 Wh).........	3.97	Btu
mth	or Millithermie..................	1.56×10^{-3}	hph
th	Thermie (= 10^3 kcal)		

1.2.12. Units of calorific value

Symbol			
$Btu.lb^{-1}$	British thermal unit per pound.....	2.326	$J.g^{-1}$
		0.556	$mth.kg^{-1}$
$Btu.ft^{-3}$	British thermal unit per cubic foot..	37.259	$kJ.m^{-3}$
		8.901	$mth.m^{-3}$
$kcal.m^{-3}$	Kilocalorie per cubic metre		
or	or............................	0.1124	$Btu.ft^{-3}$
$mth.m^{-3}$	Millithermie per cubic metre		

1.2.13. Units of power

Symbol			
ft pdl.s^{-1}	Foot poundal per second	0.04214	W
ft lbf.s^{-1}	Foot pound-force per second	1.35582	W
hp or HP	Horsepower (= 550 ft lbf/s)	0.74570	kW
Btu.h^{-1}	British thermal unit per hour	0.2931	W
		0.252	mth.h^{-1}
Btu.s^{-1}	British thermal unit per second	1.055	kW
		0.252	mth.s^{-1}
kW	Kilowatt	1.341	hp
		0.948	Btu.s^{-1}
mth.h^{-1}	Millithermie per hour	3.968	Btu.h^{-1}
mth.s^{-1}	Millithermie per second	3.968	Btu.s^{-1}

1.2.14. Equivalents of various units

Pressure

The figures give the value of one unit indicated below	Bar	Atmosphere	mm of mercury	Metre of water	Pascal (SI)
Pascal (SI)	10^{-5}	9.87 *x* 10^{-6}	0.0075	1.020 x 10^{-4}	1
Bar	1	0.98692	749.75	10.1972	10^{5}
Normal atmosphere	1.01325	1	760	10.3323	101,325
kgfcm 2	0.98066	0:96784	735.514	10	9.81 x 10^{4}
Metre of mercury	1.33377	1.316	1000	13.596	1.33 x 10^{5}
Metre of water (at 4°C)	0.09807	0.09678	73.551	1	9.81 x 10^{3}

Energy

The figures give the value of one unit indicated below	Joule	kWh	kcal or mth	• hph	Btu
joule	1	27.78 *x* 10^{-8}	238 *x* 10^{-6}	37.25 *x* 10^{-8}	948 *x* 10^{-6}
Kilowatt-hour	3.6 *x* 10^{6}	1	860	1.341	3413
Kilocalorie	4186	116 *x* 10^{-5}	1	156 x 10^{-5}	3.968
Horsepower-hour	2.68 *x* 10^{6}	0.746	641	1	2545
British thermal unit	1055	293 *x* 10^{-6}	0.252	393 *x* 10^{-6}	1

Flow rate

Value of one unit indicated below	$m^3.h^{-1}$	$m^3.s^{-1}$	$l.s^{-1}$	1000 $m^3.d^{-1}$	$ft^3.s^{-1}$	$ft^3.min^{-1}$	US gpm	US mgd	UK gpm	UK mgd
$m^3.h^{-1}$	1	278×10^{-6}	0.2778	0.024	9.81×10^{-3}	0.588	4.403	6.34×10^{-3}	3.667	5.28×10^{-3}
$m^3.s^{-1}$	3600	1	1000	86.4	35.30	2118	15,852	22.82	13,198	19.00
$l.s^{-1}$	3.6	0.001	1	0.0864	35.3×10^{-3}	2.118	15.85	22.8×10^{-3}	13.198	19×10^{-3}
1000 $m^3.d^{-1}$	41.67	11.6×10^{-3}	11.575	1	0.4085	24.5	183.47	0.264	152.85	0.220
$ft^3.s^{-1}$	102	28.3×10^{-3}	28.317	2.448	1	60	449	0.647	374	0.538
$ft^3.min^{-1}$	1.70	472×10^{-6}	0.472	0.0408	0.0167	1	7.48	0.0108	6.235	8.98×10^{-3}
US gpm	0.2271	6.3×10^{-5}	0.0631	5.45×10^{-3}	2.223×10^{-3}	0.1336	1	1.44×10^{-3}	0.833	1.20×10^{-3}
US mgd	157.7	43.8×10^{-3}	43.80	3.785	1.546	92.80	694	1	578	0.832
UK gpm	0.2728	7.58×10^{-5}	0.0758	6.54×10^{-3}	2.764×10^{-3}	0.1605	1.201	1.73×10^{-3}	1	1.44×10^{-3}
UK mgd	189.42	52.6×10^{-3}	52.61	4.545	1.857	111.4	834	1.20	694	1

Temperature

F = Fahrenheit scale

C = Celsius scale

$$F = 32 + \frac{9}{5} C$$

$$C = \frac{5}{9} (F - 32)$$

1.3.
VARIOUS OTHER UNITS

1.3.1. Radiation units

Becquerel (Bq)

This unit is used for measuring radioactivity. It corresponds to one transition of an atom per second.

Another unit used is the curie
1 curie (Ci) = 37 *x* 109 Bq

. Gray (Gy)

The measurement of the quantity of radiation received or dose absorbed by a person or a mass of matter is expressed in grays.
1 Gy = 1 joule per kilogramme
Another unit used is the rad: 1 Gy = 100 rad.

. **Sievert (Sv)**

In equal doses, the effect produced by the various types of radiation on a person varies depending on their nature and the organs exposed. This effect is measured in sieverts. The sievert is the **effective dose equivalent.**

If RBE is the **relative biological effectiveness coefficient** of the radiation:
1 Sv = 1 Gy *x* RBE
Another unit used is the rem:
1 Sv = 100 rem.

1.3.2. Units used in the sugar industry

Density

Brix weight

This is the number of grammes of saccharose for 100 g of solution.

Brix volume

This is the number of grammes of saccharose for 100 ml of solution.
Note: as calibration is performed at 15°C, if d is the specific gravity of the liquid at 15°C, with water specific gravity at VC being taken as unit, this produces:
Brix volume = Brix weight *x* d

1.3.3. Units used in the dairy industry

. **Dornic degree**

One Dornic degree is equal to one decigramme of lactic acid per litre of liquid.

2. MATHEMATICS

2.1.
ALGEBRA ARITHMETICS

Progressions

The form of an **arithmetic progression** is:
a;a+r;a+2r;...a+(n-1)r
with a being the first term, and r the common difference between any two numbers of the sequence.
Value of the nth term p:
P=a+(n-1)r
Sum of the first n terms:

$$S = \frac{(a+1)n}{2}$$

The form of a **geometric progression is:**
$a; aq; aq^2; ...aq^{n-1}$
with a being the first term, and q the common ratio between terms.
Value of the nth term p: n annuities of value a,
$p = aq^{n-1}$
Sum of the first n terms:

$$S = \frac{a(q^n - 1)}{q - 1}$$

Sum of an infinite number of terms when q< 1:

Arrangements

The total number of possible arrangements of m objects n at a time:
Am = m(m - 1)(m - 2)(m - 3) ...(m-n+1)

Permutations

The number of possible permutations with m objects:

$$P_m = 1X2x3X4x5...x\ m = m!$$

Combinations

Total number of possible combinations with m objects taken n at a time:

$$C\frac{n}{m} = \frac{m(m-1)(m-2)\dots(m-n+1)}{1.2.3.4.5.\dots(n-1)n} = \frac{A_m^n}{n!}$$

Compound interest

If C is the original capital, r the annual interest on 1 franc, A is the capital obtained after n years (compound interest):
A=C(1+r)"

Annuities

If A is the final value of a sequence of

$$A = a\,\frac{(1+r)^n - 1}{r}$$

Amortization

V = sum to be amortized.
a = annuity for amortization and interest
n = number of annuities
T = amortization rate

$$T = \frac{r}{(1+r)^n - 1}$$

$$a = \frac{Vr(1+r)^n}{(1+r)^n - 1} = V\,(T + r)$$

2.2. TRIGONOMETRY FORMULAE

(Angle measurement unit: radian)

• Fundamental relationships

$$\sin^2 a + \cos^2 a = 1 \quad \tan a = \frac{\sin a}{\cos a} \quad \cot a = \frac{1}{\tan a}$$

$$\sin a = \cos\left(\frac{\pi}{2} - a\right) \qquad \cos a = \sin\left(\frac{\pi}{2} - a\right)$$

$$\tan a = \cot\left(\frac{\pi}{2} - a\right)$$

$$\sin a = \sin(\pi - a) \qquad \cos a = -\cos(\pi - a)$$

$$\tan a = -\tan(\pi - a)$$

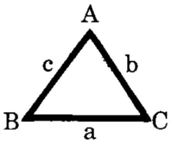
$$\cos a = \frac{1}{\pm\sqrt{(1 + \tan^2 a)}} \quad \sin a = \frac{\tan a}{\pm\sqrt{(1 + \tan^2 a)}}$$

• Solution of triangles
Oblique triangles

$$A + B + C = \pi$$

$$a^2 = b^2 + c^2 - 2bc\cos A$$

$$\frac{a}{\sin A} = \frac{b}{\sin B} = \frac{c}{\sin C}$$



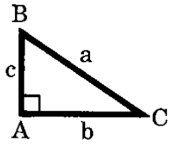
Right triangles

$$A = \frac{\pi}{2} \quad B + C = \frac{\pi}{2}$$

$$a^2 = b^2 + c^2$$

$$b = a\sin B = a\cos C$$
$$= c\tan B = c\cot C$$

$$c = a\cos B = a\sin C$$
$$= b\tan C = b\cot B$$



2.3. GEOMETRY FORMULAE

2.3.1. Plane surface areas

• Regular polygons

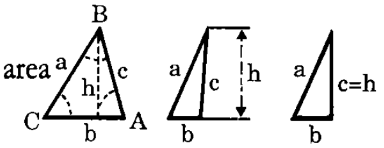
l = length of each side
R = radius of circumscribed circle
n = number of sides
r = radius of inscribed circle
S = surface area of the polygon

The sum of the angles of a polygon is provided by the formula: $(n - 2)\pi$

	R	r	l	S
Triangle	0.577 l	0.289 l	1.732 R or 3.463 r	$0.433\ l^2$ or $1.299\ R^2$
Square	0.707 l	0.500 l	1.414 R or 2.000 r	$1.000\ l^2$ or $2.000\ R^2$
Pentagon	0.851 l	0.688 l	1.176 R or 1.453 r	$1.721\ l^2$ or $2.378\ R^2$
Hexagon	1.000 l	0.866 l	1.000 R or 1.155 r	$2.598\ l^2$ or $2.598\ R^2$
Heptagon	1.152 l	1.038 l	0.868 R or 0.963 r	$3.634\ l^2$ or $2.736\ R^2$
Octagon	1.307 l	1.208 l	0.765 R or 0.828 r	$4.828\ l^2$ or $2.828\ R^2$
Nonagon	1.462 l	1.374 l	0.684 R or 0.728 r	$6.182\ l^2$ or $2.892\ R^2$
Decagon	1.618 l	1.540 l	0.618 R or 0.649 r	$7.694\ l^2$ or $2.939\ R^2$
Hendecagon	1.775 l	1.703 l	0.563 R or 0.587 r	$9.366\ l^2$ or $2.974\ R^2$
Dodecagon	1.932 l	1.866 l	0.518 R or 0.536 r	$11.19\ l^2$ or $3.000\ R^2$

• Triangle

S = surface area



$$S = \frac{b.h}{2}$$

$$= \sqrt{\{p(p-a)(p-b)(p-c)\}}$$

where $p = \dfrac{a+b+c}{2}$

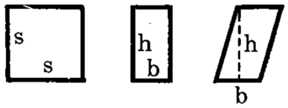
$= \dfrac{a.b.c.}{4R}$ (R = radius of the circumscribed circle)

$= pr$ (r = radius of the inscribed circle)

$$= \frac{ab}{2}\sin C = \frac{ac}{2}\sin B = \frac{bc}{2}\sin A$$

• Square, rectangle, parallelogram, trapezoid, rhombus

Square: $S = s^2$

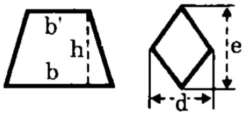


Rectangle: $S = bh$

Parallelogram: $S = bh$

Trapezoid: $S = \dfrac{b+b'}{2}h$

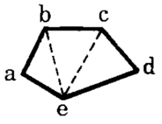
Rhombus: $S = \dfrac{d.e}{2}$



• Irregular polygons

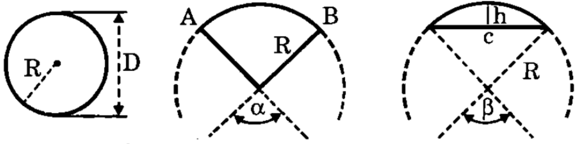
The polygon is broken down into triangles.

S = area abe + area bce + area cde



• Circle, sector, segment, annulus, ellipse

α, β in degrees



circle *sector* *segment*

Circle: $S = \pi R^2 = \dfrac{\pi D^2}{4}$

Circumference = $2\pi R$

Sector: $S = \dfrac{\text{arc } AB \times R}{2} = \dfrac{\pi R^2}{360} . \alpha$

Segment: $S = \dfrac{\pi R^2 \beta}{360} - \dfrac{c}{2}(R - h)$

$$= \frac{R^2}{2}\left(\frac{\pi\beta}{180} - \sin\beta\right)$$

Chord $c = 2\sqrt{\{h(2R-h)\}} = 2R \sin\dfrac{\beta}{2}$

Arc (AB) $= \dfrac{R\pi}{180}\alpha$

Height $h = R\left(1 - \cos\dfrac{\beta}{2}\right)$

$$= R \pm \sqrt{\left(R^2 - \frac{c^2}{4}\right)}$$

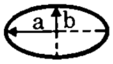
α and β expressed in degrees

Annulus

$S = \pi(R^2 - r^2)$

$= \pi(R - r)(R + r)$

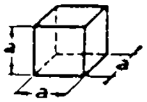
Ellipse



$S = \pi.a.b.$

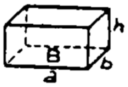
2.3.2. Surface areas and volumes of solids

• Cube



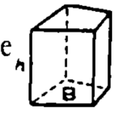
S = total surface area
V = volume
$S = 6\,a^2$
$V = a^3$

• Rectangular parallelepiped



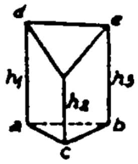
$S = 2\,(ab + bh + ah)$
$V = B \times h = abh$

• Straight or oblique prism



$V = B \times h$
B = surface area of the base
h = perpendicular distance between the two bases

• Truncated prism

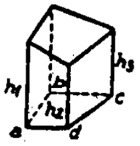


triangular base

$$V = abc \times \frac{h_1 + h_2 + h_3}{3}$$

abc = surface area of the base

quadrilateral base



$$V = abcd \times \frac{h_1 + h_2 + h_3 + h_4}{4}$$

abcd = surface area of the base

• Volume with parallel rectangular bases (obelisk)

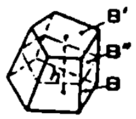
$$V = \frac{h}{2}\,[(2a + a')b + (2a' + a)b']$$

h = perpendicular distance between the two bases

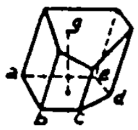
• Volume with parallel polygonal bases

$$V = \frac{h}{6}\,(B + B' + 4B'')$$

h = distance between the two bases
B and B' = base surface areas
B'' = surface area of the section parallel to the bases, passing through the middle of h.



• Prism with two oblique bases



$V = abcde \times h$
abcde = surface area of a base
h = distance from the centre of gravity of the other base to the level plane of the first one.

• Cylinder

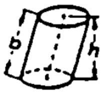
– Straight cylinder: $V = \frac{\pi d^2}{4}\,h$

– Straight cylinder with oblique section:

$$V = \frac{\pi d^2}{4} \times \frac{h_1 + h_2}{2}$$

– Oblique cylinder with parallel bases: $V = S'h$
S' = surface area of the base
h = distance between the two bases

– Cylinder with oblique bases



$V = S \times gg_1$ (S = straight cross section)
gg_1 = distance between the centres of gravity of the bases

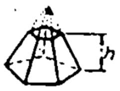
• Pyramid and truncated pyramid with parallel bases

– Pyramid
B = surface area of the base
h = distance from the apex to the level base

$$V = \frac{1}{3}\,B \times h$$

– Truncated pyramid with parallel bases
B and b = surface areas of the bases

$$V = \frac{1}{3}\,h[B + b + \sqrt{(Bb)}]$$



h = distance between the parallel bases

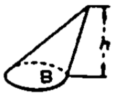
- **Cone and truncated cone**

– Straight circular cone

$S = \pi Rl$

– Straight or oblique circular cone: $V = \pi r^2 \frac{h}{3}$

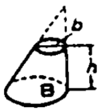
Straight or oblique non-circular cone: $V = B \times \frac{h}{3}$



In both cases, h = distance from the apex to the base.

– Truncated cone with parallel bases:

$$V = \frac{1}{3} h[B + b + \sqrt{(Bb)}]$$



B and b = base surface areas

h = distance between the parallel bases

- **Sphere, spherical sector, spherical segment, spherical zone**

– Sphere:

Total surface area = $4\pi r^2$

Volume $V = \frac{4}{3} \pi r^3 = \frac{\pi d^3}{6}$

– Spherical sector:

Total surface area = $\frac{\pi r}{2} (4h + d)$

Volume = $\frac{2}{3} \pi r^2 h = 2.0944\ r^2 h$

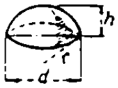
– Spherical segment

Lateral surface area = $2\pi rh$

$= \frac{\pi}{4} (d^2 + 4h^2)$

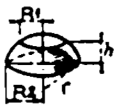
Volume $V = \pi h^2 (r - \frac{1}{3} h)$

$= \pi h (\frac{d^2}{8} + \frac{h^2}{6})$



– Spherical zone:

Lateral surface area = $2\pi rh$



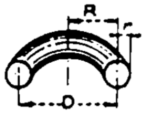
Volume

$$V = \frac{1}{6} \pi h(3R_1^2 + 3R_2^2 + h^2)$$

- **Circular torus**

Surface area $S = 4\ \pi^2 Rr$

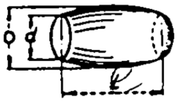
Volume $V = 2\pi^2 r^2 R$



- **Barrel**

Approximate volume

$V = 0.262\ l(2D^2 + d^2)$



- **Ellipsoid of revolution**

$V = \frac{4}{3}\pi a^2 b$ or $V = \frac{4}{3} \pi ab^2$

depending on whether the ellipsoid revolves around the small or the large axis.

a = 1/2 large axis

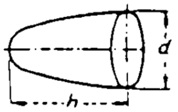
b = 1/2 small axis

- **Ellipsoid with three axes**

$V = \frac{4}{3} \pi abc$

- **Paraboloid of revolution**

$V = \frac{\pi d^2 h}{8}$

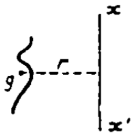


- **Surface area generated by a plane curve rotating about an axis situated in its plane but not cutting it**

Surface area $S = 2\pi rl$

l = developed length of the curve

r = radius of the circle described by the centre of gravity

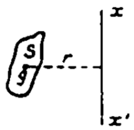


- **Volume generated by a surface rotating about an axis situated in its plane but not cutting it**

Volume $V = 2\pi rS$

S = surface area

r = radius of the circle described by the centre of gravity



2.4.
FIGURES FREQUENTLY USED IN CALCULATIONS

π	3.14159
$\log\pi$	0.49715
2π	6.28318
3π	9.42478
$\frac{\pi}{2}$	1.57080
$\frac{\pi}{3}$	1.04720
$\frac{\pi}{5}$	0.62832
$\frac{1}{\pi}$	0.31831
$\frac{2}{\pi}$	0.63662
$\frac{3}{\pi}$	0.95493
$\sqrt{\pi}$	1.77245
$\frac{1}{\sqrt{\pi}}$	0.56418

$\sqrt{\frac{1}{2\pi}}$	0.39894
$\sqrt{\frac{3}{2\pi}}$	0.69099
$\sqrt{\frac{2}{\pi}}$	0.79788
π^2	9.86960
π^3	31.00628
$\sqrt{\pi}$	1.77245
$\sqrt{2}$	1.41421
$\sqrt{3}$	1.73205
$\frac{1}{\sqrt{3}}$	0.57735
$\frac{1}{\sqrt{2}}$	0.70710

Logarithms

e = basis of Napierian logarithms

$\ln a = \frac{\log a}{\log e}$

$e = 2.718282$

$\log e = 0.43429$

$\frac{1}{e} = 0.367879$

$\frac{1}{\log e} = 2.30259$

2.5.
STATISTICS

The mean value of an expression is indicated by the symbol (-) placed above it.

2.5.1. Definitions

Sum

If we consider N values $X_1, X_2, ..., X_j, ... X_n$ their sum is: $\sum_{j=1}^{N} X_j = X_1 + X_2 + ... X_j ... X_n = \Sigma X$

Arithmetic mean

$$\overline{X} = \frac{\Sigma X}{N}$$

- **Weighted arithmetic mean**

$$\overline{X} = \frac{W_1X_1 + W_2X_2 + ... + W_nX_n}{W_1 + W_2 + ... + W_n} = \frac{\Sigma WX}{\Sigma W}$$

Median

The median of a series of number arranged in increasing order is the middle number, or the arithmetic mean of the two middle numbers (in the case of an even number of items).

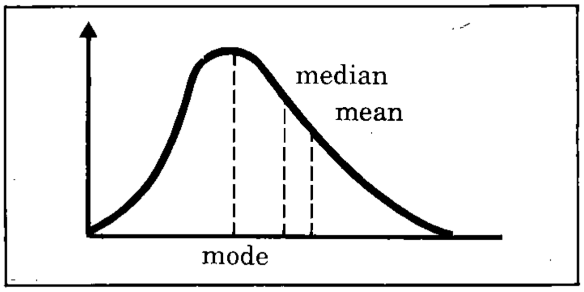
Mode

The mode of a series of number is the

most frequently occurring number, i.e., the one that has the greatest frequency.

The mode may not exist or there may be more than one.

Empirical relationship between the mean, the median and the mode



For moderately asymmetrical unimodal density curves, the following empirical relation applies:

Mean - Mode = 3(Mean - Median)

. Geometric mean G

$$G = \sqrt[N]{(X_1\, X_2\, X_3 \;....\; X_N}$$

. Harmonic mean H

$$H = \frac{N}{\Sigma \frac{1}{X}}$$

. Root-mean-square value MQ

$$MQ = \sqrt{\frac{\Sigma X^2}{N}}$$

. Average deviation AD

$$AD = \frac{\sum_{j=1}^{N} \left| X_j - \bar{X} \right|}{N} = \frac{\Sigma \left| X - \bar{X} \right|}{N} = |\overline{X - X}|$$

. Standard deviation SD

For n numbers: if x = X – ξ(deviation of the number from the mean ξ)

$$SD = \sqrt{\frac{\Sigma X^2}{n}}$$

Variance V

The variance is the square of the standard deviation.

$$V = SD^2$$

2.5.2. Property of the standard deviation

For a normal distribution, or LaplaceGauss distribution (figure 217), the following apply:

- 68.27% of cases are included between ξ-SD and ξ+SD
- 95.45% of cases are included between ξ-2SD and ξ + 2SD
- 99.73% of cases are included between ξ-3SD and ξ + 3SD

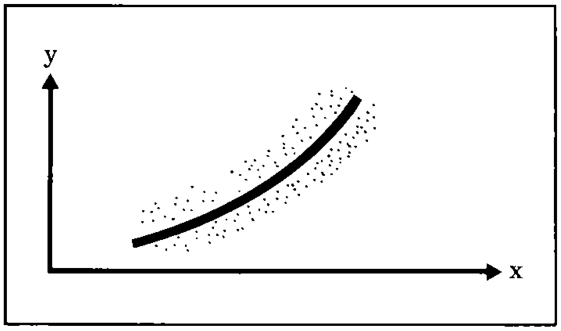
These percentages are approximately valid for slightly dissymmetrical distributions.

For slightly dissymmetrical distributions, the following empirical relation applies:

Average deviation = 4/5 (standard deviation)

2.5.3. Graphic method of curve fitting

It is often possible to draw a continuous curve approaching the particular points by means of a dispersion diagram (see figure below). Such a curve is called a fitting curve.



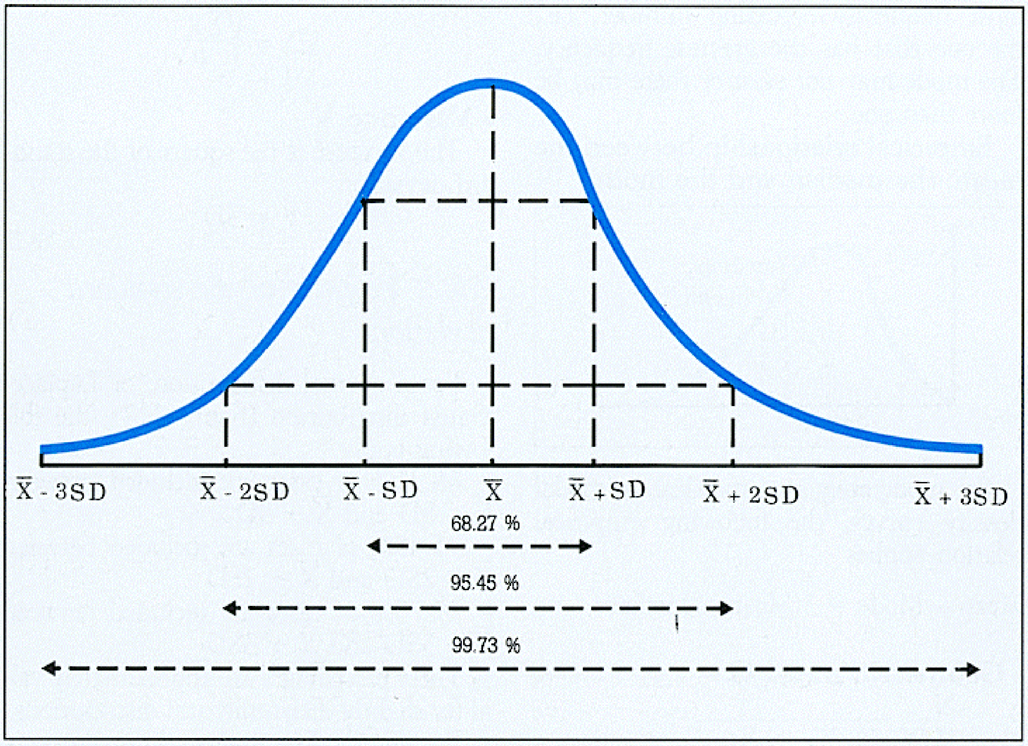


Figure 217. Normal distribution curve (Laplace-Gauss).

2.5.3.1. **Least squares methods**

Definition

Among all the curves that approach a set of points, the one that provides the closest fitting is the one that verifies the following property (see figure 218):

$Di^2 + D^2{}_2 + \ldots + D_N{}^2$ minimum.

It is called the curve of least squares.

Straight line of regression of the least squares

If we take a scatter of N points:

$(X_1, Y_1); (X_2, Y_2); \ldots (X_N, Y_N)$

(1) $Y = a_o + a_1X$ (2) $X = b_o + b_1Y$

$$a_o = \frac{(\Sigma Y)(\Sigma X^2) - (\Sigma X)(\Sigma XY)}{N \Sigma X^2 - (\Sigma X)^2}$$

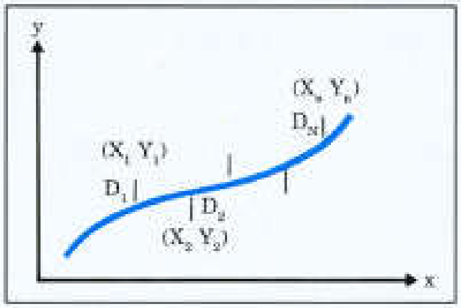


Figure 218.

$$a_1 = \frac{N \Sigma XY - (\Sigma X)(\Sigma Y)}{N \Sigma X^2 - (\Sigma X)^2}$$

(To obtain coefficients bo and bi, replace a with b, X with Y, and Y with X in the preceding formulae.)

If we take x = X - X and y = Y - Y, equations (1) and (2) can also be written in the form:

$$y = \left(\frac{\Sigma\, xy}{\Sigma\, x^2}\right) x$$

$$x = \left(\frac{\Sigma\, xy}{\Sigma\, y^2}\right) y$$

Parabola of least squares
If we take a scatter of N points:

$$(X_i, Y_i);\ 1 \leqslant i \leqslant N$$

$$Y = a_o + a_1X + a_2X^2$$

Coefficients a_o, a_l, a_2 are obtained by means of the following equation system:

$$\Sigma\, Y = a_oN + a_1\, \Sigma\, X + a_2\, \Sigma\, X^2$$
$$\Sigma\, XY = a_o\, \Sigma\, X + a_1\, \Sigma\, X^2 + a_2\, \Sigma\, X^3$$
$$\Sigma\, X^2Y = a_o\, \Sigma\, X^2 + a_1\, \Sigma\, X^3 + a_2\, \Sigma\, X^4$$

2.5.3.2. Root-mean-square error

If we take Y,,t as the estimated value of Y according to (1), a measurement of the dispersion around the straight regression line from Y to X is defined by the quantity:

$$S_{Y.X} = \sqrt{\frac{\Sigma(Y - Y_{est})^2}{N}}$$

which is called the standard deviation of Y linked to X.
The form used for calculation is:

$$S^2_{YX} = \frac{\Sigma\, Y^2 - a_o\, \Sigma\, Y - a_1\, \Sigma\, XY}{N}$$

2.5.3.3. Explained residual variation. Correlation coefficient

a) The total variation of Y; $\Sigma(Y - \varphi)^2$ can be written:

$$\Sigma\, (Y - \overline{Y})^2 = \Sigma\, (Y - Y_{est})^2 + \Sigma\, (Y_{est} - \overline{Y})^2$$

$$\Sigma\, (Y - Y_{est})^2 = \text{residual variation}$$

$$\Sigma\, (Y_{est} - \overline{Y})^2 = \text{explained variation.}$$

b) The coefficient of determination is the quotient of the explained variation by the total variation, written:

$$r^2 = \frac{\Sigma\, (Y_{est} - \overline{Y}\,)^2}{\Sigma\, (Y - \overline{Y})^2} \text{ with } 0 \leqslant r^2 \leqslant 1$$

The quantity r, root of the preceding expression, is called correlation coefficient.

r is a dimensionless number and varies from -1 to +1.

3. CHEMISTRY AND REAGENTS

3.1. SUMMARY OF CHEMICAL CONCEPTS

A **pure substance** is one whose physical constants are identical regardless of the size of the sample taken.

A **molecule** is the smallest unit of a pure substance possessing all its physical and chemical properties.

A molecule can be dissociated by chemical means, a process requiring considerable amounts of energy.

The molecule is made up of identical atoms in a pure element, and different atoms in a pure compound.

The main elementary **particles of an atom** are the **electron**, the **proton**, and the **neutron**:

- the **electron** is a particle carrying a negative electrical charge, $-e = -1.6 \times 10^{-19}$ coulombs. Its rest mass is $9.10^{9} \times 10^{-31}$ kg.

The electron has an angular momentum (spin) as it rotates around its axis; this in turn produces a magnetic dipole moment fundamental to the properties of most paramagnetic and ferromagnetic substances;

- the **proton** is a positively charged particle, ($+e = +1.6 \times 10^{-19}$ coulombs) with a mass 1,836 times that of the electron;

- the **neutron** is an uncharged particle whose mass is roughly equal to that of the proton.

The **atom** is a group of elementary particles with diameters in the range of 0.1 to 0.5 nanometres. It comprises:

- a **nucleus** containing Z protons and N neutrons. Its electric charge is +Ze . Its size is approximately 10^{-5} nanometres. The term nucleon is used to describe either protons or neutrons. The nucleus, the heavy part of the atom, is chemically stable;
- a number of Z **electrons,** of electric charge - Ze.

In an electrically neutral atom, the electrons attracted by the nucleus are in *a* state of rapid motion within a space of a few fractions of a nanometre around the nucleus and occupy quantized energy levels. They can pass from one energy level to another by either absorbing or emitting a photon.

A **photon** is a quantum of energy, i.e., a particle carrying a "grain" of energy. If we take v to be the frequency of a radiation, the energy of the associated photon is $E = h\upsilon$.

Planck's constant $h \approx 6.63 \times 10^{-34}$ J. s.

3.1.1. Atomic number - Isotopes

The **atomic number** is equal to the number of protons in the nucleus, and the **mass number A** is the sum of Z + N (number of nucleons in the nucleus).

The atomic mass is equal to the mass number multiplied by the mass of a nucleon.

Two atoms of the same chemical element differing only by the number of neutrons are called isotopes.

Isotope atoms have the same chemical properties because they have the same number of electrons. They differ only in terms of kinematics. Thus all the atoms for which Z = 8 form the element oxygen.

Isotopes are distinguished by the number of nucleons A being placed to the top left of the symbol of the atom, for example:

^{1}H light hydrogen, or protium,
^{2}H heavy hydrogen (deuterium),
^{3}H tritium,
^{35}Cl and ^{31}CI.

3.1.2. Atomic mass of the elements Mole

Within the approximations of conventional chemistry, the mass of an atom is equal to the sum of the masses of the nucleons. As these masses are extremely small, and therefore awkward to use, it was agreed to start from the mass of a certain number of atoms. The nuclide 1ZC was chosen as basic element (at the 14th General Conference on Weights and Measures, 1971).

A mole is, by definition, the amount of substance of a system, which contains as many elementary units as there are atoms in 12 g of 12 C. It is symbolized as mot.

The number of atoms contained in a mole of an element is 6.023×10^{23} (Avogadro number).

The mass of a mole of ^{12}C is exactly 12 g, and that of a mole of chlorine atoms 35.453 g; the amount of substance contained in 1 kg of H_20 is 55.533 mol.

The gramme-molecular weight of a substance is, by definition, the quotient of the mass of the substance by the amount of substance it contains: it is expressed in grammes per mole ($g.mol^{-1}$). It is now also frequently expressed in daltons. The dalton is the mass of the isotope ^{1}H.

The properties of the chemical elements are not random, but are determined by the electronic structure of the atom: two different atoms with identical peripheral layers have similar chemical properties (alkaline and halogen families, etc.). These similarities transpire in the Mendeleev table, or periodic table of the elements (figure 219).

3.1.3. Formulae of compounds

Compounds are represented by formulae comprising the symbols of their constituent elements. When the compound includes elements with different numbers of atoms, the symbols are completed by whole indices stating the proportions of the various atoms in the compound. These indices are noted on the lower right side of the symbols: for example, H_20 contains two hydrogen atoms for one atom of oxygen.

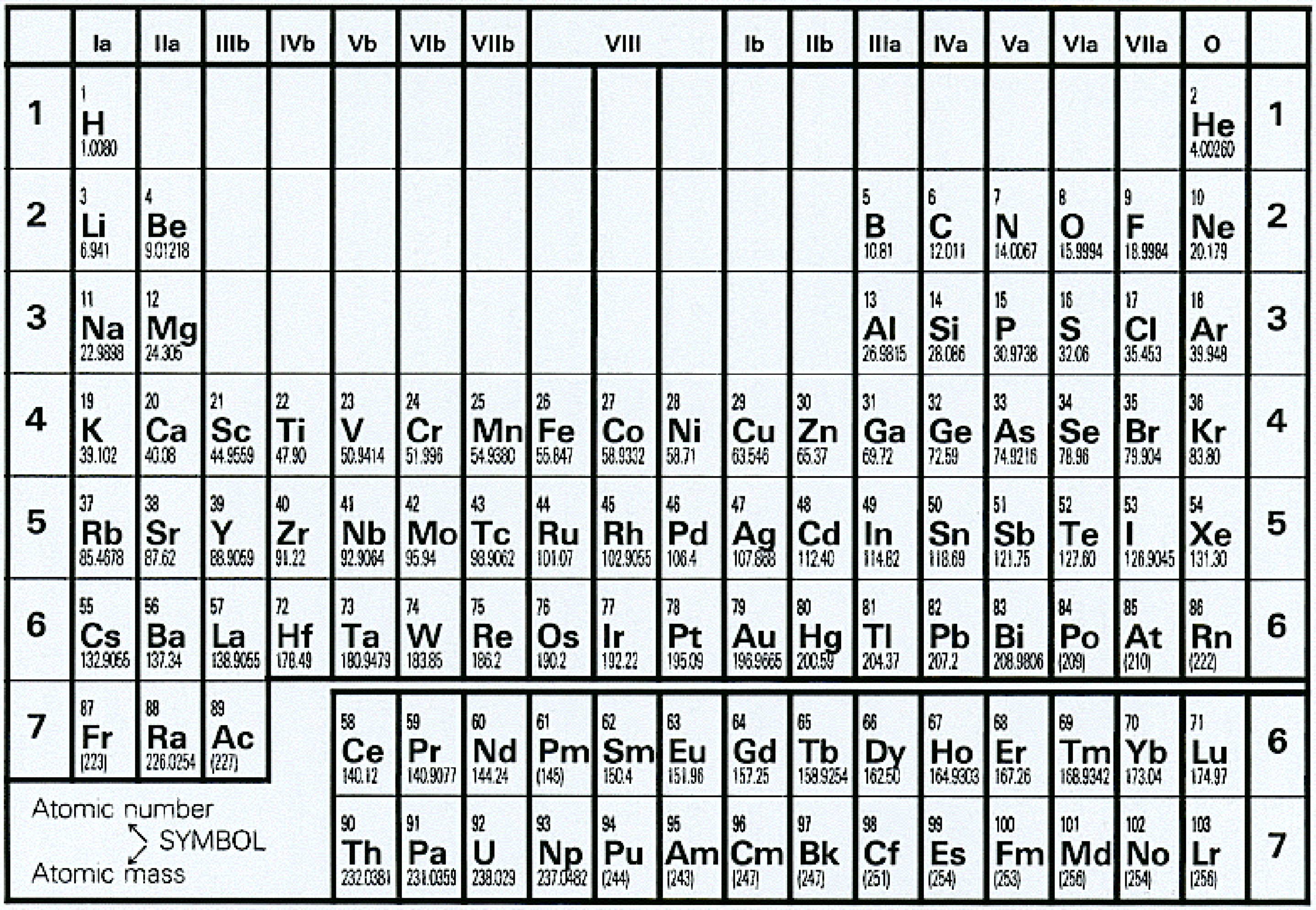
Table 54 shows the gramme-molecular weight of the main salts used in water treatment.

Formulae of organic substances often indicate how certain groups of atoms are associated within a molecule. Acetic acid is thus written CH_3COOH to show that a CH_3 group is attached to an atom of carbon, itself carrying an oxygen atom and an OH group.

3.1.4. Formulae writing rules

The complete rules concerning the Inorganic Chemistry Nomenclature were published by the Societe Chimique de France (French Chemical Society) in February 1975. Here follow a few fundamental paragraphs from this document:

(§ 2.15): in formulae, the electropositive constituent (cation) must always be placed



	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	O	
1	1 H 1.0080																	2 He 4.00260	1
2	3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.179	2
3	11 Na 22.9898	12 Mg 24.305											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948	3
4	19 K 39.102	20 Ca 40.08	21 Sc 44.9559	22 Ti 47.90	23 V 50.9414	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.546	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	4
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.22	41 Nb 92.9064	42 Mo 95.94	43 Tc 98.9062	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.4	47 Ag 107.868	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9045	54 Xe 131.30	5
6	55 Cs 132.9055	56 Ba 137.34	57 La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.9665	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.9806	84 Po (209)	85 At (210)	86 Rn (222)	6
7	87 Fr (223)	88 Ra 226.0254	89 Ac (227)																
					58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9303	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.97	6
Atomic number SYMBOL Atomic mass					90 Th 232.0381	91 Pa 231.0359	92 U 238.029	93 Np 237.0482	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (256)	7

Figure 219. Periodic table of the elements.

first, for example KCI, $CaSO_4^-$ If the compound contains more than one electropositive or electronegative constituent, the symbols within each class should be arranged in alphabetical order. Acids are treated as hydrogen salts, for example H_2SO_4 and H_2PtCl_6 for the position of hydrogen, see 6.2 and 6.32.3.

(§ 2.16.1): in the case of binary compounds of nonmetallic elements, the constituent to be placed in front is the one that figures first in the following list: B, Si, C, Sb, As, P, N, H, Te, Se, S, At, I, Br, Cl, O, F.
Example: NH_3, H_2S, SO_2, $C10_2$, OF_2.

(§ 6.2): salts containing atoms of acid hydrogen.
The names of these salts are formed by inserting the term hydrogen before the name of the anion, to indicate the presence in this salt of the substitution hydrogen. These salts can obviously not be termed acid salts.
Examples: $NaHCO_3$: sodium hydrogen carbonate, LiH_2PO_4: lithium dihydrogen phosphate, KHS: potassium hydrogen sulphide.

(§ 6.3): double salts, triple salts.

(§ 6.31): cations: in formulae, cations always precede the anions.

(§ 6.32.1): cations other than hydrogen must be cited in alphabetical order, and this order can be different in the corresponding formulae.
Example: KNaCO3: potassium sodium carbonate.

(§ 6.32.3): acid hydrogen: when rule 6.2 is not applied, hydrogen is the last cation in the formula.
Example: $NaNH_4HPO_4.4H_20$: sodium ammonium hydrogen phosphate with 4 water molecules.

(§ 6.33): anions must be written in alphabetical order, and this order can be different in the corresponding formulae.

3.1.5. Concentration evaluation

3.1.5.1. The milliequivalent

To facilitate calculations, analysis results are now frequently evaluated not in grammes per litre but rather in gramme-equivalents per litre. The sub multiple is the milliequivalent ($meq.l^{-1}$) (see page 16).
For example, as the gramme-molecular weight of chlorine is 35.5 g, if a water sample contains 2 g of chlorine per litre, this can be expressed by writing that it contains: $\frac{2 \times 1}{35,5} = 0,056$ gramme equivalent of chlorine per litre (56 $meq.l^{-1}$).

In the case of a polyvalent element, the value of the concentration unit ($meq.l^{-1}$), expressed in $mg.l^{-1}$, is the grammemolecular weight divided by the valency. For example, for calcium, a bivalent element with a gramme-molecular weight of 40 g, a concentration of one $meq.l^{-1}$ corresponds to: $40/2 = 20\ mg.l^{-1}$.

This notation has the advantage of enabling immediate calculation of saline concentrations. Taking the previous example of a water sample containing 56 milliequivalents of chlorine per litre, and if we assume this sample is a pure calcium chloride solution, the concentration in CaC12 is:

$$0,056\left(\frac{40}{2}+\frac{35,5}{1}\right)=3,1\ g.l^{-1}$$

and the corresponding calcium concentration is: $0.056 \times 40/2 = 1.1\ g.l^{-1}$.

Table 54. Gramme-molecular weights of the main crystallized salts.

Substance	Formula	Gramme-molecular weight
Aluminium sulphate	$Al_2\ (SO_4)_3,\ 18\ H_20$	666.4
Ammonium nitrate	$NH_4\ N0_3$	80.0
- nitrite	$NH_4\ NO_2$	64.0
- sulphate	$(NH_4)_2\ SO_4$	132.1
Silver chloride	AgCI	143.3
Barium hydroxide	$Ba\ (OH)_2,\ 8\ H_20$	315.5
- sulphate (barite)	$Ba\ SO_4$	233.0
- chloride	$Ba\ Cl_2,\ 2\ H_20$	244.3
Calcium carbonate	$Ca\ CO_3$	100.1
- hydrogen carbonate	$Ca\ (HCO_3)_2$	162.1
- chloride	$Ca\ Cl_2,\ 6\ H_20$	219.1
- sulphate	$Ca\ SO_4,\ 2\ H_20$	172.2
Copper sulphate	$CU\ SO_4,\ 5\ H_20$	249.7
Iron chloride (ferric)	$Fe\ C1_3,\ 6\ H_20$	270.3
- sulphate (ferrous)	$Fe\ SO_4,\ 7\ H_20$	278.0
- sulphate (ferric)	$Fe_2\ (SO_4)_3,\ 9\ H_20$	562.0
Magnesium carbonate	$Mg\ CO_3$	84.3
- chloride	$Mg\ C1_2,\ 6\ H_20$	203.3
- sulphate	$Mg\ SO_4,\ 7\ H_20$	246.5
Manganese hydroxide (manganous)	$Mn\ (OH)_2,$	89.0
- carbonate	$Mn\ CO_3$	115.0
Lead carbonate	$Pb\ CO_3$	267.2
- sulphate	$Pb\ SO_4$	303.2
Potassium nitrate	$K\ N0_3$	101.1
- permanganate	$K\ MnO_4$	158.0
- phosphate	$K_3\ PO_4$	212.3
Sodium aluminate	$Na_2\ AlO_4$	137
- hydrogen carbonate	$Na\ HCO_3$	84
- carbonate	$Na_2\ CO_3$	106.0
- -	$Na_2\ CO_3,\ 10\ H_20$	286.1
- chloride	$Na\ Cl$	58.4
- monohydrogen phosphate	$Na_2\ HPO_4,\ 12\ H_20$	358.1
- orthophosphate	$Na_3\ PO_4,\ 12\ H_20$	380.1

It is often necessary to know the balance of anions and cations rather than a detailed account of the different salts contained in a solution. Notation in equivalents makes it possible to immediately assess this balance.

3.1.5.2. Use of degrees

The notions of equivalent and millie quivalent have the advantage of being international, but degrees are still widely used for defining the degree and the ppm of $CaCO_3$ (0.02 milliequivalent per litre).

Table 55. Solution concentrations.

	Formula	**Gramme Molecular weight**	**Value of the various units in mg.l^{-1}**		
			Milli-equivalent.l^{-1}	**French degree**	**$CaCO_3$ PPM**
1) Calcium and magnesium salts and oxides involved in the water hardness	$CaCO_3$				
Calcium carbonate	$Ca(HCO_3)_2$	100	50	10.0	1.00
Calcium hydrogen carbonate	$CaSO_4$				
(calcium bicarbonate)	$CaCl_2$	162	81	16.2	1.62
Calcium sulphate	$Ca(NO_3)_2$	136	68	13.6	1.36
Calcium chloride	$CaCO$	111	55.5	11.1	1.11
Calcium nitrate	$CA(OH)_2$	164	82	16.4	1.64
Quick lime	$MgCO_3$	56	28	5.6	0.56
Calcium hydroxide		74	37	7.4	0.74
Magnesium carbonate	$Mg(HCO_3)_2$	84	42	8.4	0.84
Magnesium hydrogen carbonate	$MgSO_4$				
(magnesium bicarbonate)	$MgC1_2$	146	73	14.6	1.46
Magnesium sulphate	$Mg(NO_3)_2$	120	60	12.0	1.20
Magnesium chloride	MgO	95	47.5	9.5	0.95
Magnesium nitrate	$Mg(OH)_2$	148	74	14.8	1.48
Magnesia		40	20	4.0	0.40
	CO_3	58	29	5.8	0.58
2) Anions	HCO_3				
Carbonate	SO_4	60	30	6.0	0.60
Hydrogen carbonate (bicarbonate)	SO_3	61	61	12.2	1.22
Sulphate	Cl	96	48	9.6	0.96
Sulphite	$N0_3$	80	40	8.0	0.80
Chloride	NO_2	35.5	35.5	7.1	0.71
Nitrate	PO_4	62	62	12.4	1.24
Nitrite	SiO_2	46	46	9.2	0.92
Orthophosphate	PO4	95	31.6	6.32	0.63
Silicate as Si02	Si02	60	60	12.0	1.20

	Formula	**Gramme Molecular weight**	**Value of the various units in mg.l^{-1}**		
			Milli-equivalent.l^{-1}	**French degree**	**$CaCO_3$ PPM**
				9.8	
Sulphuric	H_2SO_4	98	49	7.3	0.98
Hydrochloric	HCl	36.5	36.5	12.6	0.73
Nitric	HNO_3	63	63	6.5	1.26
Orthophosphoric	H_3PO_4	98	32.7		0.65
4) Cations and oxides				4.0	
Calcium	Ca	40	20	2.4	0.40
Magnesium	Mg	24.3	12.1	4.6	0.24
Sodium	Na	23	23	6.2	0.46
	Na_2O	62	31	7.8	0.62
Potassium	K	39	39	5.6	0.78
Iron (11)	Fe	55.8	28	3.7	0.56
Iron (III)	Fe	55.8	18.6	5.3	0.37
	Fe_2O_3	159.6	26.6	1.8	0.53
Aluminium	Al	27	9	3.4	0.18
	A1203	102	17		0.34
5) Bases				3.6	
Ammonium	NH_4	18	18	8.0	0.36
Caustic soda	NaOH	40	40	11.2	0.80
Potassium hydroxide	KOH	56	56	7.0	1.12
Ammonia	NH_40H	35	35		0.70
6) Various salts					
Sodium hydrogen carbonate				16.8	
(bicarbonate)	$NaHCO_3$	84	84	10.6	1.68
Sodium carbonate	Na_2CO_3	106	53	14.2	1.06
Sodium sulphate	Na_2SO_4	142	71	11.7	1.42
Sodium chloride	NaCI	58.5	58.5	10.9	1.17
Sodium orthophosphate	Na_3PO_4	164	54.7	12.2	1.09
Sodium silicate	Na_2SiO_3	122	61	13.8	1.22
Potassium carbonate	K_2CO_3	138	69		1.38
Potassium hydrogen carbonate				20	
(bicarbonate)	$KHCO_3$	100	100	17.4	2.00
Potassium sulphate	K_2SO_4	174	87	14.9	1.74
Potassium chloride	KCl	74.5	74.5	15.2	1.49
Ferrous sulphate	$FeSO_4$	152	76	13.3	1.52
Ferric sulphate	$Fe_2(SO_4)_3$	400	66.6	10.8	1.33
Ferric chloride	$FeC1_3$	162.5	54.2	11.4	1.08
Aluminium sulphate	$Al_2(SO_4)_3$	342	57	8.9	1.14
Aluminium chloride	$AICI_3$	133.5	44.5	31.6	0.89
Potassium permanganate	$KMnO_4$	158	158	31.6	

3.2.
CHARACTERISTIC CONSTANTS OF SOLUTIONS

3.2.1. Specific gravities

Specific gravity	H_2SO_4	HCI	HNO_3	NaOH	Ammonia	
					Specific gravity	NH_3
1.000	1.2	2	1.6	0.8	0.998	4.5
1.005	8.4	12	10.7	5	0.996	10
1.010	15.7	22	20.0	10	0.994	13.6
1.015	23	32	28	14	0.9915	19.8
1.020	31	42	38	19	0.990	22.9
1.025	39	53	47	23	0.9875	29.6
1.030	46	64	56	28	0.986	32.5
1.040	62	85	75	38	0.983	39.3
1.050	77	107	94	47	0.982	42.2
1.060	93	129	113	57	0.979	49
1.070	109	152	132	67	0.978	51.8
1.080	125	174	151	78	0.974	61.4
1.090	142	197	170	88	0.970	70.9
1.100	158	220	190	99	0.966	80.5
1.120	191	267	228	121	0.962	89.9
1.140	223	315	267	143	0.958	100.3
1.160	257	366	307	167	0.954	110.7
1.180	292	418	347	191	0.950	121
1.200	328	469	388	216	0.946	131.3
1.220	364		431	241	0.942	141.7
1.240	400		474	267	0.938	152.1
1.260	436		520	295	0.934	162.7
1.280	472		568	323	0.930	173.4
1.300	509		617	352	0.926	184.2
1.320	548		668	382	0.923	188
1.340	586		711	412	0.922	195.7
1.360	624		780	445	0.918	205.6
1.380	663		843	478	0.914	216.3
1.400	701		911	512	0.910	225.4
1.420	739		986	548	0.906	238.3
1.440	778		1070	584	0.902	249.4
1.460	818		1163	623	0.898	260.5
1.480	858		1270	662	0.894	271.5
1.500	897		1405	703	0.890	282.6
1.510	916		1474	723		
1.520	936		1508	744		
1.530	956			766		

Table 56. The relationship between specific gravity and concentration of acid and base solutions (grammes of pure product per litre of solution at 15°C).

Table 57. The relationship between specific gravity and concentration of saline solutions (and milk of lime)
(grammes of pure product per litre of solution at 15°C).

Specific gravity	Aluminium sulphate Alz(SO4) 3. 18Hz0	Ferric chloride FeCla	Ferrous sulphate FeSOa.7Hz0	Anhydrous sodium carbonate NazCOa	Salt NaCl	Bleach CI (approx.))	Milk of lime Ca0 (approx.)
1.007	14	10.1	13.1	6.3	10.1	2.8	7.5
1.014	28	20	26.4	13.1	20.5	5.5	16.5
1.021	42	29	40.8	19.5	30.5	8	26
1.028	57	37	55.5	29	41	10.5	36
1.036	73	47	70.5	35.4	51	13.5	46
1.044	89	57	85.5	41.1	62	16	56
1.051	103	66	102	50.8	73	18.5	65
1.059	119	76	116.5	58.8	85	21	75
1.067	135	86	132	67.9	97	23	84
1.075	152	96	147	76.1	109	25	94
1.083	168	106	163	85.0	121	27.5	104
1.091	184	116	179	93.5	134	30	115
1.099	200	126	196	101.2	147	32	126
1.108	218	138	213	110.6	160	34	137
1.116	235	150	230	122	174	36	148
1.125	255	162	247	131	187	38	159
1.134	274	174	265	141.5	200	40	170
1.143	293	186	284	150.5	215		181
1.152	312	198	304	162.5	230		193
1.161	332	210	324		248		206
1.170	351	222	344		262		218
1.180	373	236	365		277		229
1.190	395	250	387		292		242
1.200	417	263	408		310		255
1.210	440	279	430				268
1.220	462	293	452				281
1.230	485	308	474				295
1.241	509	323	501				309
1.252	534	338					324
1.263	558	353					339
1.285	609	384					
1.308	663	416					
1.332	720	449					
1.357		483					
1.383		521					
1.411		561					
1.437		601					
1.453		626					
1.468		650					

Note: Bleach, the commercial term for sodium hypochlorite, is characterized by its available chlorine content, which is evaluated in chlorometric degrees. 1° chlorometric = 3.17 g of available chlorine per litre. 1 1 of 18° Cl bleach contains 57 g of available C12. 1 1 of 48° Cl bleach contains 152 g of available C12.

3.2.2. Conductivity - Resistivity

Conductivity is measured by the conductance of a water column located between two metal electrodes of 1 cm' in area, separated by a distance of 1 cm. It increases in proportion to the dissolved salts content, and varies according to temperature. Conductivity is expressed in siemens per cm (or mhos). Sub-multiples are the millisiemens per cm and the microsiemens per cm (μS.cm^{-1}); the latter unit is the most widely used in water treatment.

Resistivity is the reciprocal of conductivity and is measured in ohms.cm (Ω.cm). The two measurements are related by the following formula:

$$\text{Resistivity in ohms.cm} = \frac{10^6}{\text{conductivity in } \mu\text{S.cm}^{-1}}$$

Example: a conductivity of 10 μS.cm^{-1} corresponds to a resistivity of 100,000 ohms.cm.

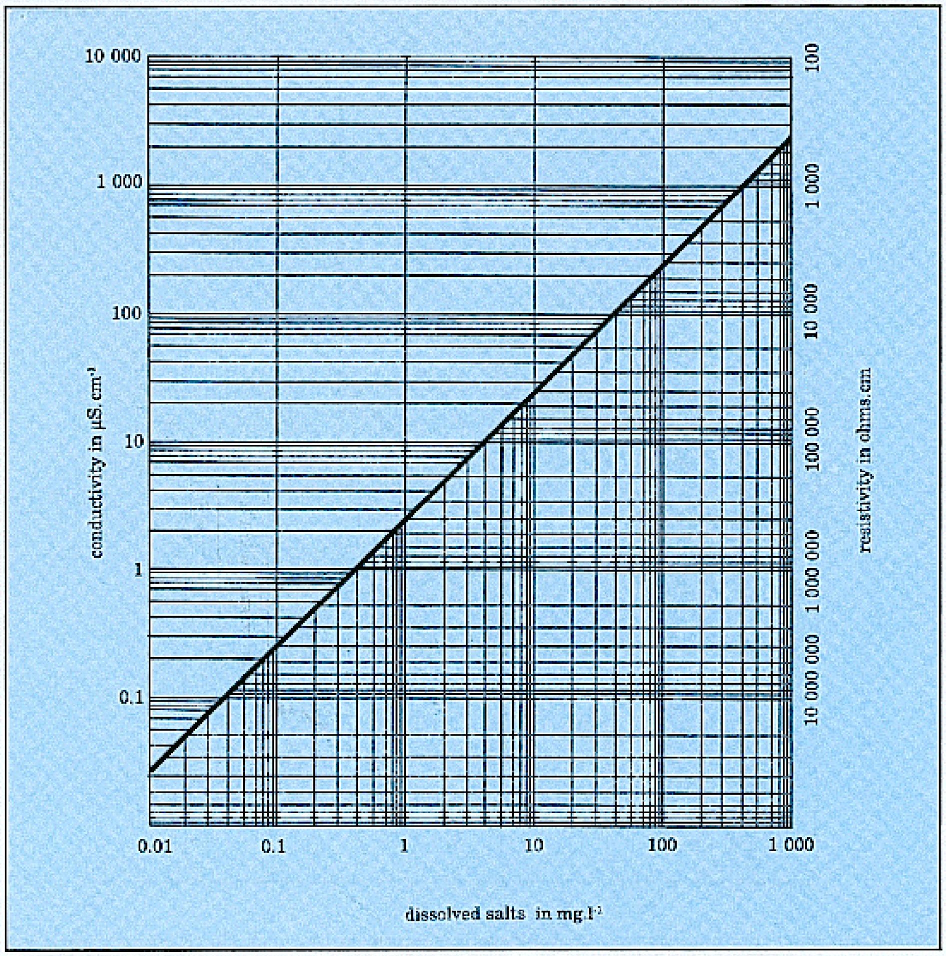


Figure 220. Conductivity versus salinity for a solution of NaCl.

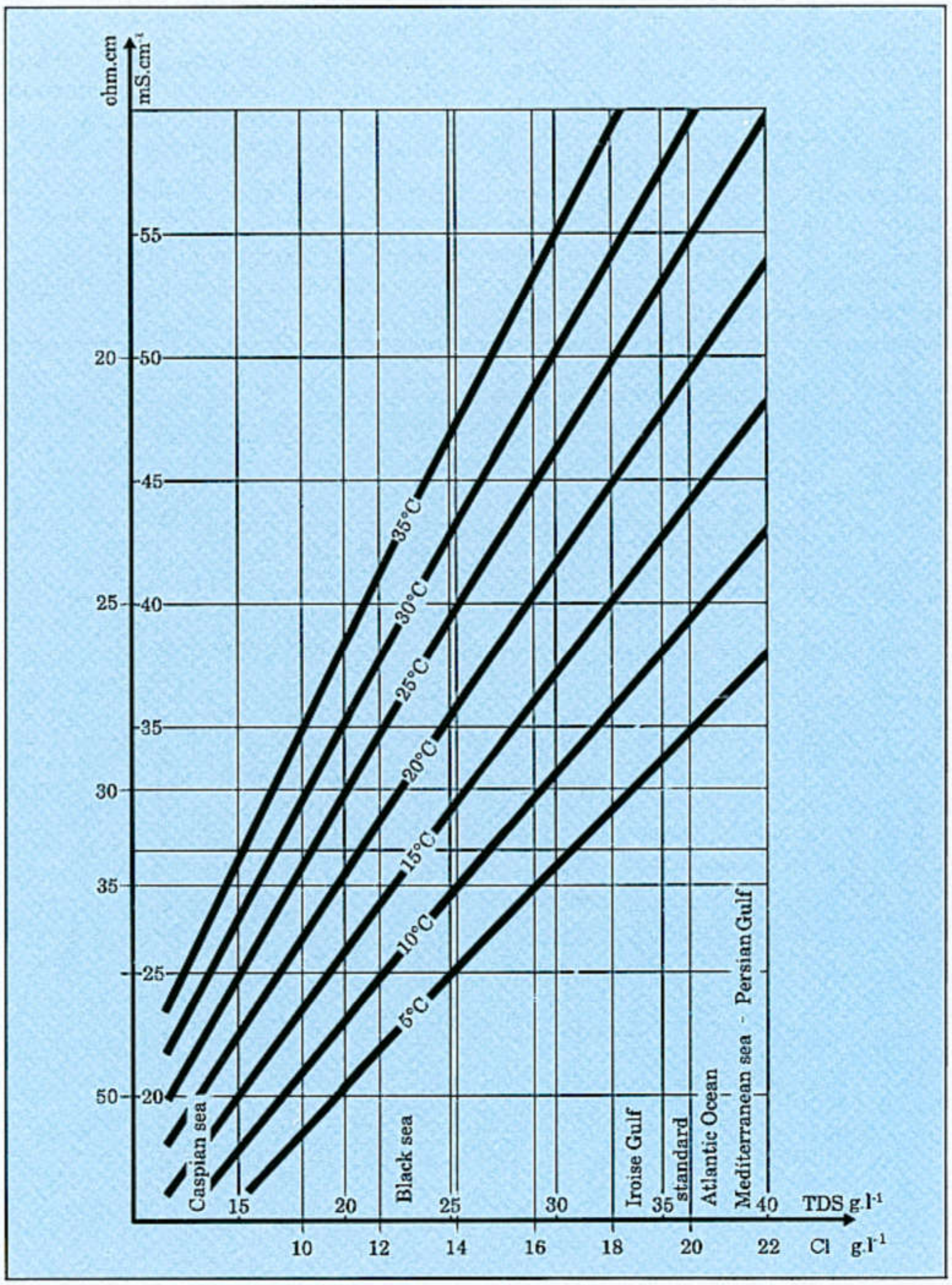


Figure 221. Conductivity of seawater.

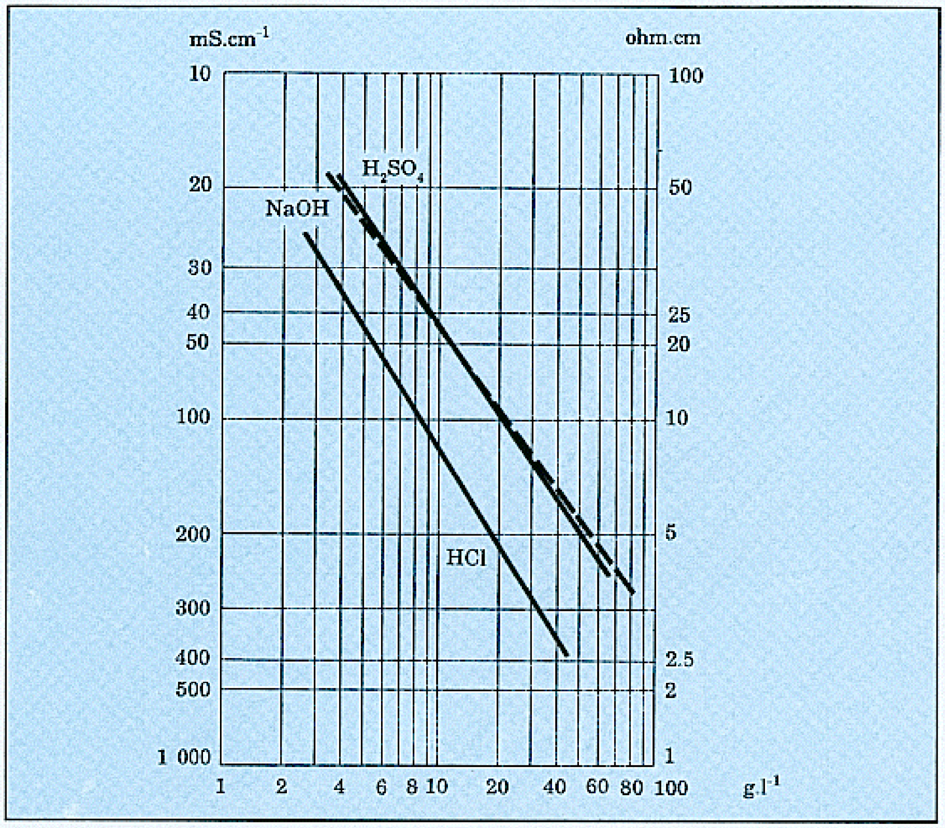


Figure 222. Conductivity of acid and caustic soda solutions.

• Calibration of resistivity meters

The resistivity measuring cells must be recalibrated periodically with N/50 or N/100 potassium chloride solutions:

$$\text{Constant of cell } K = \frac{\text{Theoretical resistivity}}{\text{Measured resistivity}}$$

Resistivity in Ω.cm		
Temperature °C	KCl N/50	KCl N/100
15	446	872
16	436	852
17	426	834
18	417	817
19	408	800
20	400	782
21	392	766
22	384	751
23	376	736
24	369	721
25	362	708

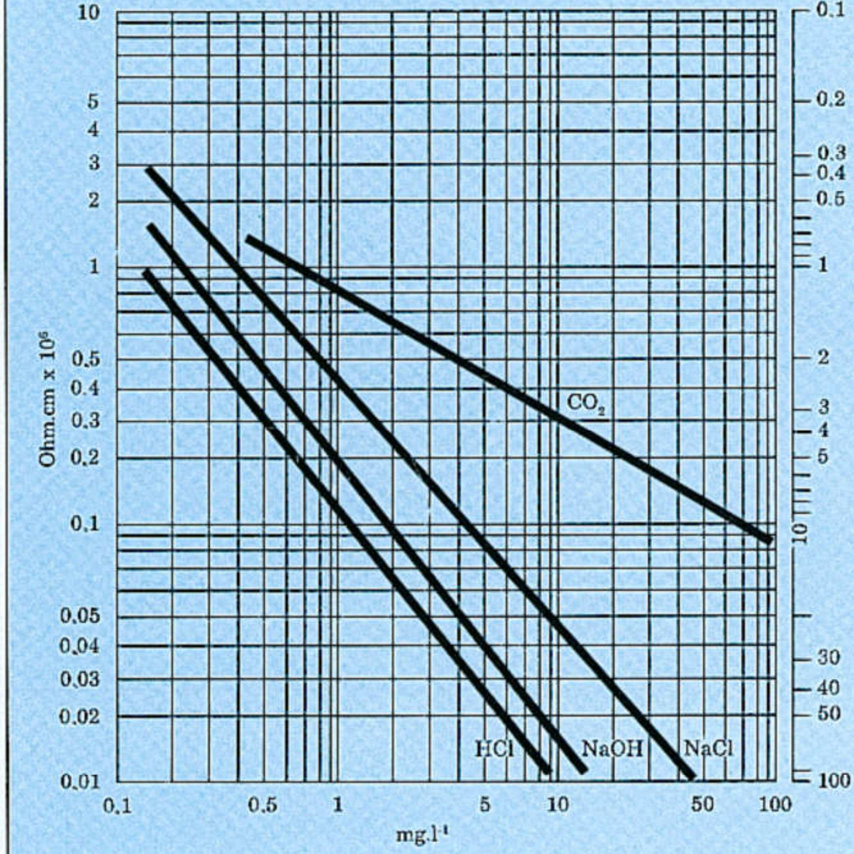


Figure 223. Influence of the concentration in specific electrolytes on the conductivity of a given water sample (25°C).

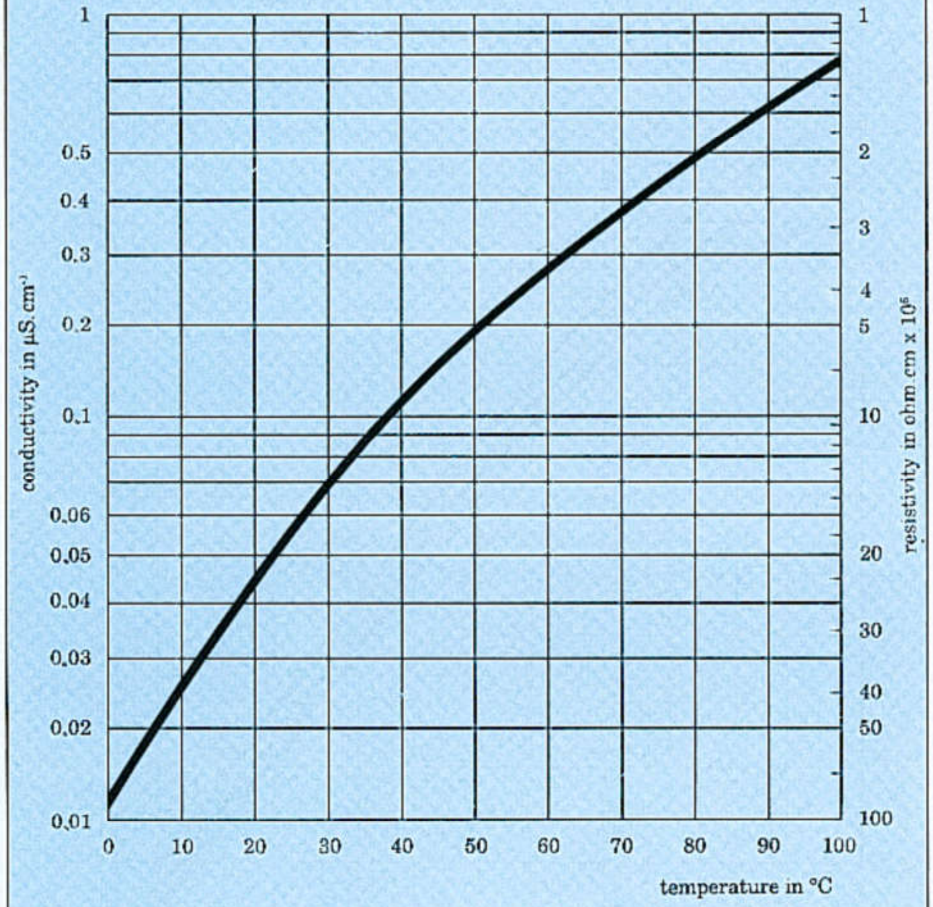


Figure 224. Conductivity of pure water versus temperature.

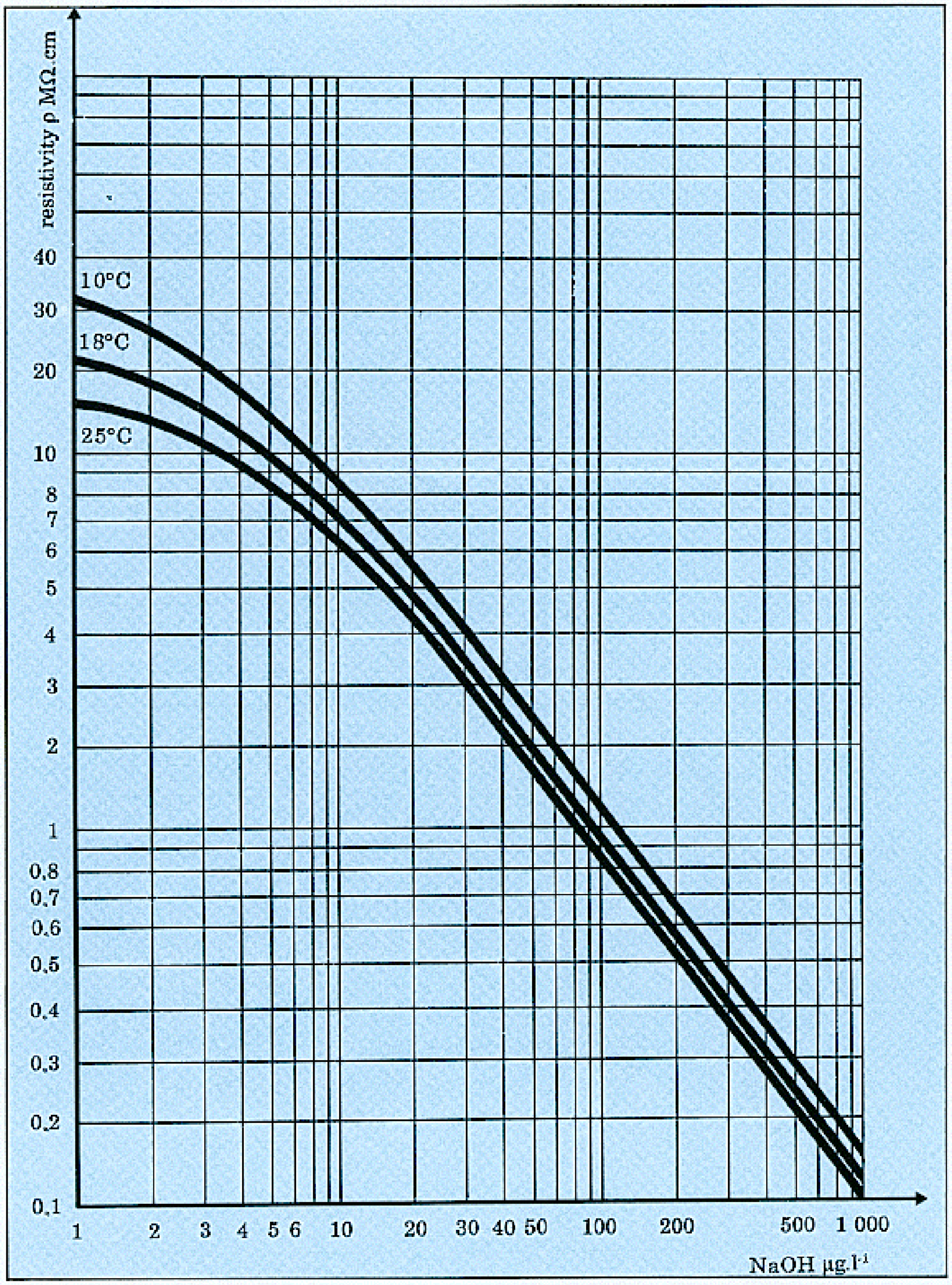


Figure 225. Effect of sodium (as NaOH) leakage on the resistivity of demineralized water.

3.2.3. Kinematic viscosity of a few liquids

Name of liquid	**Temperature** (°C)	Kinematic viscosity v ' m.^{2}s $^{-1}$
Water	0	$1,8 .10^{-6}$
-	20	$1,0 .10^{-6}$
Saturated NaCl brine	0	$2,5 .10^{-6}$
-	10	$1,8 .10^{-6}$
Acetic acid 10096	20	$1,2 .10^{-6}$
Nitric acid 95%	0	$1,5 .10^{-6}$
-	10	$1,2 .10^{6}$
Sulphuric acid 66°Be	- 10	$4,4 .10^{-5}$
-	0	$2,6 .10^{-5}$
-	15	$1,7 .10^{-5}$
-	2 5	$1,3 .10^{-5}$
-	50	$6 .10^{-6}$
Hydrochloric acid 20-21°Be	- 10	$2,6 .10^{-6}$
-	0	$2,2 .10^{-6}$
-	10	$2,0 .10^{-6}$
-	20	$1,7 .10^{-6}$
Soda lye 49%	15	$7,9 .10^{-5}$
-	20	$5,4 .10^{-5}$
-	25	$3,6 .10^{-5}$
Soda lye 41 %	15	$4,5 .10^{-5}$
-	20	$3,4 .10^{-5}$
-	25	$1,7 .10^{-5}$
Sodium silicate 38-40°Be	0	$5,5 .10^{-4}$
-	5	$2,9 .10^{-4}$
-	10	$2,05.10^{-4}$
-	20	$1,13.10^{-4}$
Aluminium sulphate 34°Be	8	$1,38.10^{-5}$
Ferric chloride 45°Be	- 15	$2,5 .10^{-5}$
-	0	$1,0 .10^{-5}$
-	20	$3,0 .10^{-6}$

NOTE: certain flocculants have a high viscosity that should be specified by the supplier (see par. 3.5.7).

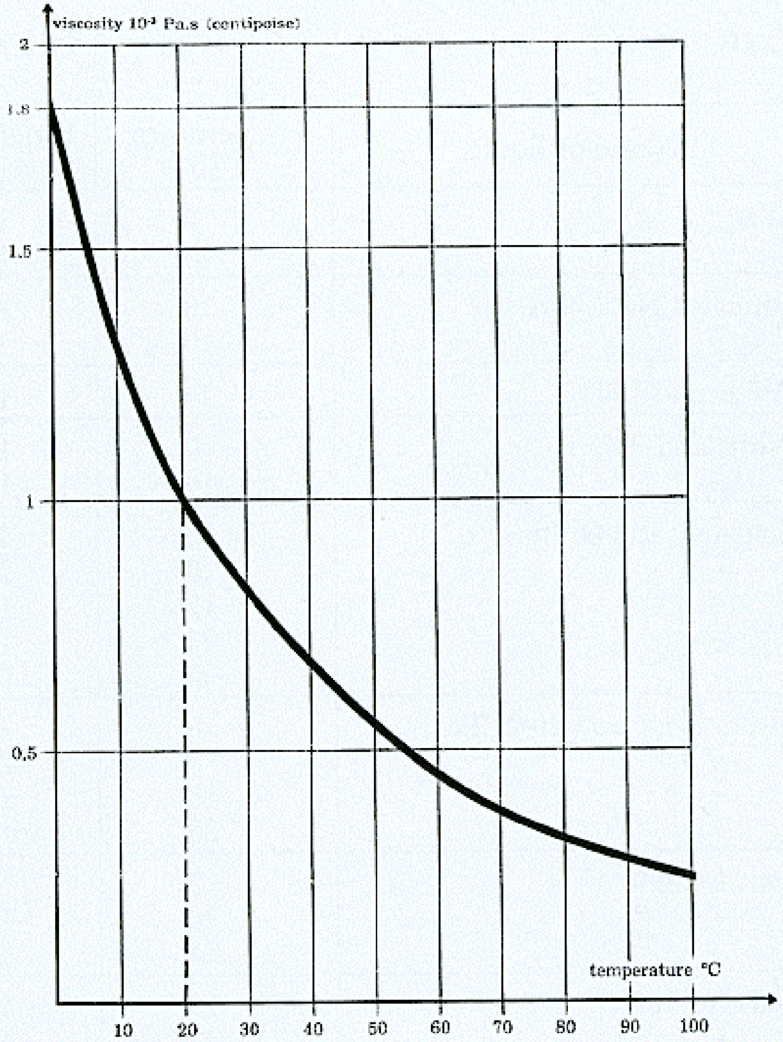


Figure 226. Absolute viscosity of water versus temperature.

3.2.4. Common solutions

3.2.4.1. Solubility

**Solubility of lime*

Temperature °C	***0***	***10***	***20***	***30***	***40***	***50***	***60***	***70***	***80***	***90***	***100***
Ca0 g.l^{-1}	*1.40*	*1.33*	*1.25*	*1.16*	*1.06*	*0.97*	*0.88*	*0.80*	*0.71*	*0.64*	*0.5*
$Ca(OH)_2$ g.l^{-1}	*1.85*	*1.76*	*1.65*	*1.53*	*1.41*	*1.28*	*1.16*	*1.06*	*0.94*	*0.85*	*0.7*
Titer of lime water in M alk. degrees	*250*	*238*	*223*	*207*	*190*	*173*	*157*	*143*	*127*	*115*	*104*

.**Solubility of a few solid reagents (1)**

(in grammes of substance according to the corresponding formula, per litre of water**).**

Substance	Formula (2)	O°C	10°C	20°C	30°C
Aluminium sulphate	$A1_2(SO_4)_3$,18 H_20	636	659	688	728
Calcium chloride	$CaCI_2$	595	650	745	1020
Calcium sulphate	$CaSO_4$ $2H_20$	2.22	2.44	2.58	2.65
Copper sulphate	$CuSO_4$, 5 H_20	233	264	297	340
Ferric chloride	$FeCl_3$	744	819	918	-
	$FeC1_3$, 6 H_20	852	927	1026	-
Ferrous sulphate	$FeSO_4$, 7 H_20	282	331	391	455
Potassium permanganate	$KMnO_4$	28	44	64	90
Ammonium phosphate	$NH_4H_2PO_4$	184	219	261	
	$(NH_4)_2H\ PO_4$	364	386	408	
	$(NH_4)_2H\ PO_4$, $2H_20$	340	388		
Ammonium sulphate	$(NH_4)_2\ SO_4$	413	420	428	
Sodium carbonate	Na_2CO_3, 10 H_20	250	305	395	568
Sodium chloride	NaCl	357	358	360	363
Sodium fluoride	NaF	40	-	42.2	-
Sodium bicarbonate	$NaHCO_3$	69	81.5	96	111
Monosodium phosphate	NaH_2PO_4, 2 H_20	615	735	888	1101
Disodium phosphate	Na_2HPO_4, 12 H_20	233	252	293	424
Trisodium phosphate	Na_3PO_4	15	41	110	200
	Na_3PO_4, 12 H_20	231	257	326	416
Caustic soda	NaOH	420	515	1090	1190

1) These figures correspond to substances dissolved in water containing no other salts.

2) When a reagent has a different formula in its commercial form than the one indicated above, its solubility must be recalculated**.**

• Solubility of calcium sulphate

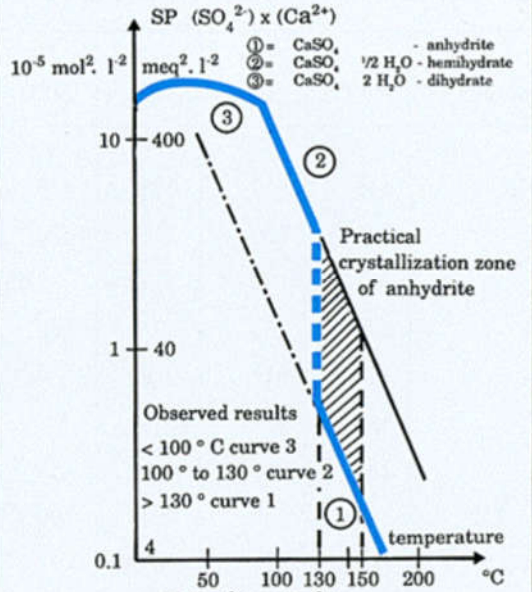


Figure 227 a. Solubility product SP of calcium sulphate in pure water versus temperature.

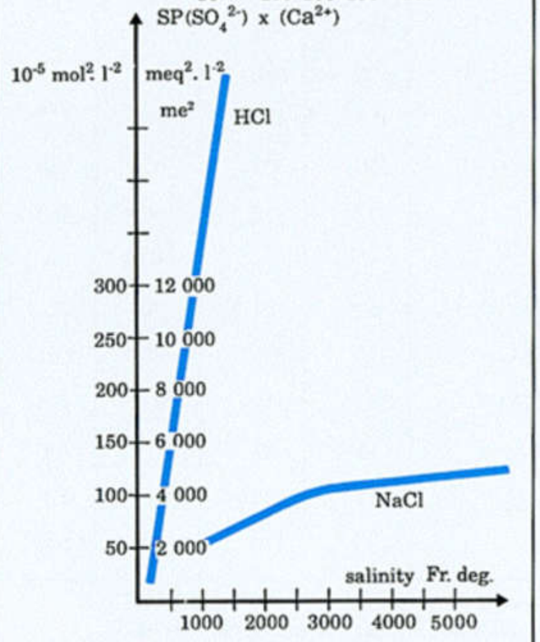


Figure 227 b. Solubility product SP of calcium sulphate versus salinity and at 25°C.

- **Solubility of silica**

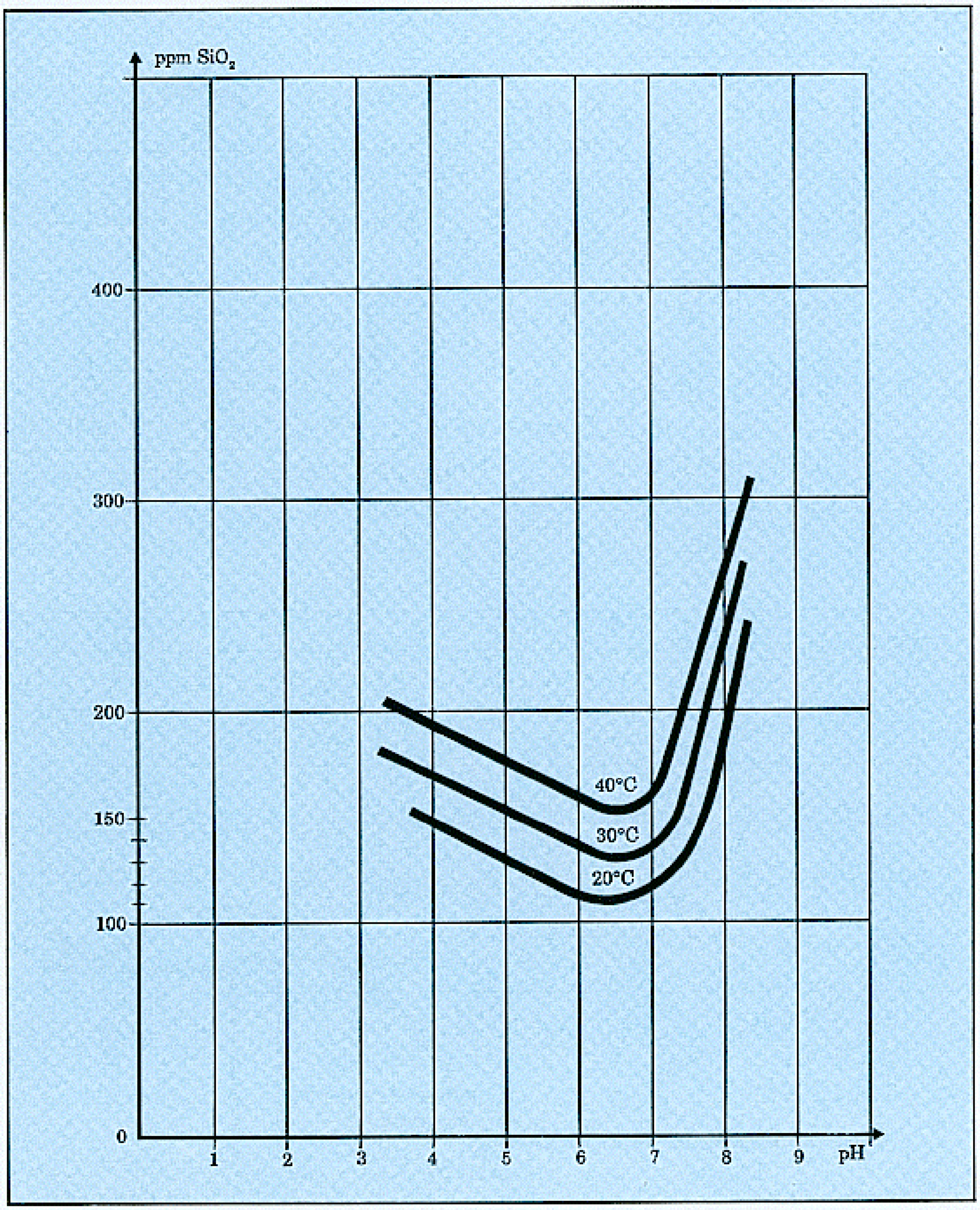


Figure 228. Solubility of silica versus pH and temperature.

Note: these figures correspond to solutions containing no polymerization inhibitors.

3.2.4.2. Caustic soda solution

pH of pure NaOH solutions

pH	**NaOH mg.l**	**pH**	**NaOH mg.l**
7.5	0.013	9.5	1.3
8	0.04	10	4
8.5	0.13	10.5	13
9	0.4	11	40

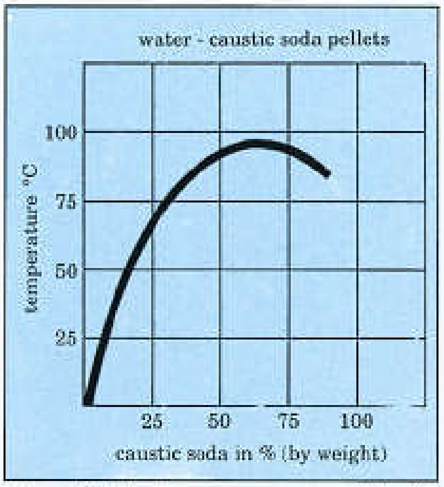


Figure 229. Maximum temperature reached when dissolving pellets.

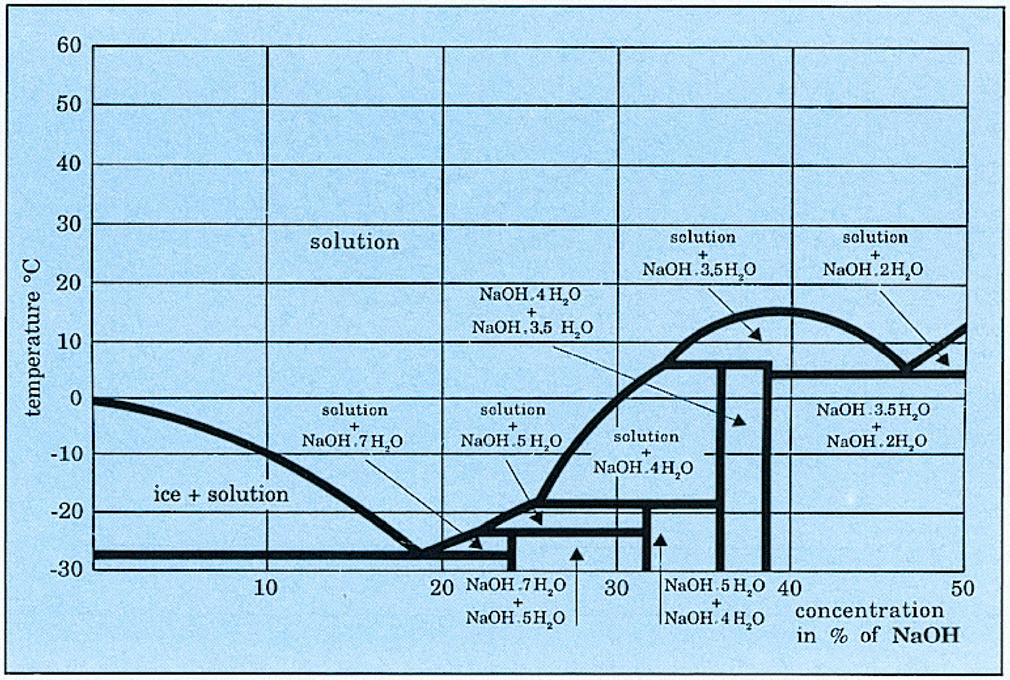


Figure 230. Solubility of caustic soda.

3.2.4.3. Sulphuric acid solutions

H_2SO_4 Concentration		**Density kg.l^{-1} 15°C**	**Melting point °C**	**Specific heat kJ.kg^{-1}, 18°C**
%	**g.1^{-1}**			
5	51.6	1.033	- 2	3.992
10	106	1.068	- 5	3.857
15	165	1.104	- 8	3.666
20	228	1.142	- 14	3.532
25	295	1.182	- 22	3.361
30	365	1.222	- 36	3.200
40	522	1.306	- 68	2.830
50	699	1.399	- 37	2.533
70	1130	1.615	- 41	1.985
90	1640	1.820	- 6	1.659
91	1660	1.825	- 11	1.597
92	1680	1.829	- 24	1.584
93	1700	1.833	- 38	1.513
94	1725	1.836	- 28	1.496
95	1745	1.839	- 19	1.484
96	1770	1.8406	- 11	1.450
97	1786	1.8414	- 5	1.434
98	1804	1.8411	+ 0	1.404
99	1821	1.8393	+ 6	1.409
100	1836	1.8357	+ 10.4	1.400

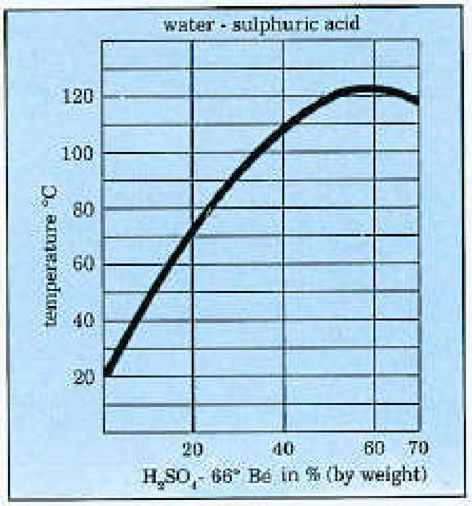


Figure 231. Exothermic reaction produced when mixing water and sulphuric acid.

3.2.4.4. Ammonia and morpholine solutions

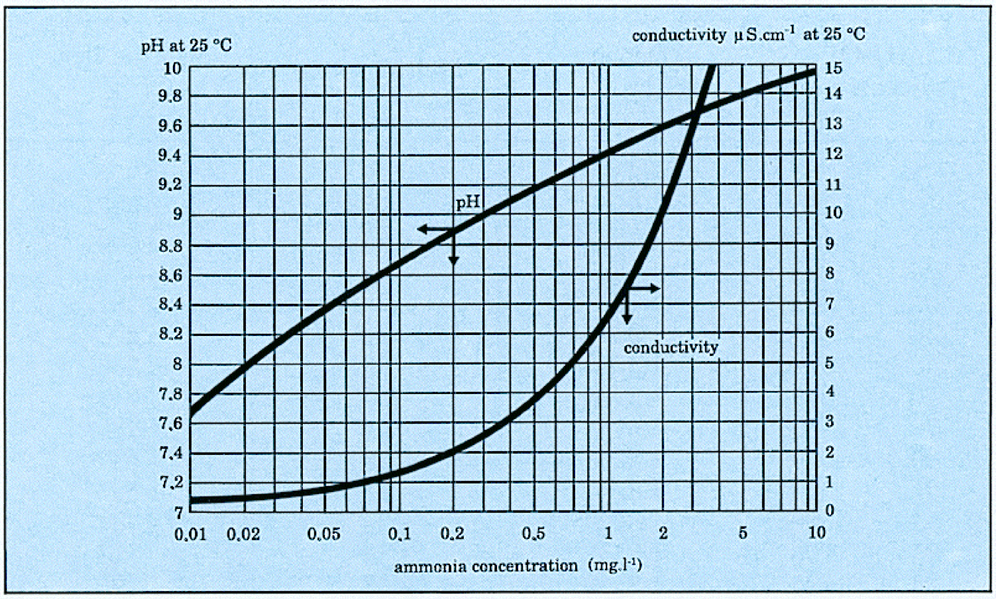


Figure 232. Ammonia solution pH and conductivity at 25°C (according to data provided by EDF laboratory).

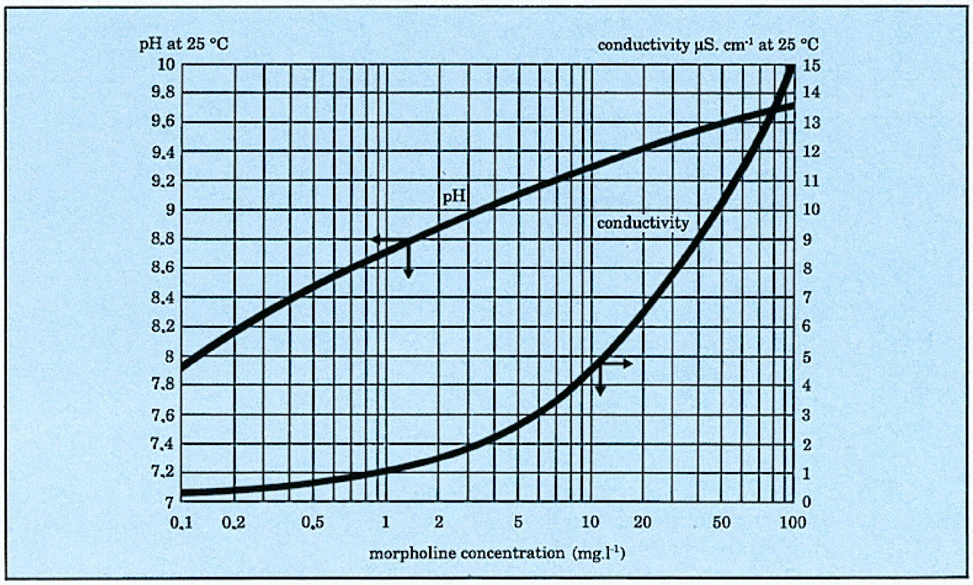


Figure 233. Morpholine solution pH and conductivity at 25°C (according to data provided by EDF laboratory).

3.2.4.5. Ferric chloride solution

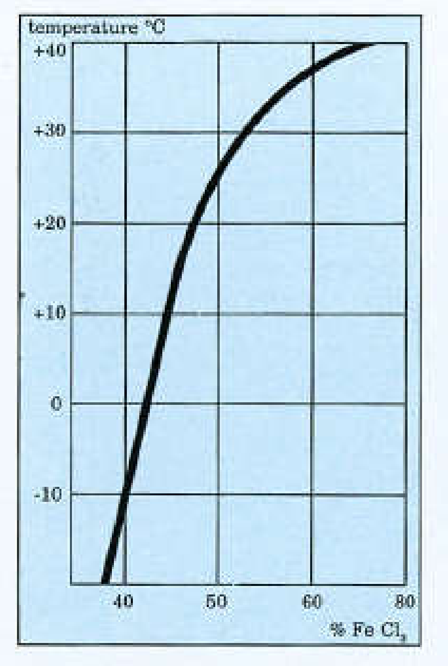


Figure 234. $FeCl_3$ solubility at different temperatures.

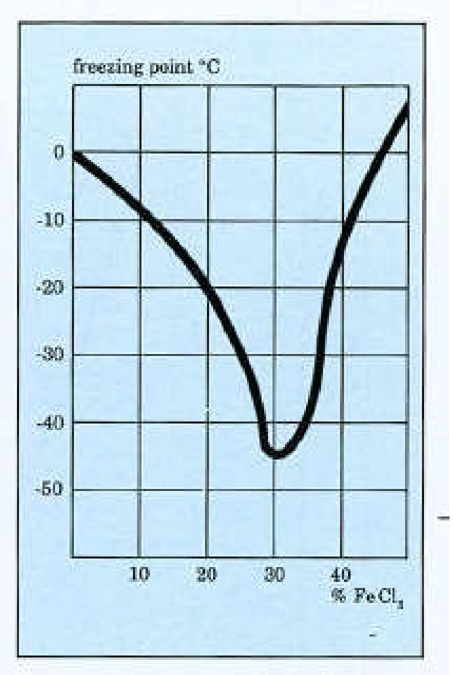


Figure 235. Freezing point of $FeCl_3$ solutions.

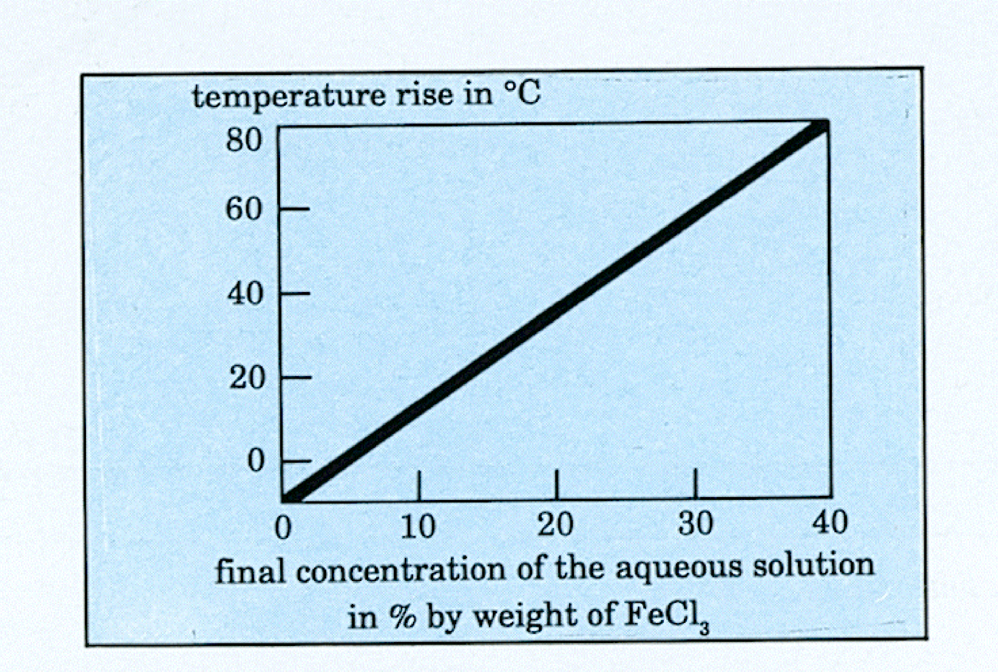


Figure 236. Temperature rise obtained when ferric chloride is dissolved in water.

3.2.4.6. Quick lime

Figure 237 shows:

- the temperature rise,
- the respective concentrations in g.l^{-1} of CaO and $Ca(OH)_2$,
- the specific gravities,

as a function of grammes of water per gramme of CaO dissolved after slaking the quick lime.

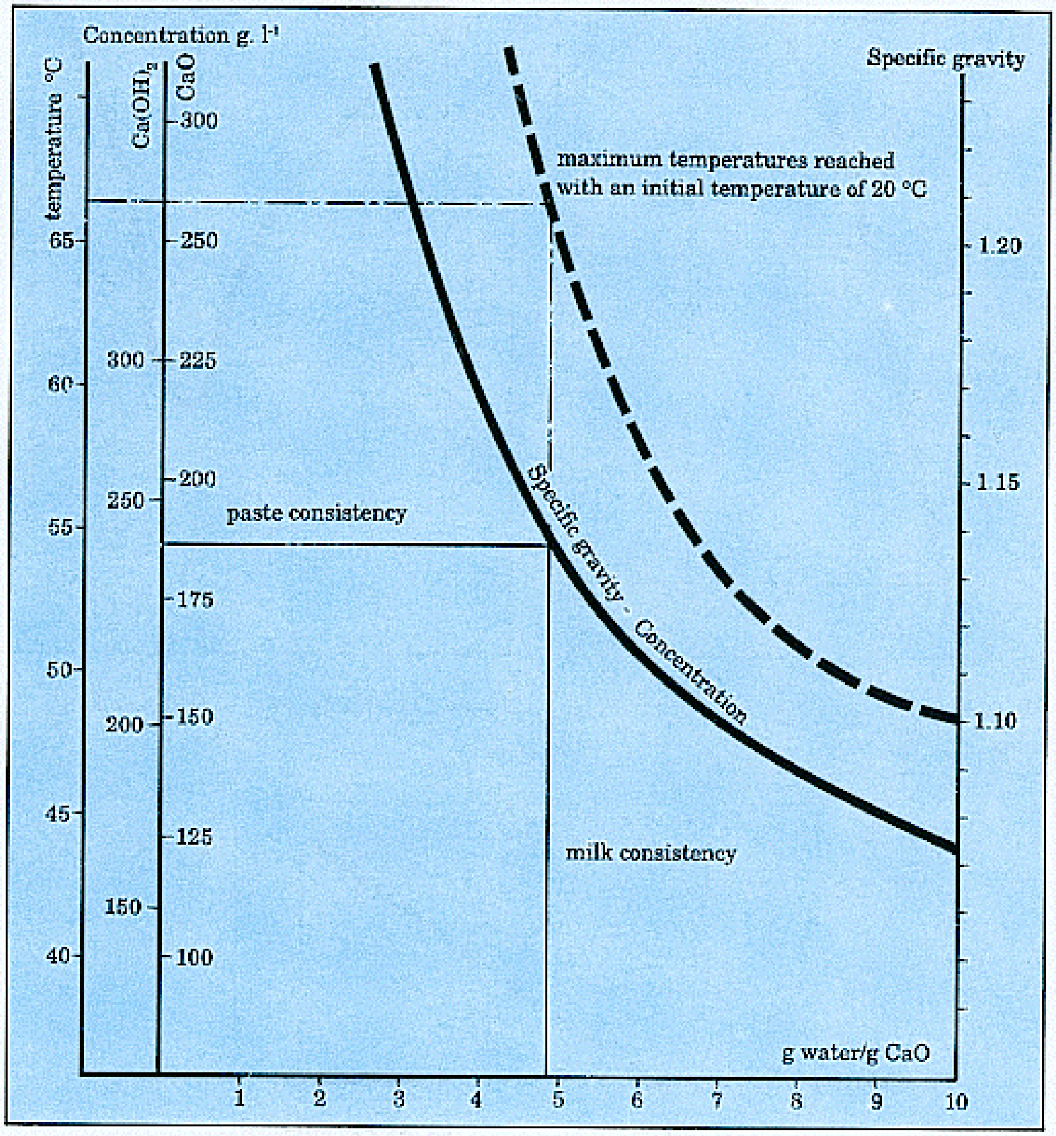


Figure 237. Quick lime slaking.

3.2.5. Table of pK values

Constants of typical acid-base couples in water at 25°C

Acid name	**Acid formula**	**Base Formula**	**pK**
Sulphuric acid	H_2SO_4	HSO_4^-/SO_4^{2-}	1.9
Chromic acid	H_2CrO_4	$HCrO_4/CrO_4^{2-}$	0.7/6.4
Oxalic acid	$H_2C_2O_4$	$HC_2O_4^-/C_2O_4$	1.2/4.1
Phosphorous acid	H_3PO_3	$H_2PO_3^-/HPO_3^{2-}/PO_3^{2-}$	1.6/6.4
Sulphurous acid	H_2SO_3	HSO_3^-/SO_3^{2-}	1.8/7.1
EDTA			2.0/2.7/6.2/10.3
Phosphoric acid	H_3PO_4	$H_2PO_4/HPO_4^{2-}/PO_4^{3-}$	2.2/7.2/12.0
Hydrofluoric acid	HF	F^-	3.2
Nitrous acid	HNO2	NO_2^-	3.4
Formic acid	$HCOOH$	$HCOO^-$	3.7
Cyanic acid	$HCNO$	CNO^-	3.8
Acetic acid	CH_3CO_2H	$CH_3CO_2^-$	4.8
Aluminium ion	$Al^{3+}aq$	$Al\ OH\ ^{2+}aq$	4.9
Carbonic acid	H_2CO_3	HCO_3^-/CO_3^{2-}	6.4/10.2
Hydrogen sulphide	H_2S	HS^-/S^{2-}	7.1/14
Hypochlorous acid	HC1O	$C1O^-$	7.3
Hypobromous acid	HbrO	BrO^-	8.7
Boric acid	H_3BO_3	$H_2BO_3/HBO_3^{2-}/BO_3^{3-}$	9/12.7/13.8
Hydrocyanic acid	HCN	CN^-	9.1
Ammonium ion	NH_4	NH_3 ou NH_4OH	9.2
Hypoiodous acid	HIO	IO^-	10.7
Calcium ion	Ca^{2+}	$CaOH^+/Ca(OH)_2$	11.6/12.6

NOTE: Strong acids and strong bases are considered to be totally dissociated.

3.2.6. COD – BOD_5 - ThOD equivalences of a few organic compounds in g per g of compound

(ThOD = total theoretical oxygen demand)

Nomenclature		COD	BOD_5	ThOD
Organic acids				
- formic	methanoic acid	0.30	0.24	0.34
- acetic	ethanoic acid	1	0.65	1.06
- propionic	propanoic acid	1.4	1.1	1.51
- stearic	octadecanoic acid	1.6	1.4-0.5	2.13
- lactic	2-hydroxypropanoic acid	0.9	0.6	1.06
- citric		0.6	0.4	0.68
- oxalic	ethanedioic acid	0.18	0.15	0.18
- tartaric	racemic acid	0.5	0.3	0.53
Alcohols				
- methyl	methanol	1.4	1.28	1.5
- ethyl	ethanol	2	1.6	2.1
- n-propyl	n-propanol	2.2	1.5	2.4
- isopropyl	2-propanol	2.2	1.2	2.4
- n-butyl	1-butanol	2.4	1.7	2.59
- glycerin	1,2,3-propane-triol	1.1	0.8	1.22
Aldehydes and ketones				
- formic ald.	formaldehyde	1.02	0.9-0.3	1.07
- acetic aid.	acetaldehyde	1.8	1.3	1.82
- furfural	2-furaldehyde	1.6	0.8-0.3	1.66
- acetone	2-propanone	1.9	0.8-0.5	2.2
- methyl ethyl ketone (MEK)	2-butanone	2.3	1.8	2.44
Carbohydrates				
- starch		0.9	0.4-0.8	1.18
- glucose		0.9	0.6-0.8	0.93

Nomenclature		COD	BOD$_5$	ThOD
Amines and amides				
- monoethanolamine (MEA)	2-aminoethanol	1.3	0.95	2.4
- diethanolamine (DEA)		1.5	0.9	2.13
- triethanolamine (TEA)		1.5	0.5	2.04
- acrylonitrile	vinylcyanide	1.4	0.7	3.17
- aniline	aminobenzene	2.4	1.5	3.09
- melamine	2,4,6-triamino-s-triazine	-	0	3.04
- methionine		-	0.4-1.4	2.07
- morpholine	tetrahydro-1,4-oxazine	-	0-0.2	2.6
- urea	carbamide	0	0.1	1.06
- dimethylformamide (DMF)		-	-	1.86
Hydrocarbons				
- n-hexane		0.8	0.3-0	3.5 3
- n-decane		1.6	1.2-0.1	3.49
- n-hexadecane		2.2	0.6-0.1	3.46
- benzene		2.8	2.1-0.5	3.1
- styrene	vinylbenzene	2.9	1.5	3.07
- toluene	methylbenzene	1.8	1.2-0.5	3.13
- lene	dimethylbenzene	2.6	1.6-1	3.12
Heterocyclic compounds				
- pyridine		0.0	0-1.2	3.03
- quinoline		2.3	1.7	2.5
Particular compounds				
- acrolein	propenal	1.7	0	2.0
- acrylamide	propenamide	1.3	0-1	2.35
- caprolactam	cyclohexanone iso-oxime	0.6	0.4	2.12
- epichlorohydrin		1.1	0	1.21
- ethylene oxide	1,2-epoxyethane	1.7	0.1	1.82
- propylene oxide	1,2-epoxypropane	1.8	0.2	2.21
- phenol	h dro benzene	2.3	1.7	2.38
Sulphur compounds				
- sulphurs	SZ-			2
- sulphocyanides	SCN-			2.2
- colloidal S				1.5
- thiosulphates	5203			0.6
- tetrathionates	SAO6			0.5
- sulphites	SO2 3			0.2

Note: The BOD of certain compounds is strongly dependent on either seeding or acclimatization conditions (ketones, SCN^-, etc.), or on initial concentration, whose increase causes reduced degradability (aromatic hydrocarbons in particular).

3.3.
CHARACTERISTIC CONSTANTS OF GASES

3.3.1. Density of gases

If M_o is the mass of a litre at 0°C, the mass of a litre at t 'C at the same pressure is:

If M_o is the mass of a litre at a pressure of 760 mm of mercury, the mass of a litre at the real pressure P is:

3.3.2. Solubility of the main gases in water

The dissolved gas content of a liquid can be calculated by means of the following formula, based on Henry's law constant (figure 238):

$$Py_i = Hx_i$$

P = total pressure of the gas.
H = Henry's law constant expressed in the same unit as P
x_i = mole fraction of the gas in the liquid.
y_i = mole fraction of the gas in the gaseous mixture

Gas	**Sp. gr. in relation to air**	**Mass per litre at 0°C and at 760 mm of mercury, in g**
Air	1	1.29349
Oxygen 0_2	1.1052	1.4295
Nitrogen N_2	0.967	1.2508
Hydrogen H_2	0.06948	0.08987
Carbon dioxide CO_2	1.5287	1.978
Chlorine $C1_2$	2.491	3.222
Ammonia NH_3	0.5971	0.772
Sulphur dioxide SO_2	2.263	2.927
Hydrogen sulphide $H2_S$	1.1895	1.539

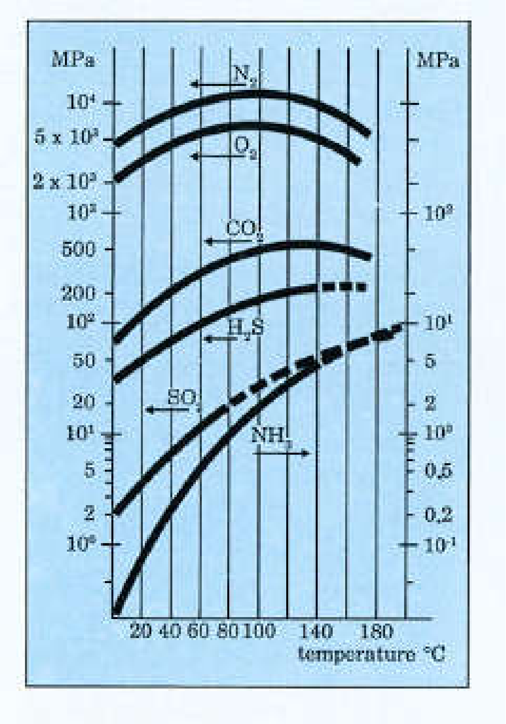


Figure 238. Henry's law constant for various gases.

Normal litres of gas per litre of water in an atmosphere of pure gas at a pressure of 1 bar.

Temperature °C	**Gas**							
	Air	O_2	N_2	CO_2	H_2S	$C1_2$	NH_3	SO_2
0	0.0288	0.0489	0.0235	1.713	4.621	4.61	1135	75.00
5	0.0255	0.0429	0.0208	1.424	3.935	3.75	1005	62.97
10	0.0227	0.038	0.0186	1.194	3.362	3.095	881	52.52
15	0.0205	0.0342	0.0168	1.019	2.913	2.635	778	43.45
20	0.0187	0.0310	0.0154	0.878	2.554	2.260	681	36.31
25	0.0172	0.0283	0.0143	0.759	2.257	1.985	595	30.50
30	0.0161	0.0261	0.0134	0.665	2.014	1.769	521	25.87
35	0.0151	0.0244	0.0125	0.592	1.811	1.570	460	22.00
40	0.0143	0.0231	0.0118	0.533	17.642	1.414	395	18.91
50	0.0131	0.0209	0.0109	0.437	1.376	1.204	294	15.02
60	0.0123	0.0195	0.0102	0.365	1.176	1.006	198	11.09
70	0.0118	0.0183	0.0097	0.319	1.010	0.848		8.91
80	0.0116	0.0176	0.0096	0.275	0.906	0.672		7.27
90	0.0115	0.0170	0.0095	0.246	0.835	0.380		6.16
100	0.0115	0.0169	0.0095	0.220	0.800			
110		0.0172		0.204				
120		0.0176		0.194				
130		0.0183						
140		0.0192						

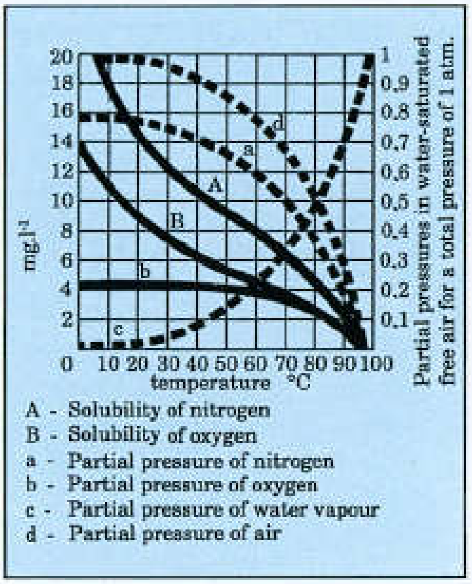


Figure 239. Solubility (in mg.l⁻¹) of air gases in water at atmospheric pressure.

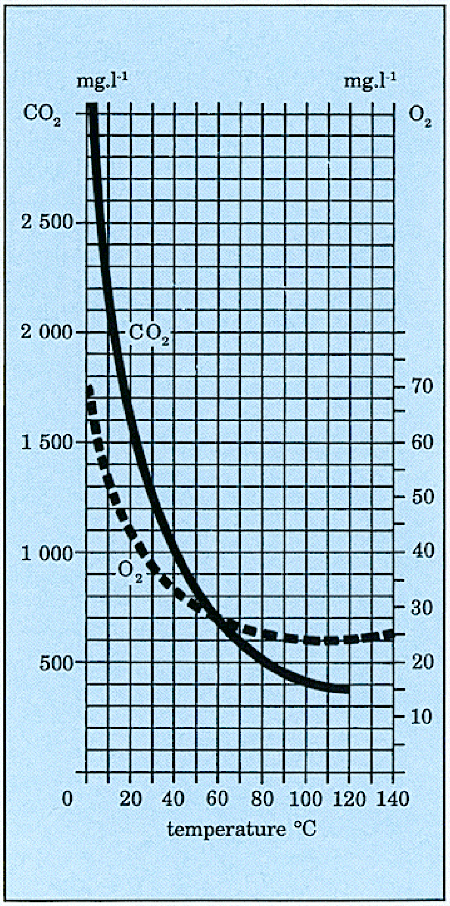


Figure 240. Solubility of CO_2 and O_2 in water (in mg.l⁻¹ of gas per litre of water) at atmospheric pressure and in an atmosphere of pure gas.

3.3.3. Kinematic viscosity of common gases

Particular cases among common gases

The table below shows the values in m^2s^{-1} of kinematic viscosity V, which varies as a function of temperature, at a normal pressure of 760 mm of mercury.

Due to pressure variations, the above figure must be corrected using the following relation (not valid for water vapour):

$$\nu' = \nu \frac{P}{P'}$$

where:

V' = corrected kinematic viscosity, in $m^2.s^{-1}$,

P' = true absolute pressure,

P = normal absolute pressure expressed in the same unit as P'.

p', the density of the fluid in kg.m 3, at temperature t' (°C) and absolute flow pressure P', is deduced from p, the density in normal conditions according to the formula:

$$\rho' = \rho \times \frac{P'}{P} \times \frac{273}{273 + t'}$$

t°C	0	20	40	60	80	100
Air	13.20×10^{-6}	15.00×10^{-6}	16.98×10^{-6}	18.85×10^{-6}	20.89×10^{-6}	23.00×10^{-6}
Water vapour	11.12	12.90	14.84	16.90	18.66	21.50
$C1_2$	3.80	4.36	5.02	5.66	6.36	7.15
CH_4	14.20	16.50	18.44	20.07	22.90	25.40
CO_2	7.00	8.02	9.05	10.30	12.10	12.80
NH_3	12.00	14.00	16.00	18.10	20.35	22.70
0_2	13.40	15.36	17.13	19.05	21.16	23.40
SO_2	4.00	4.60				7.60

3.3.4. Absolute humidity of saturated ambient air versus dew point.

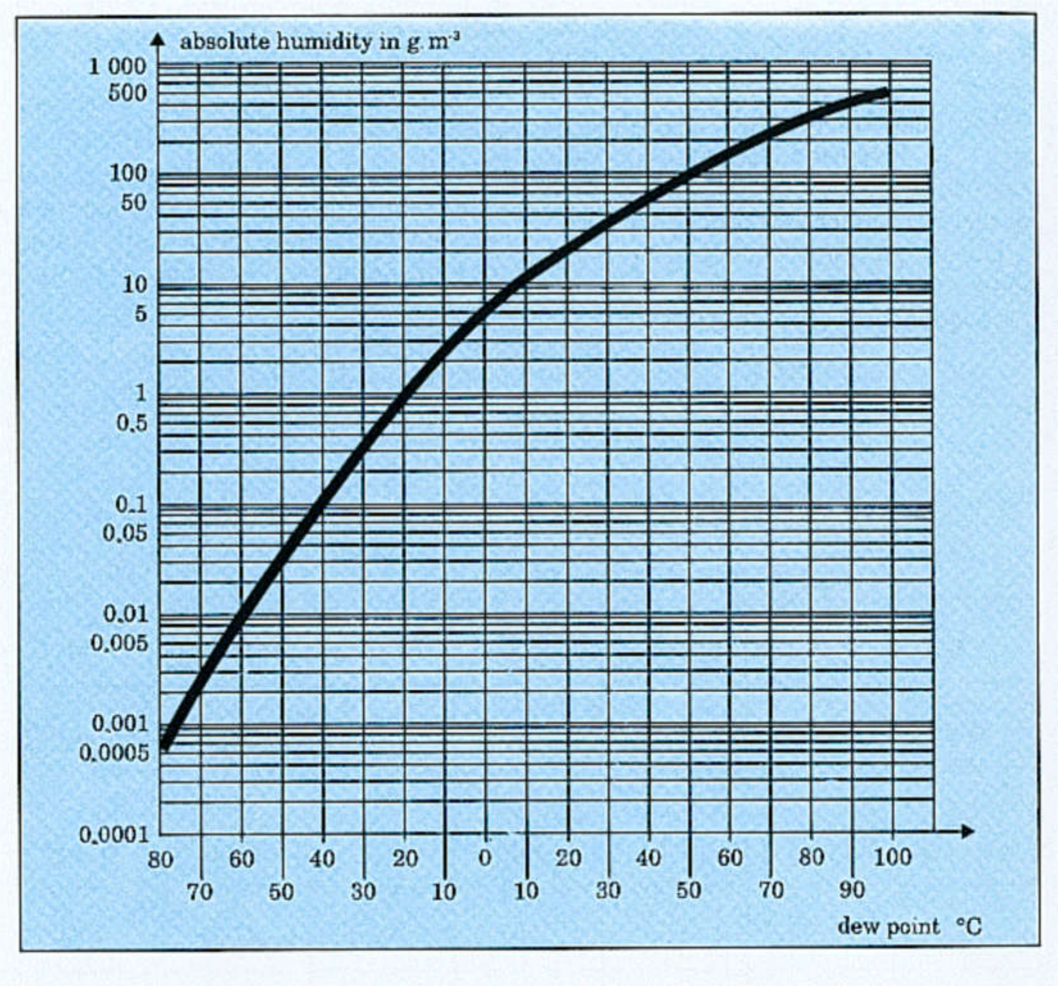


Figure 241. Absolute humidity of ambient air.

3.3.5. Chlorine

3.3.5.1. **General characteristics**

Chlorine is a greenish-yellow gas in its normal state, characterized by the following physical constants:

- sp. gr. in relation to air	2.491
- atomic weight	CI = 35.46
- boiling point at 100 kPa	-34.1°C
- freezing point	-102°C
- critical temperature	144°C
- critical pressure	7,710 kPa
- specific heat of the gas	0.518 kJ.kg^{-1} (0.124 kcal.kg^{-1})
- specific heat of the liquid	0.92 kJ.kg 1 (0.22 kcal.kg 1)

At 15°C and 760 mm Hg, 1 kg of chlorine generates 314 litres of chlorine gas, and 1 litre of liquid chlorine corresponds to 456 litres of gas. Chlorine gas is liquefied by cooling and compression under a pressure that varies with temperature:

1,000 kPa at 40°C; 500 kPa at 18°C.

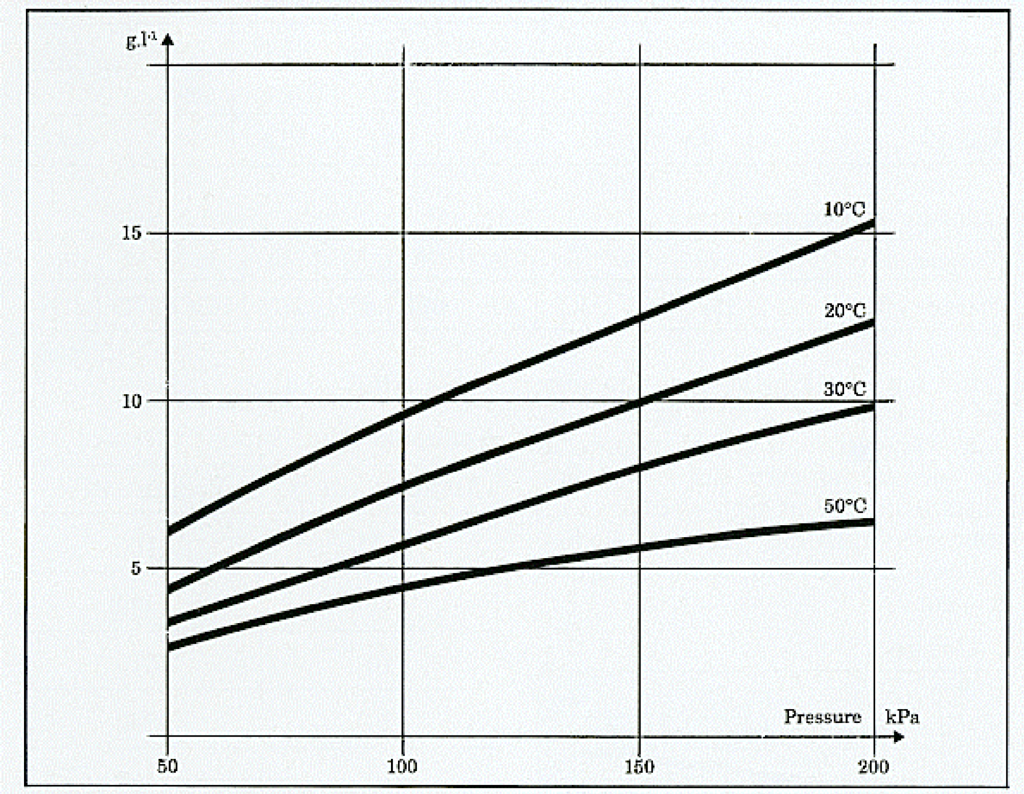


Figure 242. Solubility of chlorine in water.

3.3.5.2. The influence of temperature and pressure

Heat of vaporization

Temperature °C	0	10	20	30	40	50	60
J.mole $^{-1}$	17.64	17.14	16.59	16.01	15.47	14.88	14.30
kJ.kg $^{-1}$	249.1	242	234.1	226.1	218.2	209.8	201.5
kcal.kg $^{-1}$	56.6	58.9	56.1	54.1	52.2	50.2	49.2

Chlorine vapour pressure

Température °C	-30	-20	-10	0	10	20	30	40	50	60	70
Pressure kPa	**121**	**181**	**261**	**367**	**501**	**670**	**877**	**1127**	**1426**	**1779**	**2193**

Chlorine is an irritating and suffocating gas that is not corrosive in its pure, dry state. However, it is highly corrosive in the presence of even slight humidity.
Characterized by its high reactivity with most elements, this gas can produce explosive reactions with ammonia, hydrogen, etc.

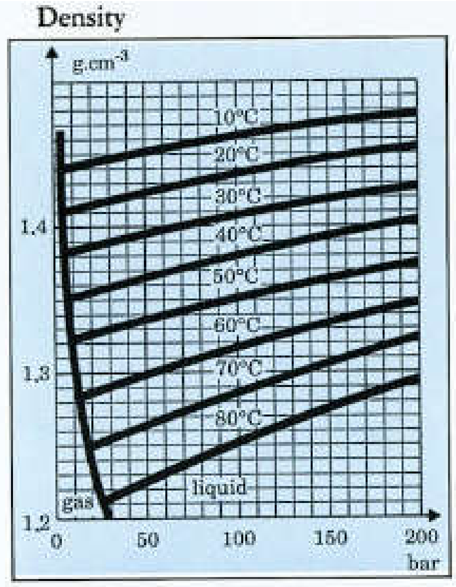


Figure 243. Density variations of chlorine.

Figure 243. Density variations of chlorine

3.3.6 Ammonia

Ammonia water vapour pressure

Temperature °C	Pressure kPa
- 31	100
0	420
10	610
20	850
30	1160
40	1570
50	1960

Legislation states that ammonia should be stored in containers certified at 2,000 kPa and tested to 3,000 kPa.

3.3.7. Ozone

3.3.7.1. Solubility of ozone in water

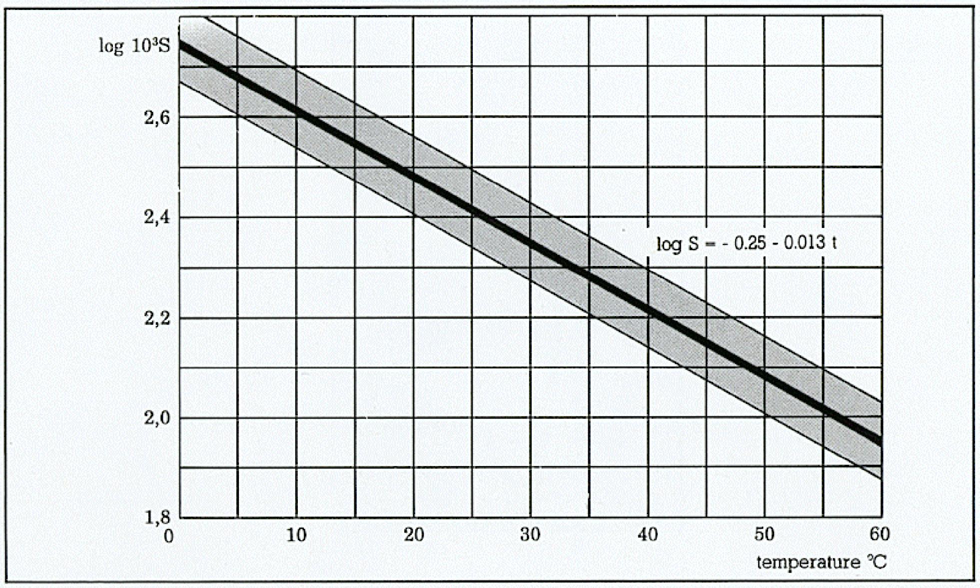
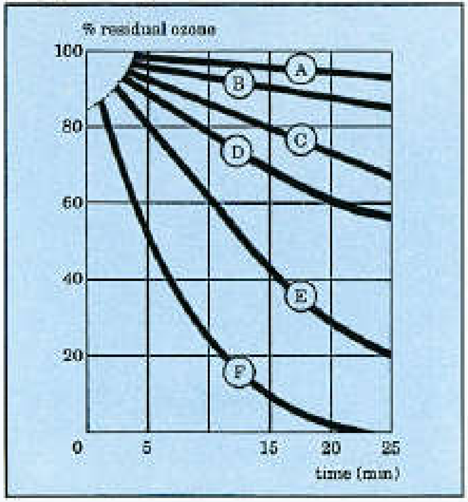


Figure 244. Solubility of ozone in water. S = mg per litre in water/mg per litre in the carrier gas.

Figure 244, Solubility of ozone in water. S = mg per litre in waterlmg per litre in the carrier gas.

3.3.7.2. Changes in the residual ozone as a function of pH and the water temperature



	Temperature °C	pH
A	1	7.6
B	10	7.6
C	15	7.6
D	20	7.6
E	15	8.5
F	15	9.2

Figure 245. Disappearance of residual ozone.

3.4. LIMITS OF PRECIPITATION OF METALS IN THEIR HYDROXIDE FORM

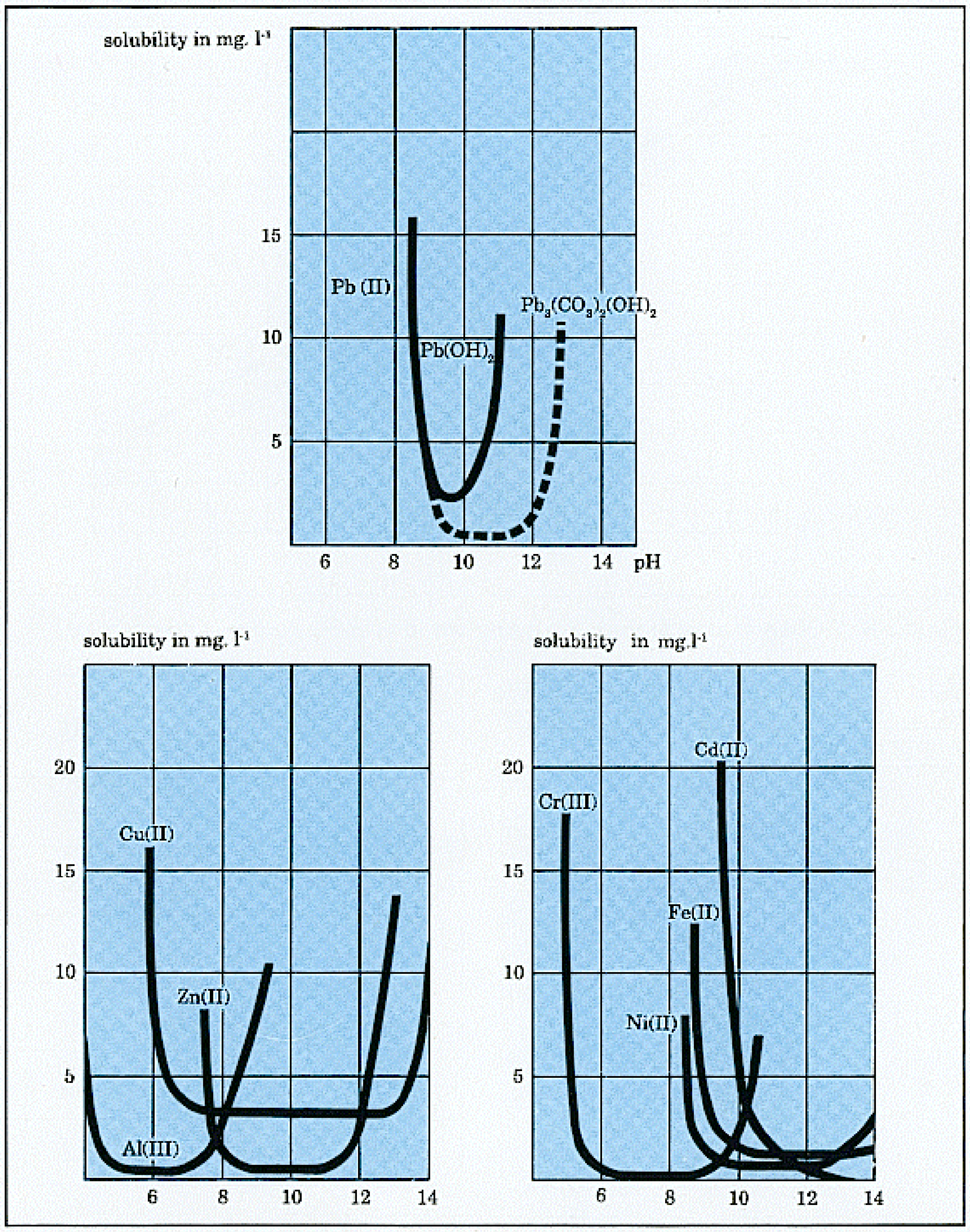


Figure 246. Solubility of metals as a function of pH.

3.5. THE MAIN REAGENTS USED IN WATER TREATMENT

3.5.1. Clarification

Reagent	Gramme-molecular weight	Use	Available forms	Characteristics	Specific gravity*	Solubility at 20°C	Crystallization point °C	Comments
Aluminium sulphate $Al_2(SO_4)_3.18H_2O$	666	Coagulation	Broken lumps Granules Powder	17 to 18% Al_2O_3	1	660 $g.l^{-1}$		Fairly safe acid product
			Liquid	7.5 to 8% Al_2O_3 (630 to 650 $g.l^{-1}$ as $Al_2(SO_4)_3.18H_2O$)	1.45		+ 3	
Aluminium hydroxy-chlorosulphate $Cl_{(m)}SO_{4(n)}$ $Al(OH)_{3-(m+2n)}$		Coagulation	Liquid	Al_2O_3 10% by weight				Acid product Many products available on the market
Ferrous sulphate $FeSO_4.7H_2O$	278	Coagulation	Green powder	20% Fe	0.9	390 $g.l^{-1}$		Fairly safe acid product
Ferric sulphate $Fe(SO_4)_3.9H_2O$	562	Coagulation	White powder	25 to 26% Fe	1.0	Very soluble		Corrosive acid product
Ferric chloride								
● $FeCl_3.6H_2O$ solid	270	Coagulation	Crystallized Sublimated	60% $FeCl_3$ 99% $FeCl_3$		1026 $g.l^{-1}$		Corrosive acid product Melts at 34°C
● $FeCl_3$(35%) in solution	162	Coagulation	Liquid	41% $FeCl_3$ (600 $g.l^{-1}$)	1.45	-	- 10	
Chlorinated copperas $FeClSO_4$	187	Coagulation	Reddish-brown solution	14% de Fe (200 $g.l^{-1}$)	1.5	-	- 8	Acid product (solution crystallized at 160 $g.l^{-1}$: -30°C). Trade name: Clairtan
Sodium silicate $nSiO_2.Na_2O$	122	Floculation (preparation of the activated silica)	Liquid	24-26% SiO_2 26-28% SiO_2 27-28% SiO_2	1.35 1.38 1.4		0	Viscous solutions
Sodium aluminate $nNa_2O.Al_2O_3.H_2O$	-	Floculation Silica removal	Crystallized	20 to 40% Al_2O_3 35% Na_2O	1	1000 $g.l^{-1}$		
			Liquid	21% Al_2O_3 (310 $g.l^{-1}$) 18% Na_2O 60% H_2O	1.48	-	- 20	

* The specific gravities of solids are their bulk densities.

3.5.2. Adds

Reagent	Gramme-molecular weight	Use	Available forms	Characteristics	Specific gravity*	Solubility at 20°C	Crystallization point °C	Comments
<u>Sulphuric acid</u> H_2SO_4	98	Demineral. Neutral.	Liquid	92% 96% 98%	1.83 1.84 1.84		- 24 - 11 0	Highly dangerous acid Considerable heat release during dilution
<u>Hydrochloric acid</u> HCl	35.5	Demineral. Neutral.	Liquid	33 to 35% HCl (380 to 410 $g.l^{-1}$)	1.18		- 30 to - 40	Highly dangerous strong acid
<u>Nitric acid</u> HNO_3	63	Demineral. Neutral.	Colourless liquid	56 to 58% HNO_3 (750 $g.l^{-1}$) 92.6% HNO_3	1.35		-	Highly dangerous strong acid. Powerful oxidizing agent capable of reacting with organic matter Fuming nitric acid

3.5.3. Bases

<u>Caustic soda</u> NaOH	40	Demineral. Neutral.	Solid in flakes Liquid	98% NaOH 33% (450 $g.l^{-1}$) 49% (790 $g.l^{-1}$)	 1.36 1.51	52%, i.e., 800 $g.l^{-1}$	 + 7 + 10	Highly dangerous caustic agent
<u>Sieved lime</u> $Ca(OH)_2$	74	Flocculation Lime softening Neutral. Remin.	Powder characterized by sieve mesh size	92 to 99% $Ca(OH)_2$	0.4 to 0.5	1.6 $g.l^{-1}$		Most widely used sieve Sieve 120, particles of 50 to 60 microns
<u>Quick lime</u> CaO	56	Flocculation Lime softening Neutral.	Powder or granules	90 to 95% CaO	0.8 to 1.2	1.3 $g.l^{-1}$		Highly hygroscopic, dangerous caustic agent Exothermic reaction during dilution
<u>Ammonia</u>	35	Demineral. Conditioning	Liquid	28% NH_3 64% NH_4OH 20% NH_3	0.92 0.95		-	Alkaline agent

The specific gravities of solids are rhea bulk densities.

3.5.4. Disinfection

Reagent	Gramme-molecular weight	Use	Available forms	Characteristics	Specific gravity*	Solubility at 20°C	Crystallization point °C	Comments
Sodium chlorite $NaClO_2$	90.5	Disinfection for preparation of chlorine dioxide	Crystallized in needles	80% $NaClO_2$	0.65	390 $g.l^{-1}$	-	Irritant Avoid contact with organic and reducing substances (wood, paper, cloth, etc.) Danger of explosion
			Solution	25% $NaClO_2$	1.21		- 8 to - 10	
Sodium hypochlorite NaClO (Bleach)	74.5	Disinfection	Greenish-yellow liquid	47 to 50° chlorometric corresponding to 150 $g.l^{-1}$ of available Cl_2	1.21		- 15	Oxidizing base Unstable solution
Calcium hypochlorite $Ca(ClO)_2.2H_2O$	179	Disinfection	Powder	92 to 94% 600 $g.kg^{-1}$ of available Cl_2	1	Highly soluble (See comments)	-	Oxidizing agent. Due to impurities contained, do not exceed a concentration of 60 $g.l^{-1}$
Potassium permanganate $KMnO_4$	158	Disinfection Oxidation	Powder of purple flakes		0.8 to 1.2	30 $g.l^{-1}$	-	Oxidizing agent
Hydrogen peroxide H_2O_2	34	Disinfection Oxidation	Colourless liquid	35% H_2O_2 50% H_2O_2 70% H_2O_2	1.13 1.19 1.29		- 33 - 43 - 38	Non-toxic irritant. Keep at a safe distance from flammable materials

3.5.5. Reagents used for carbonate removal

Sodium carbonate $Na_2CO_3.10H_2O$	286	Flocculation Neutralization Carb. removal	Solid White powder	99% Na_2CO_3	2.53	395 $g.l^{-1}$	-	Alkaline product, little danger
Magnesium chloride $MgCl_2.6H_2O$	203	Carb. removal	Crystallized	19% MgO		1.67 $g.l^{-1}$	-	
Magnesium oxide MgO	40	Carb. removal (silica removal)	Powder	98% MgO		Sparingly soluble (6 $mg.l^{-1}$)		Use the magnesium oxide obtained by precipitation

The specific gravities of solids are their bulk densities.

3.5.6 Conditioning of boiler water

Reagent	Gramme-molecular weight	Use	Available forms	Characteristics	Sp. gr.*	Solubility at 20°C	Crystallization point °C	Comments
Disodium phosphate $Na_2HPO_4.12H_2O$	358	Conditioning	Crystallized	20% P_2O_5	1.52	290 $g.l^{-1}$		Alkaline product, little danger, soluble at 34°C: 874 $g.l^{-1}$
Trisodium phosphate $Na_3PO_4.12H_2O$	380	Conditioning	Crystallized	20% P_2O_5	1.62	326 $g.l^{-1}$		Solubility at 80°C: 1570 $g.l^{-1}$

3.5.7. Polyelectrolytes

Coagulant Kemazur 4516	10^4	Clarification Filtration Flotation	Liquid (solution)	Polyamine pH = 2.5 intermediate cation	1.06	Miscible with water in any proportions	- 2	Unstable when highly diluted (< 5%) Requires no prior preparation
Coagulant Kemazur 4553	5×10^4	Clarification Filtration Flotation	Liquid (solution)	Polyamine pH = 5.5 strong cation	1.16	Miscible with water in any proportions	- 18	do.
Cationic flocculant type CS 245	1.1×10^7	Dewatering of organic sludge	Powder	Acrylamide copolymer bulk density 0.85	1 in solution	5 $g.l^{-1}$	0	Viscosity 750 cp at 5 $g.l^{-1}$
Anionic flocculant type AS 25 or ASP 25	10^7	Clarification	Powder	Acrylamide copolymer bulk density 0.8	1 in solution	5 $g.l^{-1}$	0	Viscosity 120 cp at 5 $g.l^{-1}$
Cationic flocculant type PE 23	6×10^6	Clarification Flotation	Liquid (emulsion)	Acrylamide copolymer emulsion in a solvent	1.02	10 $g.l^{-1}$	- 10	Preparation similar to that of powders
Anionic flocculant type PE 14	1.5×10^7	Clarification Flotation	Liquid (emulsion)	Acrylamide copolymer emulsion in a solvent	1.02	15 $g.l^{-1}$	- 10	do.

The specific gravities of solids are their bulk densities.

3.5.8. Oxidizing agents

Reagent	Gramme-molecular weight	Use	Available forms	Characteristics	Specific gravity*	Solubility at 20°C	Crystallization point °C	Comments
Persulphuric acid H_2SO_5	114	Oxidizing agent Cyanide removal	Liquid	200 g.l^{-1} H_2SO_5	1.3		- 25	Dangerous acid product (active oxygen 2.1%) Trade name: Caro's acid
Sodium hypochlorite	see 3.5.4.							
Calcium hypochlorite	see 3.5.4.							
Potassium permanganate	see 3.5.4.							
Hydrogen peroxide	see 3.5.4.							

3.5.9. Reducing agents

Sodium bisulphite $NaHSO_3$	84	Deoxygenation Dechlorination	Liquid	23 to 25% SO_2 (300 g.l^{-1})	1.32		+ 3	Corrosive
Sodium thiosulphate (or sodium hyposulphite) $Na_2S_2O_3$	118	do.	Powder		1.2	700 g.l^{-1}	-	Reducing alkaline agent
Sodium sulphite $Na_2SO_3.7H_2O$	252	do.	Crystallized	48% SO_2		See comments	-	Neutral agent Solubility at: 0°C 328 g.l^{-1} 40°C 1960 g.l^{-1}
Anhydrous sodium sulphite Na_2SO_3	126	do.	Crystallized	60% to 62% SO_2		See comments	-	Solubility at: 0°C 125 g.l^{-1} 40°C 283 g.l^{-1}

3.5.10. Miscellaneous

Phosphoric acid H_3PO_4	98	Nutrient	Liquid	45% H_3PO_4 61% H_3PO_4	1.45 1.72		-	Dangerous acid
Ammonium sulphate $(NH_4)_2SO_4$	132	Nutrient	Greenish powder	20 to 21% N 23 to 24% S	1.77	See comments		Solubility 0°C 706 g.l^{-1} 100°C 1040 g.l^{-1}

The specific gravities of solids are their bulk densities.

Reagent	Gramme-molecular weight	Use	Available forms	Characteristics	Specific gravity*	Solubility at 20°C	Crystallization point °C	Comments
Diammonium phosphate $(NH_4)_2HPO_4$	132	Nutrient	Solid (powder)	40% N		See comments		Solubility: at 10°C 575 $g.l^{-1}$ at 70°C 1060 $g.l^{-1}$
Calcium carbonate $CaCO_3$	100	Mineralization Neutralization Sludge treatment	Crystallized		2.70	14 $mg.l^{-1}$		Harmless Used in suspension
Sodium bicarbonate $NaHCO_3$	84	Readjustment of titers	Crystalline powder	99.7%	2.22	96 $mg.l^{-1}$		Harmless Bulk density through compaction: 0.9 to 1.4
Sodium chloride NaCl (sea salt)	58.5	Softening (regeneration)	Crystallized Granulated Pellets	97% NaCl	2.16	300 $g.l^{-1}$		Harmless
Sodium fluoride NaF	42	Fluoridation of water	White crystallized powder			43 $g.l^{-1}$		Dangerous corrosive
Citric acid $C_6H_8O_7$	192	Cleaning osmosis membranes	White crystallized powder or colourless crystals		1.52	Highly soluble		Fairly safe acid

* The specific gravities of solids **are their bulk densities.**

3.5.11. Gases

Reagent	Gramme-molecular weight	Use	Appearance	Sp. gr. in relation to air	Liquefaction at atm. pressure °C	Comments
Sulphur dioxide SO_2	64	Chromate removal Reduction	Colourless gas	2.264	-10	Highly irritating gas
Ammonia NH_3	17	Conditioning Demineralization	Colourless gas	0.597	-33	Highly irritating gas soluble in water. 33% by weight at 20°C
Chlorine Cl_2	70.9	Oxidation Disinfection	Greenish-yellow gas	2.49	-34	Highly irritating gas, solubility in water: 7.3 $g.l^{-1}$ at 20°C
Carbon dioxide CO_2	44	Mineralization	Colourless gas	1.96	-78	Must be of food-grade quality when used in drinking water

4. HYDRAULICS

4.1.
FRICTION LOSSES IN WATER PIPES

4.1.1. Empirical formulae

Many authors, including Prony, Flamant, Darcy and Levy, have attempted to calculate this head loss, and the empirical formulae they proposed were based on a few tests involving pipe work and couplings that are no longer in use. Furthermore, these formulae had limited applications and did not reflect the physical reality of phenomena, so that results obtained were sometimes very approximate. For all these reasons, they are now scarcely used.

The Williams and Hazen empirical formula, although not recently developed, is still in use in the USA. Expressed in metric units, it is written as follows:

$$J = 6{,}815 \left(\frac{V}{C_{wh}}\right)^{1{,}852} D^{-1{,}167}$$

where coefficient Ch varies with the diameter of the conduits and the inner wall surface.

4.1.2. Colebrook's formula derived from Nikuradsé's experiments

$$J = \frac{\lambda}{D} \cdot \frac{V^2}{2\,g}$$

$$\frac{1}{\sqrt{\lambda}} = -\,2 \log\left(\frac{k}{3{,}7\,D} + \frac{2{,}51}{Re\sqrt{\lambda}}\right)$$

J = friction loss, in m WC per m of pipe.

λ = head loss coefficient.

D = pipe diameter, or hydraulic diameter, in m (see par. 4.5.13 for non-cylindrical pipes).

V = flow velocity, in $m.s^{-1}$

g = acceleration of gravity, in $m.s^{-2}$ (_ 9.81 in Paris).

equivalent roughness coefficient of the pipe wall, in m.

Re = Reynolds number = $\frac{VD}{\nu}$,

where the kinematic viscosity ν of water (in $m^2.s^{-1}$) has the following values at normal pressure:

t°C	0	5	10	15	20	30	40	50	60	70	80	90	100
$\nu \times 10^6$	1.792	1.52	1.31	1.14	1.006	0.80	0.66	0.56	0.48	0.41	0.36	0.33	0.30

Selecting the roughness coefficient

The accuracy of results in friction loss calculations depends on the initially selected roughness coefficient. For water pipes, this coefficient is related both to the nature of pipe walls, to their change overtime, and the physical and chemical characteristics of the conveyed water.

- Smooth non-corrodible pipes and unlikely deposit formation
- These conditions are applied to water

with a low suspended solids content, flowing through pipes made of plastic, asbestos-cement, spun cement or any material that is non-corrodible or has a high quality smooth lining. For practical purposes, roughness coefficient k = 0.1 mm should be used, due to the slight changes that inevitably occur over time, although k = 0.03 mm is accepted in theory for new pipes.

The following table shows roughness coefficients k for all commonly used materials, under average conditions of use, including seals:

Material .	**k (mm)**	**Material**	**k (mm)**
New steel	0.1	New brass, copper, lead	0.01
plastic lining	0.03	New aluminium	0.015-0.06
non-porous, smooth lining		New spun concrete	0.03
New cast iron	0.1-1	new/smooth moulds	0.2-0.5
asphalt lining	0.03-0.2	new/rough moulds	1.0-2.0
cement lining	0.03-0.1	New asbestos-cement	0.03-0.1
Plastics	0.03-0.1	Vitrified clay	-
			0.1-1

- Corrodible pipes and likely deposit formation

When water that is relatively aggressive, corrosive, scale-forming or that has a high suspended solids content flows through this type of pipe, the mean roughness coefficient k can reach up to approximately 2 mm. The coefficient for non-chlorinated, mildly aggressive, mildly scale-forming water is k = 1 mm. For raw water with a low suspended solids content, and filtered water that is neither aggressive nor scale-forming and that has been treated for algae, it is taken to be k = 0.5 mm.

With water of average quality, head loss J in the following tables can be initially determined as the arithmetic mean of the values in the columns headed .new pipes. and "clogged pipes".

. Calculations according to the Standard Chart

This chart (figure 247), applicable to industrial pipes with walls of varying roughness, gives the different values of coefficient X, used in the Colebrook equation as a function of Reynolds number Re of real flow conditions, as well as the relative roughness of the pipe walls . $\frac{k}{D}$

Table 58 gives the different values of ratio $\frac{\lambda}{D}$ taken from the Standard Chart for a few typical values of coefficient k.

This ratio facilitates calculations by determining a global value of the friction and minor losses, Oh, expressed in metres of water column:

$$\Delta h = JL + K\frac{V^2}{2\,g} = \left(\frac{\lambda}{D}L + K\right)\frac{V^2}{2\,g}$$

where:

L = total pipe segment length in m, at flow velocity V in m.s $^{-1}$,

K = sum of the head loss coefficients corresponding to the successive minor losses in this pipe segment (see par. 4.2).

Note: if Le is the straight pipe length equivalent to the successive points of local minor losses of the pipe section, the following relations are obtained:

$$Le = \frac{K}{\frac{\lambda}{D}} \qquad \Delta h = \frac{\lambda}{D}(L + Le)\frac{V^2}{2g}$$

4.1.3. Pipes with various cross-sectional shapes

To apply the preceding formulae, the concept of hydraulic diameter Dh is used, where Dh is equal to the equivalent cylindrical tube diameter.

If S is the cross-sectional area of the pipe and p its perimeter:

$$Dh = \frac{4S}{p}$$

For a conduit of rectangular cross-section with sides a and b:

$$Dh = \frac{2\,ab}{a + b}$$

4.1.4. Circular conduits flowing partly full

Where:

- q ($l.s^{-1}$) is the flow rate in a pipe of diameter D and slope p ($mm.m^{-1}$) and filled to X% of its diameter,
- and Q (Ls^{-1}) is the flow rate in a pipe of diameter D filled to full capacity with head loss p ($mm.m^{-1}$) equal to the value of the slope.

As D and p (and therefore Q) are known factors, flow rate q is provided by the relation: q = mQ

where m is given in the table below as a function of X.

X (%)	20	25	30	35	40	45	50	55	60	65	70	75
m	0.08	0.13	0.185	0.25	0.32	0.40	0.50	0.58	0.67	0.74	0.82	0.89

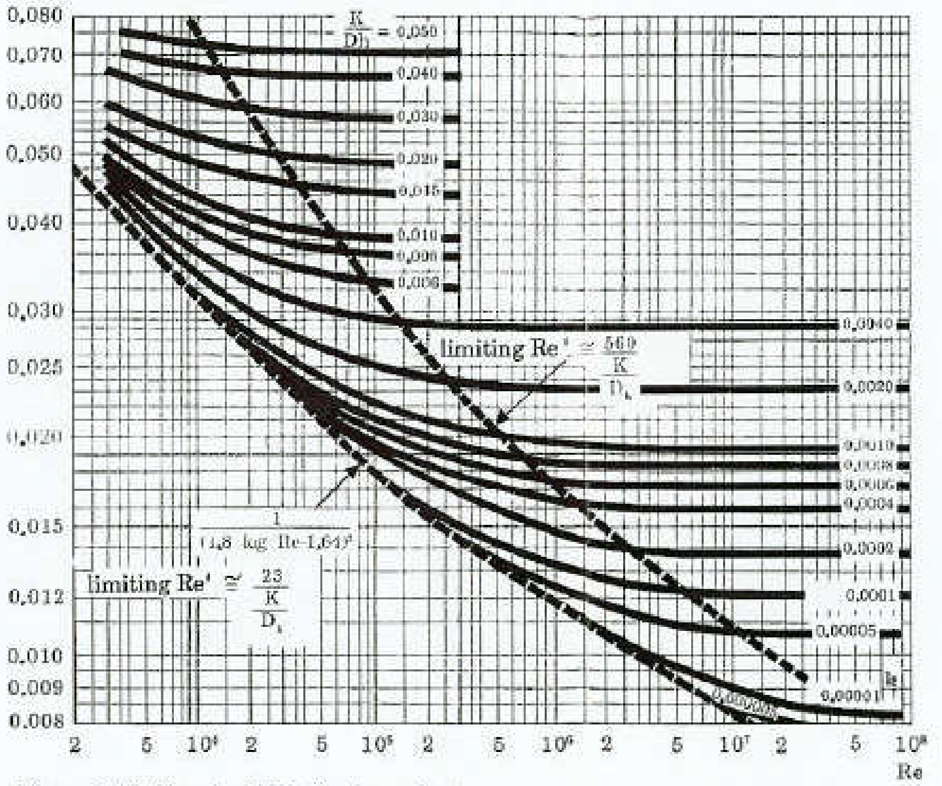


Figure 247. Standard friction loss chart.

Table 58. Varying values of ratio $\frac{\lambda}{D'}$.

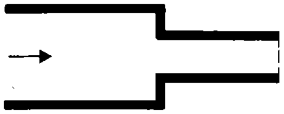
Diameter	Coefficient $\frac{\lambda}{D'}$D for a roughness equal to:			
mm	**k=0.lmm**	**k=0.5 mm**	**k=lmm**	**k=2mm**
0.025	1.26	2	2.84	
0.030	1.02	1.54	2.00	2.71
0.040	0.700	1.04	1.34	1.80
0.050	0.528	0.78	0.985	1.30
0.065	0.35	0.500	0.615	0.80
0.080	0.290	0.413	0.512	0.660
0.100	0.222	0.310	0.380	0.490
0.125	0.168	0.232	0.284	0.360
0.150	0.133	0.182	0.223	0.280
0.200	0.0935	0.128	0.153	0.190
0.250	0.0710	0.096	0.114	0.141
0.300	0.0573	0.076	0.090	0.110
0.350	0.0475	0.0625	0.0735	0.0900
0.400	0.0400	0.0530	0.0625	0.0758
0.450	0.0351	0.0460	0.0538	0.0650
0.500	0.0308	0.040	0.047	0.0566
0.600	0.0245	0.0322	0.0371	0.0477
0.700	0.0206	0.0266	0.0307	0.0368
0.800	0.0175	0.0225	0.0260	0.0310
0.900	0.0151	0.0194	0.0225	0.0267
1.000	0.0134	0.0170	0.0197	0.0234
1.100	0.01163	0.015	0.01754	0.0209
1.200	0.0104	0.01358	0.01583	0.01875
1.250	0.0102	0.0130	0.0150	0.0177
1.300	0.00946	0.0123	0.0142	0.01676
1.400	0.00878	0.01128	0.01307	0.01535
1.500	0.00827	0.0104	0.0120	0.0140
1.600	0.00737	0.00956	0.01106	0.0131
1.700	0.00694	0.00882	0.0103	0.01235
1.800	0.00655	0.00833	0.00966	0.0111
1.900	0.00605	0.00773	0.00894	0.0104
2.000	0.00586	0.00735	0.0084	0.00980
2.100	0.00538	0.00690	0.00785	0.00928
2.200	0.00513	0.0065	0.00740	0.00881
2.300	0.00491	0.00621	0.00708	0.00834
2.400	0.00466	0.00591	0.00675	0.00791
2.500	0.00453	0.0056	0.0064	0.00745
Estimated velocity range	1 to 3 $m.s^{-1}$	1 to 3 $m.s^{-1}$	≥ 1 $m.s^{-1}$	≥ 0.5 $m.s^{-1}$

4.2.
MINOR LOSSES IN PIPES, FITTINGS, VALVES, ETC. OF WATER CONDUITS

A. Sudden contraction

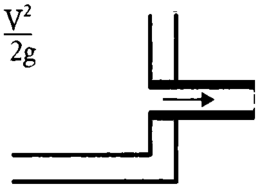
$$\Delta h = \frac{1}{2}\left(1 - \frac{D_2^2}{D_1^2}\right)\frac{V^2}{2g}$$

Δh = head loss in metres of water
V = mean velocity after contraction, in $m.s^{-1}$
g = acceleration of gravity = 9.81 $m.s^{-2}$
D_1 = pipe diameter before contraction, in m
D_2 = pipe diameter after contraction, in m



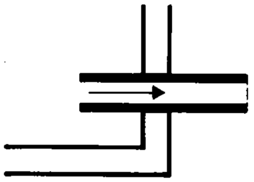
- **Specific case: outlet pipe from a large tank**

a) $\Delta h = \frac{1}{2}\frac{V^2}{2g}$



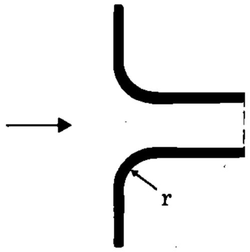
b) With pipe projecting inside the tank
(projecting length greater than half the pipe diameter):

$\Delta h = \frac{V^2}{2g}$



c) With rounded entrance fitting:

$$\left(\text{if } \frac{r}{D} > 0.18\right) \Delta h = 0.05\,\frac{V^2}{2g}$$

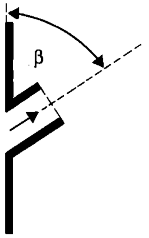


d) With oblique cylindrical fitting:

$$\Delta h = K\,\frac{V^2}{2g}$$

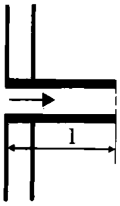
where $K = 0.5 + 0.3\cos\beta + 0.2\cos^2\beta$

β	20°	30°	45°	60°	70°	80°	90°
K	0.96	0.91	0.81	0.70	0.63	0.56	0.50



e) With standard short tube:

$\Delta h = 1.5\,\frac{V^2}{2g}$



with $2D < 1 < 5D$

B. Sudden enlargement

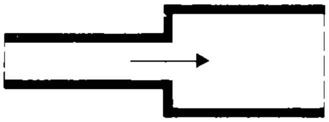
$$\Delta h = \frac{(V_1 - V_2)^2}{2g} = \frac{V_1^2}{2g}\left(1 - \frac{D_1^2}{D_2^2}\right)^2$$

V_1 = mean velocity before enlargement, in m.s.

V_2 = mean velocity after enlargement, in m.s 1.

D_1 = pipe diameter before enlargement, in m.

D_2 = pipe diameter after enlargement, in m.

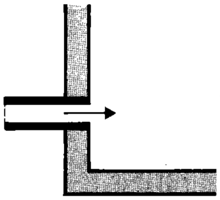


Specific case: inlet pipe into a large tank

$$\Delta h = \frac{V^2}{2\,g}$$

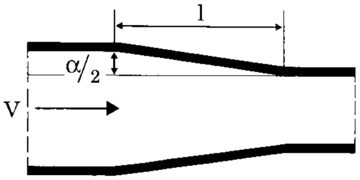
The following formula is generally where n
more appropriate:

$$\Delta h = \alpha \frac{V^2}{2g} \text{ with } 1.06 < \alpha < 1.1$$



C. Converging duct

$$\Delta h = \Delta h_1 + \Delta h_2$$



a) Friction loss (Δh_1)

Calculate the head loss Oh'1 in a cylindrical pipe of equal length, and crosssection equal to that of the larger pipe section:

$$\Delta h_1 = x\,\Delta h'_1$$

$$\text{with } x = \frac{n(n^4 - 1)}{4(n - 1)}$$

$$\text{where } n = \frac{D}{d}$$

D: pipe inlet diameter. d: pipe outlet diameter.

b) Head loss by detachment (Δh_2):

$$\Delta h_2 = K\,\frac{V^2}{2\,g}$$

V = velocity calculated in the larger pipe section, in $m.s^{-1}$

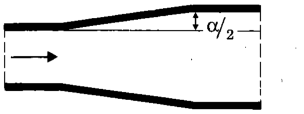
Values of K:

$n = \frac{D}{d}$	1.15	1.25	1.50	1.75	2	2.5
Apex angle						
6^0	0.006	0.018	0.085	0.23	0.5	1.5
8^0	0.009	0.028	0.138	0.373	0.791	2.42
10^0	0.012	0.04	0.2	0.53	1.05	3.4
15^0,	0.022	0.07	0.344	0.934	1.98	6.07
20^0	0.045	0.12	0.6	1.73	3.5	11
30^0	0.28	0.25	1.25	3.4	7	

D. Diverging duct
Lorenz formula: $\Delta h = \left(\frac{4}{3} \tan \frac{\alpha}{2}\right) \frac{V_1^2}{2g}$

with:

α = taper apex angle
V_1 = velocity in the pipe before enlargement

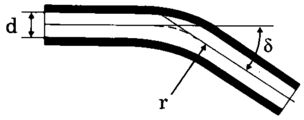


E. Elbows and bends

a) Bends:

$$\Delta h = K \frac{V^2}{2g}$$

Values of K:
r = radius of curvature of the bend, in metres.
d = pipe diameter, in metres.



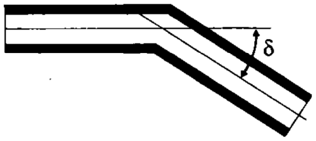
$\frac{r}{d}$	1	1.5	2	3	4
d= 22° 5	0.11	0.10	0.09	0.08	0.08
? = 45°	0.19	0.17	0.16	0.15	0.15
? = 60°	0.25	0.22	0.21	0.20 .	0.19
? = 901,	0.33	0.29	0.27	0.26	0.26
? = 135°	0.41	0.36	0.35	0.35	0.35
? = 180°	0.48	0.43	0.42	0.42	0.42

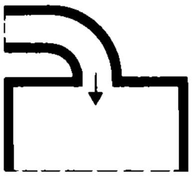
Bend opening into a full tank (total K)

d = 90°	0.68	1.64	1.62	1.61	1.61

For a "3 d bend":

$2 r = 3 d$, i.e., $\frac{r}{d} = 1.5$





b) Elbows:

$$\Delta h = K \frac{V^2}{2g}$$

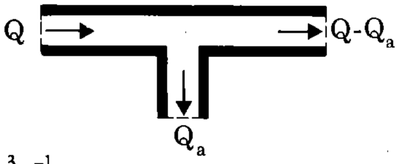
d	22.5°	30°	45°	60°	75°	90°
K	0.17	0.20	0.40	0.70	1.00	1.50

F. Pipe tees

It is assumed that:
- the fitting connections have the same diameter as the main pipe;
- the fitting has sharp angles.

a) Outlet connection:

$$\Delta h = K \frac{V^2}{2g}$$

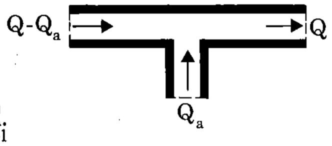


Q = total flow rate in $m^3.s^{-1}$.
Q_a = flow rate in the outlet connection in $m^3.s^{-1}$.
V = velocity of the total flow in $m.s^{-1}$.
Kb = head loss coefficient of the outlet connection.
Kr = head loss coefficient of the straight section (coupled to the main pipe).

$\frac{Qa}{Q}$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Kb Kr	(1.0) 0	1.0 0.004	1.01 0.02	1.03 0.04	1.05 0.06	1.09 0.10	1.15 0.15	1.22 0.20	1.32 0.26	1.38 0.32	1.45 (0.40)

b) Inlet connection:

$$\Delta h = K \frac{V^2}{2g}$$



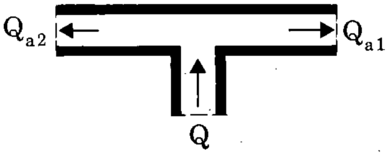
Q = total flow rate in cubic metres per second.
Q_a = flow rate in the inlet connection, in $m^3.s^{-1}$.

$\frac{Qa}{Q}$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Kb Kr	(-0.60) 0	-0.37 0.16	-0.18 0.27	-0.07 0.38	+0.26 0.46	0.46 0.53	0.62 0:57	0.78 0.59	0.94 0.60	1.08 0.59	1.20 0.55

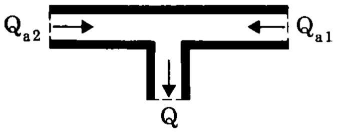
c) Symmetrical welded steel tee fitting, with flow separation

$$Kr_1 = 1 + 0.3 \left(\frac{Qa_1}{Q}\right)^2$$

$$Kr_2 = 1 + 0.3 \left(\frac{Qa_2}{Q}\right)^2$$



d) Symmetrical tee, converging flows:



$$K_{r1} = 2 + 3\left[\left(\frac{Q_{a1}}{Q}\right)^2 - \frac{Q_{a2}}{Q}\right]$$

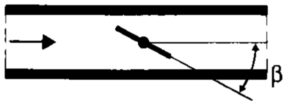
$$K_{r2} = 2 + 3\left[\left(\frac{Q_{a2}}{Q}\right)^2 - \frac{Q_{a1}}{Q}\right]$$

G. Valves and cocks.

$$\Delta h = K\frac{V^2}{2g}$$

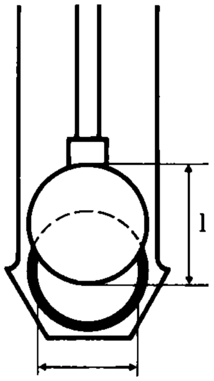
a) Rotary or butterfly valves

Depending on the valve opening angle, the head loss coefficient varies with the hydrodynamic characteristics of the disc. The table below gives a few typical values by way of indication, but it is recommended that reference be made to the manufacturers' tables for greater precision.



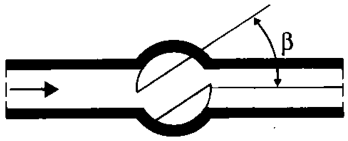
β	0° - 5°	10°	20°	30°	40°	45°	50°	60°	70°
K	0.25 to 0.30	0.52	1.54	3.91	10.8	18.7	32.6	118	751

b) Gate valves:



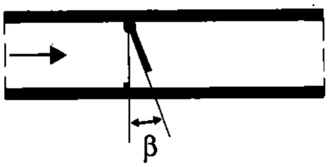
Gate lowering value $\frac{l}{d}$	0	$\frac{1}{8}$	$\frac{2}{8}$	$\frac{3}{8}$	$\frac{4}{8}$	$\frac{5}{8}$	$\frac{6}{8}$	$\frac{7}{8}$
K	0.12	0.15	0.26	0.81	2.06	5.52	17	98

c) Plug valves:



	10°	20°	30°	40°	45°	50°	55°
K	0.31	1.84	6.15	20.7	41	95.3	275

d) Flap or swing check valves:



β	*15°*	*20°*	*25°*	*300*	*350*	*40°*	*450*	*500*	*60°*	*700*
K	*90*	*62*	*42*	*30*	*20*	*14*	*9.5*	*6.6*	*3.2*	*1.7*

H. Open valves and fittings

$$\Delta h = K \frac{V^2}{2g}$$

	Typical K	Variation of K
Parallel seat valve	*0.12*	*0.08* to *0.2*
Wedge gate valve		*0.15* to *0.19*
Angle valve		*2.1* to *3.1*
Needle valve		*7.2* to *10.3*
Straight screw-down valve	*6*	*4* to 10
Screw-down stop valve, angle type		*2* to *5*
Float valve	*6*	
Plug valve		*0.15* to *1.5*
Swing check valve	*2* to *2.5*	*1.3* to *2.9*
Foot valve (without strainer)	*0.8*	
Sleeve coupling		*0.02* to *0.07*

Cv coefficients of a valve:

For some valves, and particularly regulating valves, the current trend consists of providing the flow rate coefficient C_v for the various openings rather than the actual head loss coefficient. By definition, C_v is the flow rate of water of specific gravity 1 (expressed in US gpm), which flows through the contracted pipe section for a head loss of 1 psi. This is roughly equivalent to the water flow rate in litres per min creating a head loss of *5* mbar, i.e., *0.05* m WC.

For water, we therefore obtain:

$$C_v = \frac{Q}{\sqrt{\Delta h}}$$

where Q = flow rate in US gpm
Δh = head loss in psi

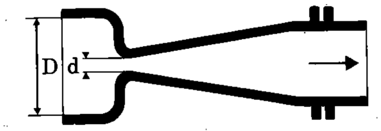
or, in decimal units:

$$C_v = 13{,}3\ \frac{Q}{\sqrt{\Delta h}}$$

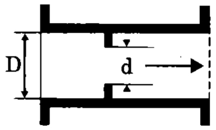
where Q = flow rate in Ls^{-1},
Δh = head loss in m WC.

4.3. CALCULATION OF NEGATIVE PRESSURE SYSTEMS

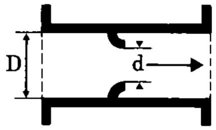
Venturi tubes



Orifice plates



Nozzles



A. Approximate calculation method

$$h = K\,\frac{\rho}{1000}\,\frac{V_2}{2g}\,(m^2 - 1),$$

i.e.:

$$\frac{D^2}{d^2} = m = \sqrt{\frac{1000\ 2\ gh}{K\rho V^2} + 1}$$

where:

h = negative pressure created by the device, in metres of water at 4°C (density 1000 $kg.m^{-3}$).

K = experimental coefficient (near 1).

ρ = density of the fluid in real flow conditions, in $kg.m^{-3}$.

V = velocity of the fluid entering the device in $m.s^{-1}$.

g = acceleration of gravity, 9.81 ms^{-2}

D = pipe diameter, in metres.

d = diameter of the throat (section of maximum constriction), in metres.

m = ratio of the pipe cross-section to the throat cross-section.

***Calculation of the opening of an orifice plate**: the actual diameter do of the opening is equal to $\frac{d}{0{,}8}$.

. **Head loss of an orifice plate** (for Re > 10^5):

$$h = \frac{K}{1000}\,\frac{V^2}{2g}$$

where

$$K = \left(1 + 0.707\sqrt{1 - \frac{d_0^2}{D^2}} - \frac{d_0^2}{D^2}\right)^2 \left(\frac{D^2}{d_0^2}\right)^2$$

for an orifice plate with sharp edges whose aperture diameter is do, expressed in the same unit as the inner pipe diameter D.

B. Precise calculation of a negative pressure measurement system: see French standards NF X-10.101, NF X-10.102 and NF X-10.110.

Installation: orifice plates, nozzles and venturi nozzles must be placed in a straight length of pipe, the length of the upstream portion being equal to at least 10 D, and the downstream portion being longer than 5 D. These minimum values are increased for slight contractions. For standard venturi tubes, the minimum straight upstream length is only 1.5 to 6 D depending on the degree of contraction (standard X 10.102 pages 9 and 10).

The length of a venturi tube is determined by the standardized shape coefficients (above standard) and the selected throat diameter D - d.

4.4. DISCHARGE OF OPENINGS AND SHORT TUBES

Discharge $Q = kS\sqrt{2gh}$ $(m^3.s^{-1})$.
Mean velocity $V = k\sqrt{2gh}$ $(m.s^{-1})$.

Where:

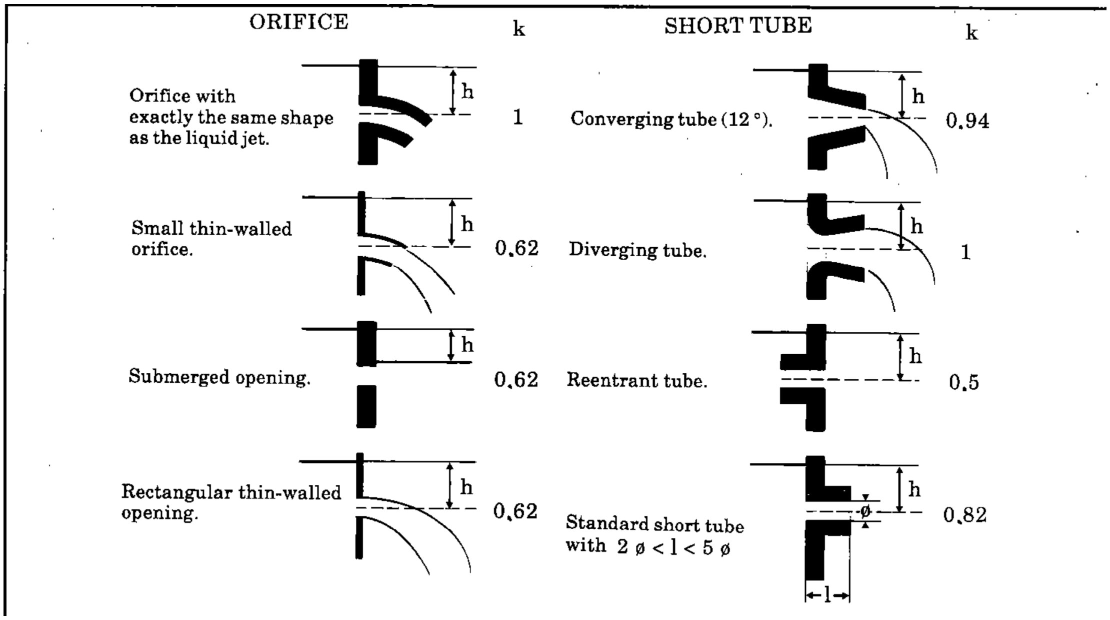
S = surface area of the opening measured at its outermost cross section (in mZ).
g = acceleration of gravity 9.81 m.s 2.
h = pressure head on the opening measured from the upstream level of liquid to the centre of gravity of the opening (in m).

Coefficient k used here and coefficient K defined in par. 4.2 are related by the equation $k = K^{-2}$.

Simplified formula with k = 0.62:

$$\underset{(m^3.s^{-1})}{Q} \cong \underset{(cm^2)}{S}\ \underset{(m)}{\sqrt{h}}$$

* **Pitot tube:** although this flow rate measurement device is not standardized, it is often used whenever difficulties are encountered in the construction or installation of a negative pressure element. For measurements in pipes, the curved end of the pitot tube detecting the pressure is generally placed along the axis of the pipe.



The resulting differential pressure h, is equal to the difference between the static pressure therefore pressure and the total, to the true dynamic pressure at the level of the pressure-indicating device. If V, is the flow velocity at a given point along the axis (in m.s), and Vm the mean flow velocity (in m.s') in the section of diameter D (in m), for flow rate Q qin m3.s') of a fluid of density p (in kg.m), the value of the differential pressure (in mm of water column) is:

$$h_c = \rho \frac{V_c^2}{2\,g} = \rho \left[\frac{0{,}2874\ Q}{D^2 \dfrac{V_m}{V_c}} \right]^2$$

where the density, under conditions of absolute temperature T and absolute flow pressure P, is calculated from *po* under normal conditions by the formula:

$$\rho = \rho_0 \cdot \frac{P}{P_0} \cdot \frac{T_0}{T}$$

When the flow is symmetrically distributed in the cross-section due to sufficient lengths of straight pipe, the diagram in figure 248 gives the values of V'" as a

function of Reynolds number Re.

For low Re values, a mean velocity must be established by moving the pitot tube in the flow cross-section.

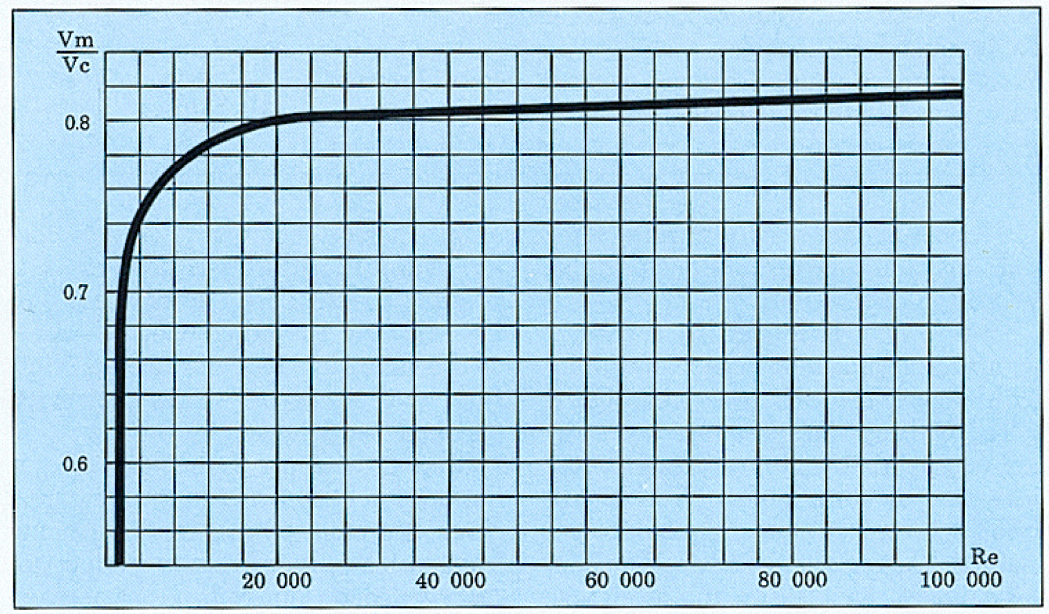


Figure 248. Values of $\frac{V_m}{V_c}$ for measurements with a pitot tube.

4.5.

WATER FLOW IN OPEN CHANNELS

A. Empirical formulae for friction loss calculations.

In friction loss calculations, the following formulae are the only ones remaining in use, and particularly the ManningStrickler formula due to its simplicity and its generalized application to all forms of uniform flow in channels or rivers.

- **Bazin formula:**

$$V = \frac{87\sqrt{RI}}{1 + \frac{\gamma}{\sqrt{R}}}$$

- **Manning-Strickler formula:**

$V = K_s R^{2/3} I^{1/2}$

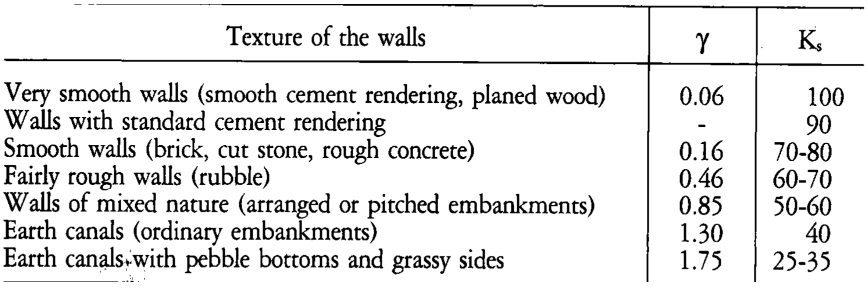
where:

V = mean flow velocity in the cross section, in m.s '

R = hydraulic radius or mean radius, in m, equal to the ratio of the crosssectional area of the channel in which the fluid is flowing (mz) to the wetted perimeter (m);

I = slope of the channel, in metres per metre;

γ and K_S = roughness constants of the walls.



Texture of the walls	γ	K_s
Very smooth walls (smooth cement rendering, planed wood)	0.06	100
Walls with standard cement rendering	-	90
Smooth walls (brick, cut stone, rough concrete)	0.16	70-80
Fairly rough walls (rubble)	0.46	60-70
Walls of mixed nature (arranged or pitched embankments)	0.85	50-60
Earth canals (ordinary embankments)	1.30	40
Earth canals with pebble bottoms and grassy sides	1.75	25-35

The nature and surface texture of the walls may limit the maximum admissible velocity in their vicinity.

Critical flow is reached in a channel with a rectangular cross-section of width 1, with water depth H, such that $Q^2 = g1^2 H_C^3$, Q being the flow rate (i.e., critical velocity $V_c = \sqrt{gH_c}$)). At greater velocities, flow is non-uniform (accelerated): it follows complex laws and requires specialized studies (mathematical models, scale models, etc.). Below this level, flow is considered to be uniform with H > Hc and V < Vc. In water treatment works, flow is usually of the uniform type, i.e., the two preceding conditions are verified.

In uniform flow, the wetted crosssection and the velocity are constant in the successive profiles, the friction loss being exactly compensated by the slope. The Bazin formula or the Manning-Strickler formula relating velocity, hydraulic radius and slope make it possible to calculate one of these values knowing the other two, i.e., three of the following four parameters: flow rate, wetted cross-section, wetted perimeter and slope.

Taking the above as the normal equilibrium level, local rises in the water level, or hydraulic jumps, resulting either from increases in velocity or from restoration of energy due to bends or obstructions, must be calculated as indicated in paragraph C below.

In water treatment works, where straight pipe lengths are generally short, level variations in the bends or obstructions have considerable relative importance.

B. Use of the Standard Chart

This chart (figure 247) giving friction loss coefficient, X, also applies to channels with walls of heterogeneous roughness. For concrete channels, the roughness coefficient k ranges, on average, from 0.5 mm (smooth rendering) to 2 mm (rough concrete under average conditions). The calculation method is the same as in pipes (par. 4.1.2) using the hydraulic diameter:

$$Dh = \frac{4\,S}{p_m}$$

where S is the section of channel filled by water and p. is the wetted perimeter, expressed in m^2 and m

C. Minor loss calculations

The same method is followed as with pipes (par. 4.2), starting downstream and based on the uniform flow velocity. Local upstream hydraulic jumps reflect the minor losses.

- Values of K3 (space between bars):

D. Head loss through a bar screen

$$\Delta h = K_1.K_2.K_3.\frac{V^2}{2\,g}$$

V = approach velocity in channel, in $m.s^{-1}$

-Values of Kl (clogging):

. clean screen Ki = 1.

. dogged screen $K_1 = \left(\frac{100}{m}\right)^2$

where m is the percent of open area remaining below the maximum tolerated dogging level.

-Values of K_2 (shape of the horizontal cross-section of the bars):

$\frac{1}{4}\left(\frac{2}{e}+\frac{1}{h}\right)$	$\frac{e}{e+d}$									
	0.1	0.2	0.3	0.4	0.5	0.G	0.7	0.8	0.9	1
0	245	51.5	18.2	8.25	4.0	2.0	0.97	0.42	0.13	0
0.2	230	48	17.4	7.70	3.75	1.87	0.91	0.40	0.13	0.01
0.4	221	4G	16.6	7.40	3.60	1.80	0.88	0.39	0.13	0.01
0.G	199	42	15	6.60	3.20	1.G0	0.80	0.3G	0.13	0.01
0.8	1G4	34	12.2	5.50	2.70	1.34	0.66	0.31	0.12	0.02
1	149	31	11.1	5.00	2.40	1.20	0.G1	0.29	0.11	0.02
1.4	137	28.4	10.3	4.60	2.25	1.15	0.58	0.28	0.11	0.03
2	134	27.4	9.9	4.40	2.20	1.13	0.58	0.28	0.12	0.04
3	132	27.5	10.0	4.50	2.24	1.17	0.61	0.31	0.15	0.05

e = space between bars.
d = width of bars.
1 = thickness of bars.
h = submerged depth of bars, vertical or oblique.
All these quantities are to be expressed in the same unit.

E. Entrainment velocity of a few substances

- Water depth 1 m, straight channels:

	Diameter in mm	Mean velocity $m.s^{-1}$
Silt	0.005 - 0.05	0.15 - 0.20
Fine sand	0.05 - 0.25	0.20 - 0.30
Medium sand	0.25 - 1.00	0.30 - 0.55
Non-compacted clays	-	0.30 - 0.40
Coarse sand	1.00 - 2.5	0.55 - 0.65
Fine gravel	2.5 - 5	0.65 - 0.80
Medium gravel	5 - 10	0.80 - 1.00
Coarse gravel	10 - 15	1.00 - 1.20

- Corrections for other water depths:

H (m)	0.3	0.5	0.75	1.0	1.5	2.5
k	0.8	0.9	0.95	1.0	1.1	1.2

4.6.
WEIRS

The discharge of weirs can be obtained from the general formula:

$$Q = \mu l h \sqrt{2 g h}$$

where:

Q = discharge, in $m3.s^{-1}$' (or Ls^{-1})

μ = weir coefficient 1 = length of weir crest, in m

h = head in m (or cm)

g = acceleration of gravity, in $m.s^{-2}$ = 9.81 in Paris).

The height of the weir crest above the bottom of the channel (upstream of the weir) is designated by P, and the width of the channel upstream of the weir is designated by L.

A. Rectangular, sharp-crested weir with a low approach velocity

$$\mu \approx 0.40$$

in the case of a tank overflow, for example

* Particular case of a circular overflow weir

$$\mu \approx 0.34$$

for an overflow of 0.20 m < dia. < 0.70 m with sufficient nappe fall to prevent any reaction downstream.

B. Rectangular-shaped, sharp-crested weir across a channel

. **Weir with suppressed end contractions** (1 = L), with unrestricted nappe flow (figure 249)

A weir is thus defined when the crest thickness a is less than half the head h, when the flow is such that it leaves a space c0 filled with air at atmospheric pressure between the head and the downstream crest wall, and when the width of the head is exactly equal .to that of the channel.

Weir coefficient μ is given by one of the following formulae:

- Bazin formula (1898), widely used in France:

$$\mu_1 = 0{,}405 + \frac{0{,}003}{h}\left|1 + 0{,}55\,\frac{h^2}{(h+P)^2}\right|$$

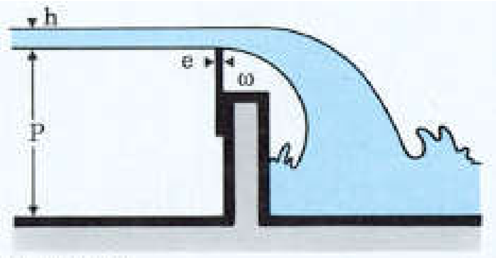


Figure 249.

- Formula proposed by the Societe des Ingenieurs et Architectes Suisses (Swiss Architects and Engineers Association S.I.A.):

$$\mu_2 = 0{,}410\left[1 + \frac{1}{1000\,h + 1{,}6}\right]\left[1 + 0{,}5\,\frac{h^2}{(h+P)^2}\right]$$

These formulae, with h and P expressed in m, can be used for heads h of 0.10 m to 0.60 m for the Bazin formula, and of 0.025 m to 0.80 m for the S.I.A. formula, which gives slightly lower results than those obtained by the Bazin formula.

Other applications:

- Bazin formula: P between 0.20 and 2 m
- S.I.A. formula: P greater than h.

Finally, h should be measured at a distance from the weir crest equal to at least five times the maximum head. If the amount of air below the nappe is insufficient (depressed nappe), the flow rate is increased and is consequently poorly defined, which is unacceptable for a metering weir.

Discharge in l.s 1 per m of crest length according to Bazin(i)

Head	**Height of weir crest in metres**								
h (m)	0.20	0.30	0.40	0.50	0.60	0.80	1.00	1.50	2.00
0.10	G4.7	63.0	G2.3	61.9	61.6	61.3	G1.2	61.1	61.0
0.12	85.3	82.7	81.5	80.8	80.4	79.9	79.7	79.4	79.3
0.14	108.2	104.4	102.6	101.5	100.9	100.1	99.8	99.3	99.2
0.1G	133.2	128.1	125.5	124.0	123.0	122.0	121.4	120.7	120.5
0.18	160.2	153.7	150.2	148.1	146.8	145.3	144.5	143.5	143.2
0.20	189.3	181.0	176.6	173.9	172.1	170.0	168.9	167.7	167.1
0.22	220.2	210.2	204.6	201.2	198.9	196.2	194.8	193.1	192.4
0.24	253.0	241.0	234.2	230.0	227.2	223.8	221.9	219.7	218.8
0.2G	287.6	273.6	265.5	260.3	256.9	252.7	250.3	247.5	246.4
0.28	323.9	307.8	298.2	292.1	288.0	282.9	280.0	276.5	275.1
0.30	361.8	343.6	332.5	325.4	320.5	314.4	310.9	306.6	304.9
0.32		380.9	368.3	360.1	345.3	347.2	343.0	337.9	335.7
0.34		419.8	405.6	396.1	389.5	381.2	376.2	370.2	367.2
0.3G		460.1	444.2	433.5	426.0	416.4	410.7	403.6	400.5
0.38		502.0	484.3	472.3	463.8	452.8	446.3	438.0	434.4
0.40		545.2	525.8	512.4	502.9	490.5	483.0	473.5	469.3
0.45		659.4	635.3	618.3	606.0	589.6	579.6	566.5	560.6
0.50			752.9	732.1	716.7	696.0	682.9	665.7	657.8
0.55			878.2	853.4	834.8	809.2	792.9	770.9	760.5
0.60			1011.1	982.1	960.0	929.2	909.3	881.9	868.7

1. Rectangular, sharp-crested weirs with suppressed end contractions.

Discharge in l.s^{-1} per m of crest length according to the S.I.A. (l)

Head				Height of weir crest in metres						
h (m)	0.10	0.20	0.30	0.40	0.50	0.60	0.80	1.00	2.00	3.00
0.02	5.4	5.4	5.4	5.4	5.4	5.4	5.4	5.4	5.4	5.4
0.04	15.5	15.1	15.0	14.9	14.9	14.9	14.9	14.9	14.9	14.9
0.06	29.0	27.8	27.5	27.4	27.3	27.2	27.2	27.2	27.1	27.1
0.08	45.7	43.3	42.5	42.2	42.0	41.9	41.8	41.7	41.6	41.6
0.10		61.2	59.8	59.2	58.8	58.6	58.3	58.2	58.1	58.0
0.12		81.5	79.2	78.1	77.5	77.2	76.8	76.5	76.2	76.2
0.14		103.9	100.6	99.0	98.1	97.5	96.9	96.5	96.0	95.9
0.16		128.5	124.0	121.7	120.4	119.5	118.6	118.1	117.3	117.1
0.18		155.1	149.2	146.2	144.3	143.2	141.8	141.1	139.9	139.7
0.20			176.3	172.3	169.9	168.3	166.5	165.5	163.9	163.5
0.22			205.1	200.1	197.0	195.0	192.6	191.3	189.2	188.7
0.24			235.6	229.5	225.7	223.1	220.1	218.4	215.6	215.0
0.26			267.7	260.4	255.8	252.7	248.9	246.3	243.3	242.4
0.28			301.5	292.9	287.4	283.7	279.1	276.5	272.0	271.0
0.30				326.9	320.4	316.0	310.5	307.4	301.9	300.6
0.32'				362.3	354.9	349.7	343.2	339.4	332.9	331.3
0.34				399.2	390.7	384.7	377.1	372.1	364.9	362.9
0.36				437.5	427.8	421.0	412.3	407.1	397.9	395.6
0.38				477.1	466.3	458.6	448.6	442.7	431.9	429.2
0.40					506.0	497.4	486.1	479.3	466.9	463.7
0.45					611.0	599.9	585.0	575.9	558.7	554.1
0.50						709.8	690.9	679.1	656.2	649.9
0.55						826.9	803.6	788.8	759.3	751.0
0.60							923.0	904.8	867.9	857.1
0.65							1048.9	1027.1	981.8	968.2
0.70							1181.0	1155.4	1100.9	1084.1
0.75							1319.3	1289.5	1225.0	1204.7
0.80								1429.5	1354.1	1329.9

1. Rectangular sharp-crested weirs with suppressed end contractions.

Weir with end contractions

The S.I.A. has proposed the following formula for μ:

$$\mu = \left[0{,}385 + 0{,}025\left(\frac{1}{L}\right)^2 + \frac{2{,}410 - 2\left(\frac{1}{L}\right)^2}{1000\,h + 1{,}6}\right] \times \left[1 + 0{,}5\left(\frac{1}{L}\right)^4\left(\frac{h}{h+P}\right)^2\right]$$

where $P > 0.30$ m; $1 > 0.31$ L; $0.025\ i < h < 0.80$ m; $h < P$.

The simplified Francis formula should also be noted:

Q = 1.83 (1 - 0.2 h) h3/2

in which the excess width on either side of the crest must be equal to at least 3 h, the head being measured at least 2 m upstream from the crest.

C. Triangular sharp-crested weir

$$Q = \frac{4}{5}\,\mu\, h^2 \sqrt{2\,gh.}\;\mathrm{tg}\,\frac{\Theta}{2}$$

where:
Q = discharge, in m3.s $^{-1}$
P = coefficient for the rectangular sharpcrested Bazin weir with suppressed end contractions (see par. 4.6.13)
h = head in m
Θ = weir apex angle

The discharge of a triangular weir can be deduced from the discharge of a rectangular weir with suppressed end contractions, with identical head and height of crest, ®y multiplying this discharge by. $\frac{4}{5}\,h\,\mathrm{tg}\,\frac{\Theta}{2}$

For Θ = 90°, the Thompson formula is sometimes used:

$$Q = 1{,}42\; h^{\frac{5}{2}}$$

This formula is only very approximate as it does not take into account the height of crest above the bottom of the channel.

4.7.
HEAD LOSS WITH UNKNOWN FLUIDS

The general head loss formula, in pipes of unknown cross-section as in channels, is:

$$\Delta h = \Delta h_0 + \Delta h_1 + \ldots$$

In turbulent flow:

$$\underbrace{\Delta h_0 = J_0\, L_0}_{\text{(friction losses)}} \quad + \quad \underbrace{10^{-5}\, K_0\, \rho\, \frac{v_0^2}{2}}_{\text{(minor losses)}}$$

$$\text{where } J_0 = 10^{-5}\, \rho\, \frac{\lambda}{D_h}\, \frac{v_0^2}{2}$$

In laminar flow the formula giving Δho is the same with:

$$J_0 = 10^{-5}\, \frac{64}{Re\, D_h}\, \rho\, \frac{v_0^2}{2},\ K_0$$

then having particular values to be calculated using specialized reference documentation.

Notation:
Δh = total head loss, in bar
? h1, ? h2, etc.. = elementary head loss per constant respective velocity segment vo, vi, etc.
Jo = friction loss coefficient, in bar per metre of pipe (or channel) length at velocity vo
Lo = pipe (or channel) length, in m, at velocity vo
Ko = sum of the minor loss coefficients at velocity vo
p = density of the fluid in real temperature and pressure flow conditions, in kg.m $^{-3}$
vo, v1, etc. = velocity values of the fluid in real flow conditions, in m.s-'
X = coefficient given by the Standard Chart (figure 247) as a function of Reynolds

$$Re = \frac{v_0\, D_h}{\nu}$$

number
(V = kinematic viscosity of the fluid in m2.s' at flow conditions - see par. 3.2.3, 3.3.3, 4.1.2), and as a function of relative roughness $\frac{k}{D_h}$ (k = roughness coefficient of the wall, in m, given in par. 4.1.2)

D_h = hydraulic diameter of the pipe (or channel) in metres; $D_h = \frac{4\,S}{p_m}$ where S the pipe (or channel) cross-sectional area filled by the fluid, in mz, and pm is the perimeter "wetted" by the fluid in this cross-section, in m. Dn is equal to four times the hydraulic radius or the typical mean radius. In a circular pipe of diameter D, Dh = D. Friction loss is calculated as in par. 4.1.2 (pipes) and par. 4.5 (channels), and minor losses as in par. 4.2 and par. 4.5.

It is often customary to express head loss values in metres of water column (WC) (taking the density of water at is1'000 kg. m^{-3} at 4°C). The preceding formulae then become:

- in turbulent flow:

$$\Delta h_0 = \frac{\rho}{1000}\,\frac{\lambda}{D_h}\,\frac{v_0^2}{2g}\,L_0 + \frac{\rho}{1000}\,K_0\,\frac{v_0^2}{2g}$$

$$= \frac{\rho}{1000}\left(\frac{\lambda}{D_h}\,L_0 + K_0\right)\frac{v_0^2}{2g}$$

- in laminar flow:

$$\Delta h_0 = \frac{\rho}{1000}\left(\frac{64}{Re\,D_h}\,L_0 + K_0\right)\frac{v_0^2}{2g},$$

where Ko has specific values to be calculated using specialized reference documentation.

4.8. MISCELLANEOUS INFORMATION

***Drainage time for a tank with constant horizontal cross-section with an opening at its base**

Drainage time in seconds is:

$$t = \frac{2\,S\,(\sqrt{h_1} - \sqrt{h_2})}{ks\,\sqrt{2g}}$$

S = surface area of the tank in cm^2.
s = area of the opening in c^2.
k = contraction coefficient of the opening (see par. 4.4).
g = acceleration of gravity: 981 cm.s z.
h_1 = initial depth of water above the opening, in cm.
h_2 = final depth of water above the opening, in cm (h_2= 0 for total drainage).

Drainage time for a conical tank

$$t = \frac{2\pi}{5}\cdot\frac{tg^2\,\frac{\alpha}{2}}{ks\,\sqrt{2g}}\cdot(H)^{5/2}$$

(assuming the opening is at the base of the cone).

Pumps

The power to be supplied, in kW, is

$$P = \frac{Q(H + h)}{r \times 366} \text{ for water.}$$

Q = required discharge, in $m_3.h^{-1}$.
H = total static head (in m WC).
h = head loss in pipes (in m WC).
r = pump efficiency (from 0.6 to 0.9).

As a rule, h should be $h < \frac{H}{10}$.

When rotation speed N becomes N' = kN, centrifugal pumps follow the formulae:

$Q = kQ$; $H' = k^2H$; $P' = k^3P$

Efficiency is virtually independent of rotation speed.

Hydraulic motors

The power supplied, in kW, is

$$P = \frac{QHr}{366}.$$

Q = flow rate in $M^3 h^{-1}$ H = water falling head in metres. r = efficiency of the turbine.

	Values of r
Water wheel	0.70 to 0.75
Propeller and Francis turb.	0.70 to 0.88
Kaplan turbine and Pelton wheel .	0.70 to 0.92

5. ELECTRICITY

5.1. UNITS, SYMBOLS

I	Current	ampere	(A)
e	Voltage of a direct current or a single-phase alternating current (line-to-neutral voltage)	volt	(V)
E	Voltage of a three-phase alternating current (line-to-line)	watt	(W)
P	Active power	volt-ampere	(VA)
EI	Apparent power	ohm	(Ω)
R	Resistance	Ohm	(Ω)
X	Reactance	ohm	(Ω)
Z	Impedance		
cos ∅	Power factor (or tan∅)		
p	Efficiency		
C	Capacitance		
L	Self-inductance		

5.2. COMMONLY USED DEFINITIONS AND FORMULAE

. **Current**

Direct current $I = \frac{P}{e}$

Single-phase alternating current:

$$I = \frac{P}{e \cos \varnothing}$$

Three-phase alternating current:

$$I = \frac{P}{E\sqrt{3} \cos \varnothing}$$

Resistance

$$R = r \frac{l}{s} 10^{-2}$$

r = resistivity in microhm-cm,
l = length in m,
s = cross-sectional area in mm^2.

Power factor or cos ∅

The intensity and voltage of an alter-amperes nating current are rarely in phase. The cosine of the angle formed by the two intensity-voltage vectors is known as the power factor.

Self-induction causes the current to lag in relation to the voltage; capacitance causes it to lead.

In both cases the active power is reduced.

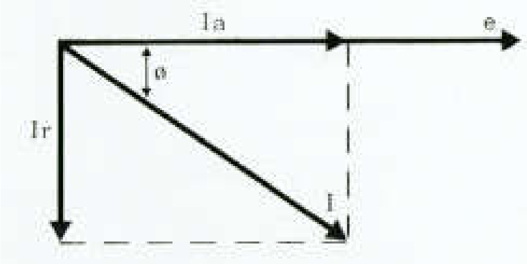


Figure 250. A circuit with self-induction.

For industrial sinusoidal current (general case):

Ia = I cos ∅ is the active current,

Ir = I sin ∅ is the reactive current.

Apparent, active, reactive power

With I being the current read on the ammeter, E the line-to-line voltage of the system in three-phase, a the line-toneutral voltage of the system in singlephase, the power is given in the following table:

	Single-phase	Three-phase
Apparent power	el	El F3
Active power	el cos ¢	El V3 cos ∅
Reactive power	eI sin ¢	El V3 sin ∅

Apparent power is expressed in volt (VA)

Active power is expressed in watts (W)

Reactive power is expressed in volt-amperes reactive (var)

A poor cos ∅ is detrimental to the energy user and the energy supplier alike, as it requires distribution systems with significant cross-sectional areas, as well as alternators and transformers with greater apparent power.

Impedance of a circuit

This is the resultant of the ohmic resistance and reactance of the circuit.

Z = $\sqrt{R^2 + X^2}$,

R = resistance,

X = reactance (inductive, capacitive).

. **Quantity of heat released by a circuit** of resistance R through which a current I passes for one second:

W (joule) = P x t = RI2

. **Star and delta connections**

Resistors and motor windings can be connected in star or delta configurations. Figure 251 shows the main characteristics of these connections.

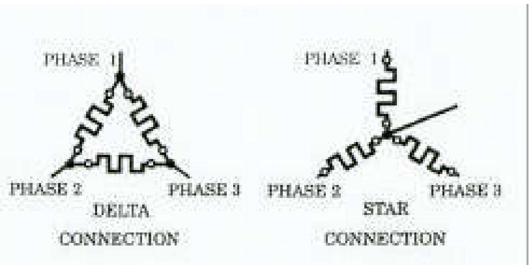


Figure 251.

5.3.
INDUSTRIAL APPLICATIONS

5.3.1. General facilities

Determining the mean cos ∅ of a facility

With Qa being the active energy consumption read on the active meter for a given period of time, and Q, being the reactive energy consumption read on the reactive meter for the same period, the mean cos ∅ of the facility during this period can be obtained from the formula:

$$\cos \varnothing = \frac{Q_a}{\sqrt{Q_a^2 + Q_r^2}}$$

Cos ∅ improvement

As the line losses through joule effect are proportional to I2, whereas the active energy consumed is only proportional to I cos ∅, the utilities penalize users whose facilities have a power factor under a specified value (approximately cos ∅ = 0.93, corresponding to tan ∅ = 0.4 in the French network).

When the reduction in cos ∅ is due to a self-inductive reaction of the facility, it is improved by a capacitor bank. The capacitor bank power (in kilovar) needed to bring cos ∅ to the desired value can only be calculated accurately after 4-6 months of the water treatment plant being operational.

Nevertheless, to compensate for a poor power factor during a transition phase, a capacitor bank can be installed whose value is approximately 10% of the total installed capacity of the plant.

Lighting and heating

The number, arrangement and power of the lighting units are generally calculated to obtain the following lighting levels, except in particular cases:

Interior lighting of facilities	
offices, control rooms, meeting rooms, laboratories	300 lux
work stations, control	200 lux
positions internal walkways	100 lux
other areas	40 lux
Exterior lighting	
works area, building approaches ,danger zones	50 lux
access to the facility, traffic routes	10 lux

The lighting levels described above are minimum acceptable values.

Interior space-heating

To calculate the power needed for space-heating, numerous factors must be taken into account: the space dimensions, orientation, thermal insulation provisions, minimum outside temperature, etc.

However, taking into account the difference between the minimum outside temperature and the maximum spaceheating temperature required, it can be assumed that the power to be installed will be approximately 2-3 watts per °C (of temperature difference) and per m3.

5.3.2. Motors

Motors currently used are of the asynchronous type; the information below applies solely to this type of motor.

. Rated power. Power input

Rated power is the power indicated in the catalogue or on the plate of the motor. It corresponds to the mechanical power applied to the motor shaft and is expressed in kW.

The electrical power input is provided by the relation:

$$\text{input power} = \frac{\text{mechanical power supplied}}{\text{efficiency}}$$

Also expressed in kW, it is the power used to establish the power balance of a facility.

A motor must be used for the frequency intended by the manufacturer. A motor designed for a 50 Hz supply will have a weaker torque if it is fed with 6O Hz.

. Efficiency

For commonly manufactured motors, efficiency p becomes greater as the power of the motor increases.

Example: motor of 50 kW p = 0.85
motor of 1 kW p = 0.70.

For a given motor, the efficiency indicated by the manufacturer corresponds to operation at full load; it decreases slightly with the load.

Example:
motor of 50 kW p = 0.85 at 4/4 load,
p = 0.82 at 3/4 load,
p = 0.80 at 1 /2 load.

.Determining the power of a motor

To determine the rated power of a motor, the following margins should be allowed, taking into account the mechanical power applied to the machine being driven (apart from particular exceptions, such as crushers and comminutors):

- 10 to 15% in the case of direct coupling,
- 20% in the case of belt transmission.

. Supply voltage

- As power varies approximately with the square of the voltage, it is imperative that the motor be designed for the exact voltage of the system.

For example, a motor developing 15 kW at the shaft at a voltage of 380 V will only provide about 12.5 kW at a voltage of 350 V.

- Most manufacturers provide boxes with six terminals allowing for both star and delta connections by moving terminal boards: the first will be used, for example, with three-phase current under 380 V, the second with three-phase current under 220 V.

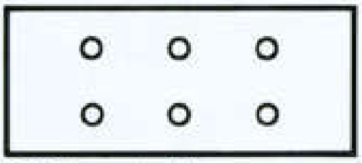


Figure 252. Six-terminal box.

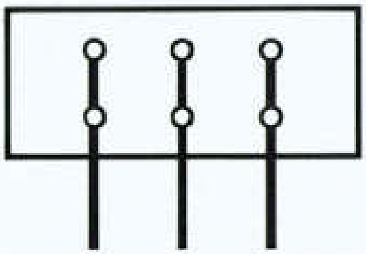


Figure 254. Delta connection. 220/380 V motor supplied with 220 V current.

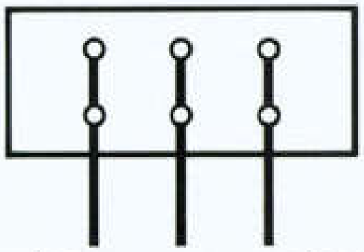


Figure 254. Delta connection. 220/380 V motor supplied with 220 V current.

If the motor is to have a star-delta switching starter, the six terminals must be brought out and designed for the following voltages:

Mains voltage	Motor voltage
220 V	220/380 V
380 V	380/660 V
440 V	440/762 V

For this type of starter, no board required in the terminal box.

Speeds of asynchronous motors

No load: asynchronous single-phase or three-phase motors have a no-load speed practically equal to the synchronous speed provided by the formula:

$$N = \frac{60 \times F}{n}$$

N = number of revolutions per minute (rpm),
F = frequency in cycles per second (Hz),
n = number of pairs of poles.

Example:

Motor - 2-pole 50Hz 3000 rpm
- 4-pole 50Hz 1500 rpm
- 6-pole 50Hz 1000 rpm
- 2-pole 60Hz 3600 rpm
- 4-pole 60Hz 1800 rpm
- 6-pole 60Hz 1200 rpm

On load: the speed is slightly lower than the no-load speed. The difference .corresponds to the slip, which is expressed by the relation:

$$g = \frac{\text{synchronous speed - on-load speed}}{\text{synchronous speed}}$$

g is comprised between 2 and 8% of the synchronous speed.

Selecting the motor and starting mode

These two points depend on the machine being driven and the conditions imposed by the utility.

As regards the machine being driven, regardless of the starting mode selected, the accelerating torque (difference between the drive torque and the resisting torque) must be sufficient to allow the is unit to reach rated speed. Two main factors are involved here:

- the gyration moment Gd2, expressed in newtons per square metre,
- the torque required to start the machine.

Certain machines, such as fans, start with virtually no load, but the mass and diameter of the rotating parts (elements characterizing Gd^2) are such that reaching rated speed requires a considerable amount of energy, almost totally transformed into kinetic energy.

With other machines (comminutor pumps, compressors), the motor must, immediately after being started, enable the machines to perform mechanical work while increasing their speed; the starting torque must therefore be taken into account here.

Across-the-line starting is normally recommended for:

- reaching rated speed more rapidly,
-reducing overall heat.

It is possible if:

- the capacity of the network is sufficient,
- the starting torque is mechanically withstood by the machine being driven.

In the case of an emergency circuit, the available power is limited and in most cases gradual starting modes have to be used.

The table below gives the characteristics of the different starting procedures:

Starting mode	Starting torque	Current demand
Across-the-line	Ts	Cs
Star-delta	0.3 Ts	0.3 Cs
Stator resistance	kTs	√kCs
Autotransformer	kTs	kCs

K is the selected coefficient of the starting torque.

The ratios of the starting current and starting torques at the rated values are given in the following table (approximate values):

Type of motor	$\frac{Cs}{Cr}$	$\frac{Ts}{Tr}$
Squirrel-cage rotor (across-the-line)	6	1.6
Squirrel-cage rotor (star-delta starting)	2	0.6
Wound rotor	1.33	0.8 to 2

Cs = starting current,
Cr = rated-load current,
Ts = starting torque,
Tr = rated-load torque.

Tr is expressed in newton-metres. If N is the speed in rpm and P is the rated power in kilowatts:

$$Tr = \frac{9564\ P}{N}$$

(formerly, the metre-kilogramme-force, 1 kgf = 9.81 N, was used).

Current input

Direct current: $I = \frac{Pr\ 10^3}{e\ \rho}$

Single-phase current: $I = \frac{Pr\ 10^3}{e\ \rho \cos \varnothing}$

Three-phase current $I = \frac{Pr\ 10^3}{E \sqrt{3}\ \rho \cos \varnothing}$

Pr is the rated power of the motor expressed in kilowatts.

.Approximate values of the current input (motor power ranging from 1 to 10 kW)

	1500 rpm	3000 rpm
Single-phase 220 V	5.5 A per kW	5 A per kW
Three-phase 220 V	4.3 A per kW	3.8 A per kW
Three-phase 380 V	2.5 A per kW	2.2 A per kW

Since cos ∅ and the efficiency decrease as the number of poles increases, the current input for a given power will be greater as the rated speed is low.

Thus the power input of a 750 rpm motor will be about 20% more than that of a motor of the same power at 3,000 rpm and 10% more than that of a motor of the same power at 1,500 rpm.

. **Supply cables**

As the permissible voltage drop at the terminals of a motor at full load is 5%, the cross-section of the supply cables must be calculated accordingly, taking particular note of the current input at full load and the length of the cable.

The table below provides an indication of the characteristics of the supply cable for a three-phase voltage of 380 V, a maximum length of 25 m, and the diameter of the stuffing box intended for the terminal box.

Motor power	Copper conductors: number and cross-sectnl area	Stuffing box dia. mm
up to 8kW	4x2.5mm^2	13
from 8 to 14 kW	4 x 4 mm^2	16
ftom 14 to 18 kW	4 x 6 mm^2	16
from 18 to 25 kW	4 x 10 mm^2	21

The fourth conductor is provided for grounding the motor, a function generally carried out inside the terminal box. Anchor bolts should not be used to ground the motor.

With a star-delta switching starter, two cables must be provided, and the conductors can be of equal cross-section. One of the two cables will include the fourth conductor for grounding the motor.

.Permissible voltage drop within distribution system

Standard No. NF C 15.100 (published by the French Standards Committee AFNOR) sets the value of the voltage drop equal to a percentage of the voltage of the system:

- 3% for lighting distribution systems,
- 5% for power distribution systems.

When motors are started, a 10% drop in voltage is generally accepted for power distribution systems.

5.3.3. Subscription

An energy supply contract must be defined as a function of the power input by the distribution system at a given moment, and optimized according to the various periods proposed by the utility.

When determining the operating costs of a treatment plant, these periods and the corresponding rate variations must be taken into account.

Here follows, as an example, an excerpt from an EDF (French national electricity board) publication regarding the general rate for average use, i.e., less than 10,000 kW in medium-voltage distribution of 5 to 30 kV (known as the EDF green rate). The rates listed are parameters to provide a general idea of variations.

Period	
Off-peak hours	10 pin to 6 am
Standard hours	6 am to 9 am 11 am to 6 pm 8 pin to 10 pm
Peak hours	9 am to 11 am 6 pin to 8 pm

Furthermore, the year is split into two periods (in France):

- the summer period from April to October (7 months), during which there are no peak hours.

Value of the kWh (August 1988 estimate)
Standard hours = a centimes per kWh
Off-peak hours = a x 0.56 centimes perkWh

- the winter period from November to March (5 months), during which the peak hours (twice two-hours) apply over

3 months, from December to February.
Off-peak hours a x 1.48 centimes per kWh (Sunday, off-peak hours all day)
Standard hours a x 3.18 centimes per kWh

Peak hours a x 6.16 centimes per kWh

The fixed annual rate for average consumption is a x 2000 centimes per kW (number of kW defined in the contract).

Many other contracts and values of the kWh can be established and negotiated with the utility as a function of the amount of power subscribe

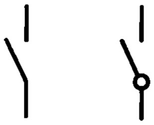
The above facts indicate simply that it is in the general interest of facilities to ensure that units with high energy consumption can be stopped or slowed down during periods where the kWh price is high. Similarly, if the facility has an autonomous power production (biogas), it could be reserved for preferential consumption during these peak periods.

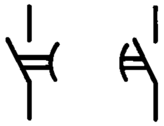
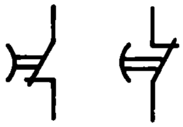
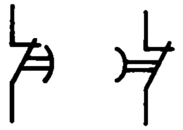
5.4.

GRAPHIC SYMBOLS FOR WIRING DIAGRAMS

(according to UTE and IEC standards)

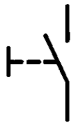
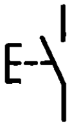
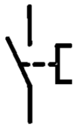
5.4.1. Contacts

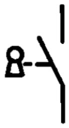
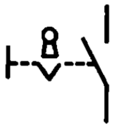
	Normally open (make) contact
	Normally closed (break) contact
	Make-break contact

	Make-break contact with central open position
	Passage contact closing momentarily on operation
	Normally open contact, delayed closing
	Normally closed contact, delayed opening
	Normally closed contact, delayed closing

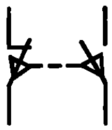
	Normally open contact, delayed closing and opening
	Normally open contact, with automatic reset
	Normally open contact, with maintained position

5.4.2. Single-pole switches

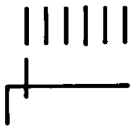
	Normally open contact, with manual reset, general symbol
	Push-button to close, with automatic reset
	Pull knob to close, with automatic reset
	Normally open rotary switch without automatic reset

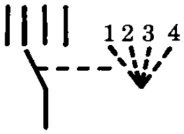
	Manual control auxiliary, key-operated
	Manual control auxiliary, latch-in type

5.4.3. Position switches

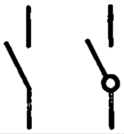
	Position switch, normally open contact
	Position switch, normally closed contact
	Two-way position switch, mechanically actuated in both directions

5.4.4. Several-way switches

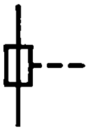
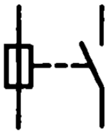
	n-way switch, n = 6

	n-way switch, n = 4
	Four-way switch with position diagram

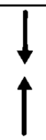
5.4.5. *Mechanical connecting devices*

	Switch
	Contactor
	Relay-fitted contactor
	Breaker
	Cut-out circuit breaker
	Isolator

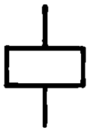
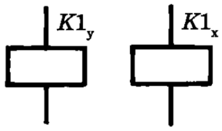
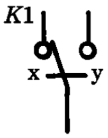
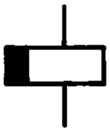
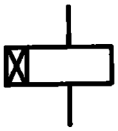
5.4.6. *Fuses and fuse switches*

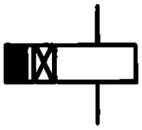
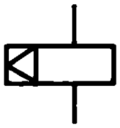
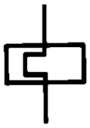
	Fuse, general symbol
	Fuse with indication
	Fuse with plunger
	Fuse with plunger with isolation
	Switch fuse
	Cut-out fuse

5.4.7. Lightning arresters and spark-gaps

	Spark-gap
	Lightning arrester

5.4.8. Control devices Electromagnetic relays

	Relay control device, general symbol
	Double-winding control device
	Bidirectional contact of a bistable relay
	Control device of a relay with delayed drop-out
	Control device of a relay with delayed pick-up

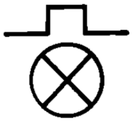
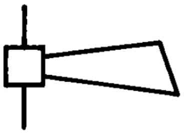
	Control device of a relay with delayed pick-up and drop-out
	Control device of a relay with mechanical latching
	Control device for a thermal relay

Detection means for overcurrent

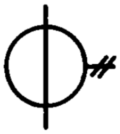
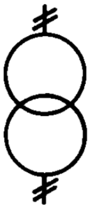
	Thermal effect
	Electromagnetic effect

5.4.9. Signalling apparatuses
(visible and audible signals)

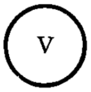
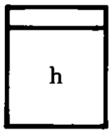
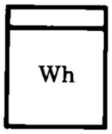
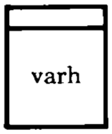
	Signal lamp

	Signal light with flashing facility
	Horn
	Bell

5.4.10. Instrument transformers

	Current transformer with one primary winding and one secondary winding
	Voltage transformer

5.4.11. Miscellaneous symbols

	Voltmeter
	Ammeter
	Wattmeter
	Power factor indicator
	Ohmmeter
	Hour meter
	Watthour meter
	Varhour meter (reactive volt-ampere-hour meter)
	Clock

5.4.12. Electrical standardizations

French electrical equipment has to conform to the rules set by the UTE (Union Technique de I'Electricité). These rules are classified in sections, of which the principal ones used in water treatment facilities are:

C 12.100, C 13.100, C 15.100

The other standards commonly encountered are:

- IEC (International Electrotechnical Commission).
- VDE (Verband Deutscher Elektrotechniker - Germany).
- BS (British Standards).
- CEI (Comitato Elettrotecnico Italiano).
- NEMA (National Electrical Manufacturers Association).
- ANSI (American National Standards Institute).

5.5.
MISCELLANEOUS NUMERICAL VALUES

• **Resistivity** of the **main conductive metals and alloys**
Resistivity at e C:
rt = ro(I + at),
where:
to = resistivity at 0°C,
a = temperature coefficient,
t = temperature in degrees Celsius.

• Voltage of a lead accumulator 2 volts per element.

• Minimum isolation of a low voltage motor per service volt 1000 O.

Nature of the conductor	Resistance microhms.cm (resistivity) at °C	Temperature coefficient
Electrolytic copper	1.593	0.00388
Annealed copper	1.538	0.0045
Aluminium	2.9	0.0039
Silver	1.505	0.0039
Pure iron	9.065	0.00625
Icon wire	13.9	0.00426
Steel wire	15.8	0.0039
Telephone silicon bronze	3.84	0.0023
Fer	18.3	0.00093
Nickel silver	30	0.00036
Constantan	SO	0
Mercury	95	0.00099
Zinc	G	0.0031

5.6.
PERSONNEL SAFETY

It is accepted that the maximum safe voltage levels are:
- 50 V for direct current,
- 24 V for single-phase current,
- 42 V for three-phase current with grounded neutral.

The safety limit of current tolerability is around 25 mA for alternating current and 50 mA for direct current.

Assuming the body's resistance lies between 2,000 and 1,000 ohms,

$$I = \frac{E}{1000} = 0.05 \text{ A}$$

therefore E = 50 V in direct current
and E = 25 V in alternating current.

6. INSTRUMENTATION

Instrumentation is represented by process diagrams generally known as:
- P&I: Piping & Instrumentation, or
- PID: Piping & Instrumentation Diagram.

The instruments or their functions are designated using general symbols defined in figure 255, with their functional identification in the upper section.

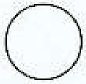
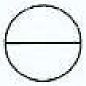
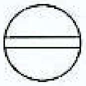
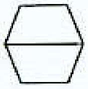
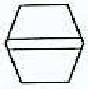
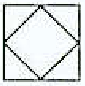
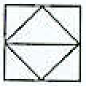
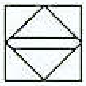
	Field mounting	**Primary location** Normally accessible to operator (1)	**Auxiliary location** Normally accessible to operator (1)
Discrete instruments		(2) 	
Computer function			
Programmable logic controller (PLC)			

Figure 255. General instrumentation symbols.

Notes: (1) When the equipment is arranged behind the panel or inaccessible to the operator, the same symbols are used with horizontal dotted lines.

(2) Position of the abbreviation identifying the nature of the analysis.

The various measurements (variables) and functions are defined in table 59, in conformity with AFNOR standard E.04.203 and ISA standard 5S.1.

Example: FIC. Flow indicating controller on a switchboard located in the main control room: 

6.1. CODING PRINCIPLE

Functional identification comprises two to four characters in capital letters, in two separate groups: - 1st group: First Letter or Variable and its modifier, common to all instruments of a same loop. - 2nd part: Succeeding Letters, designating the functions (see table 59).

Table 59. Identification of the elements used to encode a function or a piece of equipment.

	First letter		Succeeding letters		
	Measured or initiating variable	Modifier	Readout or passive function	Output function	Modifier
A	Analysis		Alarm		
B	Combustion		User's choice	User's choice	User's choice
C	Conductivity			Control	
D	Density Concentration Turbidity	Differential		Fault*	
E	Voltage		Primary element		
F	Flow rate	Ratio - Fraction			
G	User's choice		Glass viewin device		
H	Hand				High (Very high-HH)
I	Current		Indicate		
J	Power	Scan			
K	Time	Time rate of change		Auto-manu selection	
L	Level		Pilot light		Low (Very low-LL)
M	Humidity				Middle Intermediate
N	Viscosity User's choice		Supply to sensors*	User's choice	User's choice
O	User's choice		Orifice plate		
P	Pressure Vacuum		Point (test) connection		
Q	Quantity	Integrate Totalize	Integrate Totalize		
R	Radiation		Record		
S	Speed Frequency	Safety		Switch	
T	Temperature			Transmit	
U	Multivariable		Multifunction	Multifunction	Multifunction
V	Vibration			Control device Solenoid valve Control valve	
W	Weight Force		Well		
X	User's choice	Temperature compensation*	Galvanic isolation*	User's choice	User's choice
Y	Event			Relay	
Z	Position Dimension			Actuator	

Note: * Not covered by AFNOR and ISA standards.

6.2.
LETTER COMBINATIONS

Table 60 presents the most commonly found functional identifications.

A few letter combinations could be used wrongly, namely:

FE = primary flow rate measuring element, e.g., orifice plate, venturi devices, etc.
FO = flow rate limiting orifice plate,
PC = pressure controller,
PV = pressure control valve.

Other notations exist, in different conditions from those defined in figure 255, which do not correspond to the codes in tables 59 and 60. For example, placed under the symbol for a control device:

FC =failure closed.
FO = failure open.
FL = failure locked.

Table 60. Typical letter combinations defining a function or an item of equipment.

First letters			Succeeding letters											
Measured variable			Prim. elem.	Functions						Control device			Signalling	
				I	T	R	C	S	Y				L	A
Initial	Meaning	Modifier	Sensor	Indicator	Trans-mitter	Recorder or printer	Controller	Con-tacts	Various relays and computing relays	Valve, paddle	Action control and other control	Au-tono-mous	Pilot light	Alarm
	Common associations of the succeeding letters	-D,-F - J - Q - S	-E,-P -O,-W	- I -IS - G	- T -IT	- R - RS	- C - IC - RC	H (H) - S M - IS L (L)	- Y	- V	- Z	- CV - SV	H (H) - LM L (L)	H (H) - AM L (L)
A	Analysis		AE AP	AI AIS	AT, AIT	AR	AC, AIC, ARC	ASH,..	AY	AV	AZ		ALH,.	AAH,.
B	Combustion (Flame detection)		BE		BT			BSL,...			BZ		BLH BLL	BALL,
C	Conductivity		CE	CI CIS	CIT CT	CR	CC, CIC, CRC	CSH,...	CY	CV	CZ		CLH,. CLL,..	CAH,.
D	Density Concentration Turbidity		DE DP	DI	DT, DIT	DR	DC, DIC, DRC	DSH,..	DY	DV	DZ		DLH,.	DAH,.
E	Voltage			EI	ET, EIT	ER	EC, EIC, ERC	ESH, ESL	EY	EV	EZ		ELLL,. ELH,	EAH,. EALL,
F	Flow rate Flow ratio Flow quantity	FF FQ	FE, FO FQ	FL, FIS FFI FQI FG	FT, FIT FFT	FR FFR FQR	FC, FIC, FRC FFC, FFIC, FFRC	FSH,.. FFSH,..	FY FFY	FV FFV	FZ FFZ	FCV	FLH,. FFLH,.	FAH,. FFAH,
G	User's choice													
H	Hand						HC, HIC	HSH,..		HV	HZ	HCV		
I	Current		IE	II IIS	IT	IR IRS	IC, IRC, IIC	ISH,... ISHH,..	IY		IZ			IAH,. IAHH,
J	Power		JE	JI JIS		JR JRS	JC, JIC, JRC	JSHH,..						
K	Time	KQ		KI		KR		KQS						
L	Level		LE	LI, LIS LG	LT, LIT	LR	LC, LIC, LRC	LSH, LSL,	LY	LV	LZ	LCV	LLH,.	LAH,.
M	Humidity		ME	MI	MT, MIT	MR	MC, MIC, MRC	MSL MSHH,.	MY	MV	MZ	MCV MSV	MLH,.	MAH,.

NOTE: Not all combinations are mentioned: only the main ones are given.

Table 60. Typical letter combinations defining a function or an item of equipment.

First letters			Succeeding letters											
Measured variable			Prim. elem.	Functions						Control device			Signalling	
				I	T	R	C	S	Y				L	A
Initial	Meaning	Modifier	Sensor	Indicator	Trans-mitter	Recorder or printer	Controller	Con-tacts	Various relays and computing relays	Valve, paddle	Action control and other control	Au-tono-mous	Pilot light	Alarm
	Common associations of the succeeding letters	-D,-F - J - Q - S	-E,-P -O,-W	- I -IS - G	- T -IT	- R - RS	- C - IC - RC	H (H) - S M - IS L (L)	- Y	- V	- Z	- CV - SV	H (H) - LM L (L)	H (H - AM L (L)
N	Viscosity		NE	NI	NT, NIT	NR	NC, NIC, NRC	NSLL, NHSS,...	NY	NV	NZ		NLHH,.	NALL,
O	User's choice													
P	Abs/relative pressure, Differential	PD PS	PP PSE	PI, IS PDI	PT, PIT PDT	PR PDR	PC, PIC, PRC PDC, PDIC,	PSH, PDSH,	PY PDY	PV PDV	PZ PDZ PSZ	PCV PDCV PSV	PLH, PDLH,	PAH, PDAH,
Q	Quantity Metering		QE	QI QIS	QT, QIT	QR QRS		QSH/HH QSL/LL,.	QY	QV	QZ		QLL,..	QAL,.
R	Radiation		RE	RI RIS	RE	RR							RLH,.	RAH,.
S	Speed		SE	SI SIS	ST SIT	SR	SC, SIC, SRC	SSH/HH, SSL/LL,.	SY		SZ		SLH,.	SAL,. SAH,.
T	Temperature	TD TJ TS	TE TDE TW TSE	TI,TIS TDI	TT, TIT TDT, TDIT	TR TDR	TC, TIC, TRC TDC, TDIC, TDRC	TSH,.. TDSH,..	TY TDY	TV TDV	TZ TDZ	TCV TSV	TLH,. TDLH,.	TAH,. TDAH,
U	Multivariable			UI		UR								
V	Mechanical quantities (Vibrations, etc.)		VE	VI VIS	VT VIT	VR VRS		VSH,... VSHH,..	VY		VZ		VLH,. VLHH,.	VAH,. VAHH,
W	Weight or Force	WD WQ	WE	WI WQI	WT,WIT	WR	WC,WIC,WRC	WSH,..	WY	WV	WZ		WLH,.	WAH,.
X	User's choice													
Y	Event							YSH,..					YL YLH,.	YA YAH,.
Z	Position Dimension		ZE	ZI	ZT, ZIT			ZSH, ZSL,					ZLH,..	ZAH,.

NOTE: Not all combinations are mentioned: only the main ones are given.

7. HEAT

7.1.
CONCEPTS OF GASES AND THERMODYNAMICS

7.1.1. Ideal gases

A. Law of ideal gases

$$pV_m = RT$$

where:
p = gas pressure in pascals
Vm = molar volume in m^3
T = absolute temperature in K
R = constant of ideal gases:
8.314 J/(mo1.K).

B.Gay-Lussac's law

$$\frac{m\,(1+\alpha t)}{p} = \frac{m_1\,(1+\alpha t_1)}{p_1}$$

m, ml = density of a gas at pressures p, pi and at temperatures t and ti in °C.

$$\alpha = \frac{1}{273} = 0,00367$$

C. Avogadro-Ampere law

$$M=29d$$

is a relation that links the gramme - molecular weight M of a gas in $g.mol^{-1}$ to its specific gravity d in relation to the air at normal conditions of pressure and temperature. D. Specific heat

Specific heat is, by definition, the quotient of the thermal capacity divided by the mass. The thermal capacity is the ratio ., the quantity of heat dQ supplied to a $\frac{dQ}{dT}$ system and causing an increase in temperature dT. For gases, a distinction is made between the specific heat at constant:pressure cP and the specific heat at constant volume cv. The specific heat values cp of a number gases at constant pressure expressed in kJ/kg. C at 0 C and under 760 mm of mercury

Air 1	Carbon dioxide 0.88
Oxygen 0.92	Chlorine 0.48
Nitrogen 1.06	Sulphur dioxide 0.63
Ammonia 2.09	

The approximate values of the ratio

$\gamma = \frac{C_p}{C_v}$ are roughly:
for monoatomic gases: 1.67
for diatomic gases
for polyatomic gases

7.1.2. Water vapour

A. Saturating or saturated water vapour

Steam in the presence of the generating liquid phase: it is said to be dry if it does not contain a single drop of water.

Enthalpy of a vapour: this is the total quantity of heat required to transform 1 kg of water taken at 0°C into saturated steam at a temperature of t°C. It is the sum of the heat required to raise the temperature of the water from 0 to t 0C (enthalpy of the water) and the vaporization heat at t 'C, which corresponds to the energy required to transform 1 kg of water at t°C into 1 kg of vapour.

Regnault's formula, which expresses enthalpy as a function of the temperature in °C, can be used to obtain an approximate indication:

in $kJ.kg^{-1}$	2538 + 1.276 t
in $kcal.kg^{-1}$	1606.5 + 0.305 t

B. Liquid and vapour mixture

Vapour containing droplets of water, characterized in terms of its titer x: the mass of vapour contained in 1 kg of the mixture.

C. Superheated vapour

Vapour whose temperature is greater than that of the saturated vapour at the level of pressure in question. The behaviour of superheated vapour can be approximated to that of an ideal gas.

The enthalpy of superheated vapour can be calculated using the formula below:

in kJ.kg^{-1} $2538 + 1.276\ t + cP\ (t - ti)$,

in kcal.kg^{-1} $606.5 + 0.305\ t + cP\ (t - ti)$.

t - ti is the difference in temperature between the saturated vapour and the superheated vapour at a constant level of pressure. To give some indication, cp can be taken as 2.1 kJ.kg^{-1}. This formula can be used to assess the enthalpy of the water evaporated in an incinerator, which expels gases at a temperature of t; ti is, in this case, equivalent to 100°C.

D. Chart for water vapour

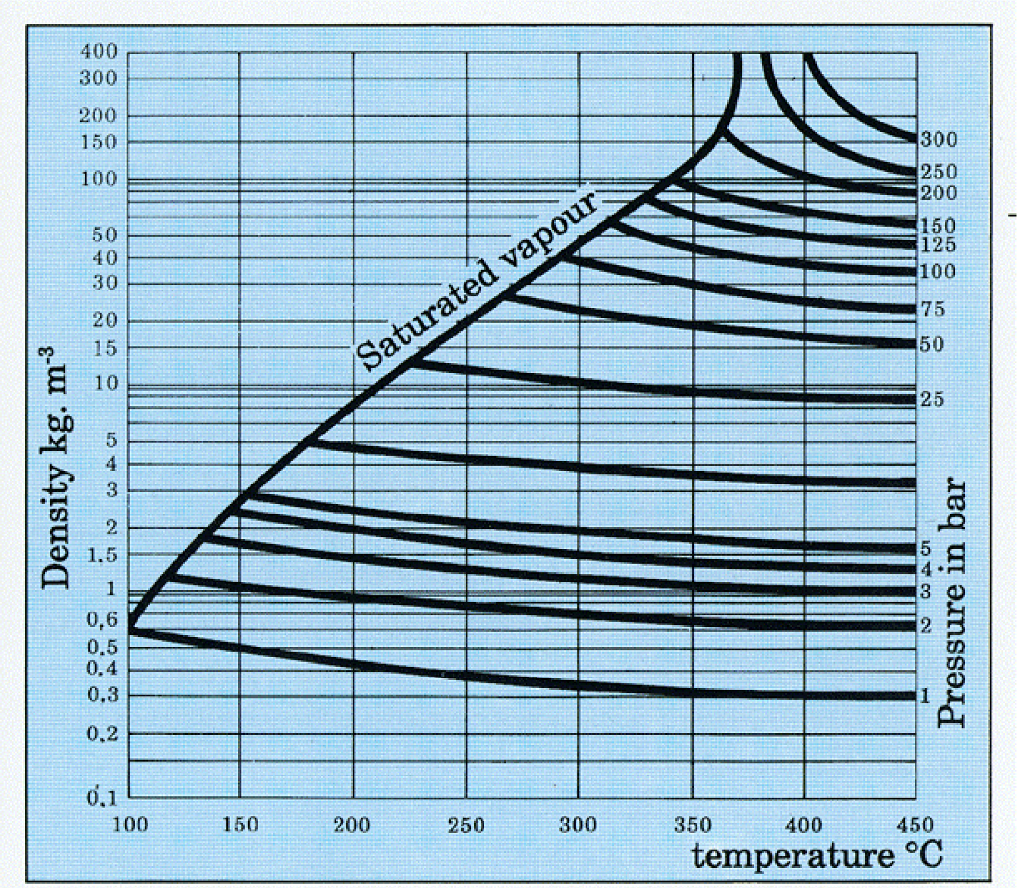


Figure 256. The density of water vapour as a function of temperature and pressure. According to Chenais (extract from French Standard NF X.10.101).

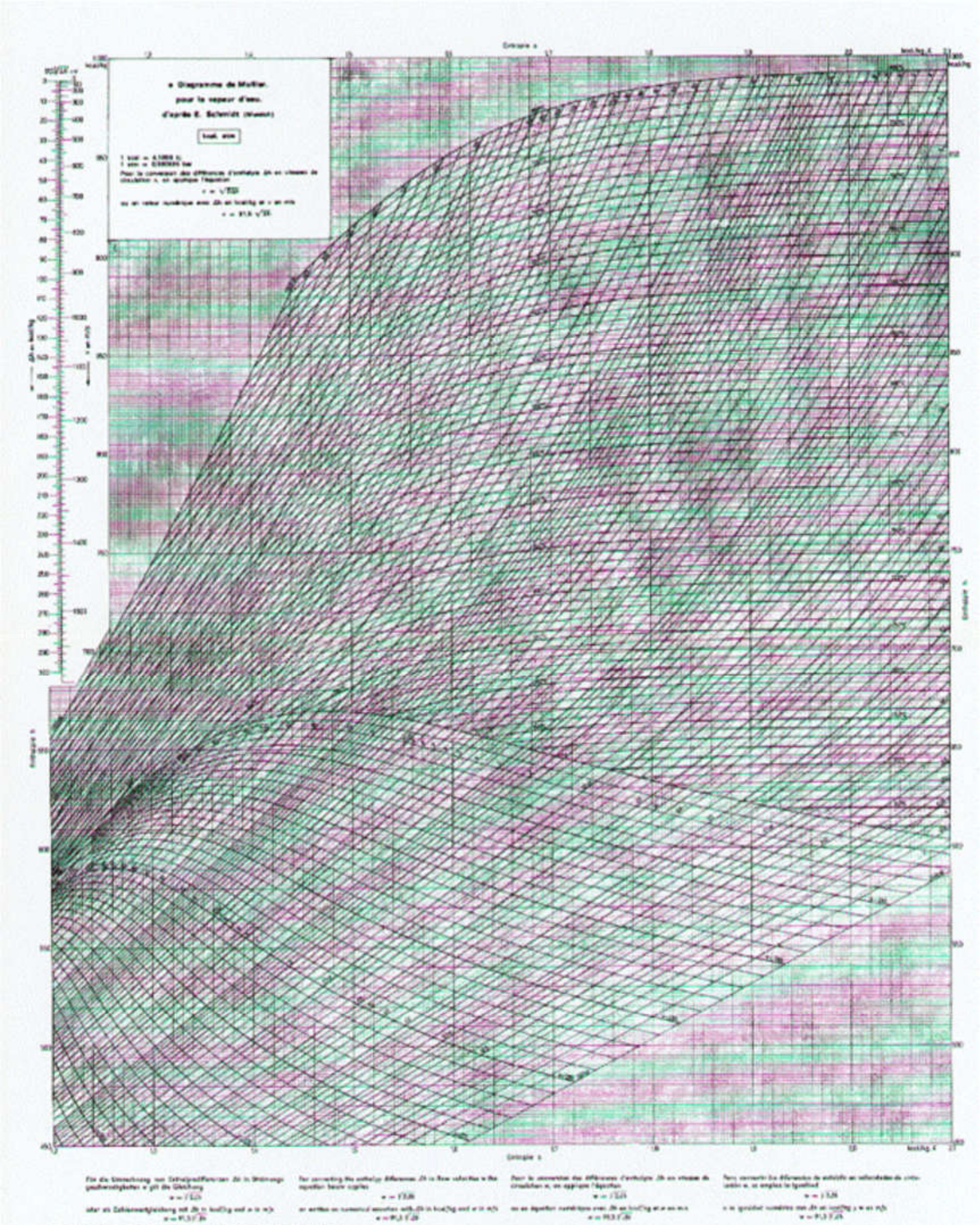


Figure 257. Mollier chart for water vapour. According to E. Schmidt (Munich).
1 kcal = 4.1868 kJ
1 atm = 0.980665 bar
To convert the differences in enthalpy Δh into flow velocities v, the following equation is applied:
$$v = \sqrt{2\Delta h}$$
or, written as a numerical value with Δh in kcal.kg^{-1} and v in m.s^{-1}:
$$v = 91.5\sqrt{\Delta h}$$

Figure 257. Mollier chart for water vapour. According to E. Schmidt (Munich).
1 kcal = 4.1868 kJ
1 atm = 0.980665 bar
To convert the differences in enthalpy Ah into flow velocities v, the following equation is applied:

$$v = \sqrt{2\Delta h}$$

or, written as a numerical value with Ah in kcal.kg ' and v in m.s 1:

$$v = 91{,}5\ \sqrt{\Delta h}$$

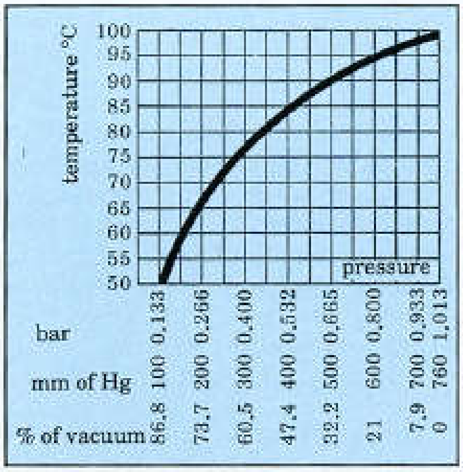


Figure 258. Boiling point of water in a vacuum.

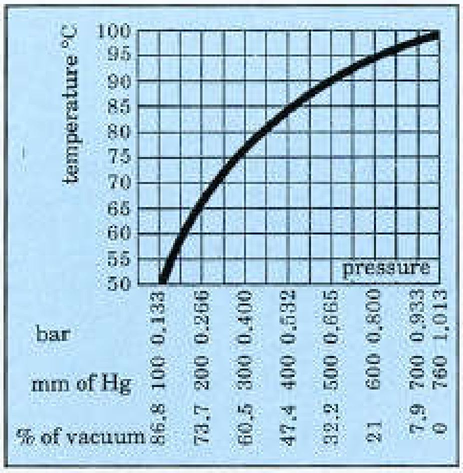


Figure 258. Boiling point of water in a vacuum.

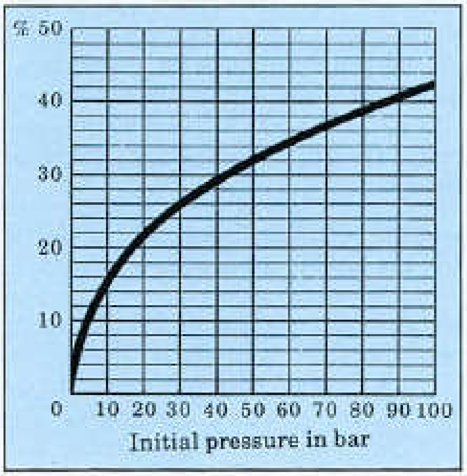


Figure 259. Percentage of water evaporating as a result of the adiabatic expansion of the saturated vapour at atmospheric pressure.

7.1.3. Wet gases

A. Definitions

Dry-bulb temperature: temperature of an unsaturated wet gas measured using a dry-bulb thermometer.

Wet-bulb temperature: temperature of a wet gas that becomes saturated on contact with a sheet of liquid.

Dew point: temperature at which the vapour contained in the gas starts to condense.

Saturated vapour pressure: partial pressure of the vapour in the gas at dew point.

Relative humidity: ratio of the partial water vapour pressure of the gas to the saturated vapour pressure corresponding to the dry-bulb temperature of the gas. It is generally expressed as a percentage.

B. Water vapour content of a gas (m)

If P is the total pressure of a gas with a gramme-molecular weight M, and p, is the partial pressure of the vapour, the water content m of a gas in kg.kg ' of dry gas is given by:

$$m = \frac{18}{M}\,\frac{p_v}{M - p_v}$$

or, in the case of air:

$$m = 0.622\,\frac{p_v}{P - p_v}$$

Thus, for water-saturated air at a temperature of 20°C and at normal atmospheric pressure P = 1.013 bar, p,. _ 0.023 bar, m = 0.0147 kg.kg^{-1}.

C. Enthalpy of a wet gas

As the heat of mixing can be considered as negligible, the enthalpy of a wet gas is equal to the sum of the enthalpies of the dry gas and the vapour.

The enthalpy of air is obtained using the formulae below:

in kJ.kg-' dry gas: 2,490 m + (1 + 1.97 m)t,

in kcal.kg-' dry gas: 595 m + (0.24 + 0.47 m)t.

7.2.
CONCEPTS OF HEAT

The flammability limits of a mixture comprising a comburent and a fuel correspond to the ratios of the minimum and maximum quantities of the products required for combustion when the conditions necessary to start the combustion process have been met.

Heat of combustion is the quantity of heat released during the combustion of a substance undergoing total oxidation. In the case of a compound, this heat is equal to the sum of the heat of formation and the heat released by the combustion of each element.

7.2.1. Calorific values

The calorific value is the combustion heat expressed in relation to the unit mass or volume of the fuel. The following heat values can be distinguished:

- **the moisture-and-ash-free calorific value**: the quantity of heat released by the combustion of the unit mass or volume of the fuel containing no humidity, mineral substances or incombustible gases;
- **the moisture-free calorific value**: the unit mass or volume of the fuel containing no humidity;
- **the as-received calorific value**: this value takes into account all the fuels in the unit mass or volume of the product.

Any hydrogen or hydrogen compounds in the fuel will take the form of water in the combustion products. The net or gross calorific value will then be defined according to whether the water is in a gaseous or liquid state.

The net calorific value (NCV) does not include the vaporization heat of the water in the combustion products (this water is therefore considered to remain in vapour form). In the International System, this value is generally expressed in kJ.kp- 1 or kJ. m-3 although mth.kg and mth.m 3 are still commonly used.

The gross calorific value (GCV) includes the vaporization heat of the water formed during combustion but not of the water present in certain gaseous fuels. The definition of the GCV assumes all the water produced by the humidity of the fuel and the combustion process to exist in a condensed state in the combustion products. The water supplied by the comburent (humid air) is assumed to remain as vapour.

The difference between the NCV and the GCV corresponds to the latent heat of vaporization of water. The NCV, which is the only value used in plant design, is deduced from the GCV following determination of the hydrogen and water content of the fuel. Table 61 gives a few average net calorific values.

For dry organic substances, the difference between the NCV and the GCV varies from 10 to 15%. The difference for domestic fuel is between 5 and 9%.

Economic studies generally make use of the concept of tonnes of oil equivalent (toe). One toe equals the energy value of a tonne of liquefied gas or 1,000 m3 of natural gas.

Table 61. Examples of average NCVs.

Designation	NCV			
	kJ.kg $^{-1}$	mth.kg $^{-1}$	kJ.m $^{-3}$	mth.m $^{-3}$
Soft coal (as received)	31,000	7,400		
MW sludge (per kg of VS)	21,000	5,000		
Domestic fuel-oil	43,000	10,000		
Household refuse	5,000 to 8,000	1,200 to 1,900		
Commercial propane			45,800	11,000
Commercial butane			44,600	10,700
Coke-oven gas			26,000 to 33,000	6,200 to 7,900
Natural gas (Lacq)			49,300	11,800
Digestion gas			22,000	5,300

7.2.2. Combustion

The conventional forms of combustion, which use air as a comburent, are as follows:

. **Theoretical combustion:** the quantity of air used is equal to the combustion capacity of the fuel (see below). This form of combustion is incomplete. **.Oxidizing and semi-oxidizing combustion:** the quantity of air supplied is greater than the combustion capacity of the fuel. Using excess air, combustion is complete in the first case and incomplete in the second.

Reducing and semi-reducing combustion: the quantity of air supplied is lower than the combustion capacity of the fuel and is completely absorbed in the first case and partly absorbed in the second.

Mixed combustion: produces smoke containing the unused oxygen and unburnt substances. This form of combustion sometimes occurs when technical difficulties are encountered.

Neutral combustion is the name given to complete combustion using the exact quantity of comburent required. This form of combustion corresponds to a theoretical concept and is difficult to achieve in practice. It can nevertheless be used as a basis on which to define a certain number of parameters corresponding to a given form of combustion.

The combustion capacity of a fuel is the quantity of air required for the neutral combustion of a unit of fuel to take place. For solid and liquid fuels, a rough estimate would be 1 Nm^3.kg $^{-1}$ of air for an NCV of 4,000 kJ.kg $^{-1}$. For gaseous fuels, the value is the same but is expressed in m^3 rather than kg under normal conditions. For municipal wastewater sludge, the approximate value is 6.5 Nm .kg^{-1} of vs.

The smoke-generating capacity of a fuel refers to the quantity of smoke produced in the neutral combustion of this fuel. In practice, the concept of the wet smoke-generating capacity is applied. Water vapour is assumed not to be condensed. The Veron formulae can be used to give a rough estimate:

- for a solid fuel: 1 $Nm^3.kg^{-1}$ per 3,500 $kJ.kg^{-1}$ of NCV,
- for a liquid fuel: 1 $Nm^3.kg^{-1}$ per 3,800 kJ.kg of NCV,
- for a gaseous fuel: 1 $Nm^3.Nm^{-3}$ per 3,500 $kJ.Nm^{-3}$ of NCV.

This figure is not valid for lean gases whose NCV is less than 8,000 $kJ.Nm^{-3}$.

7.3.
CONCEPTS OF HEAT EXCHANGE

7.3.1. Definitions

Conduction refers to the transfer of heat between two substances in contact whose temperatures differ or between two parts of the same substance that have different temperatures.

The heat flux ∅ transmitted by conduction over a length x across a surface S that is perpendicular to this flux is given by Fourier's law:

$$\varnothing = \lambda S \frac{(\vartheta_1 - \vartheta_2)}{x}$$

where $\theta1 - \theta2$ is the fall in temperature over the distance x, and λ is the coefficient of heat conduction of the material and is expressed in practice in $mth/m^2.h$ per degree Celsius

For most solids, λ is virtually a linear function of temperature: $\lambda = \lambda o (1 + \alpha\theta)$; α is generally positive for insulators and negative for metals, with the exception of aluminium and brass. However, the coefficient of heat conduction varies only slightly with the temperature. Between 0° and 100°C, the following values may be taken as rough estimates:

	W/m. K	mth/m.h.°C
Mild steel (l% carbon)	45	39
Stainless steel (72 CN 18-10)	15	13
Pine copper	384	330
Aluminium	200	175
Brass (30% zinc)	99	85
Glass wool	0.038	0.033
Expanded cork	0.040	0.035
Expanded polystyrene	0.035	0.030

The values below can be applied at ambient temperature:

- for still water: λ = 0.58 W/m.K (0.5 mth/m.h.°C),
- for still air: λ= 0.027 W/m.K (0.23 mth/m.h.°C).

The Fourier heat equation can also be written in the form:

$$\varnothing = \frac{\Delta\theta}{R} \text{ with } R = \frac{x}{\lambda S}$$

.If heat is conducted through several materials one after the other, the following is written for a total temperature drop Δθ:

$$\varnothing = \frac{\Delta\vartheta}{\Sigma R}$$

Convection is the transfer of heat within a fluid from a solid as a result of the motion that occurs either as a result of differences in density (natural convection) or as a result of mechanical power (forced convection).

In practice, the transfer of heat between a solid substance at the temperature 0 and a fluid at the temperature 0, is a particularly complex process in that it involves both convection and conduction. A coefficient of total heat transfer k can then be defined such that:

$$\varnothing = Ks(\theta - \theta 1)$$

Within the same system of units, the value of k will depend on certain physical properties of the fluid, its flow velocity and the geometry of the solid. Considerable variations in the value of k are therefore possible. The values below can be taken as an example:

	W/m^2.K	**mth/m^2.h°C**
Boiling water	1,100 to 50,000	1,500 to 45,000
Water vapour condensed into a film	5,800 to 17,000	5,000 to 15,000
Heating or coohng of water	300 to 11,000	250 to 15,000
Heating or cooling of as	1.2 to 45	1 to 40

Radiation is the transmission of the heat in the form of radiant energy. Requiring no physical medium, this phenomenon can take place in a vacuum

The Stefan-Boltzmann law gives the radiant heat flux:

$$\varnothing = k\varepsilon S T^4$$

with T being the absolute temperature of the radiating body, ε a coefficient of emission equal to 0 for a perfect reflector and equal to 1 for a blackbody, and k a dimensional constant.

7.3.2. Heat exchangers

The quantity of heat passing through a wall is written in the form:

$$Q = kS\,dm$$

where:

- S is the exchange surface area in m^2
- dm is the average temperature difference on either side of the wall. This value is determined by the logarithmic mean of the temperatures of incoming and outgoing fluids,
- k is the coefficient of total heat transfer in W/m^2.K or mth/m^2.h.°C depending on the nature and flow conditions of the fluids and the characteristics of the wall,
- Q is expressed in watts or in mth.h-1 according to the system of units adopted.

Determining the coefficient of total heat transfer

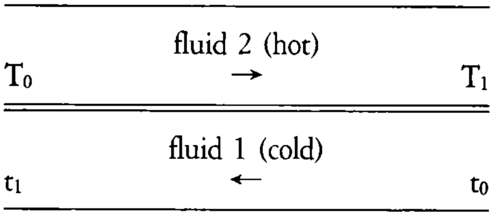
If heat is transferred by conduction and forced convection (as is the case of heat exchangers in sludge treatment facilities), a mathematical formula is used to determine a theoretical heat transfer coefficient where a cylindrical surface is used. In view of the uneven quality of the sludge and the interstitial liquid, the transfer coefficient is essentially empirical.

Examples:

- In sludge digestion, the heat transfer coefficient can take values of up to 1300 W/m^2.k (1100 mth/m^2.h.°C) for fluid velocities of between 1 and 2 m.s$^{'-1}$ - In the thermal treatment of sludge, with sludge/sludge exchangers, the heat transfer coefficient can take values of up to 350 W/m^2.k (300 mth/m^2.h.°C) for fluid velocities of between 0.5 and 1 m.s^{-1}.

Determining the logarithmic mean of temperatures

Given a countercurrent heat exchanger, in which two fluids are circulating:



The logarithmic mean is given by the relation:

$$d_m = \frac{d_1 - d_2}{\log \frac{d_1}{d_2}}$$

where: $d_1 = T_0 - t_1$

$d_2 = T_1 - t_0$

Used to calculate dm, the Hausband table (table 62) gives $\frac{d_m}{d_1}$ as a function of $\frac{d_2}{d_1}$

where $d_1 > d_2$

Table 62. Hausband table.

$\frac{d_2}{d_1}$	$\frac{d_m}{d_1}$	$\frac{d_2}{d_1}$	$\frac{d_m}{d_1}$	$\frac{d_2}{d_1}$	$\frac{d_m}{d_1}$
0.01	0.215	0.16	0.458	0.10	0.843
0.02	0.251	0.18	0.478	0.15	0.812
0.03	0.211	0.20	0.500	0.80	0.897
0.04	0.298	0.22	0.518	0.85	0.921
0.05	0.317	0.24	0.535	0.90	0.953
0.06	0.335	0.26	0.557	0.95	0.982
0.07	0.352	0.30	0.583	1.00	1.000
0.08	0.368	0.35	0.624		
0.09	0.378	0.40	0.658		
0.10	0.391	0.45	0.693		
0.11	0.405	0.50	0.724		
0.12	0.418	0.55	0.756		
0.13	0.430	0.60	0.786		
0.14	0.440	0.65	0.815		

Note: it is mathematically demonstrated that if $0,5 < \frac{d_2}{d_1} < 2$, the deviation between the logarithmic mean and the arithmetic mean is less than 5%. It is therefore perfectly reasonable to use the arithmetic mean as is the case for most exchangers in sludge treatment facilities.

7.4.

COOLING TOWERS

Hot water is cooled in contact with the air using three types of cooling towers (see page 59):

. **"Wet" or evaporative cooling towers** in which the water is in contact with the air and heat is transferred primarily through the partial evaporation of the water and the resulting increase in the moisture content of the air (between 85 and 90% of the exchange). Heat is also transferred by direct heating of the air or by convection. This transfer depends on the moisture content of the air.

"Dry" or non-evaporative cooling towers in which the water circulates in finned tubes and does not come into contact with the air; heat is transferred solely through the heating of the air.

. **Wet-dry or combined evaporative/ non-evaporative cooling towers** in which water sprayed over the tubes lowers the temperature of the air (figure 260), thus improving the efficiency of the installation.

The operation of cooling towers is defined by a number of parameters, including:

- **the cooling range**, i.e., the difference between the hot and cold temperatures of the water (values of 10°C and 12°C are often required);
- the **approach** or difference between the temperature of the cooled water and the wet-bulb temperature (wet cooling towers) or the dry-bulb temperature (dry cooling towers). This difference can attain 5 or 6°C in both cases.

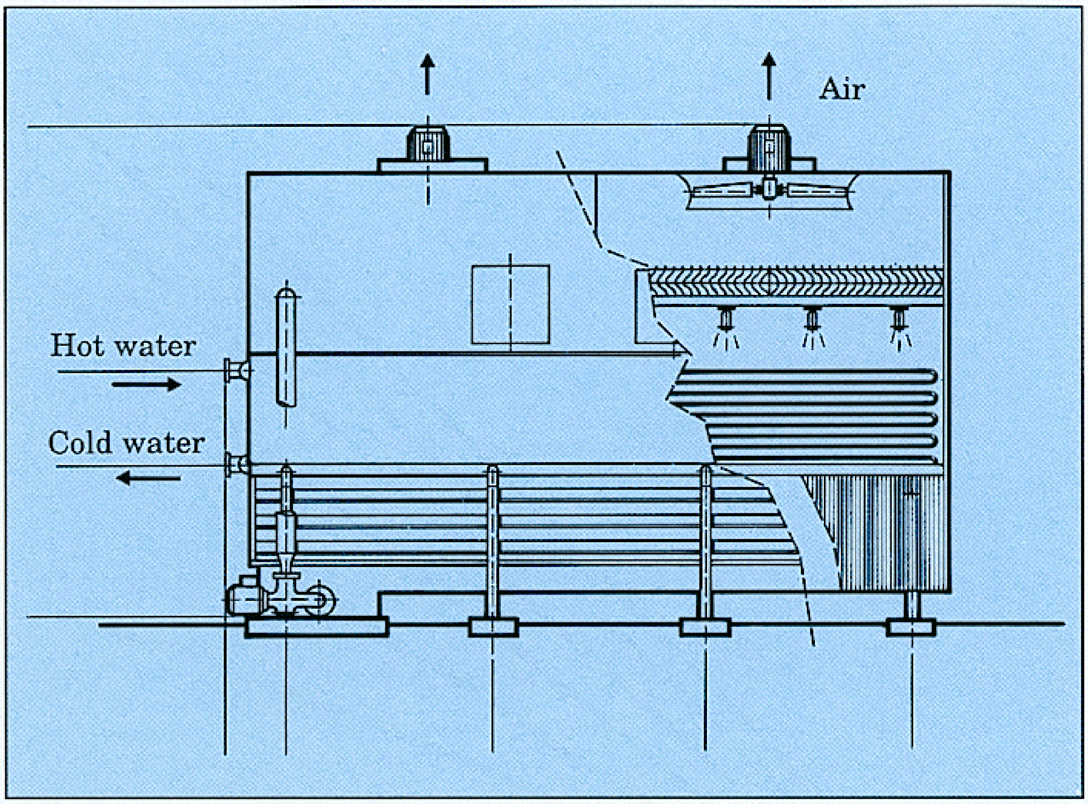


Figure 260. Wet-dry cooling tower.

In a **wet cooling tower**, the approach depending on the difference in the enthalpies of water and air is not constant when the wet-bulb temperature varies (c£ figure 261). Natural draught coolers are used primarily for high flow rates and low temperatures (the heated air is less heavy). Taking as his basis the relations of onvection and evaporation, Merkel 1925) developed an approximate equation characterizing the total heat transfer process:

M d Ce = K (H - H')S, where:

M: the mass of water being cooled,

d: the variation in the temperature of this water

Ce: the specific heat of the water,

H: the enthalpy of the saturated air at the temperature of the water,

H': the enthalpy of the air in contact with the water,

K: the mass transfer coefficient,

S: the surface of exchange.

The ratio $\frac{KS}{M}$ is considered dimension less. This value can vary between 0.7and 2

In a **dry cooling tower**, the approach is constant when the temperature varies

Cooling dirty water

When gas scrubbing water is recirculated or wastewater cooled prior to treatment, the cooling towers can suffer from scaling, fouling or even corrosion. These difficulties can be attenuated by projecting the droplets of water onto plastic gratings rather than running the water in films over a packing.

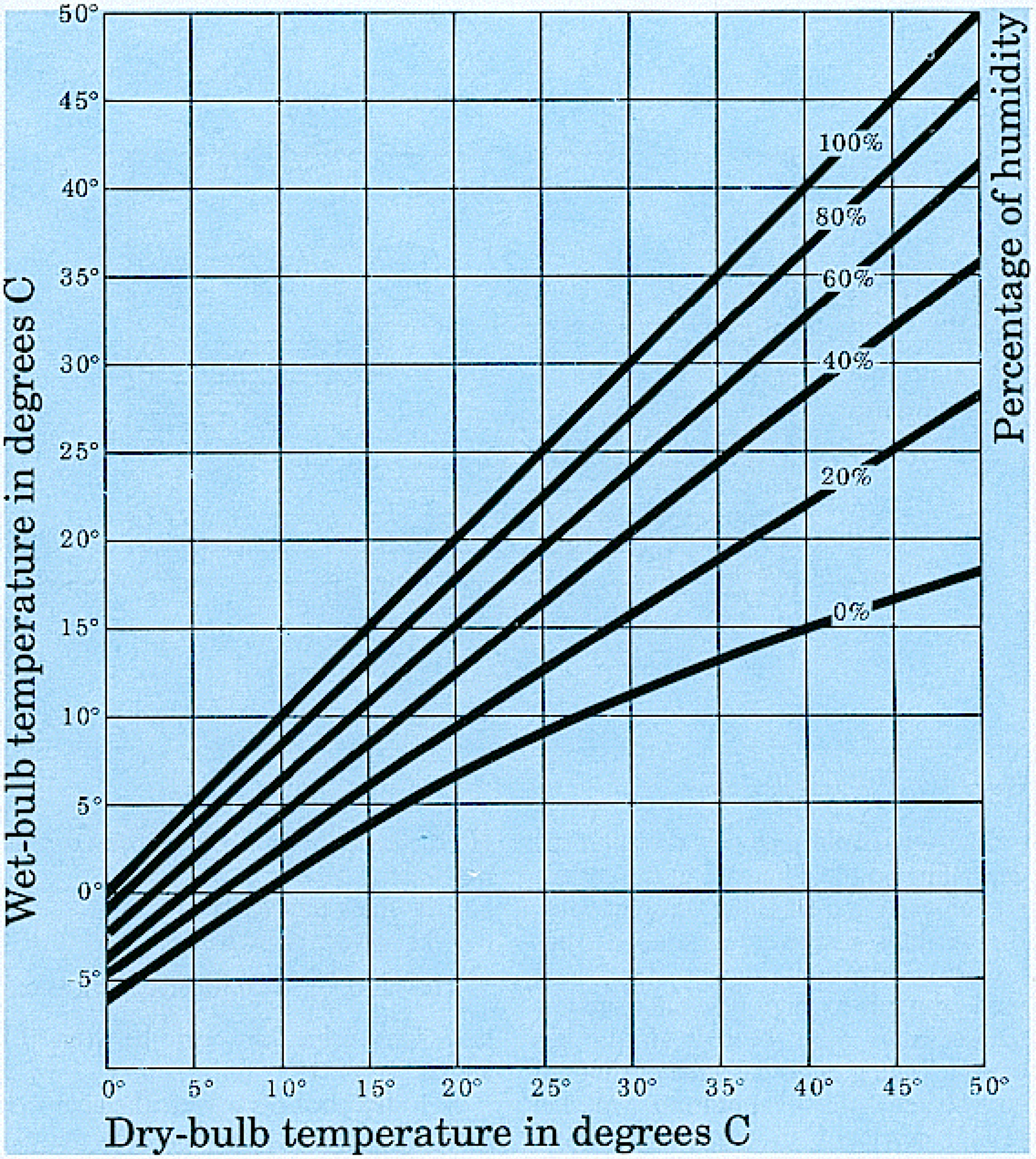


Figure 261. Temperature conversion. Dry- and wet-bulb temperatures versus relative humidity values of the air.

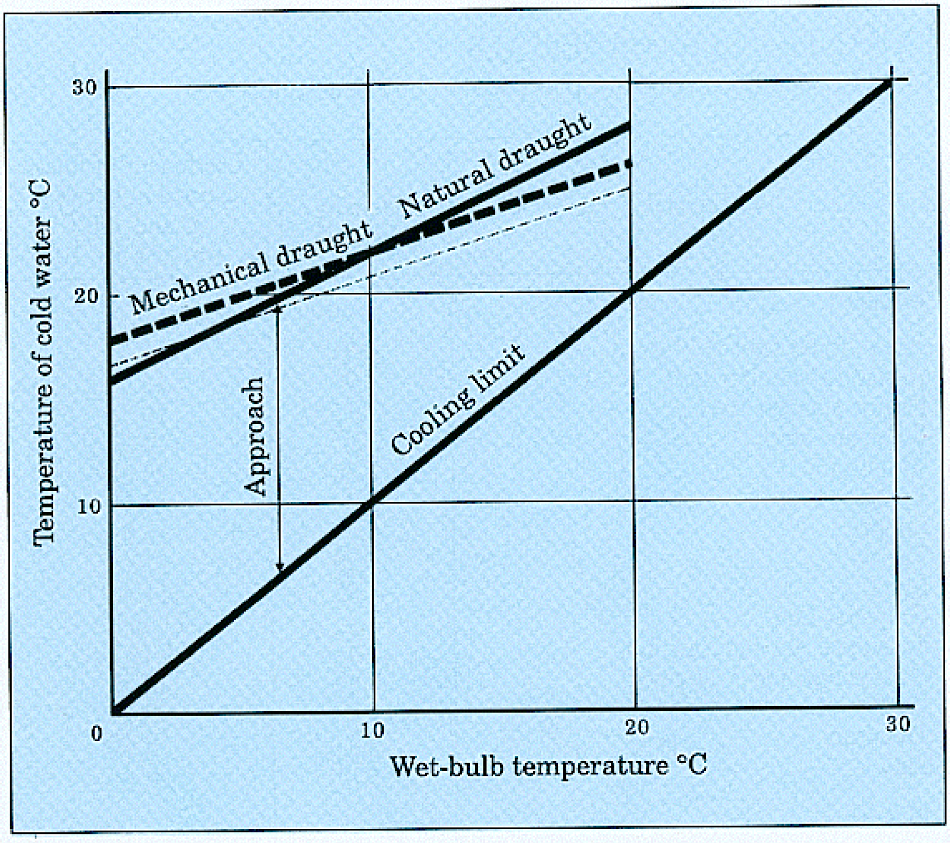


Figure 262. Influence of the wet-bulb temperature on the approach of wet cooling towers.

7.5

EXPANSION OF MATERIALS

Table 63. Coefficients of linear expansion of a few solids.

Material	**Density Kg.dm^{-3}**	**Coefficient of linear expansion between 20 and 100°C [m/m. C} x 10^{6}**
Metals		
Plain carbon steel	7.85	12.4
Austenitic stainless steel	7.9	16.5
Ferritic stainless steel	7.7	10.5
Refractory steel	7.9	15.5
Aluminium	2.70	23.8
Bronze	8.9	15.5
Copper	8.9	16.8
Tin	7.28	27
Iron	7.87	11.4
Gray cast iron	7.2	11 to 12
Spheroidal graphite cast iron	7.4	17.5 to 19.5
Brass containing 35% zinc	8.45	20.3
Lead	11.4	28.6
Titanium	4.5	8.35
Zinc	7.14	30
Plastics		
Acetal (resin) (Delrin)	1.4	130
Glass cloth reinforced epoxy (40% resin)	1.7 to 1.8	10
Glass cloth reinforced polyester 00176 resin)	1.8	30
Polyamide 6 (Nylon)	1.12 to 1.15	70 to 140
Polyamide 11 (Rilsan)	1.04	110 to 150
Polycarbonate (Makrolon)	1.20	60 to 70
PVC	1.35 to 1.45	50 to 180
Superchlorinated PVC	1.50 to 1.55	60 to 80
HDPE	0.95	110 to 140
Polymethacrylate (Plexiglas)	1.17 to 1.20	50 to 90
PP	0.9	70 to 150
PTFE (Teflon)	2.1 to 2.3	80 to 120
Impact PS	1 to 1.1	35 to 210

9
PRELIMINARY TREATMENT SYSTEMS

INTRODUCTION

Before the treatment process itself, raw water must be pretreated. This procedure consists of a certain number of operations which are exclusively physical and mechanical, aimed at removing as many elements as possible which, because of their nature and size, could hinder future treatment procedures.

Pretreatment operations are listed below (a treatment plant may include one or more of these operations, according to its size and the quality of the raw water):

- screening,
- comminution,
-grit removal,
- presedimentation,
- grease removal (frequently simultaneous with grit removal),
- oil removal,
- straining,
- removal and treatment of by-products.

The terms screening and straining need to be defined, since they are both mechanical procedures. Screening uses bar screens. The width of the openings between the very long bars in the screen rack is usually greater than 5 mm. Cleaning is done mechanically (raking). Strainers are slender structures with round, virtually square or crossed-mesh openings which, in general, are under 3 mm in size. The strainers can be either fixed or rotating, and cleaning is done either mechanically or hydraulically.

However, as a result of technological advances, straining operations may be carried out with very fine, custom made bar screens with slots less than 1 mm wide. These bar screens, like fine strainers, reduce the BOD_5 of MWW.

1. SCREENING

1.1. OPERATING CONDITIONS

Screening is the first treatment station, both for surface and wastewater. Its purpose is to:

- protect the structure downstream against large objects which could create obstructions in some of the facility's units,
- easily separate and remove large matter carried along by the raw water which might negatively affect the efficiency of later treatment procedures or make their implementation more difficult.

The efficiency of the screening operation depends on the spacing between screen bars:

- fine screening, for a spacing of under 10 mm,
- medium screening, for a spacing of 10 to 40 mm,
- coarse screening, for a spacing of over 40 mm.

Usually, fine screening is preceded by a preliminary screening operation for purposes of protection.

Screening is carried out by a manually cleaned bar screen (large in size, in order to reduce the frequency of screenings collection operations) or, preferably, by an automatically cleaned bar screen (essential in cases of high flow rates or for water with a high solids content). The automatic bar screen is usually protected by a sturdy preliminary bar screen which should also be provided with an automatic cleaning system in large facilities, and in the case of raw water containing a high volume of coarse matter.

To reduce manual operations as much as possible, screening procedures have become increasingly automated, even in small facilities. Automation is essential in situations where large amounts of plant matter (such as leaves during the autumn season) are carried by the water and arrive all at once at the bar screen, tending to mat the bars and completely clogging the screen in a few minutes. Fine screens must be automated.

The collected refuse is stored in a container of a given capacity, calculated according to the acceptable frequency of refuse disposal operations.

Usual spacings are:

- for surface waters, between 20 and 40 mm (upstream of strainer),
- for municipal wastewater: for raw water, from 15 to 30 mm (but upstream from a straining and/or lamellae settling process, fine screening is necessary); for sludge (if necessary), 10 mm or less,
- for some industrial effluents, especially agrifood effluents, fine bar screening (or at times, medium screening followed by straining).

1.1.1. Hydraulic sizing - Clogging

Under normal circumstances, the crossing velocity through the bar screen should be sufficient for matter to attach itself to the screen without producing an excessive loss of head or a complete clogging of the bars, or allowing matter to be carried by the flow; normally acceptable crossing velocities between bars average between 0.6 and 1.0 $m.s^{-1}$ and 1.2 to 1.4 $m.s^{-1}$ at the maximum water flow.

These velocities apply to the area of the clogged bar screen that is still clear. The degree of clogging (as a percentage of the clear wetted section) depends on the water quality and on the system used to recover waste from the bar screen. For automatic bar screens it can be anywhere between 10% (surface water) and 30% (wastewater with a high solids content). For manually cleaned bar screens, the area of immersed bar screen must be larger, so as to avoid frequent cleanings.

Approach velocities upstream of the bar screen are generally slow, especially in the case of fine bar screens with an open area of less than 50%; frequent sediment accumulation occurs upstream of the bar screen, which must either be prevented (by stirring) or disposed of, for instance, by daily self-cleaning.

1.1.2. Automatic control and the protection of bar screens

In general, the bar screen cleaning system works on an intermittent basis. It can be controlled in three ways: a) by a cyclic system of controllable frequencies (1 min to 1 h) and lengths of time (1 to 15 min); b) by a differential head loss indicator; c) (even better) by a combination of both systems. When the bar screen is located downstream from a pumping station, the control mechanism can be linked to the start-up of the pumps, with a built-in timer to keep the screen in operation for 1 to 30 minutes.

Automatic bar screens must be equipped with torque limiters to prevent equipment damage in case of overloading or blocking.

Normally, reciprocating cleaning bar screens, both curved and straight, include a device to ensure that the rake automatically stops moving at a point outside of the screen area, so as to avoid jamming upon restarting.

1.2.
DIFFERENT TYPES OF BAR SCREENS

1.2.1. General construction principles

1.2.1.1. Manual bar screens

To make raking easier, manually cleaned bar screens, made up of straight, round or rectangular bars, are, in general, at an angle of 60° to 80° to the horizontal. They can be travelling (on slides), or pivoting, for downstream cleaning of covered channels. In wastewater lifting stations, liftable cage screens are used instead of bar screens, thus avoiding the problem of access; however, their handling and cleaning are difficult.

1.2.1.2. Upstream cleaning bar screens

Automatically cleaned bar screens are usually cleaned from the upstream side, especially those described in this section.

There are three main types of automatic bar screens, differing from one another only with regard to some technical details. On the screen rack, the bars' cross-section is round or trapezoidal (thus lessening the risk of solid matter jamming), with sharp or rounded-off edges. Some of these bar screens allow for fine screening (and even straining) through the use of a custom made bar screen rack (of the Johnson type, where spacing ranges from a few millimetres to 0.5 mm) or a perforated steel sheet. Screenings disposal is carried out downstream of the screen.

. Type I: curved bar screens

This is the best bar screen for medium size facilities, where the water does not carry a high volume of matter and screenings are removed at a low elevation. Also, the effective cross-section of the opening is large and it is mechanically simple. Cleaning is done with one or two rakes located at the end of the rotating arm which revolves around the horizontal axis.

. Type II: straight bar screens with reciprocating cleaning mechanism

In general, the bar screen surface (at an angle of around 80° to the horizontal) stops slightly above the maximum level of liquid; it is extended with an apron. A reciprocating device (rake, doctor grab or swivelling ladle) brings up the screenings, first along the screen area and then along the apron; it then comes down away from the screen area. The screenings are removed from the elevated position by an extractor (which may be motor driven).

When handling very large flows (surface water intakes), greater for instance than 30,000 m3.h^{-1}, of water that does not have a large volume of matter, the operation can be carried out with a mobile screen which cleans only part of the bar screen, and moves laterally after each cycle.

. Type III: continuous cleaning straight bar screens

These are the best bar screens for fine screening when there is a risk of matting. Preliminary screening must be done first if there is a probability that the water is carrying coarse matter. Straight bar screens, at an angle of 80° to the horizontal, are cleaned by doctor blades, rakes or brushes driven by chains. In general, screenings are ejected by means of a motor-driven mechanism.

Figure 263. Back-cleaned screen installation.

Table 27. Upstream cleaning mechanical bar screens.

	Type of bar screen	Cleaning operation	Depth of channel m	Width of channel m	Bar spacing mm	Bar thickness mm	Height of disposal m	Water depth m
	Curved bar screen DC type	Contin.	0.75 to 1.75	0.5 to 1.6	10 to 40	10	0	0.50 to 1.5
	Hydraulic straight bar screen GDH type	Recipr.	0.75 to 2.80	0.6 to 1.2	10 to 40	10	0 to 1.2	0.50 to 1.5
Medium screening	Cable straight bar screen GDC type	Recipr.	2.00 to 10.0	0.1 to 2.6	10 to 40	10	0.65 and 1.2	1.5 to 9.5
	Rack and pinion bar screen	Recipr.	1.50 to 5.00	0.6 to 2.0	12 to 80		0.65 and 1.3	
	Grab bar screen	Recipr.	2.50 to 10.0	1.5 to 10	12 to 100			
	Fine curved bar screen GFC type	Contin.	0.75 to 1.75	0.5 to 1.6	1 to 10		0	0.50 to 1.5
Fine screening	Fine straight bar screen GFD type	Contin.	2.0 to 10.0	1.0 to 2.6	1 to 10		0.85 and 1.2	1.5 to 9.5
	Endless moving bar screen	Contin.	0.6 to 15.0	0.3 to 4.0	1 to 15		0 to 1.2	0.4 to 14.5

1.2.1.3. Back-cleaned bar screens

Some bar screens include a downstream endless chain cleaning system. With this set-up there is a risk that some of the screenings will fall back into the water downstream; however, for water carrying a high volume of matter, it may be advisable to have a back-cleaned preliminary screen with a high removal capacity (figure 263).

1.2.2. Curved bar screen, (DC type)

This type I bar screen (fig. 264) includes:

- a curved bar screen rack in a quadrant, supported by a rigid frame,
- a diametral rotating arm with two adjustable rakes, with a reduction gear, a torque limiter with a reaction arm, and a horizontal automatic stopping device,
- a noiseless extractor equipped with dampeners.

1.2.3. Fine curved bar screen (GFC

The general design of this type I bar screen is the same as the DC bar screen, except that it includes a fine screen or a stainless steel perforated sheet for spacings of less than 10 mm. Instead of rakes, polyurethane scrapers or nylon bristle brushes are used.

1.2.4. Straight bar screen (GDH type)

This type II bar screen uses hydraulic jacks to ensure a simple kinematic operation (figure 265).

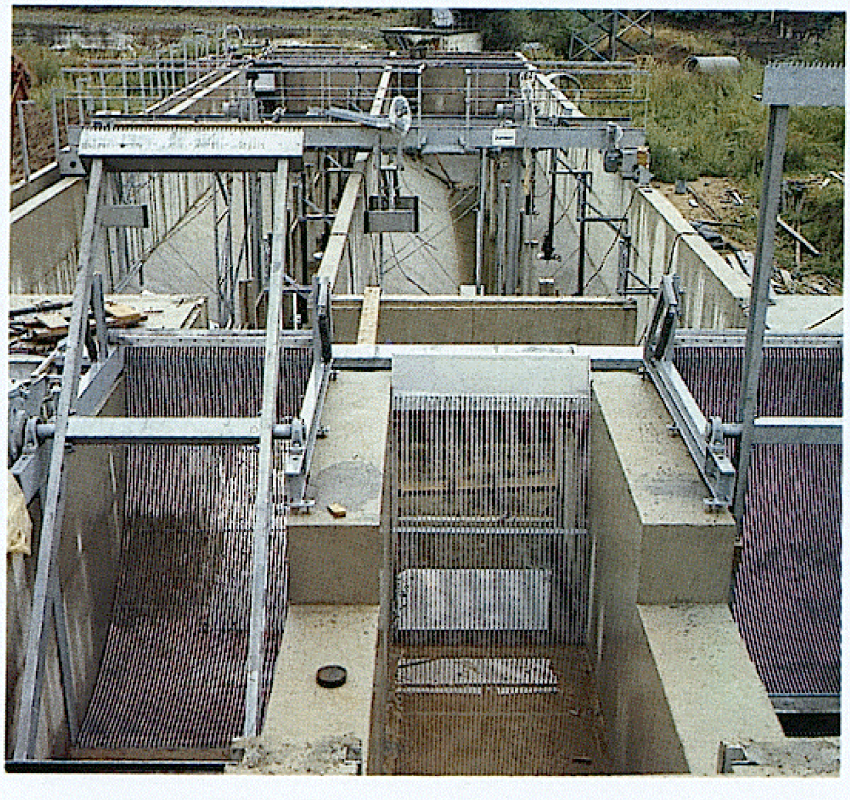
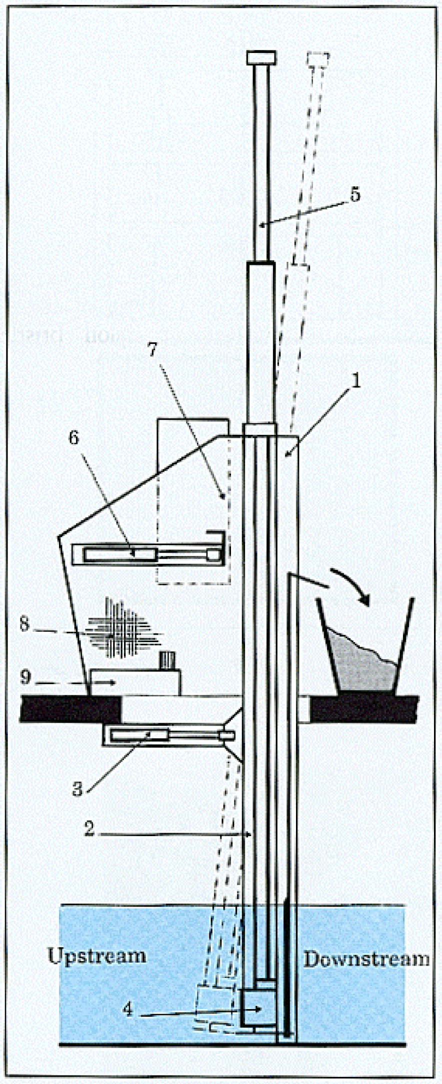


Figure 264. Curved bar screen (DC type).



1. Rigid frame with bar screen rack. 2. Moving frame. 3. Moving frame jack. 4. Rake carriage. 5. Lifting jack. 6. Ejector. 7. Electrical cabinet. 8. Latticed covers. 9. Hydraulic unit.

Figure 265. General diagram of a GDH-type screen.

It specifically includes:

- a vertical bar screen rack supported by a rigid frame (1),
- a frame (2) that tilts upstream by means of a jack (3), thus allowing the cleaning rake to descend away from the bar screen surface,
- a cleaning device made up by a rake carriage (4) which slides in the moving frame, driven by a jack (5),
- an ejector (6) driven by a jack.

1.2.5. Straight bar screen with cables (GDC type)

The rake carriage of this type II bar screen is driven by two cables. With this device, facilities can reach great depths, since pneumatic jacks drive the rake away from the frame (and descent therefore occurs away from the bar screen surface); this ensures a greater operational safety. It includes (figure 266):

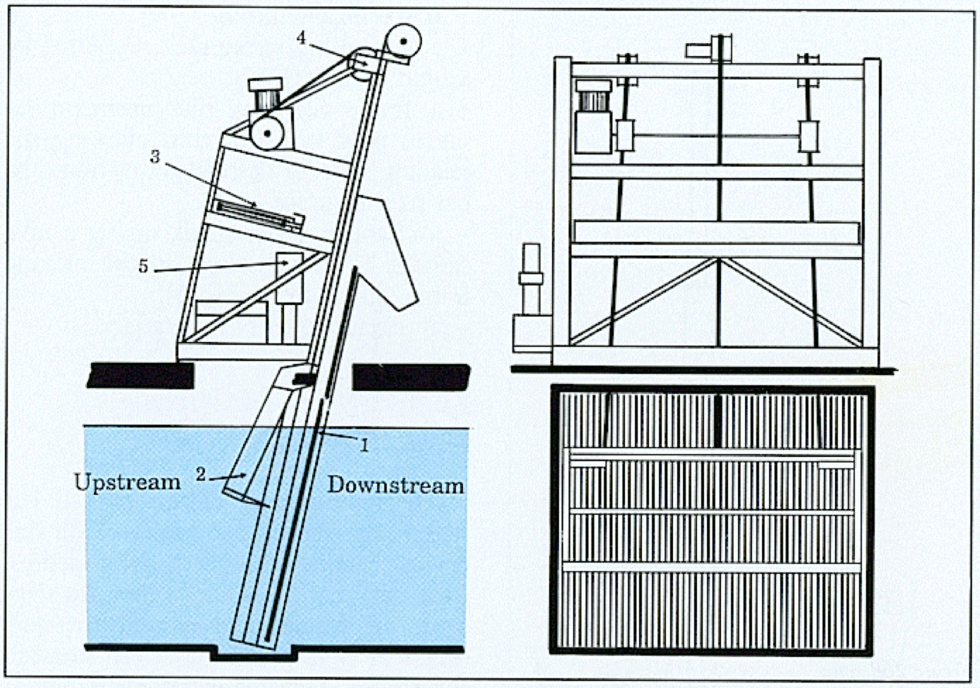
- an inclined bar screen rake on a rigid frame (1),
- a moving carriage (2), which slides on the guides of the rigid frame,
- an ejector (3) driven by jacks.

1.2.6. Fine straight bar screen

(GFD type)

This type III bar screen comprises a monobloc lifting unit, placed on guides sealed to the channel walls. Cleaning of the bar screen rack is carried out by chain-driven brushes. It includes (figure 268):

- an inclined stainless steel bar screen rack, mounted on a rigid monobloc frame,
- nylon brushes mounted on two endless chains driven by a reduction gear, for scraping and lifting of screenings,



1. Rigid frame with bar screen rack. 2. Rake carriage. 3. Ejector. 4. Jack-shaft line. 5. Hydraulic unit.

Figure 266. General diagram of a straight bar screen (GDC type).

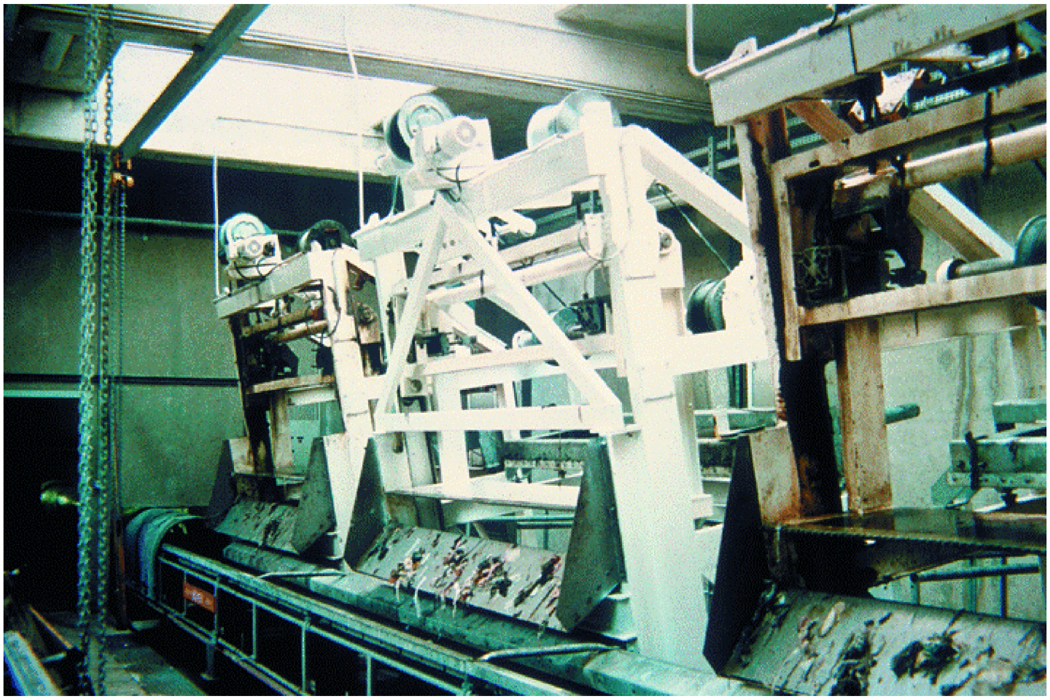


Figure 267. Straight bar screens (GDC type).

- an assembly for ejection and cleaning of lifting brushes, with a revolving brush roll driven by a chain.

Figure 268. Fine bar screens (GFD type).

1.2.7. Other bar screens

.Inclined straight bar screen with rack and pinion system

This type II bar screen is excellent for medium screening of water carrying a high volume of matter when the screenings do not require significant lifting. Because of its movable parts, its mechanical operation is simple and sturdy: all the movable parts are outside of the water, except for the reciprocating rake carried by two long hinged arms which, in turn, are held by a self-driven block which slides along the racks (figure 269).

. Vertical grab bar screen

This type II bar screen (figure 270) is excellent for heavy water flows carrying a high volume of matter, and when facilities reach great depths. The raising and lowering of the carriage which holds the grab (or ladle) is driven by two cables; the pivoting movement of the grab, hinged on the block, is driven by a third axial cable. Its construction and operation are simple, but its electrical drive (track limit switches, for instance) must be extremely reliable.

Figure 269. Rack and pinion bar screens.

Figure 270. Vertical grab bar screens.

Continuous moving screen

This machine is used for fine screening of wastewater, after preliminary screening and grit removal. Its bar screen surface is made up of a group of custom made hinged rakes (made of plastic) inscribed in a cylinder, that mesh with one another, hinged on two lateral chains (which ensure rotation of the assembly). Through the relative movement of two successive rakes, matter picked up by the machine can be removed.

1.3. COMMINUTION

This treatment is applied mainly to MWW, in order to shred solid matter carried by the water so that it may later undergo further treatment. Its purpose is to eliminate the constraints and complications brought about by the disposal and removal of coarse screening waste and to benefit from the increase in volume of the digestion gas produced. However, in practical terms, comminution has some short-comings, particularly the risk of a large accumulation of comminuted textile fibres or plants mixed with grease (clogging pumps and pipes, and possibly producing a scum layer in anaerobic digesters), which would mean that relatively frequent cleaning would have to be carried out on rather delicate equipment.

For the above mentioned reasons, comminution is no longer used in France, except on raw water at the head of the plant. However, when treating sludge, it sometimes replaces fine screening in which case it is done through a pressure comminutor, so as to obtain the desired degree of comminution fineness.

Both gravity flow and pressure comminutors are particularly well suited for treatment of MWW, due to the fact that they are capable of absorbing matter normally carried by this kind of water (after preliminary coarse screening of 40 to 80 mm, depending on the size of the machine), and reducing it into elements of a few millimetres average diameter.

1.3.1. Gravity flow comminutors (raw water)

These produce only a slight loss of head, and use little energy. The more traditional comminutors include a vertical revolving drum, with horizontal slots. In the Infilco Degrémont Griductor (figure 270 a), the drum is made up of round bars equipped with cutting teeth; there are fixed cutting rakes bolted on the frame. The machine is located within a flat-bottom, open, rectangular channel; the water goes through the drum horizontally, at which time the matter is shredded. Another model, installed in the same way, includes two revolving vertical drums, with meshing cutting teeth.

1.3.2. Pressure comminutors (raw water and sludge)

They are mounted between flanges and have to be extremely robust. They are equipped with a large electrical motor, in order to counter the possibility of clogging. In general, the comminutor system (which is in a closed casing) includes a rotating element with bars, cutting teeth and rakes, which does not make the water circulate; rather, water circulation is achieved through a pump placed in series in the conduit.

Some of these comminutors operate differently: they include a sharp revolving propeller with pumping capabilities (working at low pressure), which drives flow circulation.

Table 73. General characteristics of comminutors.

Type of comminutor	**Flo $m^3.h^{-1}$**	**Power of the electrical motor kW**
Gravity flow comminutors	5,000 to 8,000	0.25 to 4
In-line comminutors	50 to 300	7.5 to 20

Figure 270 a. Infilco Degrémont Griductor.

2. GRIT REMOVAL

2.1. OPERATING CONDITIONS

Grit removal operations remove gravel, sand and fine mineral particles from raw water, in order to prevent deposits in channels and pipes, to protect pumps and other machines against abrasion, and in order to avoid problems in later treatment stages. The normal size of particles treated by grit removal operations is equal to or greater than 200 µm; smaller particles are removed by presedimentation or settling treatments.

The theoretical principles of both grit removal and settling of discrete particles are closely related (see page 158).

In practice, the following data can be used (valid in unhindered settling for grit particles with a specific gravity of 2.65).

Table 74. Corrected settling velocity of grit particles.

d cm	**0.005**	**0.010**	**0.020**	**0.030**	**0.040**	**0.050**	**0.10**	**0.20**	**0.30**	**0.50**	**1.00**
V_c cm.s^{-1}	0.2	0.7	2.3	4.0	5.6	7.2	15	27	35	47	74
$V_{c'}$. cm.s^{-1}	0	0.5	1.7	3.0	4.0	5.0	11	21	26	33	
$V_{c''}$cm.s^{-1}	0	0	1.6	3.0	4.5	6.0	13	25	33	45	65
VI cm.s-^{1}	15	20	27	32	38	42	60	83	100	130	190

Where:

d : diameter of the grit particle,

Vc : settling velocity for a fluid with zero horizontal velocity,

Vc' : settling velocity for a fluid with horizontal velocity equal to VI,

Vc: settling velocity for a fluid with horizontal velocity of 0.30 m.s^{-1},

VI: critical horizontal velocity to entrain the settled particle.

When treating wastewater, the objective is to extract as much inorganic matter as possible, and as little organic matter as possible (as this causes problems both during removal and storage of the extracted grit). This separation procedure uses energy, which in turn lessens the efficacy of the settling procedure. So a compromise has to be made between the removal capacity (limit particle size adopted) and the acceptable amount of organic matter in the grit.

2.1.1. Grit removal in surface water

The water intake must be designed to avoid sand carry-over. If local conditions are inadequate, a grit remover must be included unless arrangements have been made to remove grit at another structure. If the facility includes a presedimentation tank, those particles larger than 300 µm can be removed by a rough grit channel with hydraulic flushing.

If the facility includes a strainer (1 to 2 mm-mesh, for instance), grit removal should be done upstream, so as to avoid any problems at the strainer itself.

In general the grit remover is a rectangular channel-type device.

Its cross-section will depend on the desired horizontal flow velocity: this velocity should be greater than the critical velocity VI of the settled particles (table 74), if sand is to be disposed of hydraulically, and lower if disposal is to be done by a bottom scraper.

The horizontal surface is calculated dividing the maximum flow to be conveyed, by the settling rate Vc of the smallest particles to be retained, corrected according to the horizontal flow velocity selected.

The grit can also be separated by cycloning (a hydrocyclone at the discharge end of the lift pumps). (See page 611.)

2.1.2. Grit removal in municipal wastewater

Since the nature of the medium is heterogeneous, separation of grit and other matter contained in the water cannot be fully carried out: the extracted grit will still contain some organic matter that settled with it; this amount can be minimised if a sweeping flow of about 0.3 $m.s^{-1}$ is maintained at floor level.

Separation can be improved by washing the grit extracted from the grit remover (see page 630), whereby the content of organic matter in the washed grit decreases to less than 30%.

Because of the nature of the extracted product, very specific equipment (vortex pumps, air lifts) must be used, so as to reduce the chance of abrasion and clogging.

In increasing order of size and effectiveness, the following are used:

- single grit channel, where flow velocity varies according to the flow rate. This structure is rarely recommended, and only for small and simple facilities. The grit is extracted manually from a longitudinal gutter with a storage capacity of 4 to 5 days;
- a grit channel improved by the inclusion of an outlet weir obeying linear equation (i.e., water depth proportional to flow rate). Flow velocity remains constant at 0.3 m.s 1. Retention time is around 1.5 to 2 min;
- circular grit chamber, used for mechanical extraction of grit and hydraulic extraction of floating matter and scum (see page 608). Retention time is around 2 to 3 min;
- aerated rectangular grit chamber, used for mechanical extraction of grit and hydraulic extraction of floating matter and scum (see page 608). Retention time is around 2 to 5 min.

The last two above-mentioned devices are increasingly used in combination with grease removal (see page 615).

2.1.3. Grit removal in industrial wastewater

Grit removal is less necessary in IWW. Aerated grit chambers used for MWW can sometimes be used for IWW, especially in agricultural and food industry effluents.

When treating effluents of the metallurgical and mechanical industry, the purpose of grit removal is to separate the very dense particles of iron oxide, of granulated oily scale with a bulk density 4. These abrasive particles that quickly, are present in initial concentrations ranging from 0.2 to several slag and of grammes per litre, and therefore should of 2.5 to be recovered by special equipment in the settle grit remover.

2.2.

CIRCULAR GRIT REMOVERS

The diameter of these tapered cylindrical structures is 3 to 8 m, with a liquid depth of 3 to 5 m.

Water enters tangentially either at the periphery of the structure or in a central cylindrical baffle; it is recovered through a submerged opening in the cylindrical wall.

The grit is deposited on a slightly sloping floor, moves due to hydraulic forces, and falls into a central hopper for storage and recovery. The sweeping velocity of the floor is kept practically constant at a level greater than 0.3 m.s 1 in three ways (characteristic of this type of structure):

- rotation of the liquid mass through a vortex effect resulting from the tangential entrance of the water,
- rotation of the liquid mass by a revolving vertical shaft, blade type mechanical mixer, whereby a specific power of 10 to 20 $W.m^{-3}$ can be maintained regardless of the flow rate, thus allowing the level of liquid to remain practically constant throughout the operation,
- gyration (in a vertical plane) of the liquid mass by blowing air into a submerged cylindrical baffle through special diffusers. With this machine, the operation can be carried out with a nearly constant level of liquid.

The grit collected in the central hopper is extracted by a pump or an air lift, and dried by gravity or sent to a mechanical recovery system.

2.3.

AERATED RECTANGULAR GRIT CHAMBERS

The width of these structures can range from 4 m (single structure) to 8 m (double structure); the liquid depth is around 4 m; the maximum length is around 30 m. They can handle large flow rates.

The shape of the floor depends on the system used to recover grit.

Water is introduced at one end of the structure, and recovered at the other end through a submerged opening; often, it goes through a downstream weir designed to maintain a constant water level.

All along this slow horizontal flow structure, there is an in-line air-injection system, equipped with special air diffusers such as Vibrairs, whereby a 15 to 30 $W.m^{-3}$ specific aeration power is achieved. The liquid can be maintained at a nearly constant level. The blown air produces cross-circulation velocity, promotes (through turbulence) the separation of the organic matter bound to the particles of grit, and partially removes floating matter.

Grit extraction is done automatically, as follows:

- by a group of air lifts operating in a pulsed fashion (recovery in the lower hoppers),
- by scraping (scraper bridge) towards a collection pit at one end (recovery by a fixed pump or air lift),
- by suction pump or air lift set up on a movable bridge, discharging the diluted grit into a lateral disposal trough.

Figure 271. Aerated rectangular grit chamber.

2.4. "METALLURGY" GRIT REMOVERS

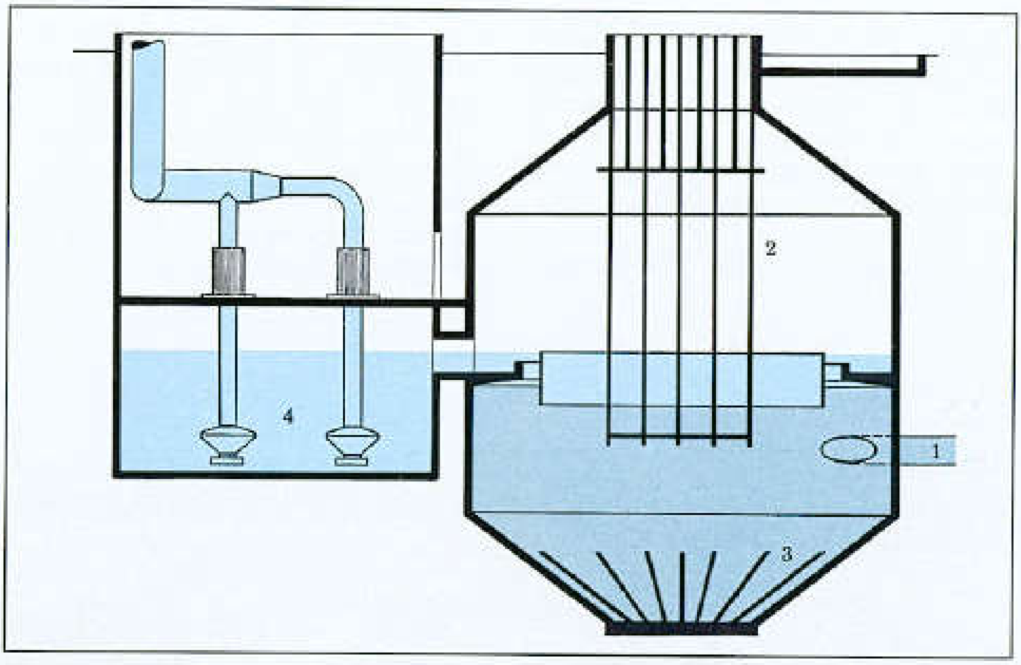
Depending on the level of incoming water, two different grit removing techniques are used:

. **tangential separators** (figure 272), frequently called "hydrocyclones°, which is incorrect since the centrifugal energy developed is low. In the case of rolling mills, hot strip mills and continuous casting mills, separators are used when wastewater inlets can go down to levels of : -10 m. These cylindroconical structures play a dual role:

- they separate discrete particles through vertical settling,
- they separate large amounts of incoming oil using a scum baffle.

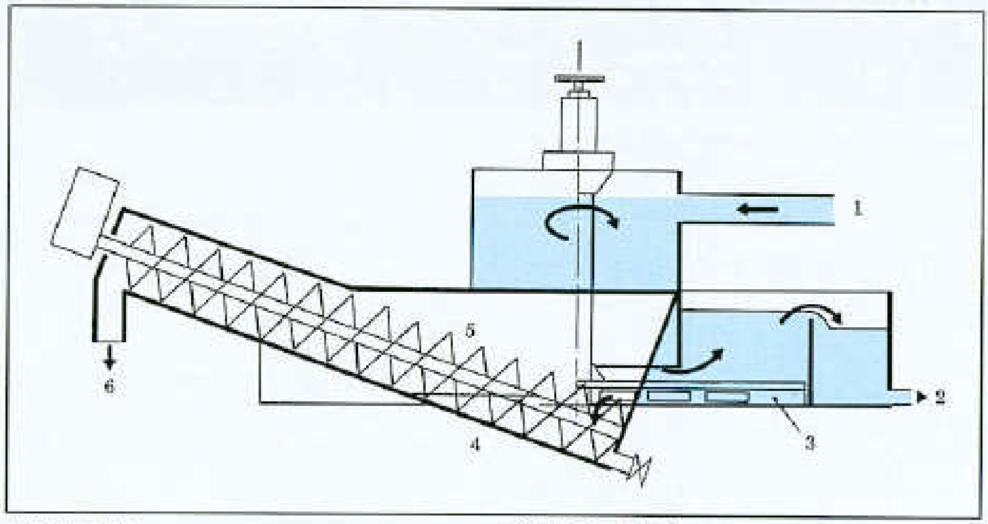
Recovery of these deposits is always carried out by a grab.

These structures built by Degrémont with diameters of 4 to 32 m, are located upstream of the settling tanks or filters. Accordingly they must be capable of removing particles upwards of 100 µm.



1. Water inlet.
2. Grab guide.
3. Floor protection.
4. Recovery of treated water.

Figure 272. "Metallurgy" tangential separator.



1. Water inlet.
2. Treated water outlet.
3. Scraper arm.
4. Peripheral sludge pit.
5. Sludge disposal screw.

Fig. 273. "Steelworks" classifier separator.

"Classifier" separators: their only role is to remove discrete particles larger than 200 or 250 gm. They are located upstream of the clarifier thickeners, and protect the sludge pumps and dewatering equipment.

Built by Degrémont in the range 5-12 m diameter, these units are fed, in general, by overhead conduits, and they comprise a circular zone for rapid settling with a low water depth. A centrally driven diametral scraper arm discharges sediments towards an outside pit, from where dry extraction is carried out through a screw or a reciprocating rake (figure 273).

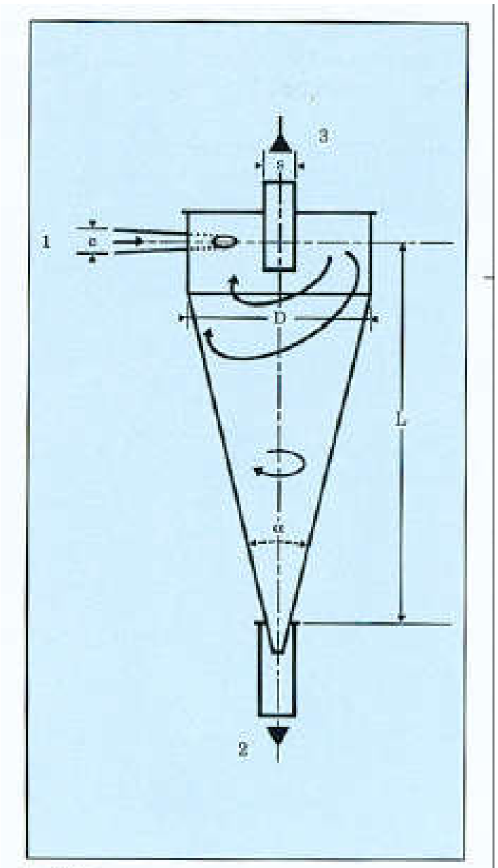
2.5.
HYDROCYCLONES

These machines separate particles through centrifugal hydraulic classification. They are made up of a cylindroconical compartment in which, because of the tangential feed, water rotates before leaving through an axial overflow pipe (figure 274).

The concentrated sludge leaves through the cone bottom (underflow). Even in the smallest machines, the centrifugal acceleration can be greater than 600 g, and the feed pressure ranges from 0.5 to 2 bar. The separation factor d50 generally expressed in gym, and improperly called removal capacity, corresponds to the particle diameter for which there is a 50% separation.

Its construction has the following characteristics: compartment diameter D, length L/diameter D ratio, diameter a of the inlet opening and diameter s of the outlet opening, and cone angle a.

Different ratios have been considered in order to define a cyclone in terms of its size; according to Rietema, typically it is as follows (based exclusively on the geometric aspects)



1. Inlet.
2. Underflow (sand).
3. Overflow (outlet).

Figure 274. Hydrocyclone.

$$Cy_{50} = \frac{d^2_{50}\,\Delta\varrho}{\eta\varrho} \cdot \frac{L\Delta p}{q} = \text{constant}$$

Where:

ϱ : water density

? ϱ : difference in densities between solid particles and water

?p : differential pressure in the machine

? : dynamic viscosity

q : output of the machine.

The experimental differential pressure variation ?p is set as a function of the throughflow rate. There are two basic types of machines:

- **Monotubular hydrocyclones**

Their diameter ranges from 150 to 800 mm for the treatment of 20 to 250 m^3.h^{-1}, flows, with d_{50} factors of 50 to 80 µm. They are protected from abrasion. They operate on concentrated sludge suspensions, or even on raw water that does not have a high volume of matter if the removal capacity can be increased.

- **Multitubular hydrocyclones**

For grit removal of larger flows with a low volume of matter, very small diameter cyclones can be used, set in parallel in one compartment, where a smaller d_{50} factor (10 µm) can be reached. Their diameter is of several centimetres, and they are made in anti-abrasive plastic material. The head loss is between 1 and 2 bar. The feed water must first go through appropriate straining.

3. PRESEDIMENTATION

3.1.FIELD OF APPLICATION

Presedimentation, which precedes clarification, is a solid/liquid separation stage of surface waters containing a very high amount of solid matter, carried out when the conventional one-stage settling procedure cannot be done. The purpose of this settling procedure is to remove most of the suspended solids in raw water, to dispose of them as concentrated sludge, and to provide the main settling stage with an acceptable water quality. The concentration threshold of suspended solids after which presedimentation becomes necessary is a function of the type of main settling tank to be used:

- 1.5 to 2 $g.l^{-1}$ for non-scraper type or sludge blanket settling tanks,
- 5 $g.l^{-1}$ for scraper settling tanks.

If grit removal has been carried out, presedimentation is the next stage, and it includes two phases of solid/liquid separation, i.e., hindered settling, and sludge thickening, the relative magnitude of which depends on the content and nature of suspended solids in the raw water, and the treatment being considered.

In general, the presedimentation stage is designed to dip occasional peaks of suspended solids of up to about 30 $g.l^{-1}$. Other than during these potential peak periods, the presedimentation tank can be bypassed. Above 30 $g.l^{-1}$, this same structure can be used but at lower flows; thus, the sludge disposal flow represents a considerable proportion of the incoming flow.

In general, it is inadvisable to consider presedimentation in water with an SS content > 50 $g.l^{-1}$; in that case, it is usually better to isolate the unit so as not to damage the equipment. A raw water holding tank can be set up upstream of the unit.

3.2. APPLICATION

In general, coagulant and/or flocculant reagents must be used to improve the quality of settled water and the hydraulic performance of presedimentation tanks.

Without a chemical reagent, the rate used in the unit must be lower than the natural settling velocity of the effluent's suspended solids which, in turn, depends on the nature and concentration of these solids (about 0.5 to 1 $m.h^{-1}$).

With an inorganic coagulant only, a fraction of the colloidal phase is removed. The settling velocity obtained with iron chloride (about 1.5 to 3 $m.h^{-1}$) is often greater than that obtained with aluminium sulphate (about 1 to 2 $m.h^{-1}$); in addition, aluminium salts produce large amounts of sludge. The treatment rate to be applied is one third of the rate necessary for optimal coagulation/flocculation.

These inorganic coagulants should only be used on water with SS definitely lower than 30 $g.l^{-1}$.

With an organic flocculant only,

settling velocity increases considerably; the colloidal fraction can be decreased if the polymer has been correctly selected. Of the three options, this is the best, because the floc produced is very compact, and the sludge very concentrated (more than 100 $g.l^{-1}$). For a treatment rate of 1 $g.m^{-3}$ of active product, applicable velocities can reach the following levels:

- 3 to 5 $m.h^{-1}$ for raw water with 30 $g.l^{-1}$ of SS;
- 8 to 10 $m.h^{-1}$ for raw water with)

10 $g.l^{-1}$ of SS.

In some cases, an inorganic coagulant and an organic flocculant can be used together. When only an organic coagulant is used, performance is usually lower than when only an organic flocculant is used.

The need for, and the sizing of a presedimentation facility are often difficult to determine. There are four basic factors that must be considered:

- nature and concentration of particles (fine sand, silt, clay, colloids, etc.);
- range and frequency of peaks,
- need to maintain quality;
- operational costs: reagents, labour.

Presedimentation tanks are rectangular (suction bridges, chain scraper) or circular (diametral scraper). Their construction is similar to that of settling tanks (chapter 10, subchapter 3). They should be preceded by a flash mixer to add the reagents, and sometimes even by a flocculator. Sludge removal by pumps is strongly recommended because of the concentration and large quantities of sludge that must be removed.

Fig. 275. Circular scraper settling tanks for presedimentation.

4. GREASE AND OIL REMOVAL

4.1.
PRODUCTS TO BE SEPARATED

Grease and oil removal operations separate products with a slightly lower specific gravity than water; through a natural or aided (chapter 3, paragraph 4.1.1) flotation effect, in a compartment with a sufficient volume of liquid.

Greases are solid products (as long as the temperature is sufficiently low), of animal (or vegetable) origin, present in MWW and in some IWW (from the agricultural and food industries) and, in low quantities, in storm water tanks, lagoons, ponds, etc. They are present either in the form of free particles or, more frequently, coalesced with different suspended solids (which must be dislodged so that flotation may occur). The separation technique used permits the recovery, not only of the grease itself, but also of floating products such as various vegetable or animal waste (slaughterhouses), soap, foam (detergents), elastomers and plastics, etc.

Grease removal is a liquid/solid separation procedure whereby a compromise is reached between a maximum retention of grease and a minimum deposit of fermentable settled sludge. Its performance is difficult to estimate because of sampling and analysis difficulties.

"Oils" is the name given to various liquid products such as vegetable oils, mineral oils and light hydrocarbons. If they are present only as traces (in surface water, heating condensates of petroleum product reservoirs), their separation is carried out by adsorption and filtration. The term oil **removal (or oil separation) is usually** used only for the removal of oil present in appreciable quantities in IWW, especially the petroleum industry (normally absent in MWW, since it is illegal to dispose of it in the sewage system).

Oil removal is a liquid/liquid separation procedure.

4.2.
GREASE SEPARATORS

4.2.1. Operating conditions

<u>4.2.1.1. Grease removal in MWW before sewage disposal</u>

This "at source" preliminary treatment is recommended, and sometimes compulsory, for many small-scale enterprises, restaurants, communities, etc. Standardised grease separators (or grease traps) are manufactured in series for maximum flows of 20 to 30 $l.s^{-1}$. These devices are designed for a retention time of 3 to 5 min and a rising velocity of about 15 $m.h^{-1}$.

If operated correctly they can retain up to about 80% of solidified grease, and store 401 of lighter matter per ls^{-1} of inlet flow. Regular cleaning is essential. Water temperature must be less than 30°C at the outlet. These devices are designed so as to avoid, as far as possible, the deposit of heavy matter; but it might be advisable to include upstream a settling tank for coarser matter, easy to clean, and with a retention time of 1 to 3 min.

4.2.1.2. Grease removal as preliminary treatment for a wastewater purification plant

A primary settling tank can separate grease that settles at the surface but, in general, it is unable to recover large amounts of grease. This situation could lead to operational difficulties.

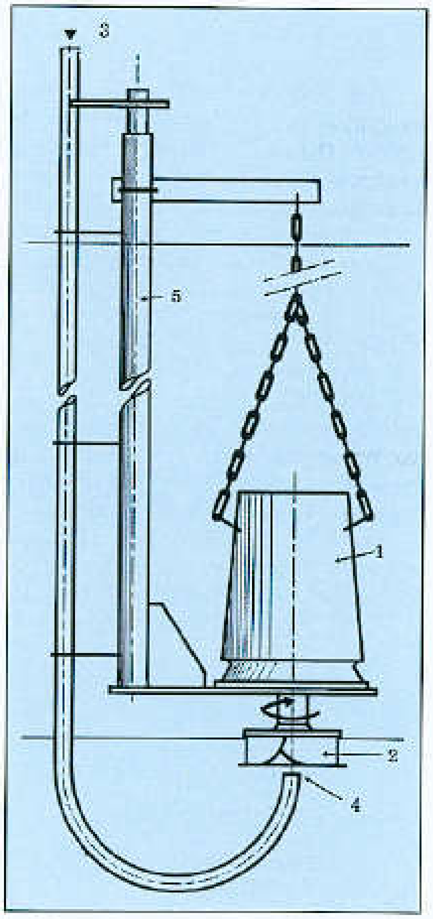
For household wastewater, grease separation is essential if there is no primary settling; its effectiveness is maximised if carried out together with grit removal. Structure size should therefore be estimated accordingly (a retention time of around 15 min), and provisions should be made to separate the organic matter settled with the grit.

In wastewater from the food and agricultural industry containing high amounts of grease to be retained (particularly slaughterhouses and the meat industry), it may be advisable to have a separate grease separator designed for a hydraulic loading of 10 to 20 m3.h-1 per m of effective surface. It would protect the sewer system because it would be located before the discharge to sewer.

These units are not designed to retain oils and hydrocarbons which, when necessary, are removed through primary settling.

4.2.2. Circular grit/grease separator

The diameter of this cylindroconical unit is 3 to 8 m, and its liquid depth (at the centre) is 3 to 5 m. It is equipped with a submerged Turboflot mixer/aerator placed along the axis. The Turboflot mixer/aerator (figure 276) includes a centrifugal pumping impeller, submerged under some 2 m of



1. Submerged motor. 2. Centrifugal impeller. 3. Air suction. 4. Air inlet. 5. Support.

Figure 276. Diagram of the Turboflot mixer/aerator.

water, driven by a submerged electrical approximately 45°. Settled grit slides on motor which releases a specific power of this slope towards the recovery point at 15 to 30 W per m^3 of liquid capacity.

The impeller:

- induces a revolving flow in the lower areas of the unit,
- creates an area of concentrated turbulence which promotes the separation of grease and coalesced matter,
- draws some atmospheric air through an open air pipe, and releases this air into the liquid in the form of very small dispersed bubbles. The air produces a slow revolving movement of the liquid mass through an air-lift effect, which promotes the collection of grease and scum at the surface.

Water is introduced tangentially into a central, submerged cylindrical baffle which surrounds the Turboflot; it is recovered through a submerged opening in the circular wall.

The lower tapered zone of the unit becomes a hopper with an angle of the bottom of the unit; this movement is aided by a sweeping velocity greater than 0.15 $m.s^{-1}$ produced by the mixer.

Once the grit that collects at the bottom of the hopper has been separated from the settled organic matter by direct mixing in the unit (air injection to the base of the air lift), it is drawn off by an air lift; the emulsion is dried by gravity or sent towards a mechanical recovery system.

The grease floating on the surface is continuously recovered by a low-speed rotating scraper assembly; the scraped grease is pushed on an inclined surface to an above-water weir and falls into a collection trough. It is generally disposed of by gravity flow into a storage skip.

Figure 277. Circular grit/grease separator.

4.2.3. Rectangular grit/grease separator

Units with a width of 4 m (single unit) to 8 m (double unit) have a liquid depth of about 4 m and a maximum length of about 30 m. They are able to treat large flows (figures 278 and 279).

The unit's cross section has a shape that works well with sweeping crossflows, with slopes that promote grit collection on the bottom of the unit. Water is introduced at the head of the unit, and recovered at the other end through a wide submerged opening in the wall, passing through a downstream weir to maintain the water level constant.

The unit, with a slow horizontal flow, is generally equipped with two interrelated mixing and aeration systems which create transverse spiral flows independent of the flow of water. This permits significant variations in the velocity of horizontal flow which can be slow without causing any problem:

- a possible preliminary grit removal zone at the inlet (which can be up to 1/3 of the unit's length), includes an in-line air-injection system equipped with custom made air diffusers such as Vibrairs, which deliver a specific aeration power of 20 to 30 $W.m^{-3}$. The blown air maintains a transversal circulation velocity, promotes (through turbulence) separation of the organic matter coalesced to the grit, and prevents the massive accumulation of large grit particles at the head of the unit;
- the rest of the unit is used for grease separation and fine grit removal; it includes a series of in-line Turboflots, which produce a slower spiral flux and allow grease to float.

Grit is automatically extracted by a reciprocating travelling bridge with a programmed sequence:

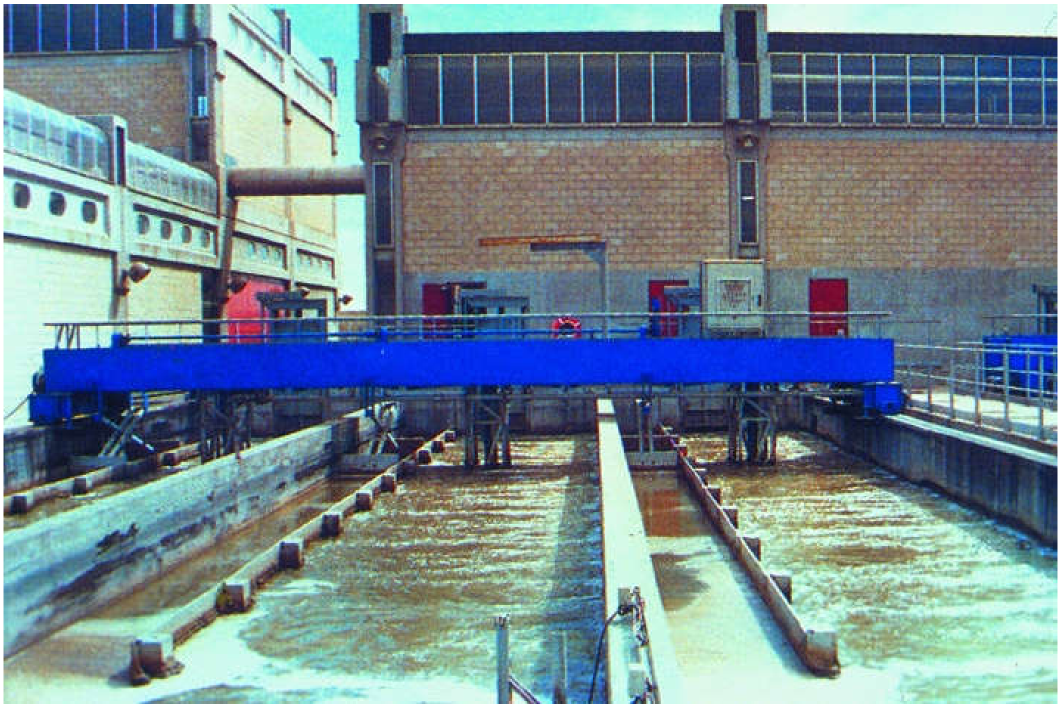


Figure 278. Rectangular grit/grease separators.

- either by scraping towards an end collection pit, followed by discharge by means of a pump or a fixed air lift,
- or by suction pump or air lift mounted on the travelling bridge, discharging the suspended grit into a side disposal trough.

The grease floating on the surface is scraped towards the end of the unit by a travelling bridge, and is removed according to a programmed sequence:

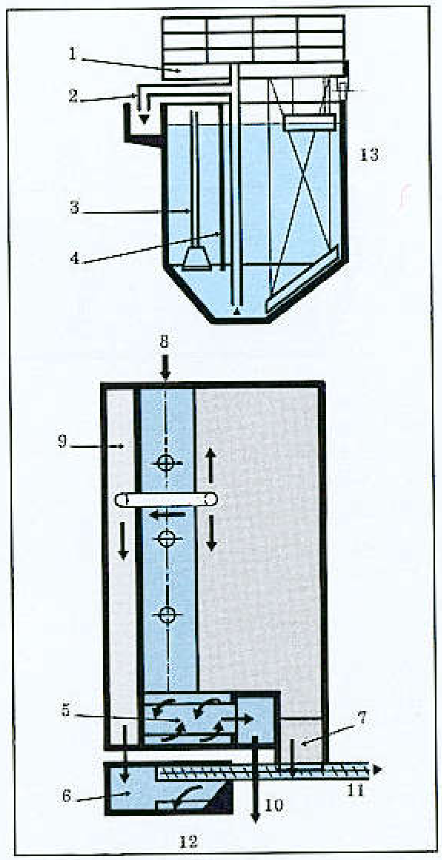
- either by pushing it onto an inclined surface and over a non-submerged weir:

dry" option - immediate recovery in a pit or skip,

- or by weir penstock (motor-driven and programmed): "wet" option - hydraulic conveying to an additional separation unit (see paragraph 6.3).

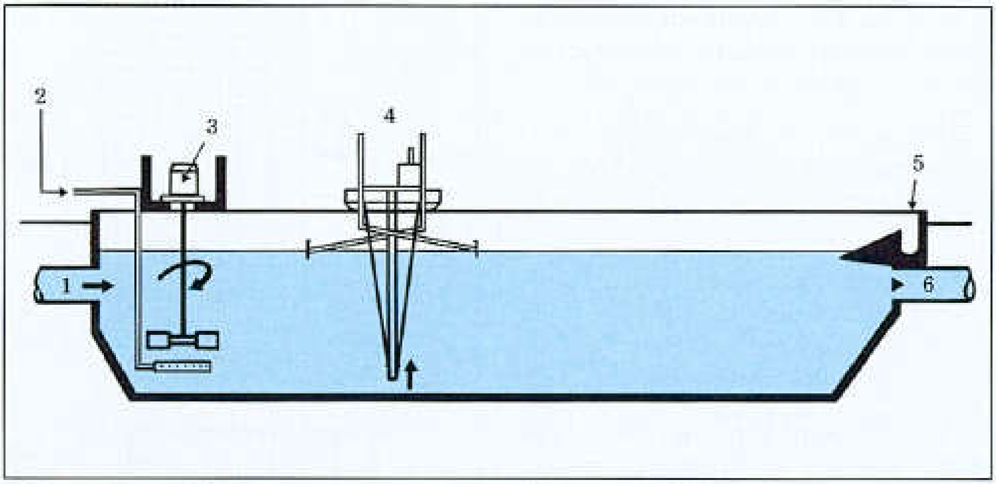
4.2.4. Rectangular grease separator with aerator/mixers at the head of the unit

For water containing small amounts of large grit particles, it may be advisable to use a variant of the unit described above, with only one or two aerator/mixers (figure 280); these devices can be of the Vortimix D type, which includes a submerged propeller on a vertical shaft, under which a controlled pressurised air flow is injected through an appropriate diffuser. This kind of aerator/mixer, to be used in large units, plays the same role as the Turboflot, with the possibility of including separately the mixing and aeration functions.



1. *Bridge, foot-bridge, scraper assembly.*
2. *Grit recovery by air lift.*
3. *Turboflot mechanical aerators.*
4. *Scum baffle.*
5. *Assembly for recovery of treated water.*
6. *Grit and grease extraction.*
7. *Grease recovery assembly.*
8. *Screened water inlet.*
9. *Grit collection trough.*
10. *Treated water outlet.*
11. *Grease and grit outlet.*
12. *Overflow outlet.*
13. *Suspended scraper.*

Figure 279. Diagram of a rectangular grit/grease separator, with in-line Turboflots.



1. Screened water inlet.
2. Pressurised air-feed.
3. Vortimix.
4. Suction and skimming bridge.
5. Grease recovery.
6. Treated water outlet.

Figure 280. Diagram of a grease separator with Vortimix at its head.

4.3. OIL SEPARATORS

4.3.1. Operating conditions

Two types of industrial effluents are involved:

- regular amount of oil (petroleum production and refining, edible oil mills, cold rolling mills, airports),
- small amount of oil, but with high accidental flow peaks (storm water from refineries, storage heating condensates, oilfired power plants, hot rolling mills).

Oils and hydrocarbons are present:

- either in a **free state,**
- or as fine but unstable mechanical emulsions, more or less adsorbed on suspended solids
- or (less frequently) as **chemical emulsions** (such as aqueous cutting fluids).

Oil separation by gravity is applicable only in the first two, and is a function of:

- specific gravity of oil which, in general, ranges from 0.7 to 0.95, but can be greater than 1 in some heavy hydrocarbons,
- temperature, the rise of which always promotes separation,
- the dynamic viscosity of the oil, which can range from several hundredths of a Pa.s to more than 0.2, a limiting value for the use of certain processes,
- the congealing point.

Oil separation in these effluents includes one or two stages:

- preliminary oil separation, or the removal of floating hydrocarbons, which can be combined with grit removal,

- oil separation which, depending on the objective, almost completely removes the dispersed hydrocarbons (table 74).

Table 74. Preliminary separators and separators.

Feed	**Preliminary separators**	**Medium separators** (40-50 mg.l^{-1} HC)	**Polishing separators** (5-20 mg.l^{-1})
Under pressure	Closed separators	Cyclones	Coalescer filters Granular media filters
Gravity	. API type , parallel plates . circular	Mechanical flotation units	Dissolved air flotation units

4.3.2. Gravity preliminary oil separators

The performance of preliminary separation units, which are generally operated without the use of a reagent, cannot be quantified:

- the hydrocarbon specific gravity and size distribution of droplets in water are usually unknown,
- the nature of the emulsion is poorly defined,
- it is practically impossible to do upstream sampling.

These devices eliminate very large and irregular peaks of oil, as well as larger droplets. There are three types:

- **longitudinal separators (API):** operate according to American Petroleum Institute standards (separation of droplets greater than 150 µm in diameter); their width ranges from 1.8 to 6 m, their water depth from 0.6 to 2.4 m.

These separators are difficult to cover (for smell reduction purposes), and sludge removal from the bottom is impractical;

- **lamellae separators:** through the use of lamellae settling procedures with plastic plates spaced at about 4 cm (figure 281), retention time has decreased from several hours to less than 60 min and even 30 min. These devices require some maintenance; also, it is advisable to use them for relatively warm water (solidification should be avoided) with small amounts of suspended solids (bottom scraping is expensive).

Since their construction is of a modular type, treatment of heavy flows requires a large number of modules (each one able to treat 15 to 30 m^3.h^{-1}, with distribution units that are both difficult to cover and to skim;

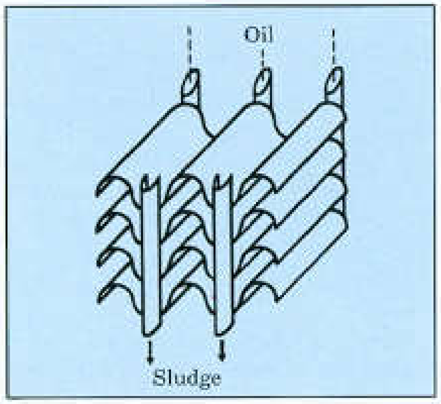
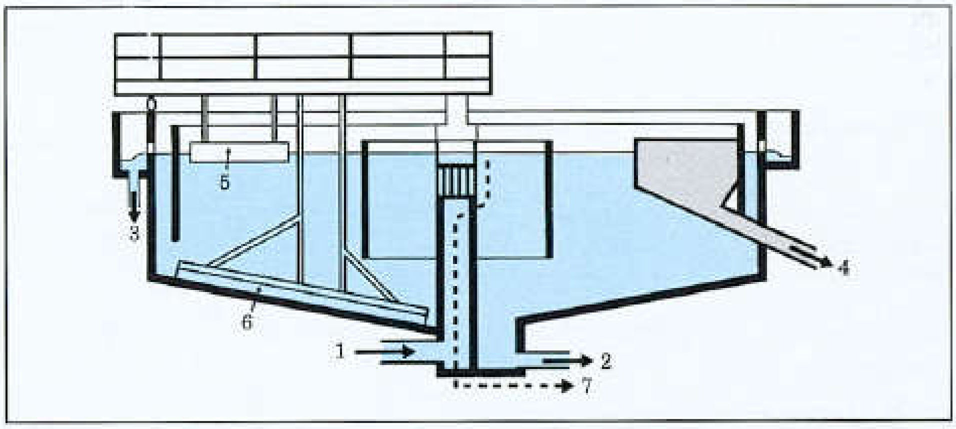


Figure 281: Lamellae oil separator modules.

- **circular separators:** separation is carried out in two successive chambers (figure 282): the first is a covered one, which prevents outgassing of light, volatile products; the second includes a bottom scraper as well as a surface skimmer.



1. Raw water inlet.
2. Sludge outlet.
3. Treated water outlet.
4. Heavy oil outlet.
5. Surface skimmer.
6. Bottom scraper.
7. Recovery of light oil, protected from the atmosphere.

Figure 282. Diagram of a circular oil separator.

4.4.

RECOVERY OF OIL AND FLOATING MATTER IN BASINS OR LAGOONS

The collection of oil layers (and/or floating matter) found at the surface of still water can be done with devices called oil recovery units, which do not carry out any purifying action on the underlying water. There are four types:

. Adjustable direction troughs and weirs

Fixed (or floating for variable water levels), they require an additional device to approach the oil layer and carry away a large quantity of water.

Figure 283. Radeg.

- **Drum or belt oil collectors**

Their main advantage is that they can recover oil with very little water and, especially in the case of belt collectors, they can tolerate a large variation in water level. For large surfaces, they also need an oil-layer skimmer.

- **Fixed mechanical oil recovery units**

The oil layer is conveyed over a great distance towards the collection zone, by water currents created by a moving pump set.

- **Movable oil recovery units**

With these floating devices (self-propelled or towed), large water surfaces (storm water tanks or lagoons) can be maintained. They take up a large flow of water, which is then cydoned or clarified.

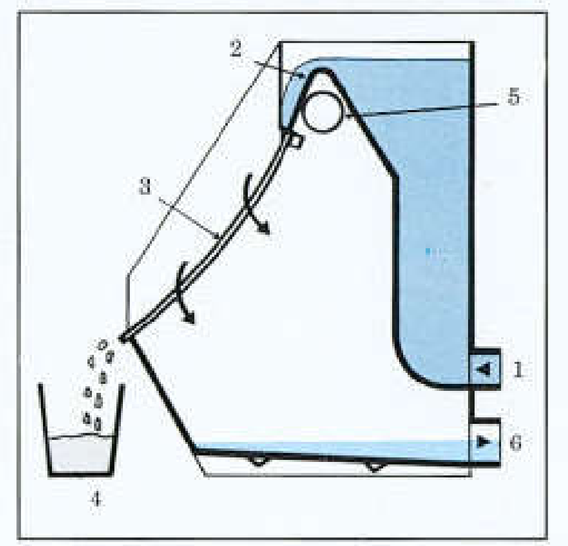
With Radeg (figure 283), there is a recovery of not only oil and grease but also, through its grinder, of papers, rags and other floating matter which are frequently found on water surfaces.

5. STRAINING

5.1. STRAINING OF WASTEWATER

In addition to mechanical bar screens with narrow slots spaced at 3 or 6 mm, necessary for some municipal wastewater treatment schemes, it may be useful to have strainers with smaller openings. That is the case for some AFI wastewater in which, together with straining, a significant portion of suspended polluting matter can be removed and, possibly, recycled.

The strainers' operating equipment is made up of perforated sheet plates or, more often, Johnson-type bar screen elements. Spacing ranges from 0.5 mm (or even 0.25 mm) to 2 mm. There are:



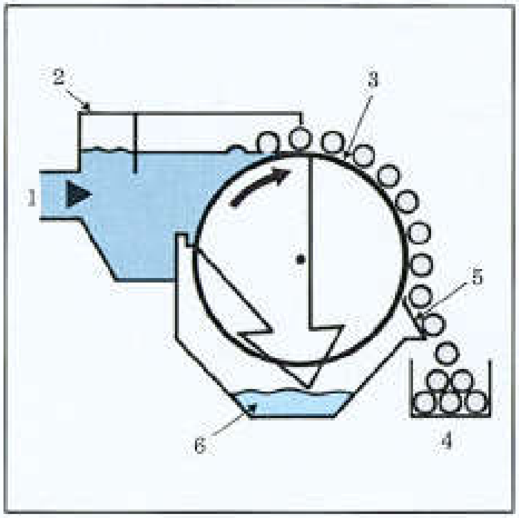
1 – Raw water inlet.
2 – Distributor flap.
3 – Strainer screen.
4 – Screenings.
5 – Observation window.
6 – Strained water outlet.

Figure 284. Diagram of a concave strainer (assisted self-cleaning).

. concave vertical bar screens (figure 284) with assisted self-cleaning and a capacity limited to 100-200 m^3h^{-1}. Since the raw water is distributed in the form of a vertical water curtain, the retained particles are carried hydraulically towards a lower container, 9

. rotating drums with a maximum capacity of 1500 $m^3.h^{-1}$:

- in some devices, most of the matter retained outside of the drum is removed by scraping, whereas the remaining mat

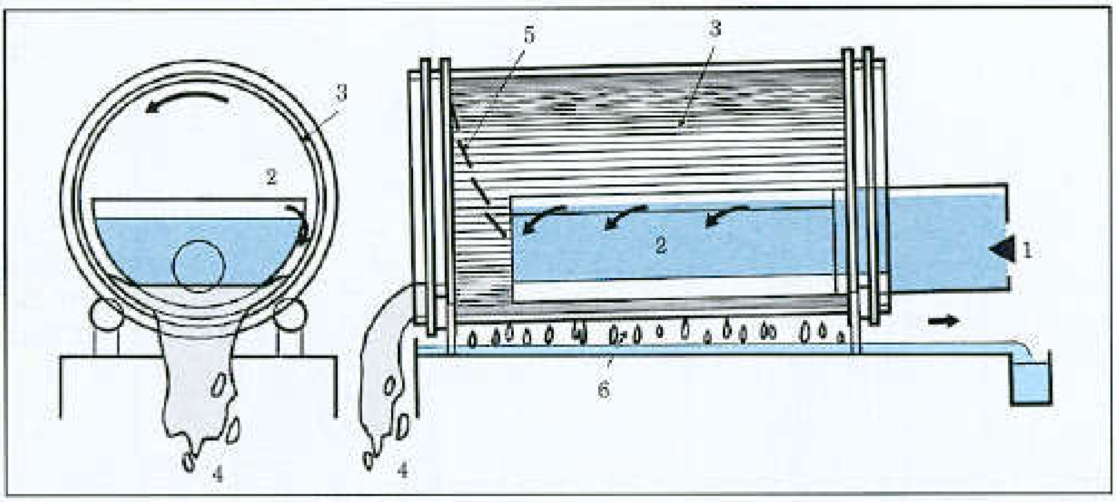


1 – Raw water inlet.
2 – Feed box.
3 – Strainer.
4 – Screenings.
5 – Doctor blade.
6 – Strained water outlet.

Figure 285. Diagram of a rotating strainer with external feed and mechanical cleaning.

ter is carried by the strained water which crosses the strainer in the opposite direction (figure 285),

- in other devices (figure 286), matter retained inside the drum is removed because of its slope, and cleaning is carried out through water spraying (also in the opposite direction).



1 – Raw water inlet.
2 – Distribution trough.
3 – Cylindrical strainer.
4 – Screenings.
5 – Screenings guides.
6 – Strained water outlet.

Figure 286. Diagram of a rotating strainer with internal feed and sprayer cleaning (Contrashear).

5.2.
STRAINERS FOR SURFACE WATER

5.2.1. Macrostraining

The filtering elements are made up of perforated sheets or, more often, of crossmesh stainless steel or synthetic fabric sheets with 0.15 to 2 mm openings.

Strainers come in the form of 15 to 6 m diameter drums, or 1 to 3 m wide bands; their 3 to 15 m height is well suited to rivers with a variable water level (figure 287).

Depending on the direction in which the water circulates, the sprinkler washing system is located over or inside the filter. Ditty wash water is removed through a trough.

In both cases, by using dihedral or semi-cylindrical shaped panels, the specific filtration surface increases (chapter 3, figures 59 and 60). The maximum capacity of these devices is several thousand m^3h^{-1},

5.2.2. Microstraining

The mesh size of the synthetic fabric filtering sheets ranges from 30 - 40 to

150 µm. They are mounted on drums. The washing equipment must be capable of intense spraying of the fabric because of the increased clogging risk due to fine sand and silt. Joint watertightness is essential. These devices have a limited capacity (figure 289).

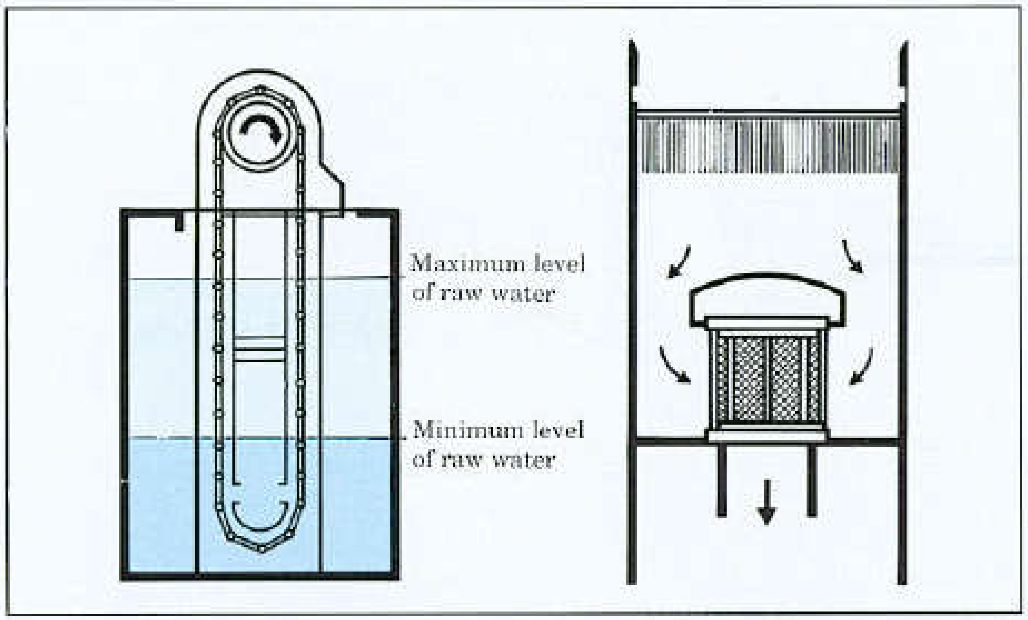
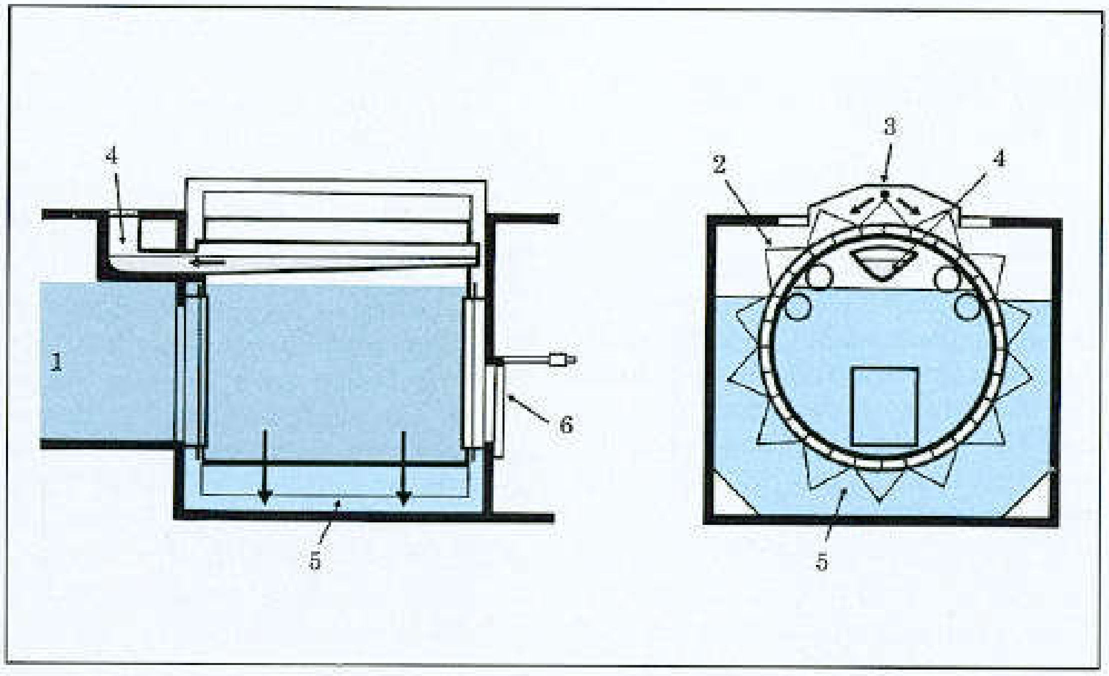


Figure 287. Band macrostrainer.

Figure 288. Rotating microstrainers.



1 – Raw water inlet.
2 – Strainer.
3 – Wash water.
4 – Wash water outlet trough.
5 – Strained water outlet.
6 – Safety valve.

Figure 289. Drum microstrainer (Geiger).

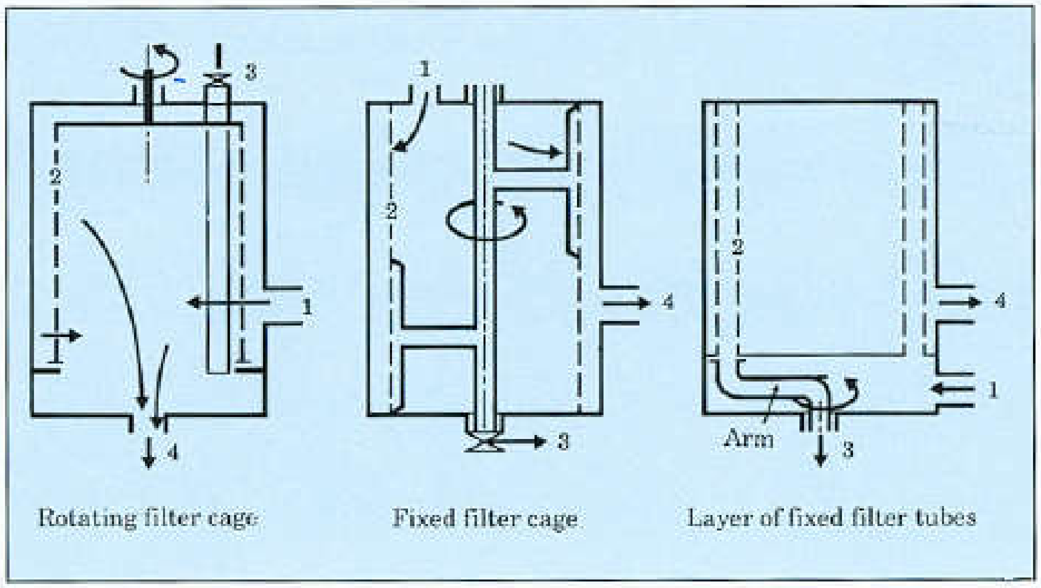
5.3.
MECHANICAL FILTRATION OR PRESSURE STRAINING

These filters (see page 182) comprise a semi-continuous washing system which ensures sludge removal by applying atmospheric pressure, in countercurrent, on a sector of the filter. Washing pressure must be consistent with the mechanical strength of the fabric.

So as to avoid irreversible clogging and excessive use of wash water, the fineness of the pressure straining system should usually be limited, for all practical purposes, to:

- 100-150 µm, for water with a large volume of organic matter and vegetable debris,
- 40-50 µm, for water containing only hard inorganic matter.

Fibres are especially troublesome, since they tend to stick to the fabric. There are three basic types of design (figure 290). Unit flow of these devices decreases with straining fineness. Above 250 µm, it can reach a level of 5,000 $m^3.h^{-1}$; and in microstraining, up to 500 $m^3.h^{-1}$. Wash water consumption, under the same conditions, ranges between 2 and 8%.



Rotating filter cage

Fixed filter cage

Layer of fixed filter tubes

1 – Raw water inlet.
2 – Strainer.
3 – Sludge.
4 – Strained water outlet.

Figure 290. Types of mechanical pressure filtration.

6. DISPOSAL AND TREATMENT OF BY-PRODUCTS

6.1.
SCREENINGS

This type of matter (see page 76) is often landfilled or buried. It can also be incinerated in a screenings furnace or in a household refuse furnace. Combustion temperature should be greater than 800°C to avoid smells. Screenings inside the works are handled as follows:

- either manually (in small facilities): a tray (perforated or non-perforated), rolling skip, movable skip,
- or mechanically: conveyor belt, continuous or reciprocating conveyor with squeegees,
- or hydraulically: trough fed by pumped water.

Because of transportation and environmental constraints, drying or compacting treatments have been given increased consideration, i.e.:

- drying (and transportation) by a movable, Sita-type, integrated compactor skip (figure 291): the water content is reduced by 75 to 80%, and the bulk density of the compacted matter in the skip is 0.75 to 0.8,
- compacting through a mechanical or hydraulic custom made press (figure 292): the compacted product may have a water content of 55 to 65%, and a bulk density of 0.6 to 0.65.

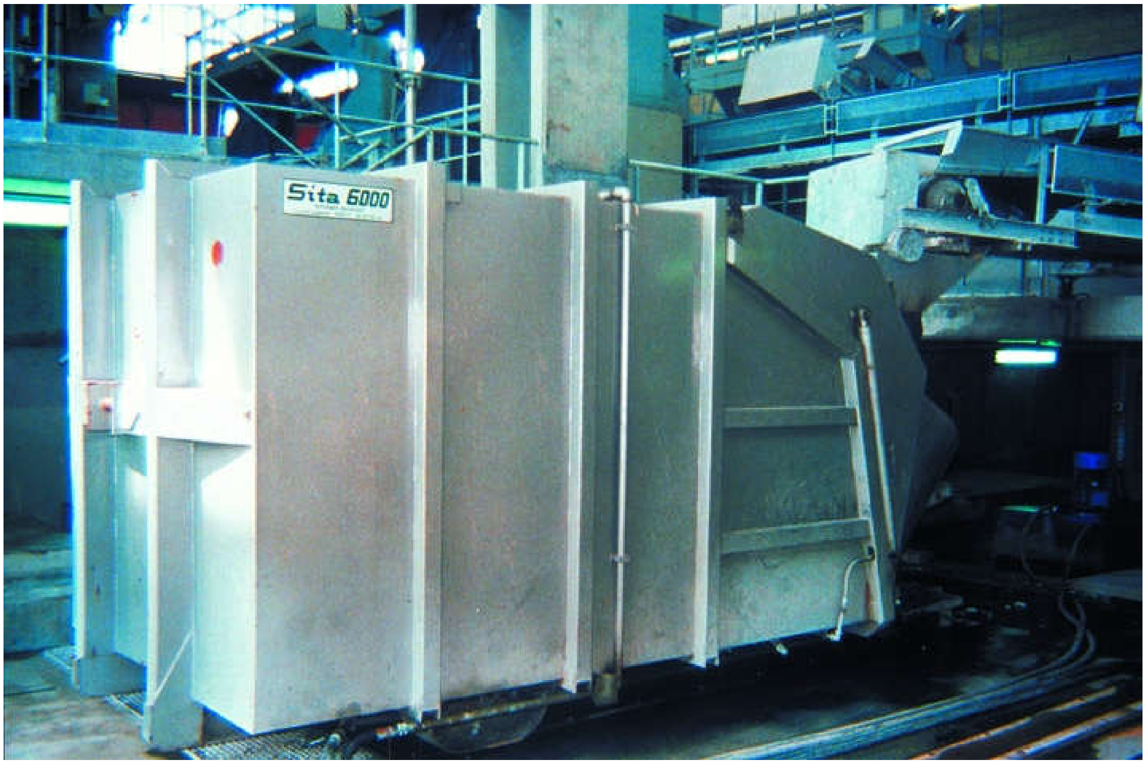


Figure 291. Sita integrated compactor skip.

Figure 292. Screenings press.

6.2.
GRIT

Grit (see page 76) extracted by a shovel from small grit channels cannot be reused, and must be buried or landfilled together with screenings.

For medium-size facilities, grit hydraulically extracted from grit removers can be separated from its water by:

- settling in a shallow tank: water is removed through filtering slabs or over a weir, -mechanical recovery (Archimedean screw, or reciprocating rake classifier) and storage in a fixed hopper or skip,
- hydrocycloning and storage in a hopper with an overflow weir,
- hydrocycloning and recovery by Archimedean screw before storage in a fixed hopper or movable skip.

Washing by make-up water on the Archimedean screw can also be considered. In large facilities, grit is sometimes washed before hopper storage, in a basin equipped with an efficient air mixing system which receives the water/grit mix pumped from the grit chambers.

A washed grit that is quite clean can be reused on-site (setting up drying beds).

Figure 293. Grit washer.

6.3.

GREASE AND SCUM

In general, grease and scum collected at the surface of grit removers, grease separators and primary settling tanks, cannot be reused. One possibility is to send this kind of waste to anaerobic digestion (after having been fine screened during its hydraulic transfer): this arrangement usually increases gas production, but at the risk of producing a scum layer.

It is preferable to store it in a skip, which could be equipped with an overflow outlet scum baffle, and then remove it periodically for burial or landfill. It can also be incinerated with sludge or screened matter, if the furnace and handling conditions allow it.

Figure 294. Grease collection.

In large facilities, grease and scum from different units are sometimes hydraulically transported towards a static flotation unit, which is equipped with a mechanical blade skimmer for dry recovery of grease, which is then stored in a skip or pit. After supplementary screening and, possibly, reheating to liquefy them, the products are pumped at a constant rate into an incinerator or sludge treatment furnace.

10

FLOCCULATION - SETTLING FLOTATION

1.ADDITION OF REAGENTS

The effectiveness of the flocculation process is directly affected by the efficiency of prior coagulation. To ensure the latter the reagent must be dispersed virtually instantaneously in a coagulation chamber, a flash-mix reactor characterized by high power input and a high velocity gradient (see page 135). Depending on the technology, the liquid's retention time varies from a few seconds to a few minutes.

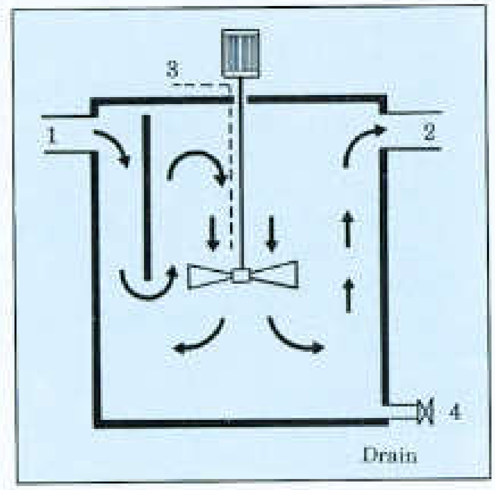
1.1.

IMPELLER TYPE FLASH MIXERS

These cylindrical (steel) or rectangular (concrete) tanks are fitted with a high speed impeller type mixer (Figure 295). Depending on their design, retention time varies from 1 up to 3 minutes, for the largest. The velocity gradient is between 250 and 1,000 s^{-1} depending upon the application.

The reagent is fed into the zone of highest turbulence, i.e., above or below the impeller, depending on the flow direction (upward or downward).

For some applications in which the velocity gradient must be adjustable according to the temperature or a varying pollution load, the impeller mixer is fitted with a variable speed drive.



1 – Water inlet. 3 – Reagent.
2 – Water outlet. 4 – Drain.

Figure 295. Mixing chamber with a flash mixer.

1.2.
STATIC MIXERS

Static mixers are placed directly in the treatment line upstream from the flocculation phase.

These units feature high velocity gradients (2,000 to 30,000 s^{-1}), and brief retention times (generally less than one second). The power dissipated is directly linked to their head loss, and the quality of the mixing is a function of their design. Unit efficiency decreases with the flow rate to be treated.

1.2.1. The Radialmix

This static mixer features hydraulic radial diffusion. comprises a nozzle located on the pipe's centre line and a diaphragm with a peripheral opening. Standard models are available for pipe diameters from 100 to 400 mm. The head loss ranges from 0.2 to 5 m of WC depending on the model and the application.

- **Radialmix type 1**

(Figure 296 a)

This mixer is best suited for inorganic reagents and polymers injected at a flow rate qi that is lower than the flow rate Q of the liquid to be treated.

It is designed to allow injection of concentrated solutions.

$0.0005\% < qi < 1\%$ of Q

The reagent is pre-diluted in the short dosing line.

- **Radialmix type 2**

The flow rate qi of liquid to be injected is higher than for the previous unit (qi > 0.5% of Q). The head loss exceeds 0.2 m of WC, and is adjusted according to the application. There are three models of type 2 Radialmix.

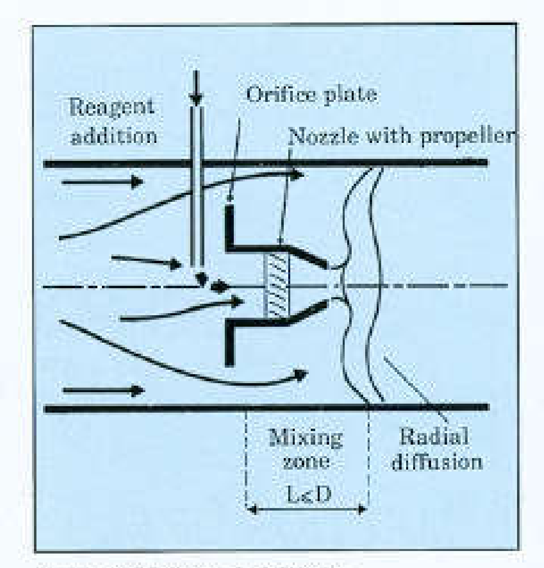


Figure 296 a. Type 1 Radialmix.

- **Radialmix 2 M**

Primarily intended for feeding reagents into liquids with a high solids content. The unit is housed in a sleeve and has a nozzle without an impeller.

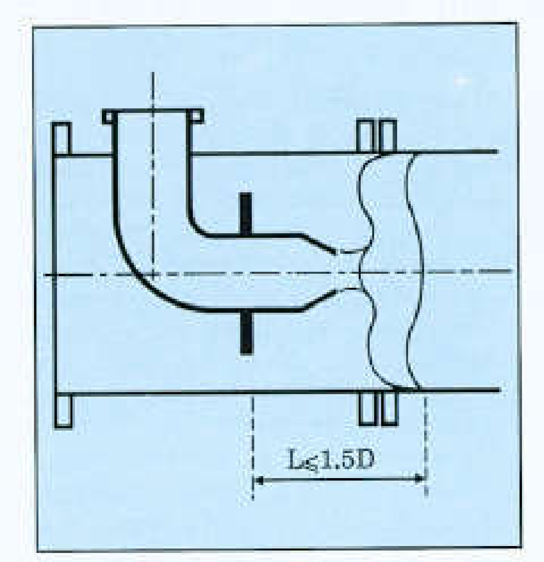


Figure 296 b. Radialmix 2 M.

- **Radialmix 2 MH**

Similar to the Radialmix 2 M, but with a nozzle and impeller. This mixer is not .suitable for fluids containing coarse or fibrous particles.

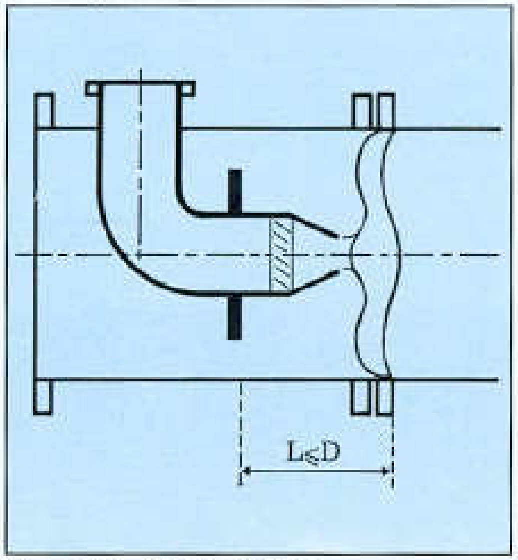


Figure 296 c. Radialmix 2 MH.

- **Radialmix 2 C**

This compact model is housed in an orifice plate and is fitted with a nozzle and impeller. It is especially suited for addition of clear reagents or liquids.

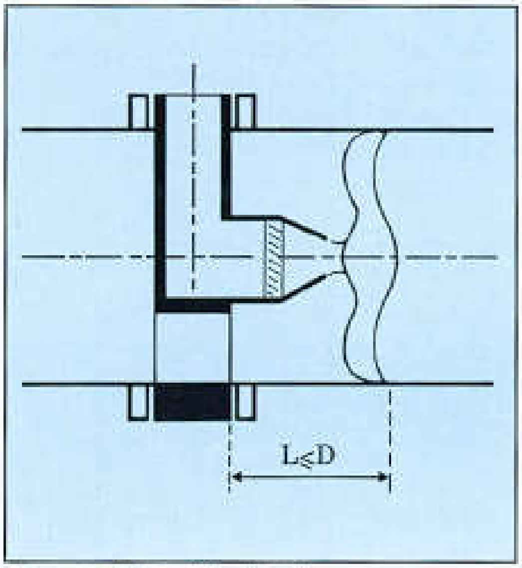


Figure 296 d. Radialmix 2 C.

1.2.2. The MSC

This cyclone-type mixer is suited for sludge conditioning applications (Figure 297). It consists of a cylindrical section equipped with sludge and reagent inlets, contiguous with a conical section in which the spiral motion ensures complete mixing. The cylindrical section also has two adjustable deflectors.

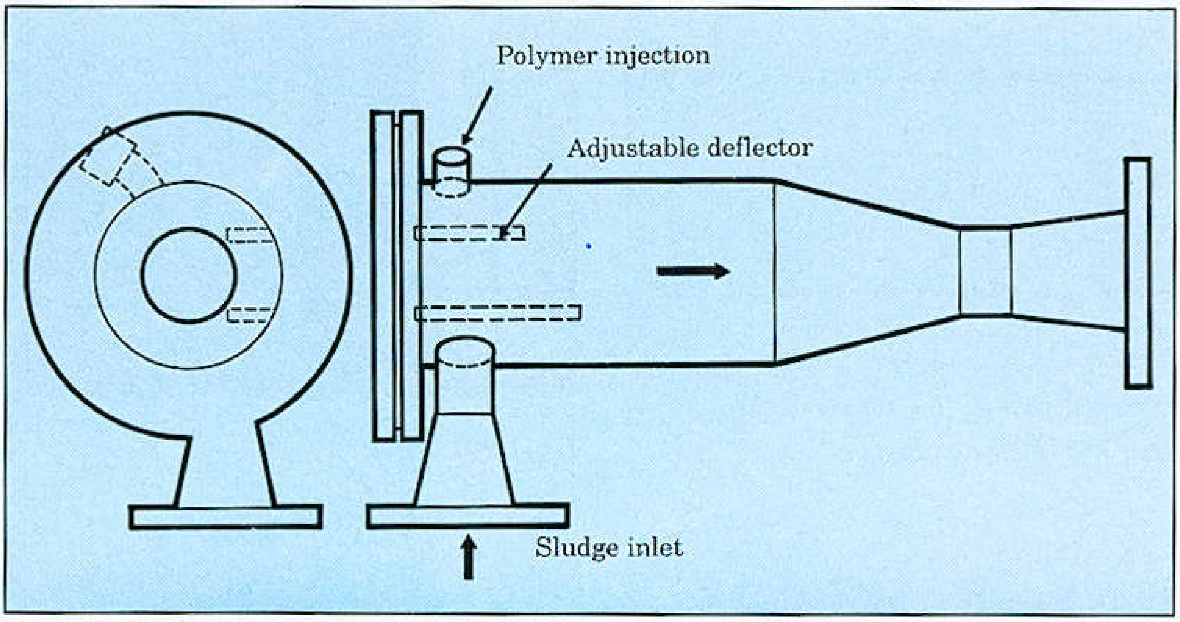


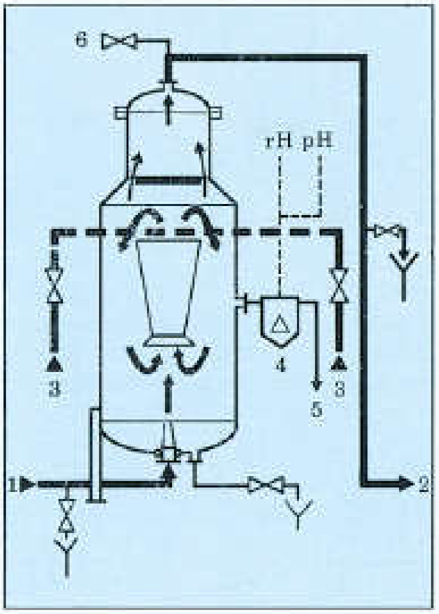
Figure 297. MSC mixer.

1.3.
TURBACTOR

The Turbactor (Figure 298) is a closed flash-mix reactor having no moving parts. It is designed to operate under pressure and consists of two sections:

- a vigorous hydraulic mixing zone,
- a contact zone which eliminates short circuits.

The unit, of plastic or protected steel construction, may be fitted with a pH and rH control system, making it suitable for neutralization or detoxication applications as well as coagulation. For these applications, the minimum retention time is two minutes, and the velocity gradient is about 600 s^{-1} for a liquid viscosity of 1 centipoise.



1 – Raw water inlet. – 2 – Treated effluent outlet. – 3 – Reagent feed. – 4 – Chamber for pH and rH probe for reagent flow control.- 5 – Recycle for rH, pH measurements. – 6 – Air blowdown.

Figure 298. Turbactor diagram.

Figure 299. Turbactor.

2. FLOCCULATORS

Flocculation is carried out in tanks known as flocculators, equipped with mixers. The mixing system, reactor volume and energy dissipation differ according to the specific application or fluid involved.

A flocculator is characterized by its velocity gradient, its contact time, and the extreme local velocities of the moving element and liquid, which shear the floc. For example, for a metallic hydroxide floc, the peripheral velocities of the moving element must not exceed 40 cm.s^{-1}

Geometry of the tank, mixing system and related equipment is defined such that:

- dead zones are avoided (areas of deposits on the bottom, for example),
- dissipated energy is recovered as turbulence (by means of peripheral deflectors in circular tanks, for example),
- short circuits between the liquid inlet and outlet are prevented.

Finally, it is important not to rupture the floc as it is transferred from the flocculator to the settling zone. Depending on the quality of the water treated, the following transfer velocities are used for surface water clarification:

- fragile metallic hydroxide floc

$$v = 0.20\ m.s^{-1}$$

- strong metallic hydroxide floc

$$v = 0.50\ m.s^{-1}$$

Flocculators may be classified in two categories:

- flocculators with a mobile mixer unit (mechanical flocculators),
- off-set baffle or static flocculators.

2.1. MECHANICAL FLOCCULATORS

2.1.1. Paddle type flocculators

The rotating unit consists of a series of paddles mounted on a vertical or horizontal shaft in regularly-spaced diametrical planes (Figure 300). The system is driven by a reduction gear mechanism that may or may not include a variable-speed drive.

The rotating unit may be driven either by a chain or directly. Direct drive eliminates risks of corrosion and the constraints of chain maintenance.

2.1.2. Propeller type flocculators

The rotating unit consists of a vertical shaft propeller with three or four blades, and is driven directly by a reduction gear system, most often equipped with a variable-speed drive (Figure 301).

2.1.3. Practical application

To produce better-quality floc, two flocculators can be used in series for a given flocculation time (Figure 302). This configuration allows:

- adjustment of the velocity gradient as a function of time,
- delayed or partial reagent feed,
- depth limitation in tanks handling large flows.

Figure 300. Paddle type flocculator.

Figure 301. Propeller type flocculator.

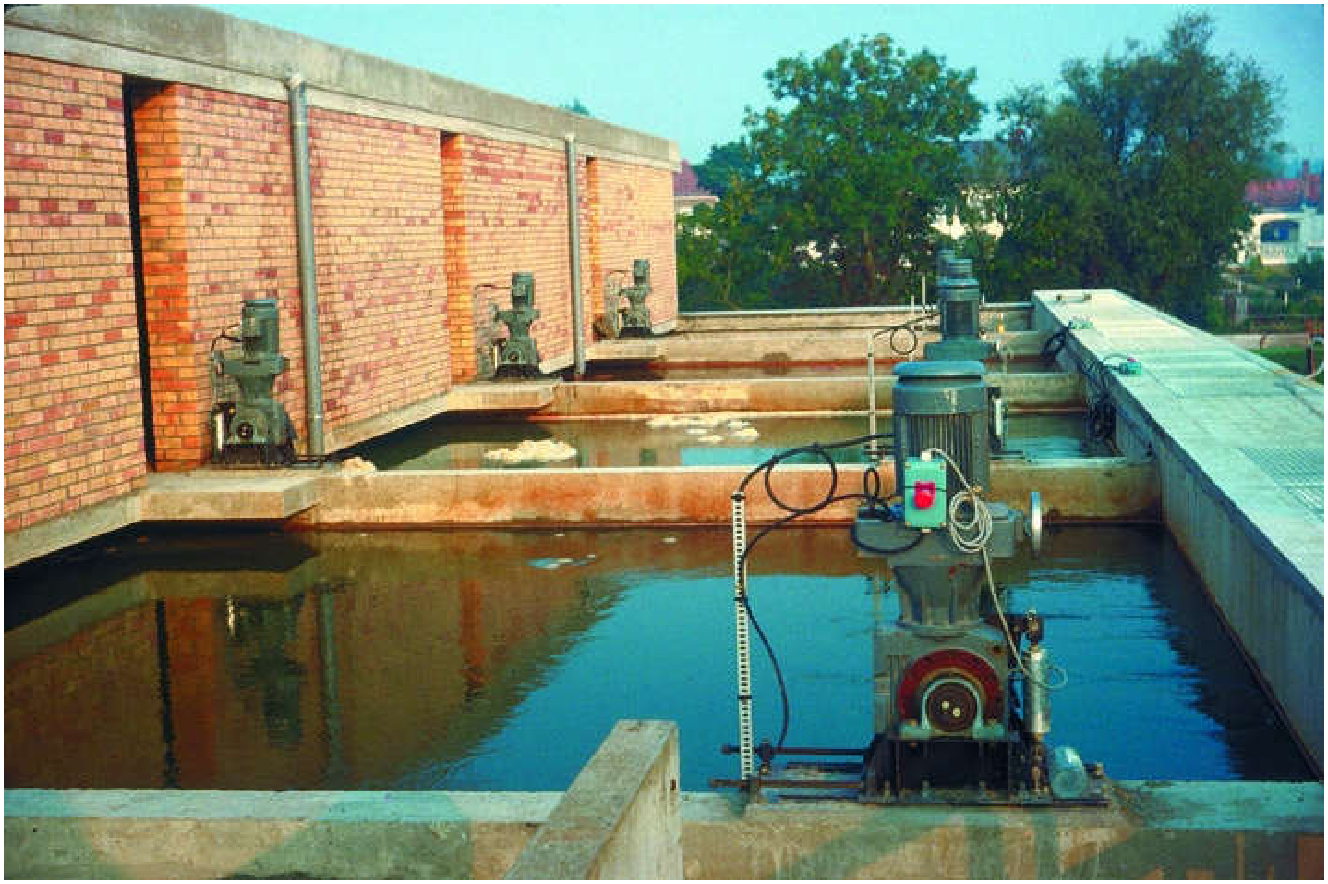


Figure 302. Moulle facility (Northern France) for LE-Dumez. Surface water clarification by flotation. Battery of four dual-cell flocculators: Flow: 4 x 300 $m^3.h^{-1}$.

2.2.

STATIC FLOCCULATORS

Much less widely used than those discussed above, these units are designed so that the flow of the liquid to be treated experiences sudden directional changes. The resulting head losses provide the energy required for flocculation. This system is used only in more rudimentary facilities.

3. SETTLING TANKS

Separation by settling can take place intermittently or continuously. Intermittent processes, or batch settling, are used only in small makeshift facilities or in biological facilities with sequenced tank operation, in which the aeration and settling phases occur in the same unit (Sequenced Batch Reactor). Generally, however, settling is a continuous process.

In a settling tank:

- the flow must be even; with good raw water distribution and uniform recovery of the settled water,
- the flow must be as non-turbulent as possible; energy dissipation at the water inlet must be gradual,
- flow, concentration and sludge removal are all essential parameters in the proper operation of the unit and the concept of solids loading or even sludge volume loading is very important:

$$\text{sludge volume loading} = \frac{\text{flow} \times \text{percentage of sludge settled in a given amount of time}}{\text{horizontal surface area of the unit}}$$

The water specialist must be thoroughly familiar with the sludge characteristics in every application. The considerable differences in treatment requirements have given rise to the wide variety of equipment described below.

3.1.
STATIC SETTLING TANKS

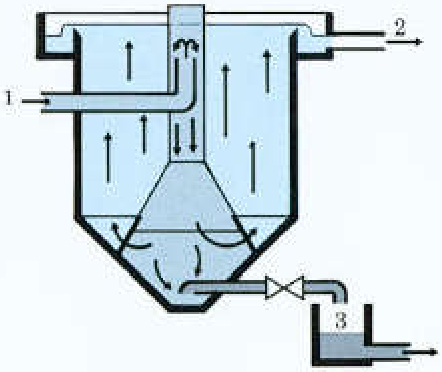
The term "static" when applied to settling tanks has come to refer to those involving neither sludge recirculation nor sludge blankets, despite the fact that settling in these units is actually a dynamic process.
Depending on the quantity and type of SS in the raw water, the volume of precipitates to be drained and the slope of the tank floor, the settler may or may not be fitted with a sludge-scraper system.

3.1.1. Plain settling tanks

3.1.1.1. Static settling tanks without scraping

- **Ordinary cylindroconical settling Tanks**

These upward flow settling tanks are used for facilities that handle small flows,



1 – Raw water.
2 – Treated water.
3 – Drain.

Figure 303. Cylindroconical settling tank.

up to about 20 $m^3.h^{-1}$, especially in physical-chemical treatment. They are also used in MWW plants serving populations of less than 1,000 or 2,000 inhabitants.

In larger facilities, this type of settler is implemented when the volume of precipitates is low and their specific gravity high. A flocculator and even a grit chamber may be provided upstream from the settler if necessary. The slope of the tank's conical section ranges between 45° and 60°, depending upon the sludge composition and the treatment process applied.

The mean upward flow velocity is 0.5 $m.h^{-1}$ for clarification of drinking water and from 1 to 2 $m.h^{-1}$ for the primary settling of MWW.

- **Horizontal-flow static settling tanks**

In this type of settling tank, formerly used for drinking water, the surface area of the settling zone, expressed in square metres, is equal to one or two times the hourly flow of the water to be treated, expressed in cubic metres. This entails vast available space and extensive civil works. Moreover, tanks require periodic draining to remove the settled sludge, restricting use of the system to cases involving low volumes of settled sludge. Static settlers are generally preceded by a mixing chamber in which the reagents are dispersed quickly, and by a slowspeed flocculation phase.

Two-stage settling tanks are a variation on horizontal-flow static settling tanks.

3.1.1.2. Static settling tanks with mechanical sludge scraping

A mechanical device for sludge scraping is used whenever the area of the settling zone exceeds 30 to 40 m^2 This permits a reduction in the steep floor slopes required for natural sludge drainage (down to 2% for light sludge), thereby making construction of large units with limited depth economically feasible.

Figure 304. Facility in Kerkh (Iraq). Capacity: 1,200,000 PE Primary settling tanks.

The scraper system is used to push the sludge into one or more hoppers from which it is extracted. Sludge scraping also promotes sludge thickening, which can sometimes be further enhanced by concentrating sumps. The rate at which sludge draw-off is performed by an automatic draw-off system, depends on the acceptable duration of storage.

Scraper settling tanks are usually used for roughing treatment of river water as well as for primary settling and final clarification in conjunction with biological or chemical treatment of wastewater. They are also used for settling heavily loaded industrial wastewater from sources such as: mines, steel manufacturing, sugar mills, coal washing, etc.

- **Circular settling tanks**

Scraper circular setting tanks, with diameter greater than approximately 10 m, are basically horizontal-flow tanks, both in terms of the settling particles, which move away from the middle toward the periphery (where the clarified effluent is recovered) and of the settled sludge moving in the opposite direction toward the centre. The complexity of the sludge scraper system depends on the application; it may be radial or diametral, and may or may not include a surface skimming system (commonly used for wastewater).

In radial scraper systems, the bottom scraper unit is mounted on rods and suspended from a supporting bridge that rotates about the axis of the tank; it may have only one scraper or a series of scraper blades arranged in echelon.

An on-board drive at one end of the bridge powers a wheel that moves along the periphery of the unit, thereby rotating the bridge (Figures 305 and 306).

In **diametral scraper systems,** the length of the scraper unit is doubled. As above, it may be suspended from a diam-

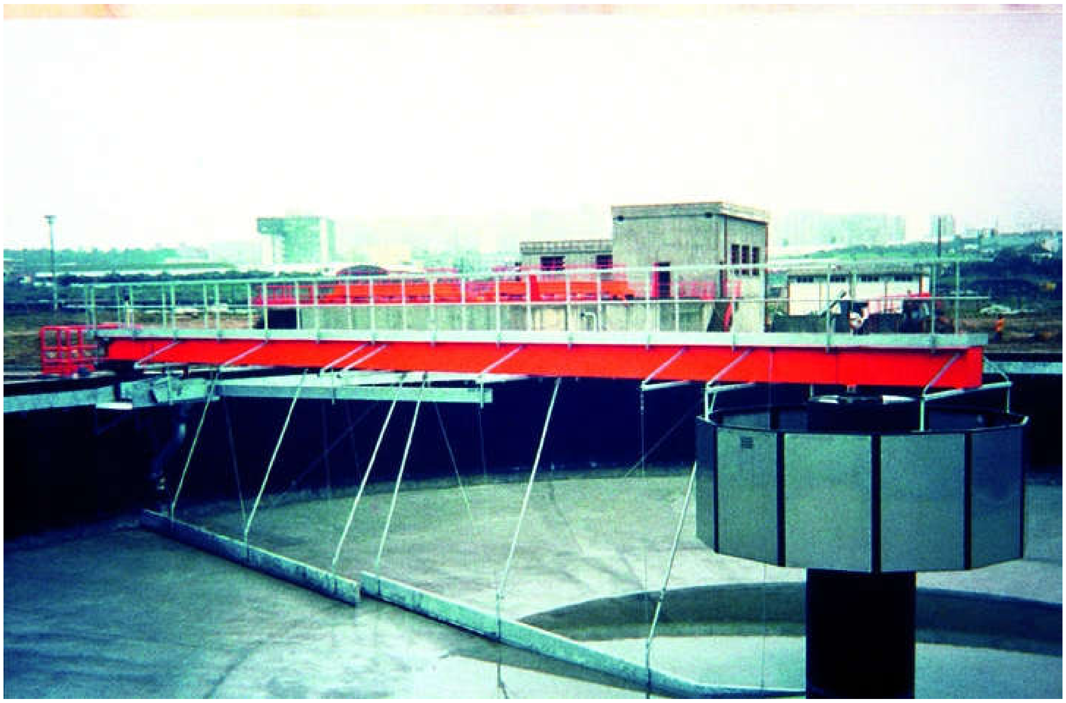


Figure 305. Type P circular scraper settling tank. General view.

etral bridge with a dual reduction gear drive at both ends. For these systems, however, a central drive is often preferred to the peripheral one, in which case the bottom scrapers (and surface skimmers where applicable) are attached to a diametral bridge. The bridge in turn is hung from a centrally-located drive unit that rotates the bridge about the tank axis.

The Centrideg central drive unit (Figure 307) is designed for higher scraper torques. It is mounted on the tank centreline, usually on a centre column made of concrete or, for small diameters, over a diametral access walkway made of either steel or concrete (for settling tanks with built-in thickeners).

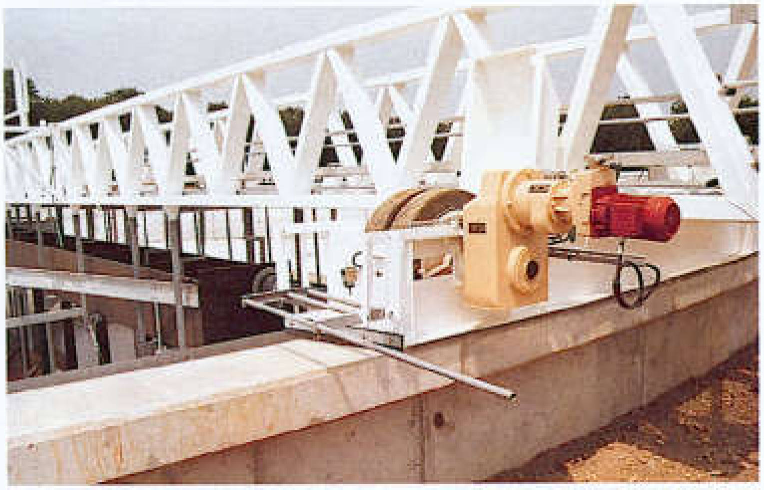
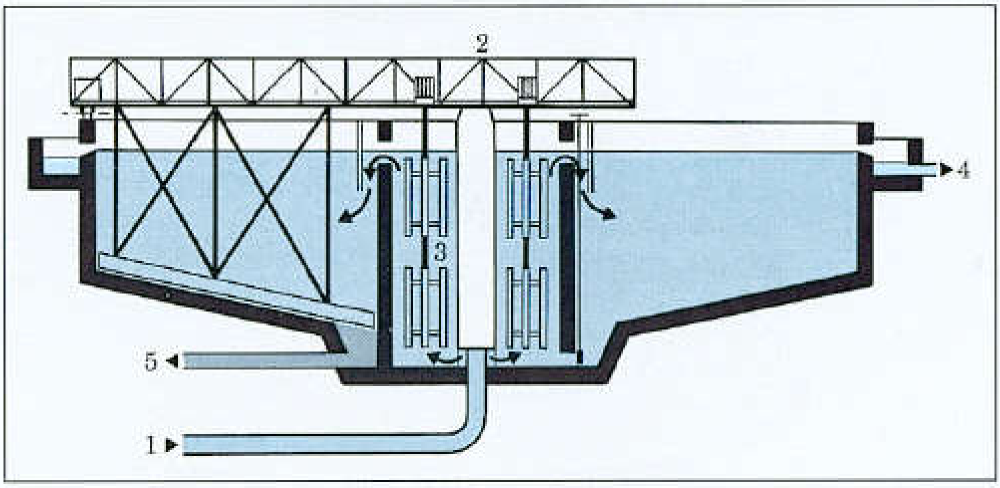


Figure 306. Type P settling tank – Peripheral drive.

Figure 307. Centrideg central drive.

In drinking water and wastewater treatment applications, scraper circular settling tanks with peripheral drive may be designed to include a central area for flocculation, with the associated slow mixers also being mounted on the supporting bridge (Figure 309). The flocculated water flows through wide orifices into the settling area, where the flocculated particles are deposited with the settleable solids.

Figure 308. Valenton (Paris area, France) facility for SLUR Flow: 300,000$\mathrm{M}^3.\mathrm{d}^{-1}$, *Central drive unit on the concrete centre column of a primary settling tank, 52 m dia.*



1 – Raw water inlet.
2 – Scraper bridge.
3 – Flocculation area.
4 – Settled water outlet.
5 – Sludge draw-off.

Figure 309. Flocculator/settling tank with peripheral bridge drive.

Figure 310. Cannes (Southern France) facility. Maximum flow: 5,500 m^3h^{-1}. Flocculator/settling tanks.

Degrémont has standardized a range of settling tanks from 6 to 60 m in diameter. The side water depths are between 2 and 4 m. The peripheral velocity of the scraper is affected by the percentage of settleable sludge contained in the influent water and by its specific gravity; in circular scraper settling tanks, the velocity is approximately 1 to 3 $cm.s^{-1}$ for wastewater applications.

- **Rectangular settling tanks**

Despite their advantage of allowing a more compact overall layout, single or multiple rectangular units are more costly than circular settling tanks, except where complete roofing or enclosure of the facility is required. Rectangular units usually have a horizontal flow pattern, a length/width ratio of between 3 and 6, and depth of 2.5 to 4 m. Sludge hoppers are located directly below the raw water inlet.

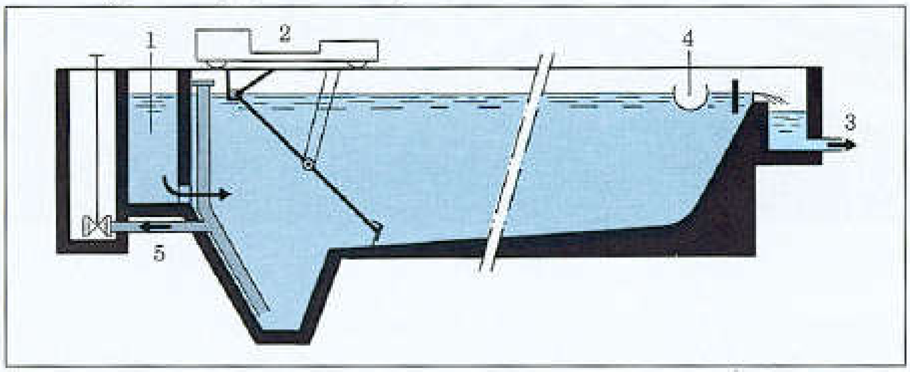
The scraper is either mounted on a cross-bridge (Figure 311) that travels back and forth along the tank, or consists of a flight-and-chain system (Figure 312). In the latter case, the bottom is scraped from downstream to upstream of the tank and the surface is scraped in the opposite direction.

In the former case, all scraper movements and bridge direction changes are fully automatic. Design of the scum recovery device located downstream, before the settled water outlet, takes into account the scraper system and may consist either of a trough at the end of a ramp, or a rotating slotted tube.

The advantage of the flight-and-chain scraper system (Figure 312) is to allow slow displacement (not exceeding 1$cm.s^{-1}$) of the many individual scrapers. On the other hand, the entire scraper system is submerged, and the maximum 6 m width of the scrapers increases the number of systems required. To avoid having a large number of hoppers, overall sludge recovery calls for the use of a cross-bridge scraper unit.

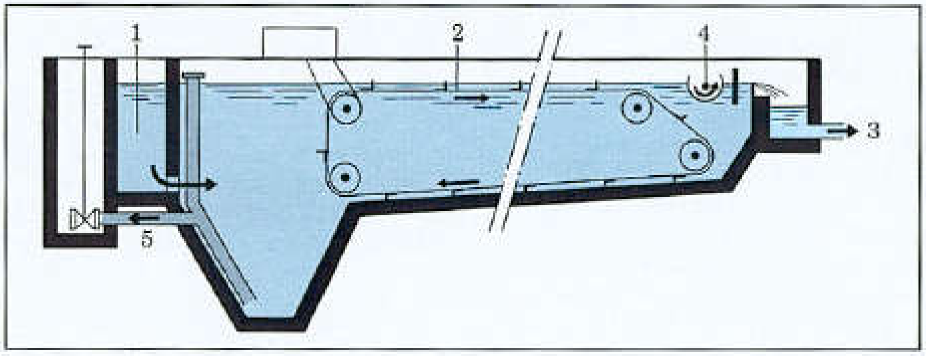
In any case, the construction of very long settling tanks is difficult, sometimes requiring the floor slope to be reduced to as little as 1% and one or more permanent sludge recovery points to be provided over the entire width of the tank floor.

It may be impossible for bridge scrapers to transfer sludge to the draw-off hoppers, especially if considerable quantities are involved and the sludge is fermentable. Suction-type rectangular settling tanks offer a solution to this problem (see page 658).



1 – Raw water inlet.
2 – Scraper bridge.
3 – Settled water outlet.
4 – Recovery of floating matter.
5 – Sludge removal.

Figure 311. Longitudinal settling tank with scraper bridge.



1 – Raw water inlet.
2 – Scraper chain.
3 – Settled water outlet.
4 – Recovery of floating matter.
5 – Sludge removal.

Figure 312. Longitudinal settling tank with chain-driven scraper.

Figure 313. Aïre effluent treatment facility in Geneva (Switzerland). Flow rate: 3.6 $m^3.s^{-1}$. One of the 8 settling tanks equipped with a flight-and-chain scraper system. Dimensions: 70 m x 18.5 m.

Figure 314. Settling tanks with scraper gantry serving multiple units (4 tanks, each 50 m x 200 m).

Other designs involve bridges that straddle and scrape several settling tanks at the same time, or bridges that span several tanks with one scraper device shifting periodically from one tank to the next (Figure 314).

3.1.2. Sédipac units

A Sédipac (Figure 315) is a two-in-one unit combining a coagulation-flocculation zone (3) with a lamellae settling zone in a single tank.

Channels (4) located on either side of the lamellae settling zone allow flocculated water to be transferred from one zone to the other, and distribute the settler influent among stilling chambers located just beneath the channels. From there, the liquid flows horizontally under the lamellae modules (5).

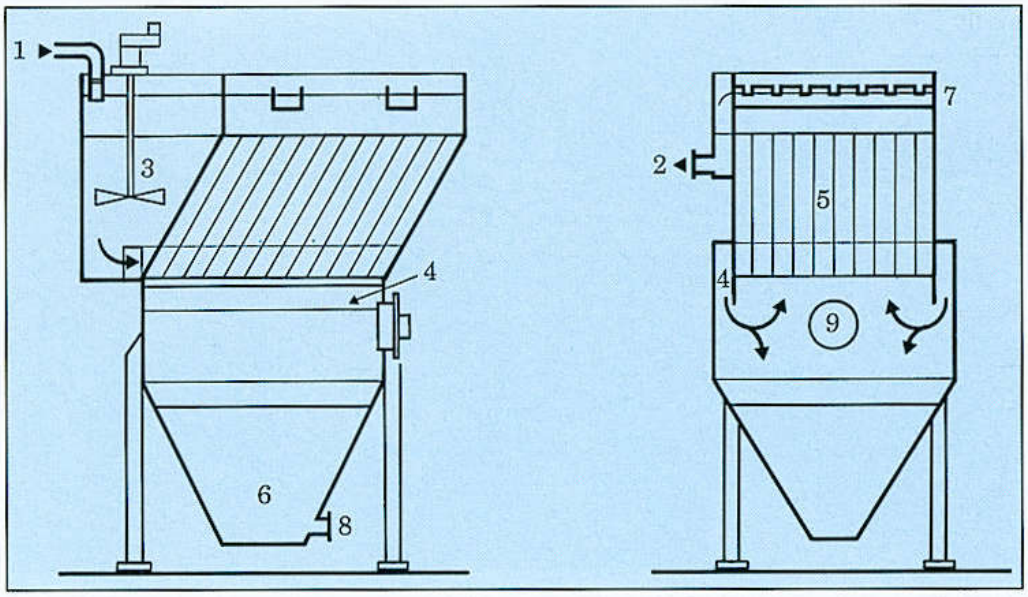
Most of the sludge settles on the bottom (6) of the unit, while the residual floc is separated in the lamellae modules. The clarified water, recovered at the surface in troughs (7), is drained through the outlet (2). An inspection manhole (9) is provided.

The lamellae modules (Figure 316), inclined at 60° to the horizontal, are made of heavy-duty polystyrene. They consist of hexagonal-section tubes with a hydraulic diameter of 80 mm and length of 1,500 mm. The large cross-section of the tubes reduces the risk of clogging in the case of fluids containing grease or fibrous particles (table 75).

The hexagonal shape has the following advantages:

- it provides the maximum orifice for a given hydraulic efficiency and module length,
- it resists bending under the weight of the sludge, as opposed to plate-type lamellae modules.

Sédipac units are used mainly to treat municipal or industrial wastewater for which flocculation time is 5 to 10 minutes.



1 – Raw water inlet.
4 – Flocculated water distribution channel.
7 – Settled water collection.
2 – Settled water outlet.
5 – Lamellae settling.
8 – Sludge removal.
3 – Flocculation.
6 – Sludge concentration.
9 – Inspection manhole.

Figure 315. Sédipac. Basic diagram.

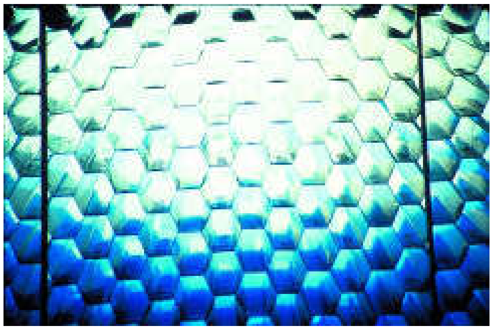


Figure 316. Degrémont lamellae modules.

Table 75. Degrémont modules.

Hexagonal modules				
Hydraulic diameter (mm)	80		50	
Spacing between plates (mm)	80		50	
Angle of inclination	60°		60°	
Length (m)	0.75	1.5	0.75	1.5
Projected surface area M^2 module/m^2 settler	5.4	10.8	8.7	17.4

3.1.2.1. Metal Sédipac units

These devices (Figure 317) are built as a single unit and are not equipped with mechanical scraping. Design calls for coating with corrosion-proof paint; all parts are accessible for preliminary shot-or sandblasting. Key unit components are:

- an impeller with a variable-speed drive
- one or more sludge draw-off valves.

The settling surface area of the units ranges from 3 to 21 m^2, with overall height from 4.4 m to 6.4 m.

Sédipac units may be incorporated into package treatment plants, and include a reagent feed system and automated control.

3.1.2.2. Concrete Sédipac units

These units are generally used to treat water with high solids loads (SS: about 0.1 to 1 g.l^{-1}) and flow rates greater than 300 m^3 h^{-1}. The flocculation time is about 5 to 10 minutes, but can be increased if the influent water quality so requires. The settling velocity may be as high as 15 m.h^{-1} calculated at the settling surface of lamellae modules (exceptionally, 18 m.h^{-1})

Concrete units are wider than the metal models and are designed with two parallel lamellae settling zones, 2 or 3 m wide each. Mechanical sludge extraction equipment is provided. The water depth is between 4 and 4.5 m, with up to 120 m^2 of settling surface area.

- **Sédipac R**

This unit is fitted with a scraper bridge (Figure 318) consisting of a transverse beam (1) with a hinged arm (2) mounted in the middle. The scraper blade (3) is attached to the end of the arm. The hinged arm circulates between the settling compartment walls (4)(5). The treated water is recovered at the surface either by troughs (6) or submerged headers.

- **Sédipac U**

This unit is fitted with a **suction** bridge (Figure 319). Designed to include easily accessible (for cleaning) distribution, channels for flocculated water, the unit

Figure 317. Metal Sédipac. Facility in Rheinfelden, Germany.

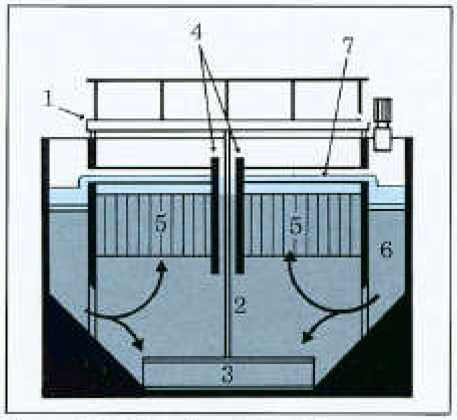


Figure 318. Sédipac R settling tank.

can be used efficiently in municipal wastewater treatment by physical-chemical processes

The suction bridge is comprised of a load-bearing beam (1) supporting a frame (2) that surrounds both settling zones (3). The draught tubes (4) are mounted on the frame. Flocculated water is distributed by the channels (6), and then is stilled in zones (5).

The treated water is recovered in the troughs across the settling zones that empty into two drainage channels (7), located on either side of the central distribution channel.

The same configuration may be applied to large lamellae units without preliminary flocculation. This is the case in primary settling tanks for MWW treatment facilities designed for small sites.

- **Sédipac C**

This unit is especially well suited for clarification of water characterized by considerable fluctuations in the SS concentration, which may reach several grammes per litre (Figure 321).

The settling zone is square and is fitted with a centrally-driven bottom scraper.

The tank floor is designed with a slope that extends downward from the middle toward the periphery, where the sludge is drained by hoppers located at each corner.

With this unit, large quantities of sludge can be removed with a minimum loss of water. Hydraulic layout is the same as that for the other Sédipac units.

3.1.3. Suction-type scraper settling tanks

Suction-type scraper settling tanks are mainly used for settling in activated sludge processes. In comparison to settlers used solely for separation, these suction type settling tanks allow recycling of significant proportions of settled sludge (equivalent to 50 to 100% of the flow treated, or more).

To avoid hydraulic disturbance caused by the transfer and recovery of a high

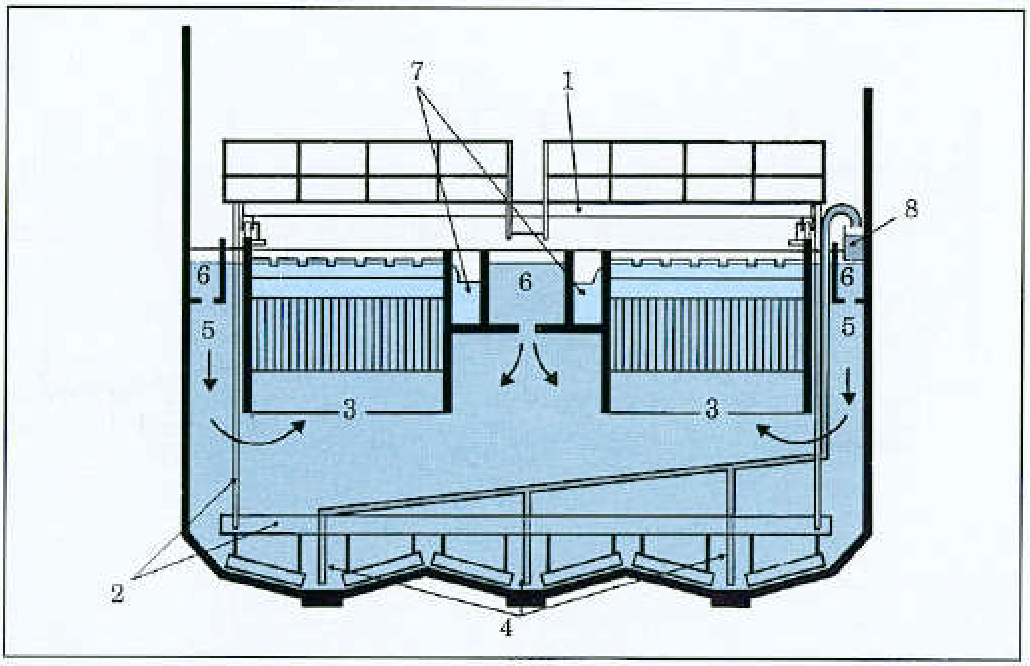
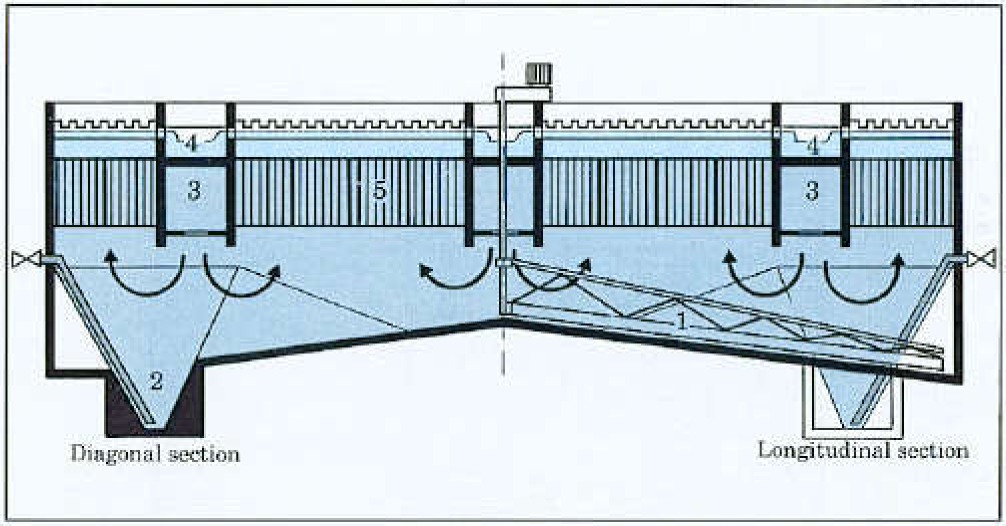


Figure 319. Sédipac U settling tank.

Figure 320. Facility in Nice (Southern France). Flow rate: 220,000 $m^3.d^{-1}$.
General view of a Sédipac U unit: 7 x 21.1 m.



1 – Bottom scraper.
2 – Sludge hopper.
3 – Distribution channels.
4 – Treated water channels.
5 – Lamellae modules.

Figure 321. Sédipac C

sludge flow at a single point, yet provide rapid sludge recirculation, it is preferable to increase the number of draw-off points.

Suction-type settling tanks, in which each scraper blade is paired with a draught tube, meet this objective. The technique can be applied to circular as well as rectangular settling tanks and many methods of operation are possible. The suction effect is most often achieved simply by using hydrostatic pressure.

3.1.3.1 Circular units

Suction-type scrapers are normally used in units with diameters greater than 20 m, and are designed for sludge that does not require scraping torque greater than 3 daN.m^2 per m of tank surface area.

The bottom scrapers are generally supported and driven by trussed arms attached to the support walkway, and have no support wheel on the tank floor. Each scraper is fitted with a PVC or HDPE draught tube placed at intervals that vary from the centre to the periphery. The tubes discharge into a recovery hopper. A telescopic sleeve with an adjustable overflow is mounted at the discharge point of each draught tube, permitting individual visual flow control. Air may be injected into the straight upright section of each draught tube, which then operates as an air lift pump.

Transfer of sludge from the movable recovery hopper to the fixed extraction pipe built into the unit is performed using a vacuum siphon with a priming device. These units may also be fitted with surface skimmers for scum removal.

In standard Degrémont radial settling tanks, the downstream branch of the siphon is located along the axis of the unit.

- **Radial suction**

SV-type (Figure 322)

The system features a peripherallydriven radial bridge rotating about a central column and is equipped with a low, partially-immersed beam, which acts as a sludge recovery trough.

The diameter is less than 40 m.

SR-type (Figure 323)

The SR-type has a radial bridge consisting of a horizontal beam, above the water. This walkway structure is made of folded steel plate or truss elements for large units. The sludge recovery tank is mounted on the walkway and partially submerged.

The diameter of such units is up to 40 m.

The alternative SRP version of this unit (Figure 324) involves extending the walkway in cantilever over one-third of the opposite radius, thereby enhancing sludge recovery in the middle zone. Another recovery tank and upstream siphon branch are included.

The diameter may exceed 50 m.

- **Diametral suction**

SD-type

In-line suction is equally applicable to the full tank diameter. In this configuration, suction devices and the activated sludge collection equipment are added to the type of centre drive described on page 644. The two-branch siphon feeds a revolving annular recovery tank serving all draught tubes (Figure 325).

The diameter is 60 m maximum.

- **Annular suction**

Succir type

The purpose of this type of unit (Figure 326) is to achieve more balanced sludge recovery in the central zone.

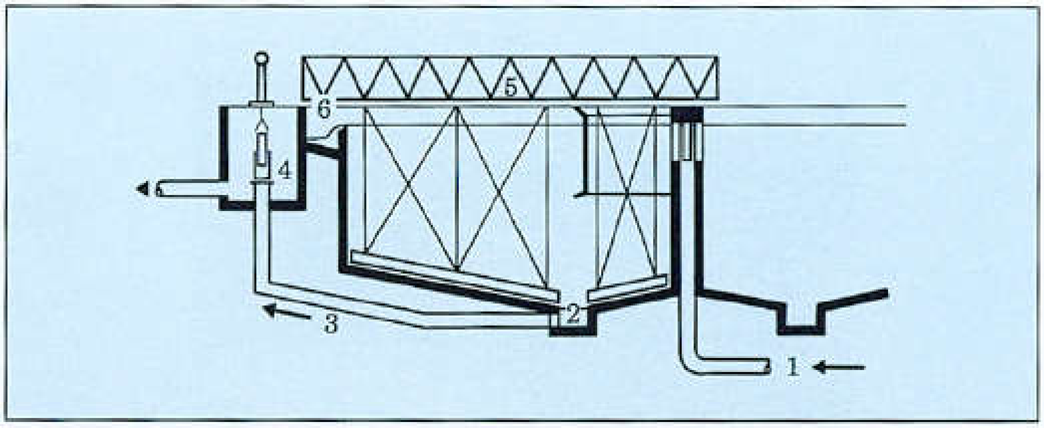
Figure 322. Zellwiller (Eastern France) facility. SV-type settling tank.

Typical design is based on the peripheral-drive radial bridge. Most of the draught tubes, which rotate with the bridge, are arranged concentrically with the unit, at one-third of its radius. The others are in line with the scrapers. The diameter ranges from 30 to more than 50 m.

A simplified use of this technique - and one suitable for small units only - involves annular extraction points embedded in the tank floor.

Figure 323. Ploegsteert-Comines (Belgium) facility. Flow: 22,650 $m^3.d^{-1}$. Aerial view of SR-type settling tanks.

Figure 324. Mulhouse (Eastern France) facility. Flow.' 98,135 $m^3.d^{-1}$. SRP-type settling tank.



1 – Feed.
2 – Circular trough + cover plate with calibrated orifices.
3 – Recirculated sludge.
4 – Sump with telescopic adjustment valves.
5 – Standard scraping equipment.
6 – Recovery of settled water.

Figure 325. Diagram of a simplified Succir settling tank.

Figure 326 Roanne (Central France) facility. Flow: 30,000 $m^3.d^{-1}$ Succir type setding tank, 54 m dia.

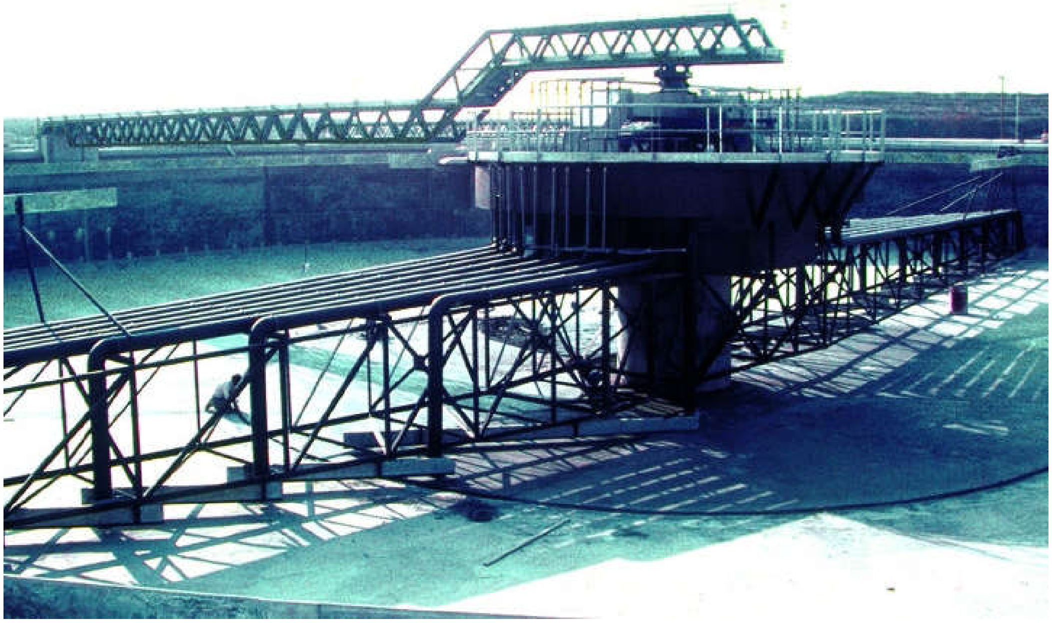


Figure 327. Valenton (Paris area, France) facility for SIAAP. Flow: 300,000 $m^3.d^{-1}$. SD-type settling tank, 52 m dia.

3.1.3.2. Rectangular units

A rectangular layout is not as suitable as a circular one for the construction of large unit surface areas: special attention must be paid to ensuring even flow distribution at the inlet and settled water recovery points, and to preventing the occurrence of unscraped floor zones. These tanks usually have horizontal flow with a basically flat bottom.

The design principle of suction and scraping devices for rectangular tanks is the same as for circular units. According to the size of the unit, sludge is recovered either by siphon(s), pump(s) or air-lift(s), and scum is drained through a trough or a slotted tube.

The scraper device is usually an automatically operated bridge travelling back and forth along the tank at speeds varying from 3 to 4.5 $cm.s^{-1}$, depending on the length of the tank. The scraper bridge is calculated for a scraping torque of less than 20 daN per metre of tank width. The end carriage has either elastomer tyred wheels for rolling directly on concrete with lateral guide rollers, or steel rollers for rail-mounted units.

- **SLP-type (for small units)**

The sludge is lifted by air-lifts) into a lateral trough or directly into the adjacent aeration tank (Figure 328).

The width may be up to 7 m and the length up to 35 m. Water depth: 2.5 m to 3 m.

- **SLG-type**

Sludge extraction is generally achieved using hydrostatic pressure, by means of a vacuum siphon fitted to the bridge. The siphon transfers sludge from the recovery tank to a lateral gutter. Mobile suction along the longitudinal axis may be supplemented by fixed extraction points along the transverse axis.

This type of construction should be considered for units up to 20 m wide and 70 m long (Figure 329).

- **Special design**

Cross-flow settling tanks

This alternative is especially worthwhile when it allows an improved, more integrated layout of the aeration and set ding tanks. However, even distribution of mixed liquor at the inlet is particularly important (Figure 330).

Distributed fixed-extraction settler with additional mobile suction

Most recirculated sludge is removed using a series of fixed air-lifts, placed all along the tank centre line and emptying into a general recovery channel (Figure 331). A travelling bridge with scrapers and air-lifts scrapes the floor and provides additional recirculation.

Figure 328. SLP-type settling tank,

Figure 329. Strasbourg (Eastern France) facility. Flow: 242,000 $m^3.d^{-1}$. *SLG-type settling tank. 18 units, 20* m x *66* m *each.*

Figure 330. La Minière (Paris area, France) facility. Flow: 12,000 $m^3.d^{-1}$. Cross-flow settling tank, 21 m x 29.5 m.

Figure 331. Nice (Southern France) facility. Flow: 220,000 $m^3.d^{-1}$. One of 12 secondary clarifiers, 15 m x 60 m.

3.2.
SOLIDS CONTACT UNITS

3.2.1. Sludge blanket units

In this type of settling tank (also known as a clarifier), the sludge formed through flocculation is retained as an expanded blanket. Water flows regularly and evenly up through the sludge blanket. The raw water is introduced at the base of the sludge blanket via a distribution system that promotes continuous mixing. The water flocculates as it passes through the "sludge filter" and emerges clarified in the upper portion of the unit.

If water is fed continuously into the bottom of the sludge blanket, the sludge eventually ceases to remain suspended in the liquid (see page 145). Instead, it settles gradually in some zones, ultimately forming **a compact mass of settled sludge** in which the water has created preferential channels, thus destroying the efficient contact between the water passing through the sludge blanket and the sludge that forms it.

On the other hand, if water is allowed to enter **intermittently**, quickly and at a high flow, and then is stilled for an extended period, the sludge mass is seen to **remain in a regular suspension**. All the sludge is entrained toward the top as the water flows in, but then settles regularly during the subsequent stilling period, as it would do in a jar at absolute rest. The resulting sludge mass is uniform in every respect.

Jar tests may be conducted in laboratory to measure the maximum rising velocity to which a sludge blanket can be subjected; this is the sludge cohesion coefficient (see page 353). This maximum rising velocity depends on a number of factors: raw water composition, coagulant and flocculant dosages, temperature, etc.

3.2.1.1. The Pulsator clarifier

This is the most widely used clarifier in the world; more than one million cubic metres of water are treated every hour in Pulsator clarifiers.

This simple sludge blanket-type clarifier is highly reliable, flexible and can be easily adapted to existing tanks to increase their treatment capacity.

Generally used for water clarification, it allows rising velocities between 2 and 4 $m.h^{-1}$, or even higher in special cases, depending on the sludge cohesion coefficient.

The clarifier (Figure 332) comprises a flat-bottom tank, with a series of perforated pipes (9) at its base, through which the raw water is injected to ensure even distribution over the entire floor of the clarifier. A series of perforated pipes or troughs (2) at the top of the tank allow uniform collection of the settled water, avoiding flow variation from one unit component to another.

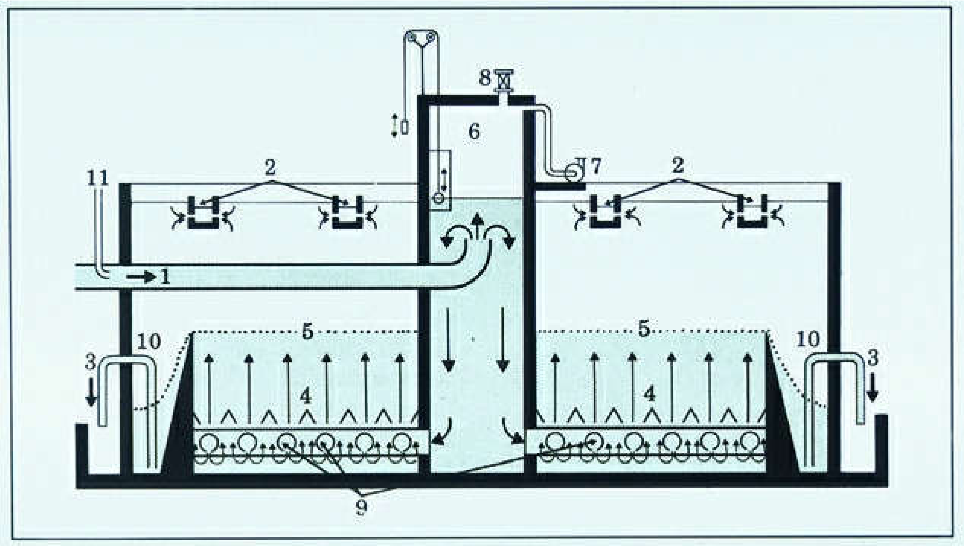
Different methods may be used to feed the distribution system intermittently. They all involve storing a certain volume of raw water for a certain amount of time, then discharging it instantaneously into the unit.

The most economical means of achieving this is to take the raw water into a chamber from which air is sucked by means of a vacuum device (7) displacing an air flow that is approximately equal to one half of the maximum flow rate of the water to be treated. The chamber is connected to the distribution system at the base of the clarifier.

During the filling phase, the raw water level rises gradually in the chamber. When it rises 0.6 m to 1 m above the clarifier water level, an electric relay actuates a valve (8) that is thrown open to connect the chamber with the atmosphere. Atmospheric pressure is therefore immediately exerted on the water stored in the chamber, which rushes into the clarifier.

These units are usually calibrated so that the chamber drains into the clarifier in 5 to 20 seconds, whereas it takes 20 to 40 seconds to fill.

The suction in the chamber is created using a fan or blower operating as a vacuum pump. The opening and closing of the air release valve are controlled by the chamber water level.



1 - Raw water inlet.
2 - Clarified water outlet,
3 - Sludge removal.
4 - Stilling baffles.
5 - Upper level of sludge blanket.
6 - Vacuum chamber.
7 - Vacuum pump.
8 - Air release valve.
9 - Raw water distribution system.
10 - Sludge concentrators.
11 -Reagent feed

Figure 332. Pulsator clarifier

The main distribution system, located in the lower portion of the clarifier, has a large cross-section to reduce head loss. The orifices along the laterals are positioned to permit a homogeneous sludge blanket to form in the lower part of the clarifier. The blanket pulses up and down and tends to expand due to the added reagents and the impurities borne by the raw water; its level rises regularly. The excess sludge flows into hoppers (10) provided in one section of the clarifier and becomes concentrated there. Sludge is drawn off periodically through the pipes (3). One major advantage of the unit is that if too much sludge is drawn off, the resulting water loss does not affect the sludge blanket; operational integrity remains the same.

The unit has no mechanical sludge mixing system that would break up the floc particles already formed. Given the high concentration of the sludge blanket, and its role as a buffer, poor adjustment of the treatment rate or a variation in the raw water pH have no immediate negative effects; a slow variation in the turbidity of the settled water is observed, but this does not produce any massive loss of the sludge in the clarifier.

It is easy to convert an existing tank, filter or reservoir into a Pulsator, thereby modernizing old facilities and increasing their flow capacity two or three times over. Examples of this type of retrofit are the facilities in Buenos Aires, Argentina: 1,300,000 $m^3.d^{-1}$, and Alexandria, Egypt: 240,000 $m^3.d^{-1}$.

3.2.1.2. Larnellae Pulsator clarifier or Pulsatube

Installing Degrémont modules above the sludge blanket of the Pulsator clarifier results in superior water quality with the same settling velocity as a conventional unit, or allows an increase in settling velocity which can range from 4 to 8 $m.h^{-1}$ (Figure 334).

Figure 333. Palermo II facility for drinking water supply for Buenos Aires (Argentina). Flow: *36,000* $m^3.h^{-1}$. *Surface water clarification. Four Pulsator clarifiers, 99.5* m x 27 m.

However, in the latter case, special attention should be paid to the raw water distribution and settled water collection systems, for an increase in the flow modifies the hydraulic regimen through the systems.

The floc particles that have escaped from the sludge blanket are deposited on the lower walls of the modules and accumulate there in a thin layer until their cohesion allows them to slide back down into the sludge blanket.

3.2.1.3. Superpulsator clarifies

The Superpulsator (Figure 336) is a compact and economical sludge blanket unit derived from the Pulsator.

Figure 334. Lamellae Pulsator clarifier or Pulsatube.

Figure 335. Boudouaou facility for drinking water supply for Greater Algiers (Algeria). Flow: 540,000 m^3.d^{-1}. Surface water clarification. Six Pulsatube clarifiers. Unit area: 551 m^2.

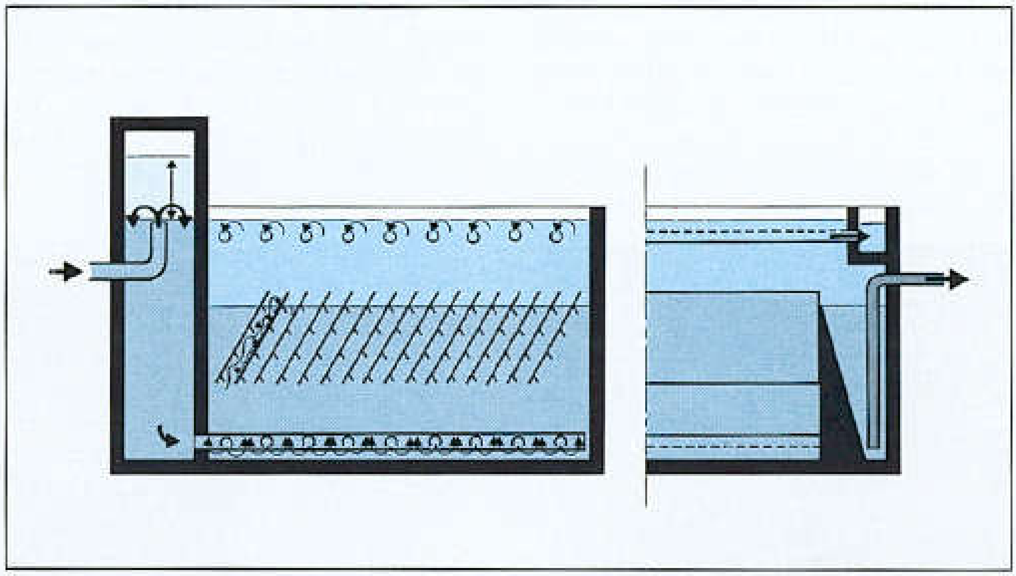


Figure 336. Superpulsator: cross-section.

The Superpulsator utilizes the lamellae settling effect to combine the respective advantages of sludge contact settling, sludge blanket pulsing and sludge densification. It has several features in common with the Pulsator but extends the range of application of the latter. The design principle of the raw water feed with distribution at the base of the unit is the same as that of the Pulsator.

The mixture of coagulated water and flocculated sludge rises vertically in parallel streams, through the deep area located between the bottom distribution pipes and the inclined plates, which thus are fed uniformly. The stilling baffles used in the Pulsator are not needed for this unit.

The flocculated water, which is evenly distributed, then enters the parallel plates slanted at a 60° angle to the horizontal and perpendicular to the sludge concentrators. Deflectors fitted to the underside of each plate provide support and create mixing movements conducive to flocculation. (Figure 337).

The deflector plates serve to maintain sludge blanket concentration that is twice as high as that of a Pulsator operating at the same rising velocity.

Figure 337. Sludge circulation between the plates of a Superpulsator.

This high concentration of the sludge blanket makes the Superpulsator an effective filter for impurities - a major advantage of deep, concentrated-sludge blanket clarifiers.

As in the Pulsator, the upper level of the sludge blanket is limited by its over flow into the concentrator zone, which is exempt from the uplift forces caused by the rising velocity. The settled water is collected by a network of collectors. The unit's operating flexibility allows rapid start-up. Rising velocities used in clarification range from 4 to 8 m.h^{-1}.

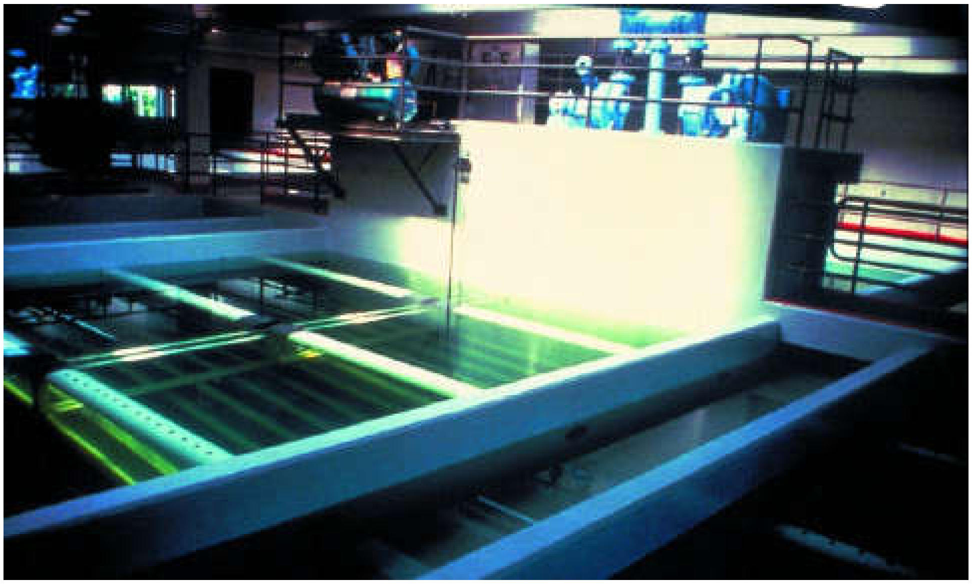
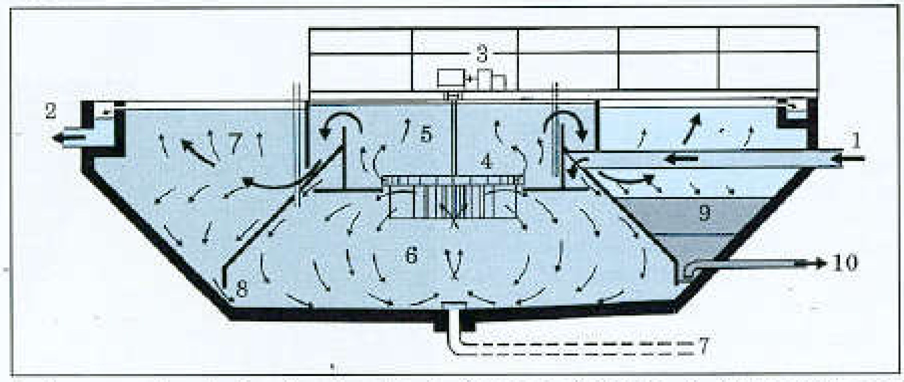


Figure 338. Burlington (Vermont, U.S.A.) facility. Flow: 1,500 m3.h^{-1}. Retrofitting two existing tanks with Superpulsators.



1 – Raw water inlet. 2 – Treated water outlet. 3 – Drive unit. 4 – Turbine. 5 – Primary mixing zone. 6 – Secondary mixing zone. 7 – Clarified water. 8 – Sludge recirculation. 9 – Sludge concentrator. 10 – Excess sludge. 11 – Drain.

Figure 339. Accelator clarifier.

3.2.2. Sludge recirculation units

In this type of unit, the sludge is separated from the clarified water in a settling zone, then recycled to a mixing zone equipped with either mechanical agitation (Accelator, Turbocirculator, Claricontact) or hydraulic agitation (Circulator). The raw water with the added reagents is injected into the same mixing zone.

3.2.2.1. Accelator clarifier

The Accelator clarifier (Figure 339) has a central reaction zone surrounded by a settling zone. The two zones are connected at the top and bottom.

A turbine located in the upper portion of the reaction zone circulates the water to the settling zone. The sludge deposited in the settling zone returns to the central zone by induced flow. The resulting sludge "enrichment" allows rapid flocculation and the formation of a dense precipitate.

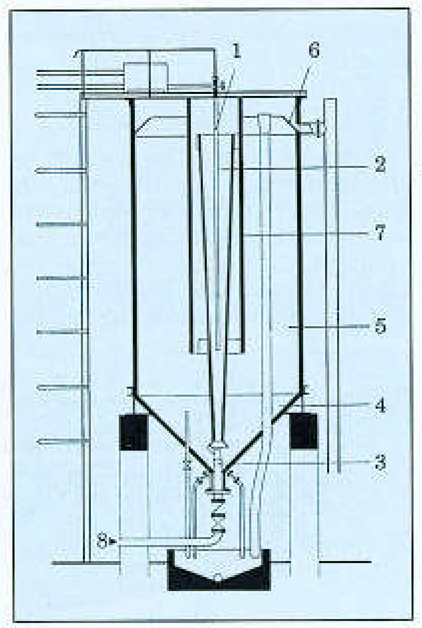
In some cases a bottom stirrer is provided to mix the raw water with the sludge and the reagents and to prevent accumulation of heavy deposits that could clog the unit. One or more sludge hoppers are provided for extraction of excess sludge in as concentrated a state as possible.

The Accelator IS is a variation on the Accelator equipped with a scraper in the lower portion of the unit. The scraper promotes thickening of the sludge that is pushed to the sludge hoppers in the floor for extraction.

3.2.2.2. Circulator clarifier

The Circulator (Figure 340) is a very simple piece of equipment whose small diameters are perfectly suited for medium-sized facilities.

This type of clarifier has a hydraulic device specially designed to accelerate reactions through a methodical recirculation of the precipitates formed by the reagents and influent water. It is also widely used to achieve flocculation and accelerated settling under pressure.



1 – Reagents. 2 – Reaction zone. 3 – Ejector. 4 – Sludge concentration. 5 – Settling zone. 6 – Settled water collector. 7 – Skirt. 8 – Raw water inlet.

Figure 340. Circulator clarifier for carbonate removal.

The unit has a conical floor to help the sludge slide toward the ejector for recirculation. It has no moving parts.

The Circulator can usually clarify or soften water with a retention time of 45 minutes to 2 hours depending on the specific case; the maximum admissible rising velocity is 2.5 $m.h^{-1}$ for clarification and 5 to 7 $m.h^{-1}$ for softening.

- **Scraper Circulator**

For large-diameter units that cannot have a sufficient floor slope, a scraper bridge is used to bring the sludge continually to the middle; design is identical to that of static settling tank scraper systems (page 643).

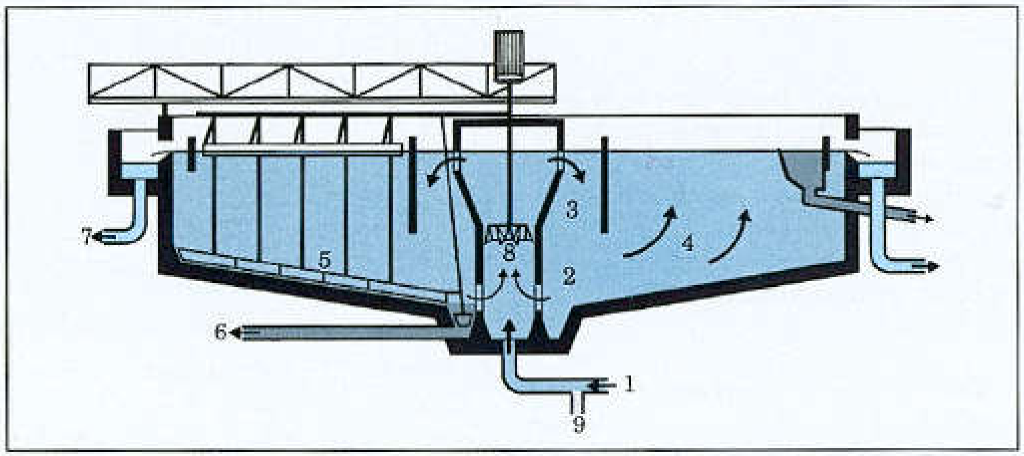
3.2.2.3. Turbocirculator clarifier

In this unit (Figure 341), precipitates are recirculated by a special impeller. The impeller prevents damaging fragile metallic hydroxide precipitates which would not withstand recirculation by an ejector. This feature makes the unit suitable for clarification as well as softening applications, by accommodating significant flow rate variations and high rising velocities, comparable to those of the Circulator.

The reaction zone, located in the middle of the unit, allows excellent control over the coagulation, flocculation, softening and even oxidation reagents. A scraper system continually brings the sludge to the centre, where it is then collected by the recirculation system or pushed to the hoppers for concentration and periodic extraction.

3.2.2.4. CLARICONTACT clarifier

In this unit (Figure 343), an air-lift system is implemented to recirculate the thickened and scraped sludge into the flocculation zone, thereby permitting monitoring of sludge quality. The volume and the contact time (hence, the flocculation time) are defined based on water characteristics. A scraper system allows the sludge to thicken as it is pushed toward the hoppers, from which it is peri



1 – Raw water inlet. 2 – Sludge recycling. 3 – Floc maturation. 4 – Settling zone. 5 – Scrapers. 6 – Excess sludge. 7 – Treated water outlet. 8 – Impeller for mixing raw water and recycled sludge. 9 – Reagent feed.

Figure 341. Turbocirculator clarifier.

Figure 342. James MacLaren Industries Inc. (Canada). Primary settling of effluents. Turbocirculator 55 m dia.

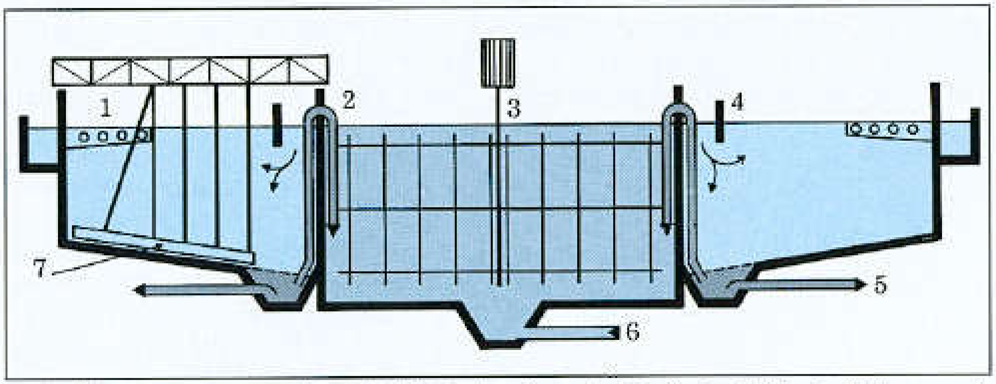
odically removed after becoming concentrated

3.2.2.5 Thermocirculator clarifier

This unit (Figure 344) is used for combined lime softening and magnesium oxide-based silica removal for some boiler feedwater applications (medium pressure). It also allows partial deaeration (oxygen).

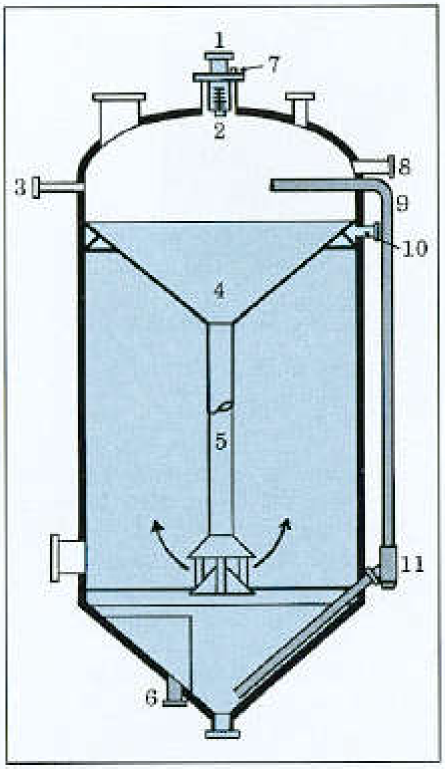
Treatment occurs under low pressure equivalent to the vapour pressure, at a temperature selected between 102° and 115°C depending on the case. This temperature range allows complete and rapid reactions, further facilitated by sludge recirculation. This is performed by a "steam-lift" pump, located outside the unit, and easy to check for proper operation.

The unit is fitted with a steam regulator and a water level regulator. Its upper portion may include a deaeration zone fed with settled water, in which case the heating steam goes through the deaeration chamber before it heats the raw water.



1 – Settled water recovery trough. 2 – Air-lift. 3 – Flocculator. 4 – Distribution baffle. 5 – Sludge removal. 6 – Raw water inlet. 7 – Scraper.

Figure 343. Claricontact clarifier.



1 – Raw water inlet. 2 – Spray. 3 – Reagent inlet. 4 – Funnel. 5 – Flow shaft. 6 – Sludge removal pipe. 7 – Non-condensible gas outlet. 8 – Heating steam inlet. 9 – Recirculated sludge. 10 – Condensed water outlet to filtration. 11 – Steam ejector.

Figure 344. Thermocirculator.

3.2.3. Densadeg clarifier/thickener

The Densadeg is an external recirculation unit based on the lamellae settling principle. It is a fast, compact and adaptable unit, unaffected by variations in raw water composition and flow rate. The unit reduces the volume of settled sludge, which can then be dewatered without further thickening.

The RPL Densadeg has three main components (Figure 345):

R - Reactor: the reactor is made up of three successive chambers. Chambers 1 and 2 provide rapid flocculation with mixing by an axial-flow impeller that recirculates the flow within the reactor. In chamber 3, plug flow conditions prevail to allow slow flocculation. Following coagulation, the raw water (5) is injected at the base of the agitated reactor. The flocculant is fed in (6) at the base of the turbine. Sludge from the presettler-thickener is recirculated externally (7).

The design of the reactor promotes the formation of dense floc; rising velocities in the lamellae settling zone may exceed 20 $m.h^{-1}$ for clarification and 30 $m.h^{-1}$ for lime softening.

P – Presettler-thickener: most of the floc settles in this zone. The lower portion is fitted with a thickening picket fence (9) and a bottom scraper (10). The thickened sludge is drawn off through a pipe (14) from the central sludge hopper. Part of the sludge is recirculated to the raw water inlet pipe (7), thereby ensuring optimum sludge concentration in the reactor at all times. The excess sludge is drained by gravity or pumped away. The sludge is thick enough to be transported to the dewatering system without any additional thickening.

L - Lamellae settling: this settling chamber, fitted with hexagonal-section Degrémont modules (11), removes the residual floc. The settled water is recovered (13) by a system of collection troughs (12). Depending on the size of the unit, the sludge is collected by gravity or scraping (15), extracted in (16) and recycled to the head of the reactor.

The Densadeg can be used in a variety of applications: production of drinking or process water (clarification, lime softening), treatment of waste filter backwash water, treatment of industrial wastewater (flocculation, precipitation), or MW (physical-chemical treatment, tertiary treatment for phosphate removal, etc.).

Depending on the treatment goals, the relative sizes of the lamellae settling zone and of the prethickening zone can be varied. Thus, if the purpose is simply to concentrate the suspended solids in the raw water, without attempting to achieve the best possible quality of settled water, a unit without a lamellae zone (Densadeg RP) is sufficient. One such application involves the treatment of filter backwash water in facilities not equipped for in-line settling: in-line coagulation, biological iron removal. This also applies for treatment of mine water, and some IWW. On the other hand, if highquality settled water is the priority treatment goal, and if there is no need to achieve maximum sludge thickening, then the Densadeg RL (Figures 346 and 347) is appropriate.

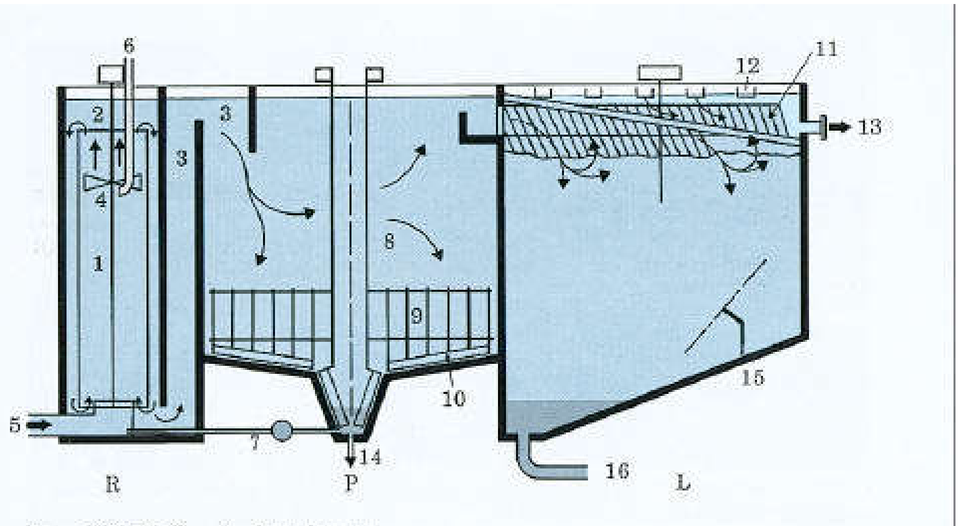
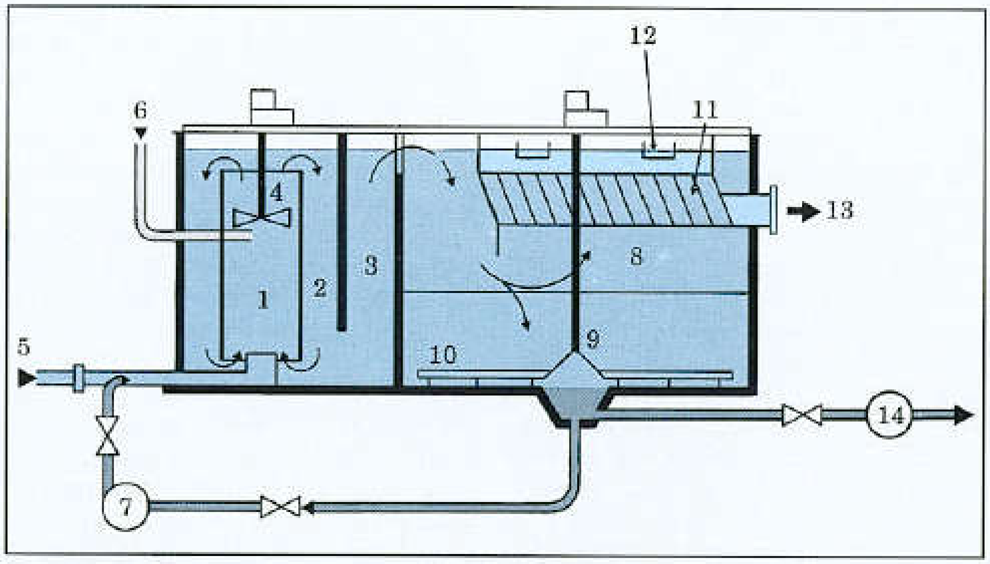


Figure 345. RPL Densadeg. Basic diagram.



1,2,3 – Flocculation chambers.
4 – Propeller.
5 – Raw water inlet.
6 – Reagent feed.
7 – Recirculation pump.
8 – Flocculated water inlet.

9 – Drive shaft.
10 – Scraper.
11 – Modules.
12 – Collection troughs.
13 – Treated water outlet.
14 – Sludge draw-off pump.

Figure 346. Densadeg RL – Basic diagram.

Figure 347. Extension of the LE-Dumez facility in Morsang-sur-Seine (Paris area, France). Clarification of water from the River Seine. Flow rate: 3,800 $m^3.h^{-1}$. RL Densadeg clarifier. Settling velocity in the lamellae zone: 22.5 $m^3.h^{-1}$.

A steel version of the Densadeg is also available (Figure 348).

Figure 348. Franken 11 (Germany) facility. Flow rate: 150 m^3.h^{-1}. Clarification of river water for the production of process water. Steel Densadeg clarifier.

3.3.
GRANULAR CONTACT MEDIA CLARIFIERS
THE GYRAZUR

The main difference between this device and sludge contact precipitation units lies in the use of larger nuclei. While in the preceding devices the size of the elementary calcium carbonate crystals is about 0.01 mm, a "catalysing" media is used here, generally involving sand with initial particle size of 0.2 to 0.4 mm, contained in a conical receptacle. The calcium carbonate precipitates by crystallizing on the surface of the grains, between which water percolates upward at a high rate. The large number of grains guarantees a rapid and complete reaction.

These units have three advantages:

- relatively compact,
- able to operate under pressure; when associated with pressure filters, they can be used for carbonate removal with no pressure break between units,

- instead of sludge, they create beads 1 to 2 mm in diameter which dewater very rapidly.

Since catalytic lime softening involves crystallization of the calcium carbonate of the water with the granular media, dispersing agents must not be used. The process is not applicable to water containing too much colloidal matter, iron or magnesia. To prevent precipitation of magnesium oxides, the magnesium hardness of the raw water (MgH) must conform to the relation MgH < TH - M alk.

The Gyrazur can be used to produce carbonate-free water with low SS, as the solids are mainly a result of impurities in the lime used (lime grit).

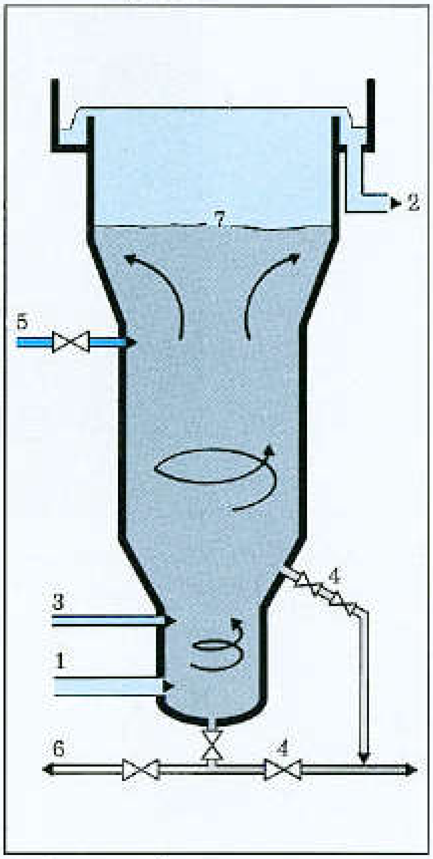
The Gyrazur (Figure 349) is a metal unit comprised of a stack of three cylinders with diameter increasing from bottom to top, connected by truncated conical sections. This geometry contains practically twice as much granular media as a conventional conical unit of like upper diameter and height.

The raw water is introduced horizontally and tangentially (1) into the lower cylinder so as to impart an upward spiralling motion that makes the media expand and move.

The lime, in the form of highly diluted milk of lime or lime water, is injected directly into the media at (3), which is slightly above the raw water inlet and thus in a highly turbulent zone that facilitates rapid mixing.

The treated water, separated from the media in the upper cylinder (7), is recovered at the top of the device and drained out through (2).

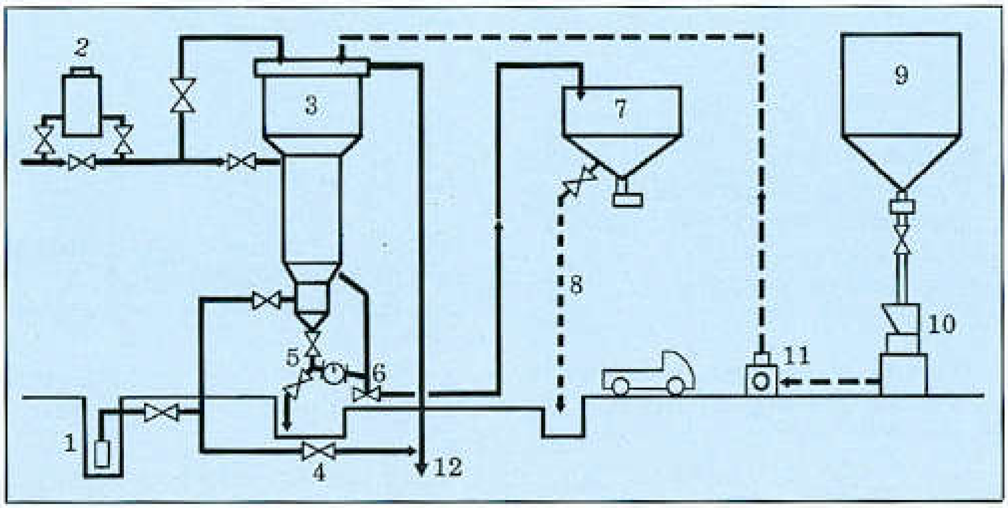
Since the grains of the media grow continually, the largest must be removed periodically from the base of the device (4), and replaced by new small nuclei introduced through (5).



1 – Raw water inlet.
2 – Treated water outlet.
3 – Reagent addition.
4 – Media removal.
5 – Addition of new nuclei.
6 – Drain.
7 – Upper level of the media.

Figure 349. The Gyrazur reactor.

High rising velocities, from 30 to 70 m.h^{-1} are possible in the separation zone. Gyrazur models may be designed to accommodate flow rates from 50 to 2,000 m3.h^{-1}. The Gyrazur reactor can also be used for removal of carbonates using caustic soda. Layout is shown in Figure 350.



1 – Raw water lift station. 2 – Sand loading chamber. 3 – Gyrazur. 4 – Bypass. 5 – Drain. 6 – Ejector. 7 – Grain storage silo. 8 – Bead removal. 9 – Lime silo. 10 – Volumetric feeder. 11 – Metering pump. 12 – Treated water outlet.

Figure 350. Lime softening facility using the Gyrazur.

Figure 351. LE-Dumez facility in Villeneuve-la-Garenne (Paris area, France). Maximum flow rate: 1,800 m^3.h^{-1}. Lime softening of groundwater using a Gyrazur reactor. View of the reagent feed point at the base of the unit.

3.4.
SLUDGE DRAW-OFF DEVICES

3.4.1. Internal collection

- **Without scraper**

The sludge is concentrated in:
- single gravity hoppers (plain static settlers, metal Sédipac units),
- multiple gravity hoppers (Accelator, Pulsator, etc.).

The slope of the hopper walls must be greater than the angle of repose of the sludge.

- **With scraper**

The sludge at the bottom is pushed by a scraper device toward one or more recovery points, designed to avoid deposits. In some cases, such as wide rectangular settling tanks, the tank itself must be fitted with a scraper due to the prohibitive cost of providing sufficient slope to allow gravity flow.

With suction systems, sludge can be collected without hoppers.

3.4.2. Recovery

Sludge recovery may be by gravity flow, provided that a sufficient head is available and that sludge characteristics (viscosity, thixotropy, texture, etc.) permit. Otherwise, the sludge must be recovered directly by pump, and recycled where applicable.One means of recovering sludge directly, without hoppers or scrapers,
involves submerged, self-propelled suction devices with PLC multidirectional control.

Sludge draw-off is intermittent except in specific cases involving:
- external recirculation,
- a high risk of clogging.

3.4.3. General configuration

Sludge draw-off lines must be designed to eliminate the risk of clogging. The following guidelines must be adapted to the sludge characteristics:
- sufficient line velocity should be provided at least periodically, to prevent deposits,
- pipe diameters should be sufficient,
- pipe runs should be as straight as possible,
- pump suction lengths should be minimized,
- perforated pipes should be used for recovery only over short distances and with highly fluid sludge,
- drainage and rinsing of pipes (water and compressed air flushing) or even mechanical raking out (steel industry) should be provided.

Figure 352 shows two configurations applicable to concentrated industrial sludge for:
- direct recovery,
- recovery via an intermediate storage sump.

This configuration allows visual control and accommodates different instantaneous flows between the settling tank draw-off process and sludge removal.

3.4.4. Sludge removal devices

DEVICE	USE	COMMENTS
ISOLATING DEVICES		
Pinch valves	Any sludge	Sleeve selection based on resistance to chemical agents
Spherical or taper plug valve	Industrial sludge	Taper plug valves for abrasive sludge
Telescopic valves	MWW sludge	Visible flow
Butterfly valves	Drinking water sludge	Partial flow valves for large diameters and highly fluid sludge
Siphons	Suction-type settling tanks	Avoid pipes through walls and isolation valves
PUMPS		
Vortex pumps	Any sludge	Except sludge with high concentrations
Eccentric rotor	Concentrated sludge	
Diaphragm pumps	Concentrated sludge with high pressure discharge	
Archimedes' screw	Activated sludge	High flows
Air-lift	Abrasive, only slightly concentrated sludge	Low lift heights. Can accommodate large particles

3.4.5. Automation

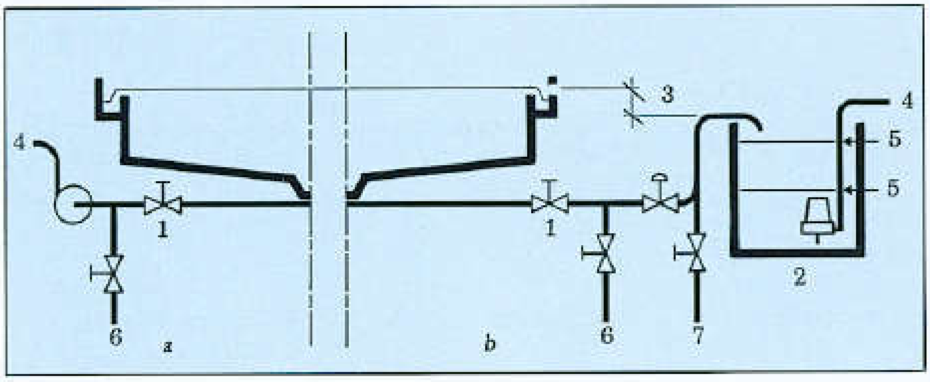
Since sludge draw-off is almost always intermittent, it is a process worth automating. Depending on the application, the controls can be set up according to different parameters:

- frequency/duration using a timer (especially if the flow treated is constant and if the concentration of extracted sludge is of little import),
- flow rate (variable frequency but constant duration of extraction),
- concentration of the sludge (measured ultrasonically or estimated based on scraper torque measurement),
- settling tank sludge level (detected by an ultrasonic or optical probe),
- other.

Automated devices are described in Chapter 21, page 1130.

3.4.6 Scum

Usually, matter floating on the surface must be separated from sludge. In general, the skimmer directs it toward a hopper or trough connected in turn to a sump in which the scum is concentrated. The profile and diameter of the connecting structure must take into account the "stickiness" of the scum; automatic cleaning devices are often included.



1 – Isolation valve.
2 – Intermediate sump.
3 – Head required on the draw-off pipe.
4 – Sludge outlet.
5 – Level sensor.
6 – Flushing water connection.
7 – Vertical pipe drainage.

Figure 352. Examples of IWW sludge recovery: a – direct; b – with intermediate sump.

4. FLOTATION UNITS

4.1. GENERAL TECHNOLOGY

Flotation units may be circular or rectangular. Rectangular ones are normally used in drinking water treatment because they can be used as part of a single structure combining the flocculator, flotation unit and filters with minimum space requirements.

If necessary, preliminary testing may be done on a laboratory (Flottatest, Figure 353) or semi-industrial pilot plant scale (Figure 354).

Figure 353: Flottatest.

In terms of hydraulic characteristics, especially when treating water with high SS concentrations, a circular flotation unit is preferable to a rectangular one: for a given unit capacity, the distance between the top of the water/air bubble mixing chamber and the bottom of the scum baffle is shorter and bubble distribution may be kept virtually uniform over the entire horizontal cross-section of the vessel.

4.1.1. General description of a flotation unit

The operating principle described in Figure 3 5 5 applies to both circular and rectangular flotation units. The raw water (11), which may have already undergone chemical flocculation (12) in a flocculator (13), is injected into a mixing

Figure 354. Mobile flotation unit. Flow rate: 10 $m^3.h^{-1}$.

chamber (1) where it is placed in contact with air-saturated water (9) that has passed through a pressure-release valve, resulting in the formation of small air (or gas) bubbles that attach to the solid particles. Being of lower specific gravity than the water, the particle/ bubble composite is separated out in zone (2) and collects at the surface. The resulting sludge is recovered by a surface skimmer and channelled out through a trough (4). The water separated from the particles is recovered under a scum baffle (5) before it is collected and drained off in (6).

Pressurized water is obtained:

- either by **recycle pressurization,** i.e., part of the treated water is recycled (7) and brought into contact with pressurized air (or gas) (14) in a saturation vessel (8);
- or by **full flow pressurization,** in which all the liquid to be treated is pressurized.

The pressurized water is injected into the mixing chamber (1).

For some applications and for large-diameter units, the flotation unit is fitted with a bottom scraper to facilitate the removal through (10) of any sludge that settles on the floor.

Comments:

a) The mixing chamber serves two purposes:

-to combine the water to be treated with the pressurized water,

- to dissipate the kinetic energy from the mixture before the latter passes into the separation zone.

b) The floated sludge layer may in some cases reach a thickness of several dozen centimetres and be extremely stable (thickening of activated sludge). In other cases it is not as thick and/or is more fragile (flotation of metallic hydroxide floc or oils).

c) The number of surface skimmer blades depends on their rotational veloc-

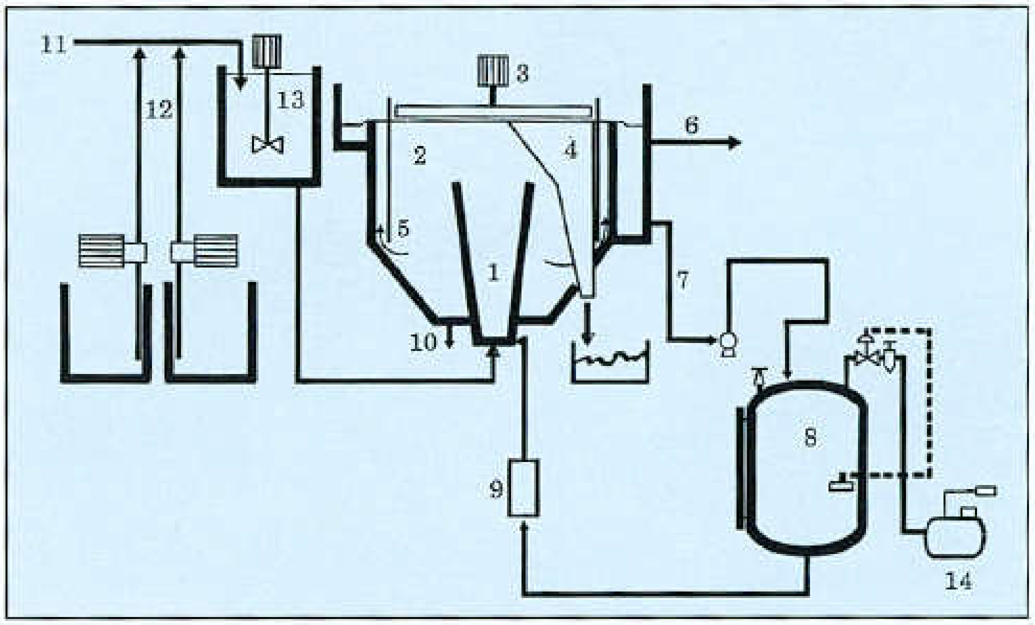


Figure 355. Flow sheet of a flotation facility.

ity, the distance between two blades and the amount of sludge to be removed. The risk of deaeration or rupture of the sludge must be avoided.

4.1.2. Saturation vessels

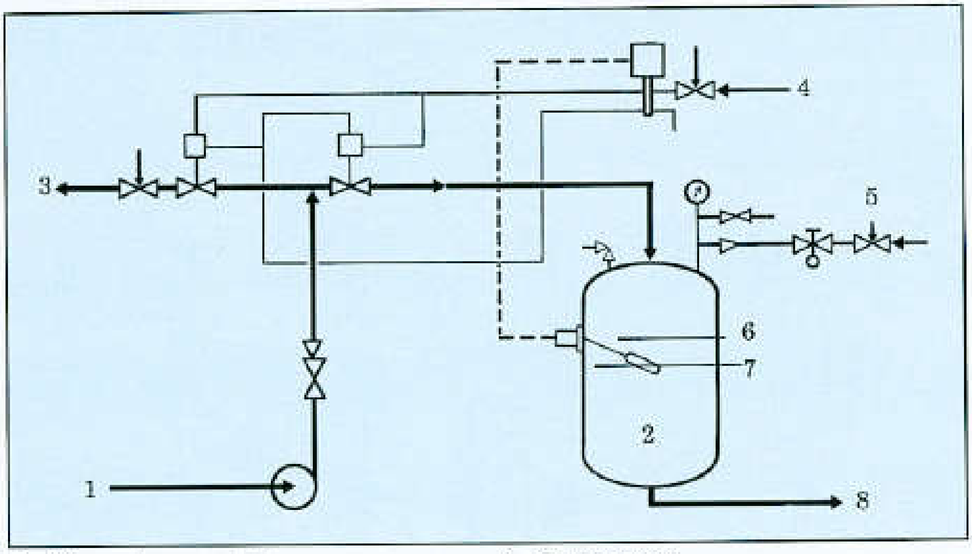
These gas-dissolving units are made of galvanized steel or have internal protection. They may be vertical or horizontal.

The standard Degrémont vessels have a contact time ranging from a few dozen seconds up to one minute. Vertical units are used for flow rates under about 300 $m^3.h^{-1}$.

Different types of regulation prevent the pressurization gas from discharging directly into the flotation units. Figure 356 shows one configuration that is widely used because of its simplicity.

4.1.3. Recovering floated sludge

Floated sludge to be recovered from the receiving hopper may require deaeration before pumping. The pumps must have a positive suction head.



1 – Water to be pressurized.
2 – Saturation vessel.
3 – Recycle.
4 – Valve control air.
5 – Compressed air.
6 – High level contact.
7 – Low level contact.
8 – Pressurized water.

Figure 356. Diagram of a pressurization system.

4.2.

CIRCULAR FLOTATION UNITS

4.2.1. Flotazur BR

The Flotazur BR, made of metal, has been standardized for diameters up to 8 m. It is fitted with a dual scraper system, for the surface and the bottom (Figure 357).

Depending on the application and the diameter, the Flotazur BR has between two and six surface skimmers (1) and only a single bottom scraper (2). The system's central drive motor reduction gear (3) is connected by an arm (4) to the middle component (5) with the other end resting on a roller (6) that moves along a track. The bottom scraper is suspended from one of the scraper arms.

The floated sludge receiving trough (7) is long and has an access ramp, the upright part of which is designed to ensure contact with the scraper at all points. Downstream, the sloped guides allow gradual return of the skimmer into the water with the minimum of disturbance.

4.2.2. Sediflotazur

The Sediflotazur is a concrete unit standardized for diameters up to 20 m. The scraper principle is similar to that of the Flotazur BR. The difference is that the scraper system is pulled by a peripherallydriven walkway to which the bottom scraper is attached.

For unit diameters greater than 15 m, two diametrically opposed sludge drainage troughs are provided, both to minimize sludge retention time at the surface (avoiding deaeration) and especially to prevent overloading at the trough inlet.

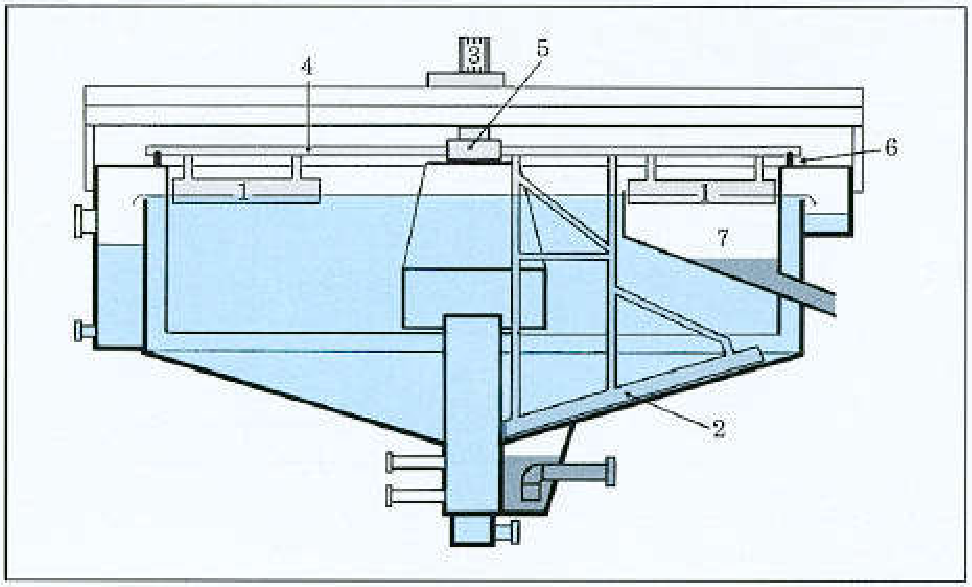


Figure 357. Flotazur BR.

Figure 358. Barrancabermeja (Colombia) facility for Ecopetrol. Flow rate: 3,000 $m^3.h^{-1}$. Flotation of oily water. 4 Sediflotazur units, each 15 m dia.

4.3. RECTANGULAR UNITS

4.3.1. Flotazur P

The Flotazur P (Figure 359) is a combined flocculator (1) and rectangular flotation unit (2). It is especially suited for treatment of lightly loaded waters giving light, fragile floc. The rising velocity is between 5 and 8 $m.h^{-1}$ with the proportion of pressurized water ranging from 6 to 12%.

After a retention time of 15 to 30 minutes in a flocculator equipped with slow stirrers (usually two compartments), the water enters the parallel mixing chambers (3) directly, where it comes into contact with the pressurized water (4). The floated sludge is removed at the opposite end (7) by a travelling scraper bridge (5) that scrapes the portion of the tank where the sludge thickens (about a third or half) without disturbing the expansion zone above the mixing chambers. Depending on the dimension of the tanks, the scraper bridge is driven by a pneumatic piston (6) or an electric motor. A chain scraper may be provided.

These devices have been standardized for surface areas up to 120 m^2 and are not usually fitted with a bottom scraper.

4.3.2. Flotazur L

Primarily intended for highly loaded water requiring high pressurized water recycle rates, this unit (Figure 361) is not as widely used as circular units.

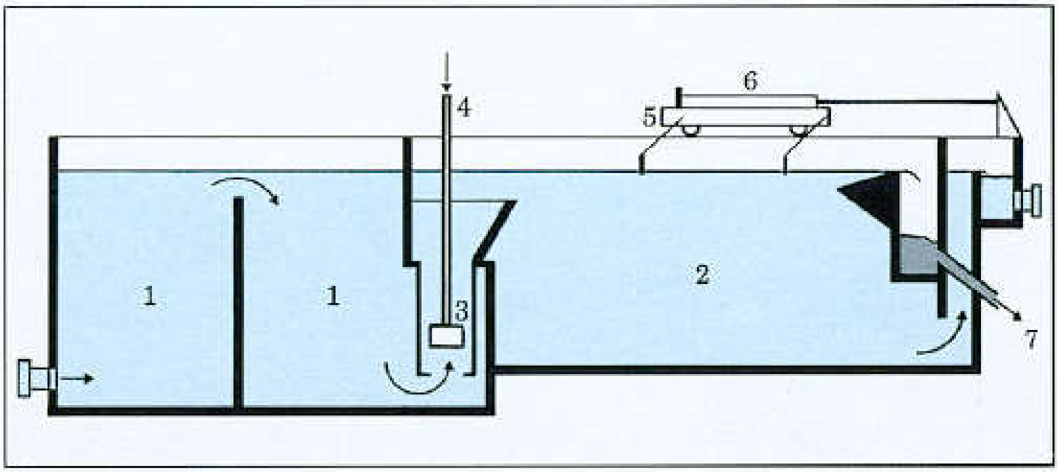


Figure 359. Flotazur P.

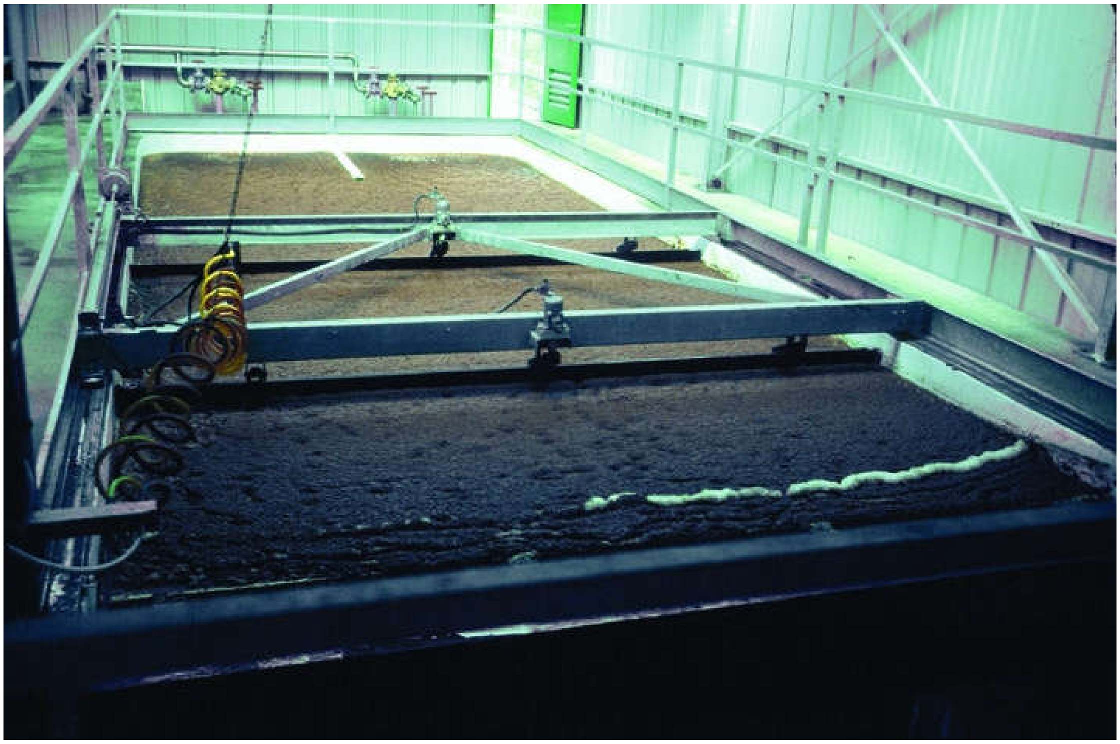
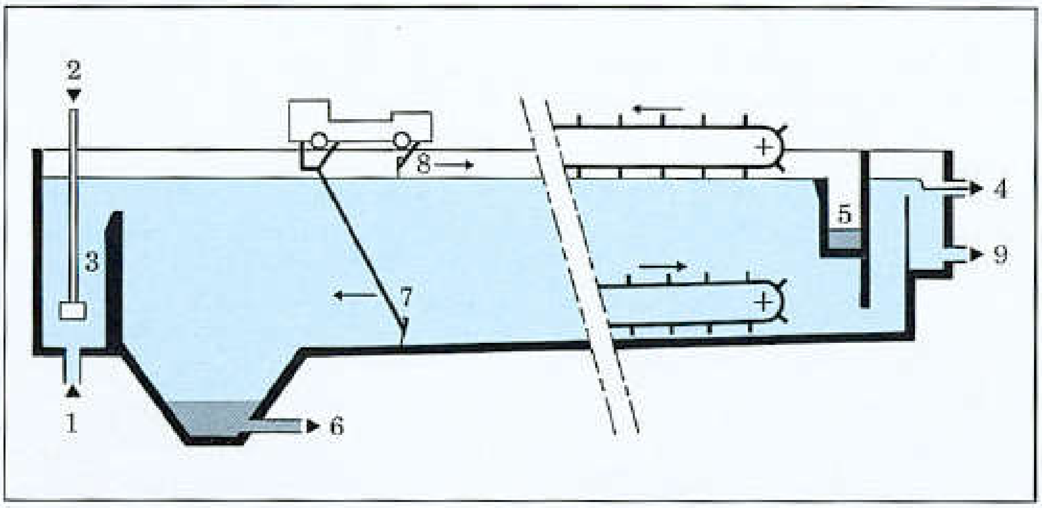


*Figure 360. Facility at Pontrieux (Western France). Drinking water supply. Flow. 200*m^3.h^{-1}. *Clarification of river water by flotation. View of the sludge and the Flotazur P scraper system, with a surface area of 27*m^2.

The Flotazur L has the same arrangement as the Flotazur P for mixing the water to be treated with the pressurized water. The scraper system removes the surface scum and, if necessary, the sludge at the. bottom (chain scraper or scraper bridge).



1 – Raw water inlet.
2 – Pressurized water inlet.
3 – Mixing zone.
4 – Treated water outlet.
5 – Float outlet.
6 – Sludge removal.
7 – Bottom scraping.
8 – Surface skimming.
9 – Water recycled to pressurization.

Figure 361. Flotazur L.

4.4.
FLOTATION UNITS FOR SLUDGE THICKENING

4.4.1. General

The flotation units used in the treatment of water with high SS concentrations (several grammes per litre.) have the following characteristics:

- a modified mixing chamber design,
- greater depth, providing more than 80 cm for storage of larger quantities of sludge, thereby promoting thickening,
- a scraper system with a large number of scraper arms,
- sludge removal troughs designed to increase the volume of the sludge removed each time the scraper arm passes,
- the option of mounting an anti-odour cover on the scraper arms.

In this application, the **full flow pressurization** technique is generally used.

Although rectangular tanks may be used, circular tanks allow greater efficiency, especially for the larger sizes, using simple equipment with minimal maintenance requirements.

4.4.2. FE flotation units

FE flotation units are circular devices made of metal that have been standardized for diameters up to 8 m. The scraper principle for this device is the same as that of the **Flotazur BR.**

4.4.3. FES flotation units

FES flotation units are circular units made of concrete, based on the same scraper principle as the Sediflotazur. The model has been standardized for units up to 20 m in diameter. For diameters greater than 15 m, these units are equipped with two diametrically opposed sludge drainage troughs.

Figure 362. Maxéville (Eastern France) facility for the Champigneulles brewery. Flow rate: 600 m^3 h^{-1}. One of two 20 m dia. Rotation units.

11

AEROBIC BIOLOGICAL PROCESSES

1. ACTIVATED SLUDGE

1.1 INSTALLATION LOADING AND OPERATIONAL CHARACTERISTICS

The purification efficiency of an activated sludge plant depends on two factors simultaneously:

- fixing, by adsorption and oxidation, of the polluting elements by the bacterial mass (or biological floc),
- effective separation of this floc from the purified interstitial water.

In the activated sludge reactor, bacterial mass is accumulated due to sludge recycling; sludge age thus increases with the available biomass quantity and has a somewhat slowing effect on the bacterial activity; however, in the development phase (see page 297) which is the phase of most of the bacterial flora, this effect is not predominant and, generally speaking, the quantity of pollution retained is all the greater because the bacterial mass is considerable.

For continuous removal of the soluble carbonaceous pollution, the purification efficiency is greater the lower the **F/M ratio** (see page 296) and the greater the sludge age. This might not be the same for concomitant nitrification or phosphate removal.

Purification processes by activated sludge are thus classified in families. However, it is customary to relate these processes not only with F/M ratio but also with **BOD loading.** There are two reasons for this:

- the requirements of clarification - usually carried out by settling - make it necessary not to exceed maximum concentrations of SS (g.l^{-1}) of the activated sludge liquor. For the limits of F/M ratio there are thus corresponding limits of loading in **BOD_5 or COD** (kg/m^3. d) calculated on the volume of the biological reactor,
- a minimum retention time in the biological reactor is necessary to facilitate the

phenomena of adsorption and to dampen the effect of peaks, particularly common in municipal effluents. Table 76 summarizes the usual classification by loading level of the processes of removal of carbonaceous pollution by activated sludge. The stated efficiencies assume the case of proper separation of all the elements that can be settled from the activated sludge liquor.

Table 76. **Classification of processes using activated sludge.**

Type	**F/M kg BOD_5/kg SS.d**	**BOD loading (Cv) kg BODs/m^3.d**	**Sludge age in days**	**BOD_5 removal efficiency p on MWW**
Low loading	F/M < 0.15	Cv< 0.40	10 to 30	? > 90% Nitrification possible
	F/M < 0.07 (extended aeration)			
Medium loading	0.15 < F/M < 0.4	0.5 < Cv < 1.5	4 to 10	? ~ 80 to 90% Nitrification possible at elevated temperatures
High loading	1.2 > F/M > 0.4	1.5 < Cv < 3	1.5 to 4	? < 80%

Very high loadings (F/M> 1.2) are sometimes used in an initial roughing stage where the pollution is basically removed by adsorption and retaining of particles in the biological floc.

With concentrated industrial wastes, purification efficiencies are greater than those indicated above.

It is customary to compare the F/M ratio to the mass of aerated sludge present 0.5 in the aeration tank alone, because it is usually in this reactor that most of the activated sludge is found and that the medium is aerobic. However, in certain processes, the volume of sludge present in the clarifier may be of the same order of magnitude as or even greater than that of the aerated sludge. The preceding classification must then be modified

Figure 363 characterizes the development of purification according to the F/M ratio.

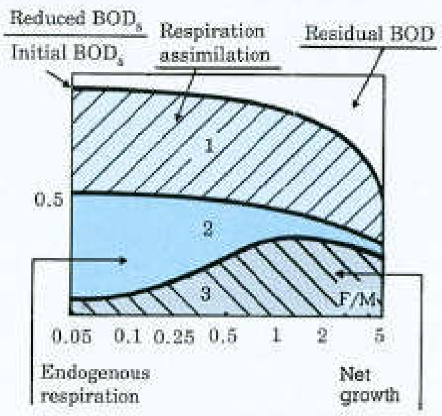


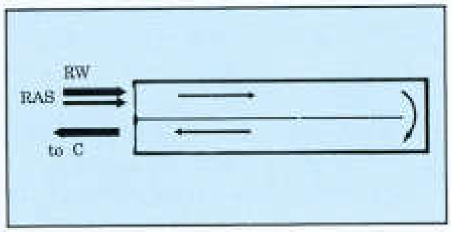
Figure 363. Development of purification as a function of the F/M ratio.

1.2.
POSSIBLE ARRANGEMENTS OF ACTIVATED SLUDGE TANKS

Independent of the loading criteria (and sludge age), the hydraulic arrangement of the biological reactor and the relations between reactor and clarifier make it possible to distinguish various systems of activated sludge treatment.

1.2.1. Plug flow tank

The waste to be treated and the recycled sludge enter more or less at the same point at the head of the tank which is arranged in such a way as to form a long channel (Figure 364).



RW = raw water
RAS = returned activated sludge
C = clarifier

Figure 364. Principle of plug flow.

The substrate concentrations and the oxygen demands of the activated sludge liquor vary throughout its flow path. This is why the installed oxygenation power normally decreases from upstream to downstream (tapered aeration)

This type of tank is the oldest. It is used particularly in the case of nitrification and is especially suited to large. plants. Usually sized for considerable retention times (5 to 6 h at average flow), it is sometimes used on a high rate basis with retention times of 1 to 2 h and liquor concentrations of SS of 1 to 2 $g.l^{-1}$ (a process called modified aeration).

For any reaction that is not zero, the plug flow reactor makes it possible to achieve the best purification efficiency. However, a perfect hydraulic design is impossible and would lead to excessively costly construction. A longitudinal dispersion factor is unavoidable (see page 288).

1.2.2. Completely mixed tank

The aim is to obtain a completely homogeneous reactor presenting, at all points, identical concentrations of microorganisms, dissolved oxygen and residual substrate (Figure 365). The raw effluent is immediately dispersed in the reactor, and the interstitial liquid represents the treated effluent.

Nevertheless, the theoretical concepts of complete mixing are rarely fully adhered to in practice, particularly with large units. They are only achieved practically in certain package units (Oxyrapid). The advantage of complete mixing is to limit overloads due to pollution peaks (daily, for example).

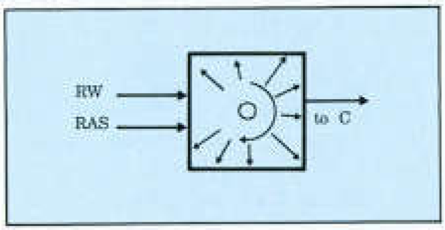


Figure 365. Principle of complete mixing.

1.2.3. Closed loop basins

This technique (Figure 366) is similar to that of the completely mixed one. However, the relatively great length of the loop, and the very localized arrangement of the aerators, lead to quite considerable variations in the dissolved oxygen content throughout the basin.

When the aerators used are of the horizontal type, the reactor is often called an "oxidation ditch°. If they are of the vertical type, it is often called "Carrousel". It is always possible to connect several basins in a loop in series uniting with each other.

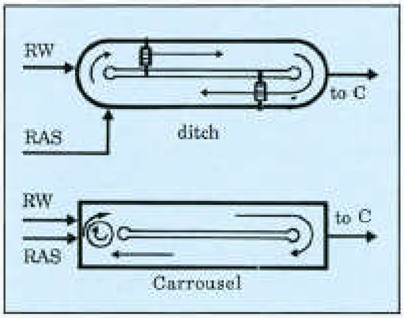
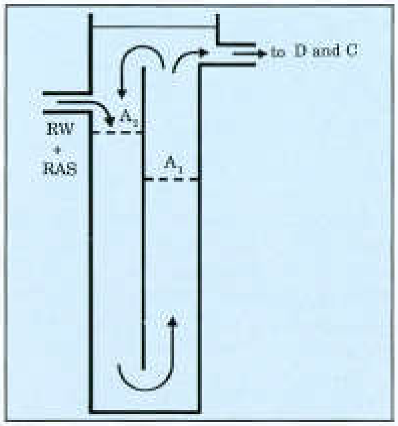


Figure 366. Closed loop basins.

There is a particular type of closed loop reactor to point out: the deep well reactor (Figure 367). In this small diameter vertical reactor (generally less than 3 m) that may be up to several dozen metres deep, the depth allows an increase in the oxygen transfer efficiency. Air is introduced in the rising branch A_1 to ensure external recycling of the liquid mass in the vertical plane and, at the same time, in the descending branch A_2. Hydraulic operation of the system is difficult.



RW = *raw water*
RAS = *returned activated sludge*
D = *deaeration*
C = *clarification*
A = *air injection screen*

Figure 367. Deep well reactor.

1.2.4. Cascade tank

This type of reactor (Figure 368) comprises a series of completely mixed tanks through which the activated sludge liquor flows successively. It follows kinetics similar to those of the plug flow tanks, while making use of compact reactors of simple construction. It adapts quite well to treatments combining the ammonium and phosphorus removal with that of the carbonaceous pollution.

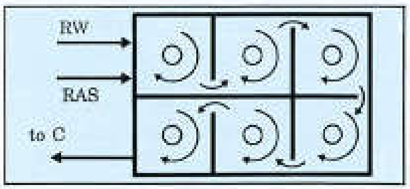


Figure 368. Cascade tank.

Figure 368. Cascade tank.

1.2.5. Stepped feed tank

(incorrectly called "step aeration°). The inflow of wastewater is organized in step fashion in the aeration tank, which is comprised of a series of cells successively traversed by the liquor, which "zigzags" forward. The recycled sludge is introduced at the head of the tank. Oxygen needs are thus much better distributed than in a plug flow tank and, for the same SS concentration at the inlet of the clarifier, the mass of activated sludge present in the reactor is also greater.

Degrémont have perfected various regulating systems for this stepped feed process (Figure 369).

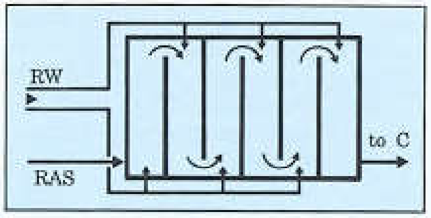


Figure 369. Stepped feed tank.

1.2.6. Contact-stabilization process

This process, initially known as Biosorption (Infilco-Degrémont) consists of mixing the raw wastewater with the recycled activated sludge only after a long period of re-aerating it, with this period allowing the oxidation and assimilation of the stored organic matter (Figure 370).

In the contact phase, purification is basically ensured by adsorption, with only partial synthesis of the new bacterial mass. It lasts 20 to 40 minutes on MWW.

The volumes of the two zones are comparable in size.

1.2.7. Adsorption – bioaeration process

This process consists of carrying out the biological purification in two separate phases each including a reactor and a clarifier. It is used on raw wastewater and consists of

- a phase with very high loading (high rate), greater than 2 kg BOD_5 per kg SS per day,
- a phase with medium loading (medium rate) (F/M ratio of 0.3 kg BOD_5 per kg SS per day).

The purpose of this process is to develop two completely different bacterial floras in the two stages. In the first, the phenomena of adsorption dominate and a reduction of about 30 to 50% BOD_5 is sought. In the second stage, the mechanisms of oxidation and synthesis are predominant. Nitrification is possible if the F/M ratio is sufficiently low.

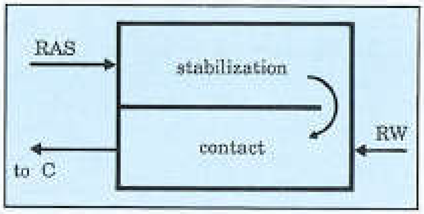


Figure 370. Contact-stabilization process.

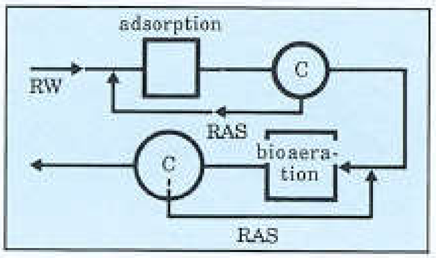


Figure 371. Adsorption-bioaeration process.

1.3.
THE CLARIFIER AND RECYCLING

Separation of the bacterial floc from the interstitial liquor, or clarification, is usually achieved by settling.

In a continuous purification process, this clarifier, separated from the actual reactor, is called **secondary settling tank.** In intermittent processes (in batch run) or alternating processes, settling can be ensured in the actual reactor. On highly concentrated activated sludge liquors, separation by flotation may sometimes be used.

Activated sludge tends to flocculate, with a specific gravity quite near that of water. Its ability to settle, monitored by the SVI (sludge volume index), or Mohlman index (see page 297), depends on a certain number of factors that affect the characteristics of the bacterial floc: the presence of industrial wastes, the dissolved oxygen content, the variation in the microorganisms load conditions throughout the treatment cycle, the aeration mode, the temperature, etc. The settleability and the concentration of activated sludge determine, with the flow of treated water and the total throughflow (raw wastewater flow + recycled flow) the proper operation of secondary settling tanks.

They provide two equally important functions:

- clarification of the wastewater,
- thickening of the recycled sludge.

Rising velocity and solids loading

(SS) are typical parameters for sizing the having a small diameter. It may be 4 to secondary settling tanks whose guide values are as follows for MWW:

Activated	**Rising velocity**		**Solids loading (SS)**	
	Daily $m^3/m^2.d$	**Maximum** $M^3/m^2.h$	**Average** $kg/m^2.h$	**Maximum** $kg/m^2.h$
Medium rate	15-30	1.2-1.8	3-6	8
Low rate	8-15	0.8-1.2	2-5	6

The rising velocity corresponds to the flow of treated water alone. Solids loading is calculated on the total throughflow.

However, the preceding values must sometimes be considerably reduced with a sludge that settles poorly. Sludge volume load (see page 642) is then quite often representative of the spatial sludge load of the clarifier. In the case of sludge bulking with SVI's of 300 or 400 $ml.g^{-1}$ and for concentrations of 1 to 2 ($g.l^{-1}$) the rising velocity must be adjusted to several dozen $cm.h^{-1}$.

Other elements, inherent in the very design of the clarifier, are important for the results of clarification: the means of collection of the treated water, weir loading rate (which normally should not exceed 15 $m^3/h.m$).

The **depth** of the structure is one of the main sizing parameters. It must be sufficient to give the sludge the required time to thicken and, at the same time, to allow the inevitable fluctuations of the sludge blanket due to variations in hydraulic operating conditions.

A 3 m minimum straight tank height is recommended for circular units 5 m for units of large diameter (40 to 50 m). The maximum admissible rising velocities in practice are highly dependent on this height when the sludge volume is considerable.

The recycle rate, which determines the concentration of suspended solids of the recycled sludge, governs the volume occupied and the retention time of the sludge in the clarifier. If it is insufficient, the volume of sludge stored is too great: the top sludge level nears the collecting weirs and the water quality deteriorates. This results in a risk of anaerobic conditions and, in some cases, denitrification, with the activated sludge rising to the surface. If it is excessive, the clarification may be disturbed by the excess hydraulic energy introduced. For MWW activated sludge with proper settleability, a recycle rate adjustable from 50 to 100% of the average flow is satisfactory. For sludge that is very difficult to settle, a rate of 200% may be necessary.

The effectiveness of a clarifier also depends on its shape. The best results are obtained by vertical flow settling implemented in deep units with a highly sloping bottom (at least 50° to horizontal) but the construction of such units, of limited diameter, is expensive. Units with large surfaces have slightly sloping bottoms and are often equipped with bridge or flight scrapers pushing the sludge into pits whence it is recovered for recycling and removal of the excess fraction. However, mechanical scraping is not the most appropriate method for sludge that is often light and flocculent.

A more effective sludge recovery system is that of **"suction settling tanks"** (see page 652). It allows:

- high recycle flow without creating excessive sludge velocities at the bottom of the unit,

Figure 372. Valenton plant, France, for the SIAAP. Flow: 300,000 $m^3.d^{-1}$. Biological purification of Paris MWW by activated sludge. 4 clarifiers 52 m dia.

- a more orderly recovery of the sludge over the **entire** surface of the floor, avoiding excessively long sludge retention times in the clarifier.

The risk of degradation of the sludge is considerably reduced. This arrangement is absolutely necessary for large-sized tanks operating under difficult circumstances (hot countries, poor settleability of sludge). The draught tubes are mounted on a movable bridge (rotating or travelling back and forth); each one is connected with a short scraper sweeping the adjacent surface.

Degrémont largely developed the technology of these suction settling tanks.

The sizing of an activated sludge treatment plant depends **equally** on the aeration unit, the clarification unit and its recycling system. Sizing of these elements is interdependent. For example, making the clarifier large will make it possible to accommodate greater concentrations of activated sludge and, consequently, shorter retention times in the biological reactor. Figure 373 shows that there is a minimum total volume for a set purification efficiency. This minimum does not necessarily correspond to the economic optimum

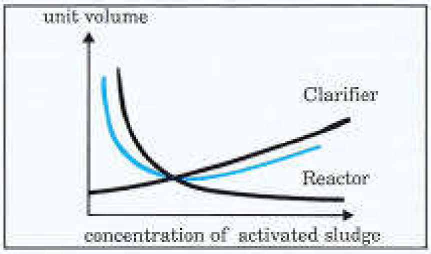


Figure 373. Variation of unit volume in an activated sludge system for a given purification efficiency.

1.4
AERATION SYSTEMS

1.4.1. Efficiency criteria and comparison of aeration systems

Aeration systems in an activated sludge tank have a dual purpose:

- to provide the aerobic microorganisms with the oxygen they need, generally taken from the air,
- to cause sufficient homogenization and mixing so as to ensure close contact between the live medium, the polluting elements and the water thus oxygenated.

These systems usually consist of an apparatus or a group of apparatus placed in a tank of determined volume and shape, accomplishing these two functions simultaneously.

1.4.1.1. Oxygenation capacity under standard conditions (OX.CAP.)

This basic criterion (OX.CAP.) makes it possible to determine the oxygenation capabilities of an aeration system.

It represents the oxygen mass that can be transferred by the system, per hour per cubic metre of tank, into fully deoxygenated water, (i.e., under maximum transfer conditions).

(OX.CAP.) = $K_L a.Cs$ (O_2 in kg/h.m^3 of tank)

- K_La in h^{-1} is the overall transfer coefficient and characterizes the oxygen transfer from the gas phase (air) to the liquid phase (water) (see page 277),
- Cs in $kg.m^{-3}$ is the oxygen saturation concentration in the water.

Typically, the system's oxygenation capacity should be established and monitored under the effective conditions of use in the activated sludge; however, under these circumstances, measurements are quite difficult and liable to be erroneous; this is why it is generally preferred to evaluate a system's effectiveness in clean water and at standard conditions, i.e.:

- at a temperature of 10°C (20°C in some English-speaking countries),
- under the normal atmospheric pressure of 1,013 mbar (i.e., 10.33 m WC),
- at a constant dissolved oxygen concentration of 0 $mg.l^{-1}$.

To convert the test values in dean water to the values in standard conditions, it is necessary to apply several correction factors depending:

- on water temperature,
- on absolute pressure at the measuring site, sum of the atmospheric pressure and the average relative water pressure Hm at this site (Hm = H x Z).

H is total water depth. The relative pressure coefficient Z, which is a characteristic of the aerator/tank combination, can be summarily evaluated for H 4 m, but must be subjected to a more elaborate evaluation for greater water depth. Finally, the total correction for conversion into standard conditions is written:

$$(OX\text{-}CAP.)_n = (OX.CAP.)_m . T_n$$

where:

$$T_n = \frac{C_s\,(10°C)}{C_s\,(t)} \times \frac{10.33 + Hm}{Patm + Hm} \times 1.024^{(10 - t)}$$

$(OX.CAp.)_n$, and $_m$ = under standard conditions and in measured conditions in clean water, respectively,

T_n = total correction coefficient,

$C_s(10°C)$ and (t) = values of oxygen saturation at the absolute pressure of 10.33 m of water, at 10°C and at the test temperature of the water, respectively,

Patm = atmospheric pressure at the measuring conditions, in m of water,

t = temperature in °C of the water at the measuring conditions.

1.4.1.2. Performance criteria

If the standard oxygenation capacity is known, several criteria can be determined, helping to choose and/or to compare aeration systems:

- **hourly oxygen transfer capacity,** relative to the entire tank:

AH = (OX.CAP.) x V in $kg.h^{-1}$ of dissolved oxygen,

where V = volume of the tank in m^3,

- **specific oxygen transfer capacity,** representing the quantity of oxygen transferred per unit of energy consumed:

$$AS = \frac{(OX.CAP.) \times V}{PA}$$

in kg dissolved O_2/kWh gross or net, where PA = power of the aerator in established condition in kW (motor input power or actual power at the rotor shaft),

- **oxygen transfer efficiency,** which is the percentage of the mass of actually dissolved oxygen compared to the mass of oxygen introduced, in a compressed air system. It can be calculated by adopting a mass of oxygen of 0.3 $kg.Nm^{-3}$ of air:

with Q = flow of air in $Nm^3.h^{-1}$.

The aerator/tank combination is inseparable and any performance of an aeration system must be linked to the complete definition of the combination. For example, it is known that oxygenation performance can be increased under exceptional circumstances: considerable specific power (per m^3 of tank) for surface aerators, or low air flow for fine bubble systems.

1.4.1.3. Converting standard conditions into actual conditions

Comparing aerators in clean water is not truly representative of the performance recorded in actual conditions in the liquor. As a matter of fact, oxygen transfer can be greatly influenced by installation conditions, the nature of the wastewater and the quality of the sludge, and hydraulic and biological operating conditions.

Under current conditions, it is customary to use a correction coefficient T to be applied to the above defined criteria, to convert standard conditions to actual conditions:

Actual conditions
= standard conditions x T,
where coefficient T is itself the product of three secondary coefficients T_p, T_d, T_t.

- **Tp: oxygen transfer correction coefficient(pure water-liquor equivalence),** often called a in English, depends on the nature of the water and, in particular, on its concentration of surface-active agents, fats, suspended solids, etc., on the aeration system itself and on the shape of the tank.

- **Td: oxygen deficit coefficient.**

The oxygen transfer capacity is proportional to the oxygen deficit $C_s - C_x$

C_s : oxygen saturation under actual conditions: salinity, atmospheric pressure, temperature, etc. C_X: oxygen content of the liquor.

Under standard conditions (at 10°C), C_S is constant and equal to 11.25 $mg.l^{-1}$, and C_X is zero.

Td is thus equal to $\frac{C_s - C_x}{11.25}$

C_s is affected by:

- salinity of the water: the multiplying correction factor to be used is equal to:

$$\frac{475 - 2.65\ S}{475}$$

where S is the salinity in $g.l^{-1}$

- temperature (see page 509). The saturation concentration drops when the temperature rises,
- atmospheric pressure (generally only the effects of elevation are taken into account).

Cx is usually taken as between 1 and 2 $mg.l^{-1}$.

- **T_t: transfer rate coefficient.**

A rise in temperature increases the gasliquid transfer rate: the correction is equal to $T_t = 1.024^{t-10}$ where t is expressed in °C.

It is noted that, while the coefficients T_d and T_t are independent of the aeration system, the transfer coefficient T_p definitely is not. For this reason, the oxygenation capabilities of the various aeration devices do not vary in the same way when converting standard conditions into actual conditions, and the comparison, to be objective, should be made in the latter conditions; unfortunately this requires.

that T_p be known, and its precise definition requires delicate measurements carried out in a pilot biological treatment unit fed with the wastewater being studied.

The coefficient T_p can be considerably lower in the case of fine bubble diffusion of air than in the case of coarse bubble diffusion or of surface aeration, particularly due to the influence of the surface-active detergents.

The method explained above of converting standard conditions into actual conditions is suitable, where the oxygen transfer efficiencies are not too high (up to 25%, for example) and the water depths are moderate (up to 5 m), but it is not applicable for high performance aeration systems and for great depths, because it does not take the gradual reduction of the oxygen content of the air bubbles into account, which may then become considerable causing a reduction in the transfer coefficient.

As the actual performance in liquor is generally less than that at standard conditions, the oxygen impoverishment of the air bubbles is lower and, for this reason, the effect of reduction of the transfer coefficient due to this impoverishment is less. Failure to take this parameter into account thus leads to an underestimation of performance in actual conditions in liquor, all the more pronounced as the usual coefficient T_p of the system deviates from 1.

Determining with sufficient accuracy the actual aeration performance in liquor in a deep tank requires a fairly complex method, with various undetermined points requiring iteration. Degrémont uses a special computer program, perfected with the help of oxygenation tests used as models, carried out in up to 25 m submergence and reaching efficiencies in the 85% range.

1.4.1.4. Other comparison criteria

The comparison also involves other supplementary criteria which are not easily calculable and can only be qualitatively evaluated:

- mixing, which should allow sweeping velocities sufficient to avoid deposits and to ensure successful homogenization, etc., - the constant nature of the specific oxygen transfer capacity in the various operational modes,
- the reliability of all the components such as reducer, compressor, diffuser, conduits, etc.

It is of little use if, for example, an aerator has excellent oxygenation capabilities at the cost of insufficient hydraulic mixing or a risk of clogging, which results in a drop in oxygenation capacity and the production of anaerobic deposits in the tank.

1.4.2. Surface aerators

1.4.2.1. Different types of aerator

Surface aerators are divided into three groups.

The two most important ones are **low speed** aerators:

- **vertical axis type,** which take in water either through a draught tube or not, then spray it laterally into the air,
- **horizontal axis type (roller** or brush), which sweep the water with a submerged portion of the blades and spray it downstream.

The third group comprises **high speed, vertical** axis aerators driven directly by an electric motor at 750 or 1,500 rpm without an intermediate reducer. The impeller, generally placed inside a short tube, is of small diameter. The mechanical assembly is often supported by one or more floats, so as to be easily placed on the water and to provide considerable mobility. This type of aerator has the advantage of being inexpensive, but it consumes large amounts of energy (specific oxygen transfer capacity rarely exceeds 14 kg/kWh net) and has a low mixing capacity. It is better suited for lagoons than for activated sludge tanks, where deposits must be avoided. These units are produced for a power range of 2 to 50 kW or more.

1.4.2.2. Vertical axis, low speed aerators. The Actirotors

This type of unit is as old as the activated sludge process itself (Manchester 1916).

The advantages of these aerators are:
- simplicity of installation and use,
- their energy consumption,
- their mixing capabilities.

They are still very widely used despite their relative lack of flexibility of use (particularly if the number of units in the tank is low) and certain risks of nuisance (aerosols, noise). These nuisances can be avoided by judicious covering of the spray, and by soundproofing the drive assembly.

The sequencing of operation by PLC (see page 1143), a constraint often necessary to adjust the oxygenation to the demands, may promote partial denitrification.

Actirotors are vertical surface aerators developed by Degrémont Several thousand are in operation.

(a) The impeller and shaft

The impeller of the Actirotor (Figure 374) is of the completely open type, which eliminates any possibility of clogging or packing. It includes a closed, hollow hub on which thin, streamlined pumping blades and blades for dispersing the spray are attached.

This balanced impeller is supported and driven by a tubular shaft, fastened on a high output drive assembly calculated, according to AGMA standards, for a service life of over 80,000 hours in conditions of intensive use.

The peripheral velocity of the impeller, at full power, varies according to models between 4 and 4.5 $m.s^{-1}$, i.e., rotation speeds from the 100 rpm range for small units to 40 rpm for large models (75 kW). Operation at limited power can be obtained by a two-speed or variable speed motor (1).

(b) Installation

The assembly is often mounted on fixed support: a walkway or, even better, a circular platform surrounded by a semi-rigid, anti-aerosol, anti-noise skirt, flush with the liquid level (Figure 375).

---

(1) Another method of regulating the input power and thus the oxygen transfer capacity which is sometimes used consists in adapting the submergence of the aerator by variations in the liquid level. This arrangement has the disadvantage of a very low mixing capacity at limited submergence and hydraulic surges on the clarifier if the water level variations are rapid.

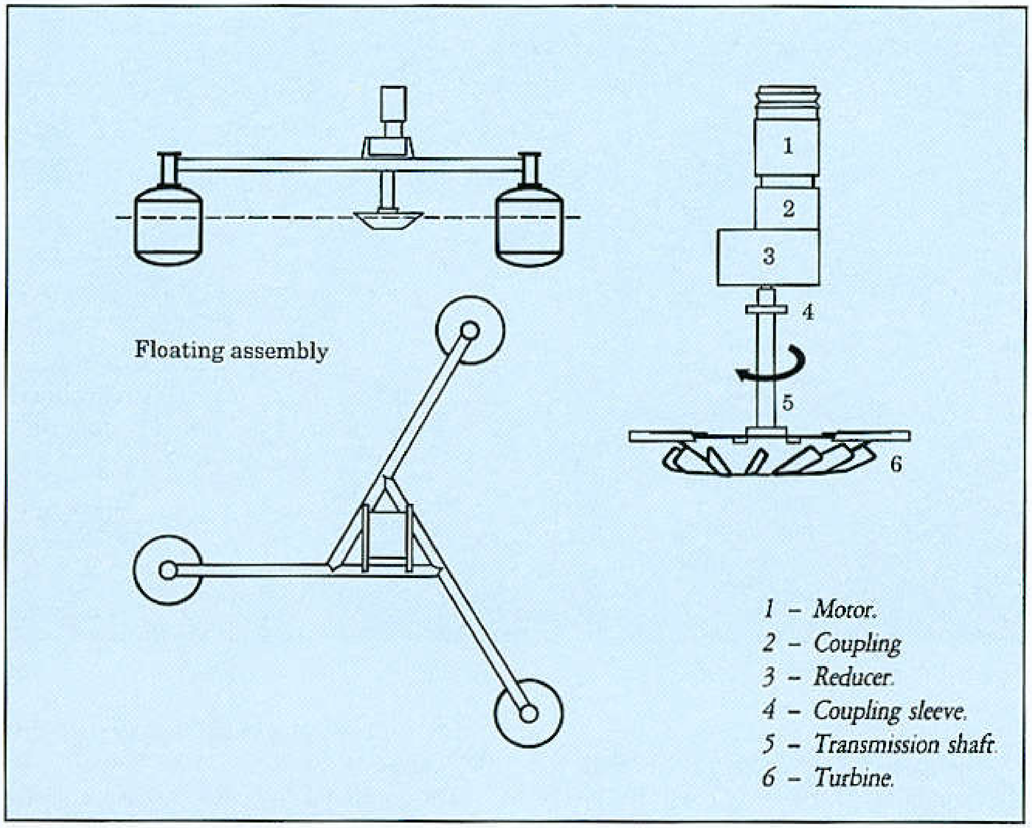


Figure 374. Actirotor surface aerator.

Figure 375. 75 kW R 8020 Actirotor installed on a reinforced concrete walkway.

An assembly on stabilized, floating equipment (with the space between the three ballasted floats calculated so as not to slow down the circulation flow caused by the aerator), maintained in position by guide cables or an articulated arm, can allow great variations in the liquid level while keeping the impeller fairly constantly submerged.

In the case of a low rate tank, an innovative arrangement - Manège type (Figure 376) -allowing the aerator to move by itself on the structure, can ensure effective mixing despite a low overall specific power. This solution is also advantageous in aerated lagoons.

Figure 376. Manège type Actirotor.

(c) Power

The power absorbed at the shaft of the impeller of the Actirotor is of the form $P = K \times NP \times D^5 \times N^n$, where D is the diameter of the impeller, N the rpm, Np a power factor depending on the geometry of the impeller and its submergence. The exponent n of the velocity equals approximately 2.7 in normal conditions of use.

As any surface aerator, the Actirotor takes full power at startup; the power at steady speed is lower because the adjacent liquid mass is put into rotation, with the drop being all the greater:

- if the tank is "flat" (high surface/depth ratio),
- if the specific power is greater (circular tanks usually require anti-rotation baffles).

(d) Nominal specific oxygen transfer capacity

The nominal specific oxygen transfer capacity of the Actirotors varies from 1.8 to 2.3 kg/kWh net (mechanical energy measured on the shaft of the aerator) according to the conditions of installation and use.

For a given aerator/tank combination, this value can be influenced by several factors, in particular:

- specific power (i.e., the power consumed, expressed per m^3 of tank volume): a typical specific power is in the 40 $W.m^{-3}$ range. U to a maximum in the 100 $W.m^{-3}$ range, its increase tends to increase the specific oxygen transfer capacity,
- the surface/depth ratio of the tank: the optimal specific oxygen transfer capacity is generally obtained when the side of the square (or the diameter) is 2 to 2.5 times the water depth.

(e) Actual oxygen transfer capacity

For mainly domestic wastewater, the correction coefficient T for conversion into actual conditions is generally good, with the oxygen transfer correction coefficient T_p being near 1.

(f) Mixing

The mixing effect must ensure that the sludge is kept suspended and that the mixture is homogeneous, but it must also produce floor sweeping velocities (in the 0.2 to 0.3 $m.s^{-1}$ range depending on the quality of the sludge) avoiding deposits, which is often the determining requirement.

The mixing effect is influenced by two main parameters.

- specific power: which must be in the 30 to 40 $W.m^{-3}$ range for activated sludge of domestic wastewaters; mainly industrial effluents may require greater power (according to the viscosity of the interstitial liquid and the nature of the SS), to be determined on a case by case basis,

- **the gyration radius** of the tank - by analogy with channel flow, gyration radius is defined as the ratio of the volume to the wetted surface. When the gyration radius increases, mixing improves.

Certain types of aerators must be equipped with a draught tube. Due to their considerable pumping capacity, Actirotors do not require this accessory, except in special cases.

1.4.2.3. Horizontal axis, low speed aerators. The Rolloxes

These units are similar to the vertical aerators in their simultaneous functions of oxygenation by aerial spray and mixing by moving the liquid mass. They are intended for moderately deep, closed loop aeration basins (ditches) in which they cause a horizontal flow.

Figure 377. Reims plant, France. 5,250 $m^3.h^{-1}$. Biological purification of MWW by activated sludge. 2 tanks each 3,750 m^3 and equipped with six 37 kW R 6016 Actirotors.

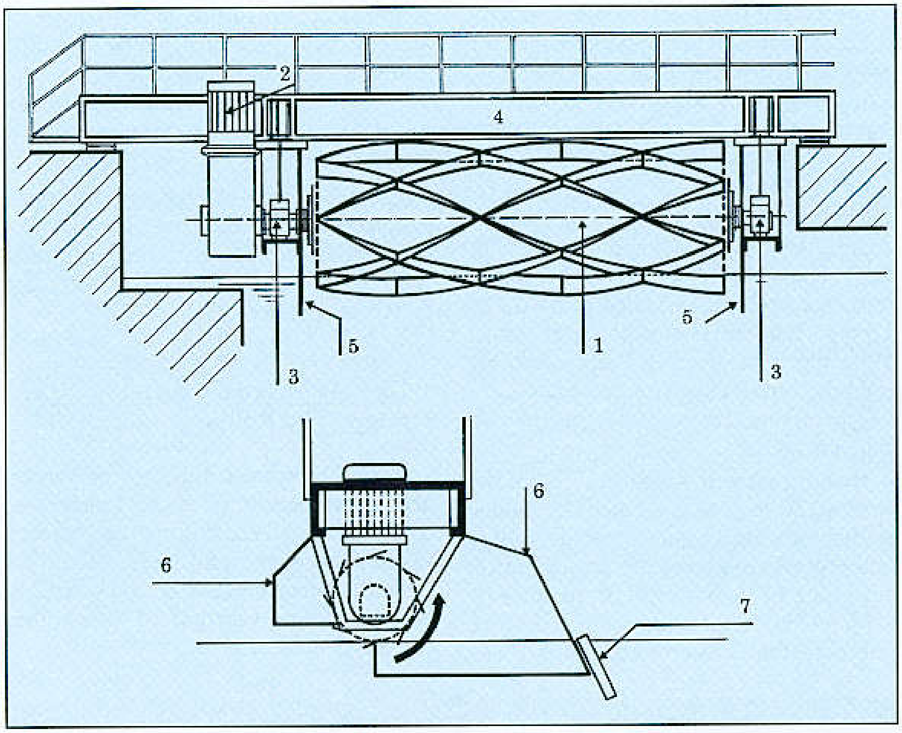


Figure 378. The Rollox.

1 – Rotor.
2 – Drive motor-reducer assembly.
3 – Bearings.
4 – Walkway chassis.
5 – Protective screen.
6 – Hood.
7 – Baffle.

(a) Rotor body

The rotor of the Rollox is made up of a horizontal cylinder (diameter: 700 or 900 mm) on which is welded a series of long, thin blades sloping in herring-bone pattern; their arrangement ensures a constant, submerged, total blade surface during rotation, causing balanced operation without variation that would be harmful to the drive assembly (Figure 378).

The oxygenation rotor is supported by two heavy-duty, watertight end bearings protected by an anti-splash casing. This arrangement guarantees the bearings' service life.

The high output drive assembly is calculated according to AGMA standards for a useful life of over 80,000 h in conditions of intensive use.

The Rollox is generally produced as a monobloc assembly, with the skeleton supporting the oxygenation rotor also serving as the access walkway; hoods upstream and downstream of the rotor ensure considerable reduction of noise and aerosol formation. Downstream, a submerged, inclined baffle promotes the entrainment of bubbles into the liquid mass.

(b) Power

Rolloxes are manufactured in two ranges:

- Rollox 700 (net power: 3 kW per m of roller length) up to 18 kW net,
- Rollox 900 (net power: 4 kW per m of roller length) up to 34 kW net.

(c) Specific oxygen transfer capacity

Nominal oxygen transfer capacity varies from 1.7 to 2.2 kg per kWh net according to conditions of installation and use.

As for vertical axis aerators, the oxygen transfer correction coefficient T_P is close to 1 with domestic waste.

(d) Mixing

The principle of the rotor ensures a high pumping capacity under typical installation conditions. On MWW, a specific power in the range of 30 $W.m^{-3}$ of ditch makes it possible to ensure a sludge circulation velocity greater than 0.5 $m.s^{-1}$.

1.4.3. Aeration by compressed air

Aeration by compressed air consists in blowing air into the liquid mass at depths varying from 1 m to sometimes more than 10 m. The devices used are divided into three major groups based on the size of the bubbles produced:

- coarse bubbles (dia. > 6 mm): vertical tubes, large orifice diffusers,
- medium bubbles (dia. 4 to 5 mm): various diffusers make it possible to reduce the dimension of the bubbles released: valves, small orifices, etc,
- fine bubbles: diffusion of air through porous material or finely perforated elastic membranes.

Figure 379. Rollox type 740 installed in an oxidation ditch.

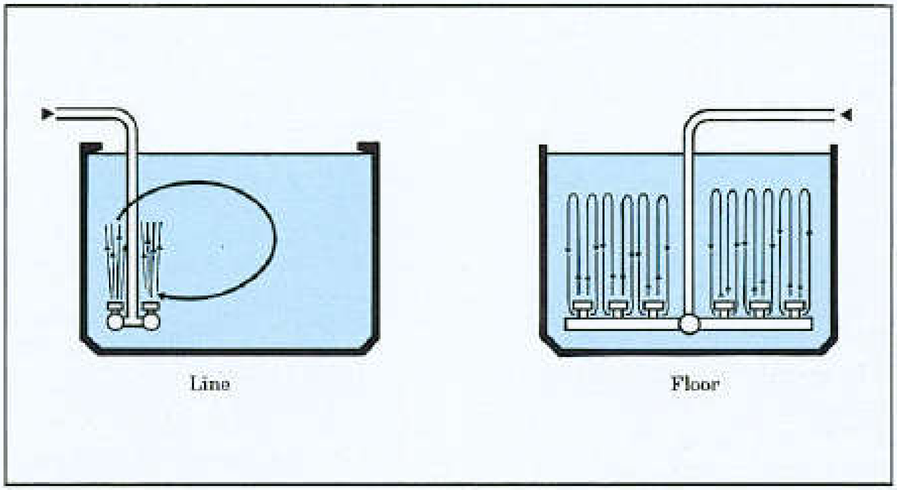


Figure 380. Linear and floor arrangement.

1.4.3.1. Oxygen transfer efficiency

The nominal oxygen transfer efficiency of a given system in clean water varies with the depth at which air is injected (approximately linear between about 2.5 and 8 m). Depending on the nature of the diffusers and the conditions of installation and use, when air is injected at 4 m depth (with water depth in the same range), this standard efficiency varies from:

- coarse bubbles: 4 to 6%,
- medium bubbles: 5 to 10%,
- fine bubbles: 15 to 30%,

These considerable differences under standard conditions are reduced under actual conditions, with the oxygen transfer correction coefficient T_p generally lower for fine bubbles:
- coarse and medium bubbles: T_p varying from approx. 0.8 to 1.0,
- fine bubbles: T_p varying from approx. 0.5 to 0.7 (MWW).

Nevertheless, the net energy gain of the fine bubbles remains considerable and generally justifies using them, despite a higher installation cost.

The oxygenation efficiency of a given system is influenced by several factors:

- the nature of the diffusers and their depth of submergence,

- the specific power output in relation to the flow of air injected: in coarse and medium bubble systems, increasing the flow generally translates into a higher efficiency (increase in turbulence); in fine bubble systems, the efficiency rather tends to decrease (greater coalescence of the bubbles),

- the hydraulic flow pattern caused by the arrangement of the diffusers (see also mixing). Oxygenation efficiency is generally optimal in the floor arrangement due to a very good distribution and a maximum retention time of the bubbles in the liquid mass,

- the tank cross-sectional area.

1.4.3.2. Mixing

- **Linear arrangement:** the air lift effect created by the concentration of the air in a limited zone causes gyration (or spiral flow) of the liquid mass. This arrangement creates a considerable floor sweeping velocity (Figure 380).

- **Floor arrangement:** this arrangement is particularly well adapted to deep tanks (Figure 380).

In general, for equal specific powers, the mixing of an aeration tank is more effective with a compressed air system than with a surface aerator, provided:
- that the air diffusion level is near enough the floor, particularly in the floor arrangement,
- that the liquid surface/depth ratio in the linear (or point-wise) arrangement is maintained within acceptable limits. There is an optimal ratio for each system.

For activated sludge treating MWW, the required mixing power is ensured for aeration rates varying from 4 to 8 $Nm^3.h^{-1}$ of air per m^2 of liquid surface in the tank.

Figure 381. Aeration tank with porous *discs.*

1.4.3.3. Porous disc DP 230

This is the reference as regards fine bubbles, and is the result of 50 years of experience in the field of porous diffusers of mineral composition. The disc (Figures 381 and 382) is composed of grains of artificial corundum (alpha alumina), bonded by a high-temperature vitrified ceramic binder; the grain size chosen ensures a good compromise between a sufficiently high oxygenation efficiency and operational durability (very gradual plugging) in continuous use. The material successfully resists most concentrated, aggressive chemical products.

The discs, attached on PVC or stainless steel supports, are mounted on submerged feed pipes grouped in a line or spread over the bottom of the tank.

The discs, generally installed in tanks 3 to 8 m in depth, ensure a high nominal oxygenation efficiency in the 20 to 25% range with a 4 m depth. The head loss of the diffuser (porous disc + equal distribution orifice) is in the 0.03 (new disc) to 0.06 (dogged disc to be regenerated) bar range under normal conditions in use.

The injected air must be suitably filtered

Figure 382. Porous disc in use.

beforehand (dust content < 15 mg for 1,000 Nm^3).

The risk of clogging by the sludge is related to the frequency of interruption of aeration (which must be minimized). In the case of particularly scale-forming water (calcium carbonate or sulphate), a system for sequential feeding of dilute (hydrochloric or formic) acid in the injected air makes it possible to avoid the risk of mineral clogging.

With these operational precautions, porous systems can generally ensure 10 years or more of continuous use; after this period the discs can be regenerated by refiring

1.4.3.4. Vibrair diffusers

These are medium bubble air diffusers particularly adapted to a linear arrangement.

The Vibrair consists of a molded polyethylene body on which is located an integral vibrating valve; the valve includes a rod crossing the air distribution orifice of the body; the constant movements of the rod in the orifice prevents it from clogging. This innovative arrangement allows a low unit air flow and thus a great number of points of introduction in the liquid mass, which promotes the oxygenation efficiency and mixing.

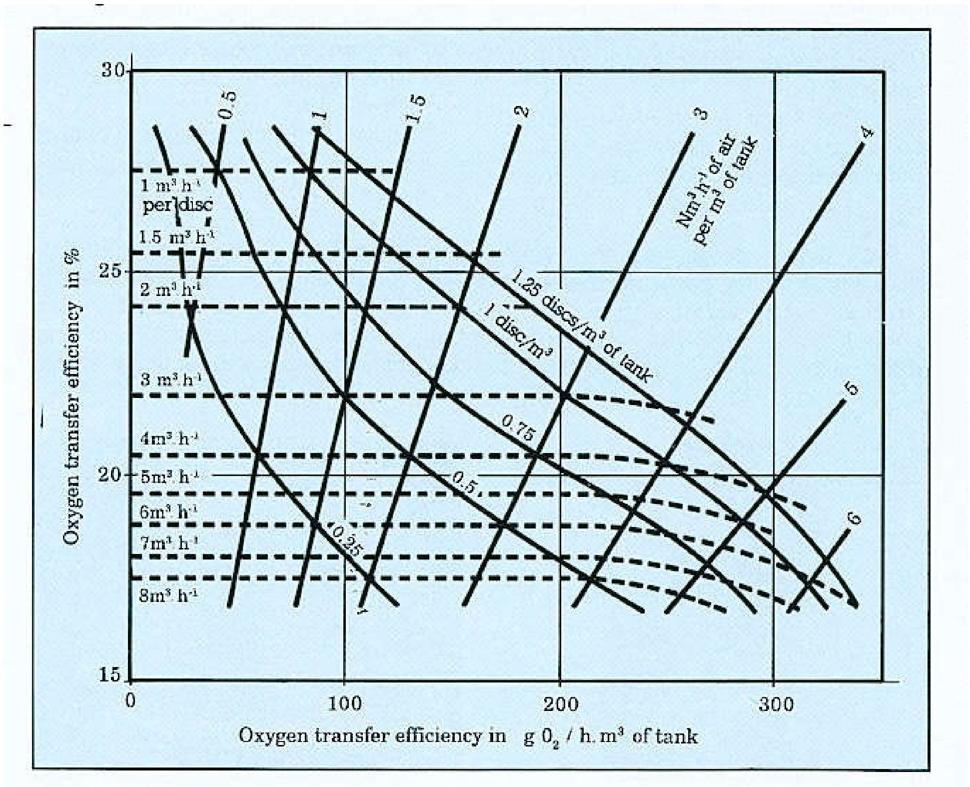


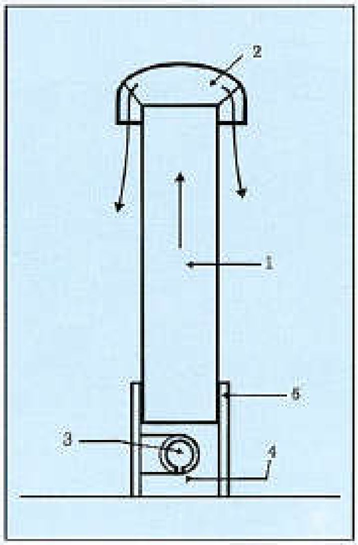
Figure 383. Efficiency curves. DP 230 type porous disc.

Figure 385. Aeration tank equipped with Vibrair diffusers.

Figure 384. Vibrair diffusers.

Two models (Figure 384) allow unit flows of from 1 to 3 Nm^3.h^{-1} and 2 to 10 N m^3.h^{-1}, with a distribution head loss in the 0.02 bar range.

The nominal oxygen transfer efficiency of the Vibrairs is 8 to 12% at 4 m submergence. Their simplicity (coarse filtration of air) and their operating safety make them particularly well suited to small and medium installations. They allow discontinuous operation of the air feed system.



1 – Air lift tube.
2 – Flow inversion bell.
3 – Feed pipe.
4 – Calibrated orifice.
5 – Fixed legs.

Figure 386. Diagram of a Dipair.

1.4.3.5. Dipair diffusers

Dipairs are submerged static aerators specially adapted to a floor arrangement in a deep tank (Figure 386).

The aerator is basically comprised of:

- an air lift tube (1) completely open inside, located directly above a large diameter orifice (4) (dia. ≃15 mm) arranged below the common feed pipe (3),
- an upper bell (2) covering the tube and ensuring an intense turbulence with inversion of the emulsified flow direction.

As a static unit, the Dipair has no risk of wearing out. Built from polypropylene and stainless steel, it has high resistance to corrosion.

Figure 387. Tarascon facility in southern France for Cellulose du Rhône. Flow: 36,000 $m^3.d^{-1}$. Deep aeration tank with Dipairs.

- **Air flow:** the air flow per aerator is variable between 30 and 60 $Nm^3.h^{-1}$, with a head loss of approx. 0.03 bar at full flow (in the calibrated orifice).
- **Oxygen transfer efficiency:** for an 8 m deep tank the nominal oxygen transfer efficiency in clean water varies from 22 to 26% according to the specific power in the tank. In actual conditions, the oxygen transfer correction coefficient T_p can be taken equal to 0.9.

- **Mixing:** the flow pumped by aeration, at its full air flow, is approx. 150 $m^3.h^{-1}$. The flow induced is several times greater.

1.4.3.6. Flexible membrane diffusers

- **Oxazur diffuser**

These are medium bubble air diffusers particularly suited to floor arrangement and developed for attached growth reactors with granular beds (Figure 388).

The air diffusion is effected by an orifice about 1 mm in diameter. This orifice is made through a flexible molded elastic membrane made of special elastomer housed in a polypropylene body.

Figure 388. Oxazur diffuser.

The air flow per diffuser is about 1 to 2 $Nm^3.h^{-1}$ for a head loss in the 0.05 bar range. The nominal oxygenation efficiency of an Oxazur system, promoted by the very good distribution of the air in the granular mass, is 10 to 15% at 4 m submergence.

Figure 389. Flexazur diffuser.

- **Flexazur diffuser**

In this tube-shaped diffuser (Figure 389), diffusion of the air in fine bubbles is achieved by a thin, flexible, elastic membrane perforated with numerous small diameter orifices (in the 0.2 mm range).

The innovative perforation method makes it possible to obtain a good oxygen transfer efficiency and a low head loss.

The nominal oxygen transfer efficiency of the Flexazur is 25 to 30% at 4 m submergence, with a head loss (diffusion + distribution) of between 0.03 and 0.05 bar.

1.4.4. Mixed aeration - Separate aeration/mixing operations

Separation of the two operations makes it possible to maintain effective mixing despite a possibly low or zero air flow:

- air supply can be limited to the oxygenation needs alone,

Figure 390. Palo Alto plant (California, USA). Aeration tank equipped with Vortimix aerators, for treating

- sequential stops of the aeration can ensure periods of anoxic conditions (for denitrification) while preserving the homogeneity of the mixture.

The possibility of a high hydraulic efficiency of the impeller ensures a good overall energy efficiency.

1.4.4.1. Vortimix vertical flow aerator

This unit consists of:

- a vertical axis mechanical rotor with submerged, low speed (constant or adjustable) turbine creating a downflow,
- a device for compressed air injection under the impeller.

The total energy consumption is in the same range as that of a low speed surface aerator; it can become lower when mixing problems are prevalent.

This type of equipment is particulary suited to cold regions and/or when aerosols must be avoided.

- **Rotor power:** 10 to 100 kW net range.
- **Air and oxygen transfer efficiency**

- Volume of air dispersed: 30 Nm^3 per net kWh at the turbine, i.e., a range of air flows of from 300 to 3,000 $Nm^3.h^{-1}$, at a pressure of between 0.25 and 0.5 bar according to the depth at which air is injected.
- Nominal oxygen transfer efficiency in clean water varying from 30% at full load to 45% at low air flow with the air sparger submerged at 3 m and a liquid depth of 5 m.

- **Mixing**

In MWW treatment, mixing requires a specific power (developed by the turbine) of from 15 to 30 $W.m^3$ with air injection and 5 to 10 $W.m^3$ without air.

1.4.4.2. Air infection and the horizontal brush type aerator

It is possible to connect one (or more) horizontal aerators with low speed impellers and air diffusers in a closed loop ditch (see page 720).

A brush of high hydraulic efficiency can ensure a sufficient circulation velocity with a specific power in the range of 2 to 5 $W.m^{-3}$ of tank.

Proper dispersion of the bubbles, promoted by the horizontal liquid flow, can ensure a good overall energy efficiency, often better than that obtained with diffusers alone.

1.4.4.3. Mixers - Aerators (Jet type aerators

These units, generally submerged in the tank, include a hydraulic pumping rotor (featuring high speed with direct drive by electric motor) directly drawing in atmospheric air and releasing it in fine bubbles in the pumped flow.

The advantage of their simplicity carries the disadvantage of an energy efficiency which is usually low: the nominal specific oxygen transfer capacity is often lower than 1 kg per kWh, due to limited air suction capacity.

1.4.5. Use of pure oxygen

1.4.5.1. Applications

Pure oxygen, in a closed reactor, can be used in several cases:

- **Activated sludge units with continuous operation in an oxygen environment**

- Covered biological treatment works located in sensitive environments (deodorizing necessary).
- Treatment of concentrated IWW containing primarily biodegradable pollution.

- **.Activated sludge units with variable loading**

For example, units in tourist areas with oxygen demands in peak season far greater than the yearly average (conventional aeration tank with seasonal "doping" with pure Oz).

- **Forced pre-oxygenation of wastewater or liquors**

- For the purpose of preventing odours (case of injection into pipe systems under pressure),
- or for the purpose of oxygen enrichment before treatment by biological filtration in closed pressure vessels (see page 739).

1.4.5.2. Advantages

- As a result of the very high partial pressure of oxygen, oxygenation capacities are available that are several times greater than those available with atmospheric air alone; hence the ability to satisfy the demands of more concentrated activated sludge subjected to greater BOD loadings. A certain reduction in the volume of the biological reactors is thus possible.

- Due to the bw volume of gas used for oxygenation, the possible deodorizing unit for the closed reactors is sized considerably smaller.

1.4.5.3. Use

- **Activated sludge reactors**

The most common use of an oxygenenriched gas is that of closed tanks in which the air space above the liquor is maintained at a high partial pressure of oxygen.

However, purifying highly concentrated waste, by means of pure oxygen and in closed tanks, has the disadvantage of slowing down the evacuation of the free CO_2 produced by bacterial respiration.

*Figure 391. Leykam plant Austria. Treatment ofpaper mill effluents. Flow: 856*M^3 *h^{-1}. Pure oxygen activated sludge reactor.*

To limit the production of this gas, the alkalinity of the liquor is increased or air stripping is practised. This is why the adoption of the Degrémont system in two steps (oxygen followed by air) is often advantageous. The use of pure oxygen in the first cells of the reactor makes it possible to limit energy consumption and the size of the plant for the removal of most of the pollution. The use of air in the last cells makes it possible to remove the free CO_2 and reduce the phenomena of degassing and foaming in the clarifier. It helps in removing the residual pollution and ensures nitrification where applicable.

In order to limit the losses as much as possible, the Oz reactor generally comprises several cells crossed by the gaseous mixture in succession. The rate of oxygen use in the reactor is near 90%.

The inlet of pure oxygen is normally controlled by the pressure in the atmosphere of the reactor. For safety, the latter is equipped with a detector of hydrocarbons in the air space.

- **Separator**

The separation of the activated sludge is, in general, carried out in a settling tank, with the removal of the highly concentrated sludge normally allowing a lower recycle rate than in the case of standard aeration.

In certain cases, if an appreciable loss of SS is acceptable in the treated water (for example, pretreatment of a highly concentrated waste prior to discharge to a municipal plant), separation by dissolved air flotation makes it possible to reach an optimal concentration of the sludge in the reactor straightaway.

- **Oxygenation and mixing devices**

The surface aerators are of the low speed type, made of stainless steel, with the drive assembly located outside and a hydraulic seal.

In the case of considerable load variations, systems that separate the oxygenation and mixing operations and make it possible to ensure mixing with very low energy consumption are recommended.

For small units, the use of open tanks and primary negative pressure systems (in which the gas is introduced at low pressure at the throat of an ejector through which the contents of the tank are recycled) makes it possible to considerably reduce investments.

1.4.5.4. Production of oxygen

The most favourable case is by far the one in which the pure oxygen is available in an oxygen duct running nearby and coming from a steelworks or a large independent production unit.

If this is not the case, in small plants, the oxygen is supplied in liquid form and stored in insulated containers equipped with evaporators.

For larger plants, two technologies are possible: that of molecular sieves (Pressure Swing Adsorber or PSA) up to capacities of 30 $t.d^{-1}$, or that of cryogenic stations starting from 10/20 $t.d^{-1}$. Generally, the gas produced has a purity level of 95 to 99% O_2.

1.5.
PACKAGE UNITS

1.5.1. General

The most common arrangement of activated sludge treatment plant is that of separate units. The aeration tanks are connected to the clarifiers by channels or conduits with possible deaerating units in between; the sludge recycling equipment is located outside the clarifiers or is integrated with them. This design allows a large variety of plant possibilities and is highly adaptable to local construction norms as well as to the constraints imposed by the nature of the terrain or the water table. However, it leads to a greater land use than with the package units.

These **package** activated sludge plants are **standardized.** They make it possible to treat MWW in a range of several hundred to approximately 20,000 users, on an extended aeration basis, and beyond that with medium loading

They unite the aeration and settling phases in a single structure. They simplify the hydraulic systems and ease of access. The aesthetics of the units are improved and it is easier to cover them

The pretreatment of raw water comprises automatic screening, grit and grease removal, with automatic storage of the residues (separate or combined, according to their method of collection) with a view to weekly removal. Depending on each case, the pretreatment unit can be integrated with the biological purification unit (ease of access) or located upstream

(for example, in the form of a prefabricated metal assembly for small plants).

The package Degrémont units, classified according to increasing capacity, are listed below:

Minibloc AP	100 to 500 population (concrete version for up to 2,500 users).
Compact MA	1,000 to 10,000 population (designed with mechanical aeration or air injection).
Compact Alterné (Alternating)	1,000 to 10,000 population
Compact Chenal (Ditch)	1,000 to 20,000 population
Oxyrapid R	20,000 plus

1.5.2. Extended aeration units

These units are designed with a view to unsupervised operation, without permanent staff, according to the following criteria:

- simple process (without primary settling) with completely mixed aeration tank, safe, at the expense of large unit sizing,
- operation with low labour cost and reasonable energy consumption.

They can be equipped with a programmable logic controller that ensures:

- management of the oxygenation of the activated sludge, by sequencing based on the loading curve of the unit and/or the hourly electricity rate of the local utility, while maintaining minimum mixing,
- management of sludge recycling and extraction.

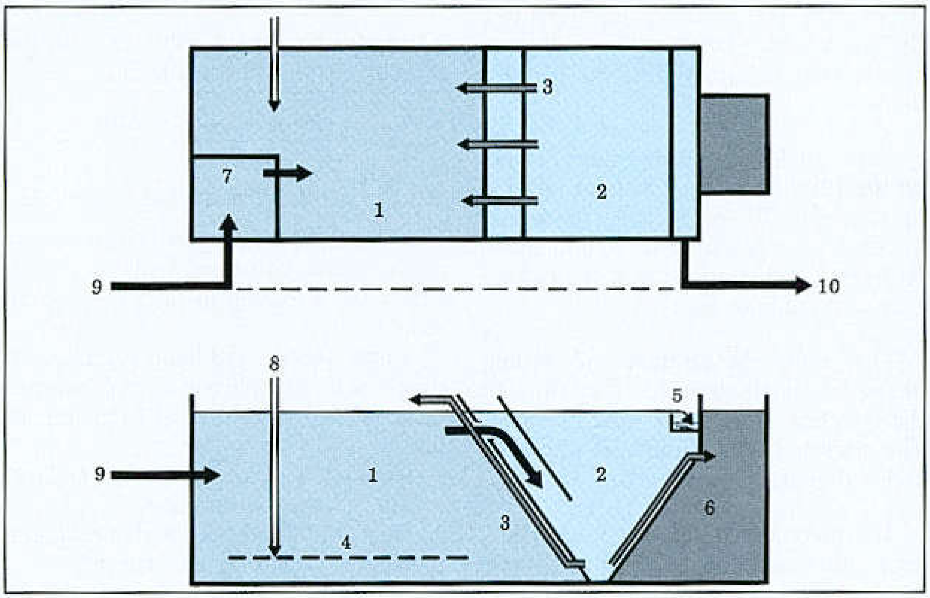
The biological reactor allows simultaneous stabilization of the sludge. The installation of a thickening GDE screen on a storage silo is a simple means (nevertheless requiring the use of polymer) of obtaining a thickened liquid sludge (6 to 8% SS), thus considerably reducing the volumes to be removed. The silo can be aerated and mixed to ensure an additional stabilization effect by aerobic digestion.

1.5.2.1. Minibloc AP

The Minibloc (Figure 392) combines the various compartments needed for the process of the treatment - aeration (1), clarification (2), recycling of the sludge (3), and possible lifting of the raw or treated water, in a single shop-fabricated, parallelepipedal steel tank.

Aeration is ensured by injection of compressed air (4) (Vibrair, Oxazur or Flexazur diffusers). The air is supplied by a blower located on the unit, inside a soundproof hood; the blower also feeds a battery of air lifts (3) operating in parallel, in an alternately sequenced manner, and ensuring recycling of the settled sludge towards the aeration compartment.

The treated water collecting weir (5) may be protected by a scum baffle to retain the floating matter, collected periodically by an air lift.



1 - Extended aeration.
2 - Clarification.
3 - Sludge recycling.
4 - Air diffusers.
5 - Weir.
6 - Sludge storage.
7 - Manual screening and coarse screening.
8 - Process air inlet.
9 - Raw water inlet.
10 - Treated water outlet.

Figure 392. Diagram of an AP Minibloc (100 to 500 users).

Figure 393. Dampierre-en-Burly facility, France. Capacity: 400 population equivalents. Minibloc AP.

The Minibloc is prefabricated in 5 models for 100 to 500 users.

A watertight wooden cover avoids all risk of accident and allows the installation of the unit in urban areas (very low noise level, below 45 dB if requested).

1.5.2.2. Compact M.

The MA consists of a monobloc concrete structure with easy access, without underfloor conduits, and equipped with a scraper bridge that moves back and forth. It can be equipped with either surface aeration or air injection (Figure 394).

(a) Unit with surface aeration

The unit is comprised of a square or rectangular aeration tank for the activated sludge and an integral clarifier, semicircular in shape and with a nearly flat bottom and a common access footbridge. **Aeration tank (1):** mixing and aeration are carried out by one or more Actirotor surface aerators (3), located on a circular platform mounted on posts and accessible from the footbridge; there can be a semi-rigid skirt to control the noise of the spray and to prevent atmospheric contamination (elimination of aerosols). The oxygenation capacity of the aerator normally allows periods of non-aeration ensuring anoxic phases favourable to partial denitrification in the aeration tank.

Clarifier (2): the introduction of the liquor from the aeration tank is carried out in the centre of the semi-circle by a flow inversion pipe (8) in an inlet zone defined by a submerged baffle (4); this inlet zone, of great capacity, ensures the dissipation of the energy of the flow introduced and the deaeration of the liquor before settling.

The sludge which settles at the bottom of the unit is scraped by a rotating bridge (5) with alternated semicircular operation, equipped with one (or two) air lift tube(s) (6) capable of a considerable flow (roughly 150% of the mean flow to be treated); the sludge recovered by the air lift is recycled by gravity to the aeration tank. The compressed air necessary for the air lift is supplied by a centrifugal blower located on the fixed footbridge.

The clarified water is recovered by overflowing weir into a peripheral trough (7) or by laterals with submerged orifices. The scum and other matter floating on the surface can be retained: a hinged skimmer blade attached to the travelling bridge then directs them toward an automatic lateral scum box to be stored in a drainable tank.

An alternative design provides for a rectangular settling tank equipped with a similar sludge withdrawal system (Figure 395).

(b) Unit with air injection

This unit is a completely circular unit with a flat or slightly sloping, truncated cone-shaped bottom. Vertical, radial, internal walls define sections constituting an activated sludge aeration tank, a clarifier, possibly a compartment combining the pretreatment stages, and the sludge storage tank (Figure 396).

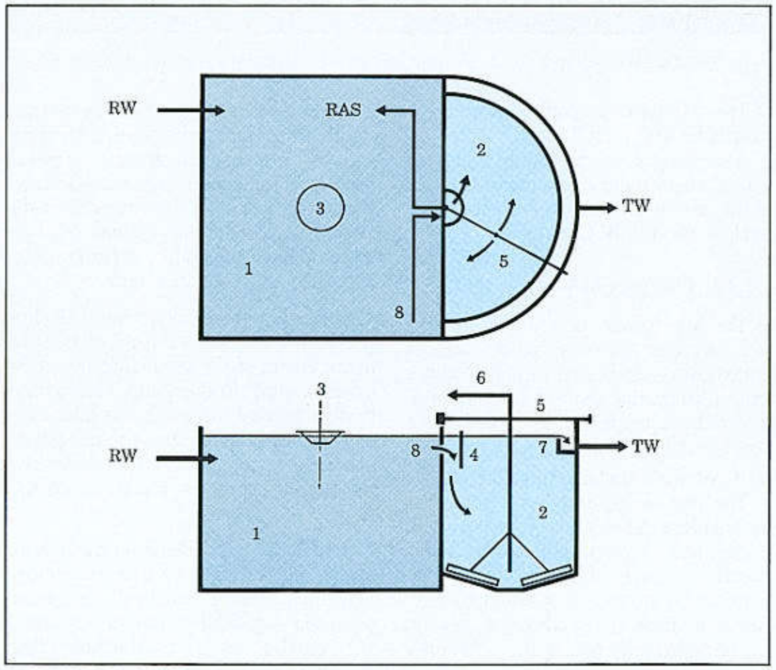


Figure 394. Diagram of a Compact MA with surface aeration.

Figure 395. Compact MA with a rectangular settling tank.

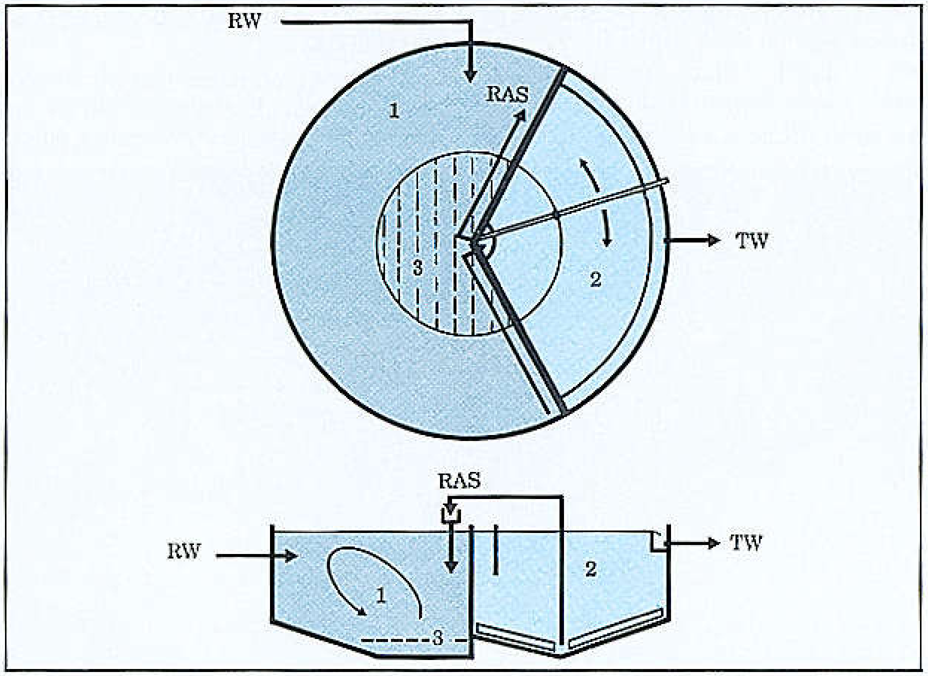


Figure 396. Diagram of a Compact MA with air injection.

Aeration tank (1): mixing and aeration are carried out by air diffusion through medium bubble diffusers (3) (Vibrair, Oxazur) or fine bubble diffusers (porous discs or Flexazur). The air injected is supplied by one (or several) blower(s) located in a separate building or possibly outdoors in a soundproof enclosure.

Clarifier (2): is similar in design to the preceding model, the only difference being that the angle of the sector is variable.

Note: it should be noted that on these Compact MA units, structurally differentiated in some cases (depending on the terrain or the environment), submerged aeration can be replaced by mechanical aeration or vice versa.

1.5.2.3. Compact Chenal (ditch)

This is a package, circular unit made in concrete, comprising an outside ring-shaped aeration ditch with a flat bottom, and a slightly sloping, central, circular clarifier with scraper (Figure 397).

Aeration ditch: horizontal circulation of the mixed liquor, homogenization and oxygenation are ensured by one or several horizontal mechanical aerators of the Rollox type or similar.

Clarifier: is of the scraper type with sludge collection at the centre, and recycling by means of a submersible pump and a separate well. The mixed liquor is fed in through a central circular baffle; the treated water is collected in a peripheral trough.

Alternative: if the operations of circulation and oxygenation are to be separated, the mechanical aerators can be replaced by:

- one or more submerged circulation rotors with large diameter impellers (1),
- an assembly for injecting air in, with medium or fine bubble diffusers (2) (Figure 398).

1.5.2.4. Compact Alterné or Alter 3 (alternating

Alternating operation systems consecutively use two identical capacities for the aeration phase then for the settling phase.

Figure 397. Waremme plant, Belgium. Oxidation ditch with Rollox for MWW treatment.

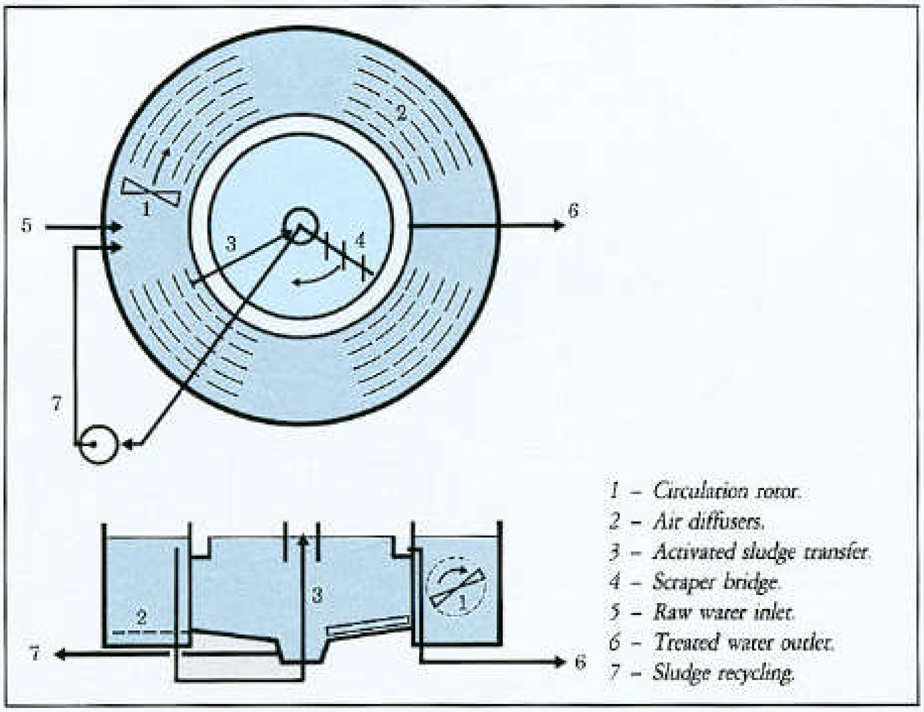


Figure 398. Compact Chenal (ditch). Alternative with circulation rotors and air diffusion.

Mobile equipment is not submerged (in particular the scraper bridge). The denitrification rate is relatively high. Degrémont have long experience with these alternating systems.

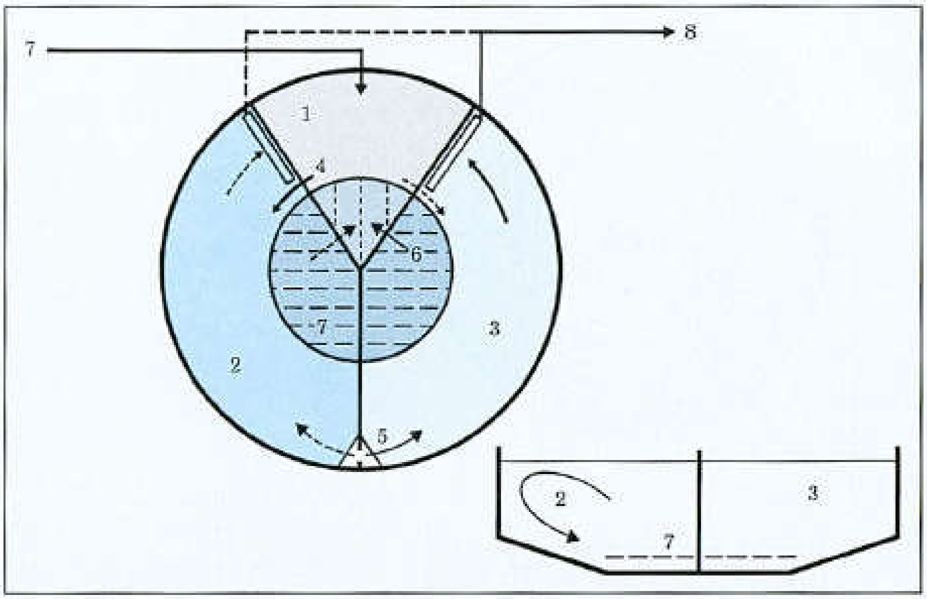
The unit includes (see Figure 399):

- an inlet zone (1), constituting an activated sludge tank with continuous aeration,
- two zones (2 and 3) with alternating aeration/clarification operations, operating on an adjustable cycle.

The operation of the cycle is as follows:

- the pretreated raw water is introduced into the zone (1), and aerated and mixed continuously,
- a continuous transfer (4) of liquor is established by gravity from zone (1) to zone(2), with mixing and aeration, possibly in sequence,
- a second transfer of liquor (5), of equal flow, is established by gravity from zone (2) to zone (3), without mixing or aeration, in which the clarification of the treated wastewater is carried out by sludge settling; the clarified water is recovered from (3) and drained by gravity,
- the sludge settled in (3) is partially stored, but recycling this sludge by air lift (6) from (3) towards zone (1) reduces concentration in (3) and maintains a sufficient solids concentration in (1).

In the following cycle, after an intermediate period during which preliminary settling is initiated in (2) (by stopping



1 – Inlet zone. 2,3 – Alternate zones. 4,5 – Gravity transfers. 6 – Sludge recycle. 7 – Raw water inlet. 8 – Treated water outlet.
Figure 399. Compact Alterné (1,000 to 10,000 users).

mixing in this zone), the operations of zones (2) and (3) are reversed and the sludge deposited in (3) in the preceding cycle is resuspended.

Aeration and mixing are ensured by air injection.

The absence of a scraper bridge allows complete covering of the unit at ground level with only a few access hatches, allowing the unit to be almost totally concealed.

1.5.3. The Oxyrapid R

The Oxyrapid R, intended for medium rate biological treatment of wastewaters of large conurbations, is the development of considerable experience acquired by Degrémont in the field of large, package units featuring complete mixing and short retention times.

The Oxyrapid R (Figure 400), which is usually rectangular in shape, includes:

- a completely mixed aeration tank located along the axis of the unit,
- one or two lateral clarifiers with vertical flow, equipped with travelling scraper bridges,
- rapid recycling of the sludge, with adjustable flow (up to 300%), ensured by a battery of air lifts fed by the aeration blowers.

The careful distribution and introduction of the aerated liquor into the clarifier makes it possible to reach high rising velocities and to make good use of the sludge blanket.

The unit can be constructed in lengths of 120 m or more.

By its design, the Oxyrapid R is well suited for producing package treatment "modules" possibly incorporating the primary settling tank.

1.5.3.1. Aeration tank (2)

This tank has vertical walls and a flat bottom. The raw water is introduced across the length of the unit by a submerged pipe (1) provided at various points with calibrated distribution orifices.

Mixing (in double gyration) and aeration of the activated sludge is carried out by air injection (5) using medium bubble diffusers (Vibrair, Oxazur) or fine bubble diffusers (DP 230, Flexazur), arranged on a false floor.

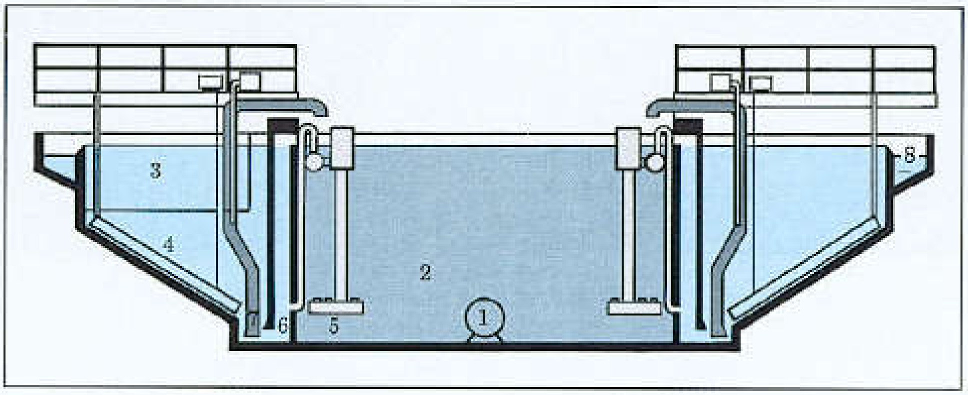
1.5.3.2. Clarifiers (3)

Clarification is carried out in two (or possibly a single) rectangular channels (3) integral with the aeration tank, with moderately sloping bottoms and mechanical scraping (4) drawing the deposited sludge towards a longitudinal trough at the foot of the dividing wall. The aerated liquor enters via flow inversion pipes that deliver it below a large cross-section baffle. The treated water is recovered by longitudinal external troughs (8) with, if desired, an extension of the overflow length by regularly arranged channel elements.

The scum and other matter floating at the surface of the clarifier are scraped by the travelling bridge towards a scum box at the end.

Recycling the settled sludge: this is ensured by a battery of air lift tubes (6) regularly arranged along the dividing wall between the aeration and clarification zones, collecting the settled sludge and delivering it directly into the activated sludge mass, in spiral motion.

According to operating conditions and the sludge quality, the recycling flow can be intermittent or continuous.



1 – Raw water inlet.
2 – Aeration zone.
3 – Clarification zone.
4 – Scraper.
5 – Air diffusion.
6 – Sludge recycling.
7 – Excess sludge drawoff.
8 – Treated water collection.

Figure 400. Oxyrapid R (with scraper).

Excess sludge drawoff: this is carried out by manually or automatically operated air lifts:

- mostly in concentrated form: collection by a draught tube (7) on the travelling bridge (with centrifugal blower on it) sucking up the sludge at the bottom of the clarifier,
- for the rest, in dilute form: collecting at several sites, directly in the aeration tank.

Automation: a programmable logic controller is well suited to manage the oxygenation, the recycling of sludge and the drawoff of excess sludge.

Various sensors can be added for measurement and alarm functions, possibly for servo-control, such as a raw water and/or treated water flowmeter, dissolved O_2 analyzer (acting on the air production), detection probe for the top sludge level during clarification, turbidity of treated water, etc.

Figure 401. Harelbeke facility, Belgium. Purification of municipal wastewater by Oxyrapid R.

2. ATTACHED GROWTH

2.1.
TRICKLING FILTERS

2.1.1. Trickling filters with traditional fill

These have a certain number of advantages compared to the activated sludge processes:
- less supervision,
- significant energy savings, as the air is usually supplied by natural draught through the bed,
- often fairly quick "recovery" after a toxic shock,

but there are numerous disadvantages:
- lower purification efficiency for equal BOD loadings,
- risk of clogging,
- greater sensitivity to temperature,
- no control of the air draught (lack of oxygenation and odours),
- limited height,
- supply or resupply of adequate material sometimes difficult,
- higher construction cost,
- excess sludge is not generally stabilized.

2.1.2. Trickling filters with plastic fill

Trickling filters with plastic fill make it possible to overcome some of the disadvantages. In particular, the high void ratio of the materials used considerably reduces risks of clogging. In addition, as the weight of plastic fill is much less than that of mineral fill, it is possible to design taller plants, thus reducing the land surface occupied. Another advantage lies in the greater developed surface area and the improved natural draught of air, which consequently make it possible to work with greater BOD loadings.

Plastic fill trickling filters are particularly suited for IWW treatment:
- pretreatment of concentrated wastewater from agrifood industries (dairy farms, etc.),
- treatment of water from refineries, etc.

A high treatment efficiency (greater than about 80% on the BODO should not be expected from a trickling filter with plastic fill. Such an efficiency would be difficult to obtain and would cause prohibitive capital and running costs. Likewise, water with very high BOD_5 concentrations (greater than about 2,500 $mg.l^{-1}$) should not be treated by this means since other techniques such as methane fermentation make it possible to obtain better results with lower energy consumption and the production of a valuable biogas by-product.

2.1.2.1. General arrangements

(a) Shape of the trickling filter and hydraulic distribution

In general, to ensure a good hydraulic distribution of the wastewater, trickling filters are circular or polygonal in shape (fed by rotary distributor). For rectangular trickling filters, the distribution can be achieved by fixed distributors, or a combination of fixed and rotary distributors.

The disadvantage of fixed systems, with their smaller orifices, is their requirement of a means of access for the periodic clearing of the distribution orifices. This periodic clearing must be expected with most wastewaters because whatever the quality of pretreatment, the presence of debris capable of clogging the water distributing orifices is inevitable.

(b) Structure of the trickling filter

In the case of ordered materials, since plastic fill is self-supporting, the outside structure can theoretically be calculated only to resist wind load. The outer walls of the filter are generally built around a frame of concrete, wood or metal posts; a plastic sheeting is then stretched over, avoiding splashing from the outside.

In the case of random fill, the outer casing must normally be calculated to resist the water pressure throughout the height of the bed.

Aeration systems: aeration is ensured by openings set at the base of the bed. In the case of covered beds (Figure 402), these openings are connected by ducts to blowers. The minimum surface of the openings must represent 2% of the developed surface area of the tower. It is advisable, however, for industrial wastewaters heavily loaded with pollutants, to have a greater surface area. In the case of low temperatures, it is desirable to allow for the possibility to partially close the air inlets, by a system of flaps, for example.

Supporting the media: the media is supported either by a grating or by a system of small metal or wooden beams

The means varies according to type of media chosen. The design of this support must be carefully studied because most often the bed begins to clog at this level.

(c) Hydraulic recycling

To avoid clogging of a trickling filter due to excessive growth of the biofilm, it is necessary to work with a minimum hydraulic load, variable according to the type of wastewater and the nature of the material chosen. In most cases, it is necessary to carry out recycling. The instantaneous hydraulic loading, continuous or discontinuous, is between 1.5 and 5 m^3/m^2.h. Recycling is normally carried out directly at the outlet of the trickling filter. If the production of SS is high, it may be preferable to carry out this recycling from the settling tank located downstream, but then the latter must be larger.

(d) Protection

From the cold: trickling filters with plastic media behave like cooling towers. In winter, a considerable lowering of temperature can be observed. In cold countries, it is advisable to limit thermal losses by using a twin shell (cladding) construction and a cover as well as by controlling the ventilation.

From corrosion: particular attention must be paid to protecting the metal parts, especially in the distribution area and on the support floor. Corrosion can be expected in the case of H_2S release and with high water temperature.

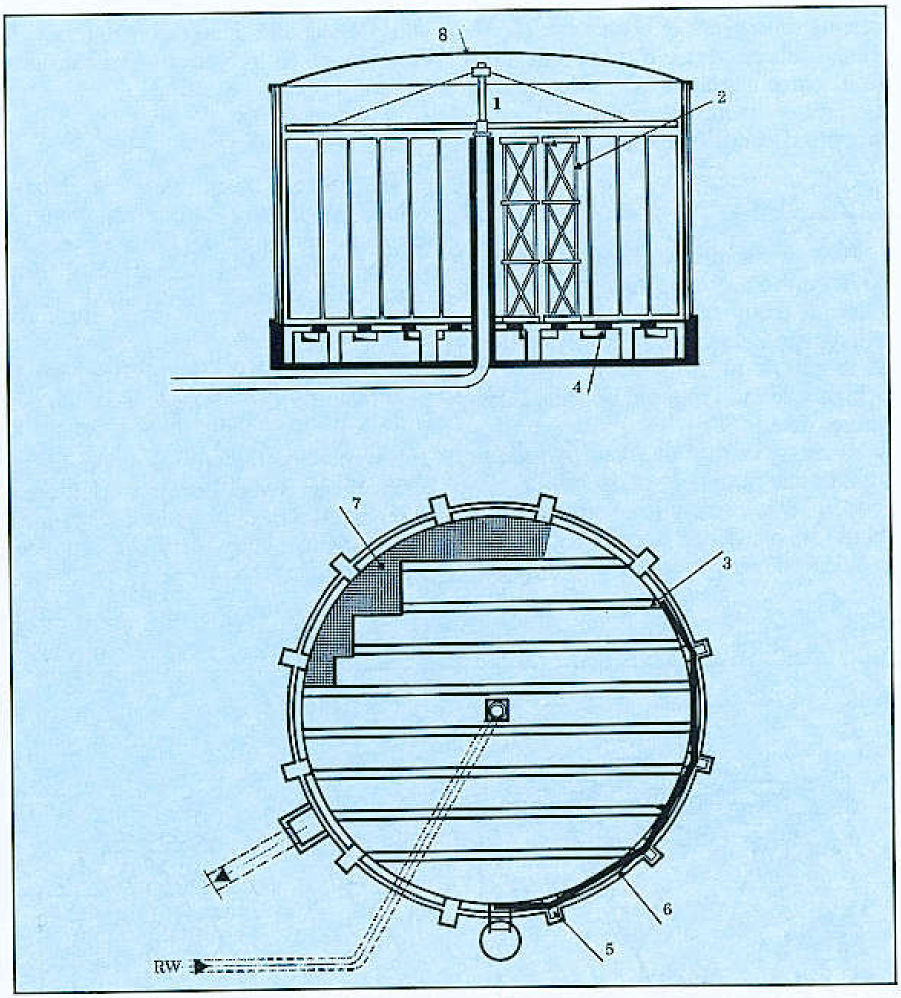


Figure 402. Cross-section of trickling filter with plastic fill.

1 – Rotary distributor.
2 – Ordered packing (stacked).
3 – Support beams.
4 – Openings for aeration.
5 – Posts.
6 – Cladding.
7 – Support grating.
8 – Possible cover.

From environmental nuisance: when treating some types of wastewater (breweries, distilleries, etc.), trickling filters can be a source of considerable odours. It is then necessary to cover them and some times to deodorize the drawn air.

2.1.2.2. Media

Most of the media (Figures 403 and 404) available on the market meet the following requirements:
- large specific surface area, varying from 80 to 220 M2.rri 3,
- high void ratio to avoid clogging (often greater than 90%),
- lightness, so that they can be used to considerable heights (4 to 10 m),
- sufficient mechanical strength. It should be noted that once in regular use and loaded with zoogloea and trickling water, the media can weigh between 300 and 350 kg.rri 3. Figures of 500 kg.m 3 are often taken into account for calculating the supporting system,
- biologically inert,
- chemical stability.

The plastic media differ in shape (which governs the surface area/volume ratio), in honeycombing, in the weight/ volume ratio and in the nature of their constitutive material (generally PVC or polypropylene).

Two broad categories of media exist:
- those using ordered packing,
- those using random fill.

It seems that the average service life of plastic media is about ten years. The need to replace the media is caused by various phenomena: fouling, crushing, support defects, etc.

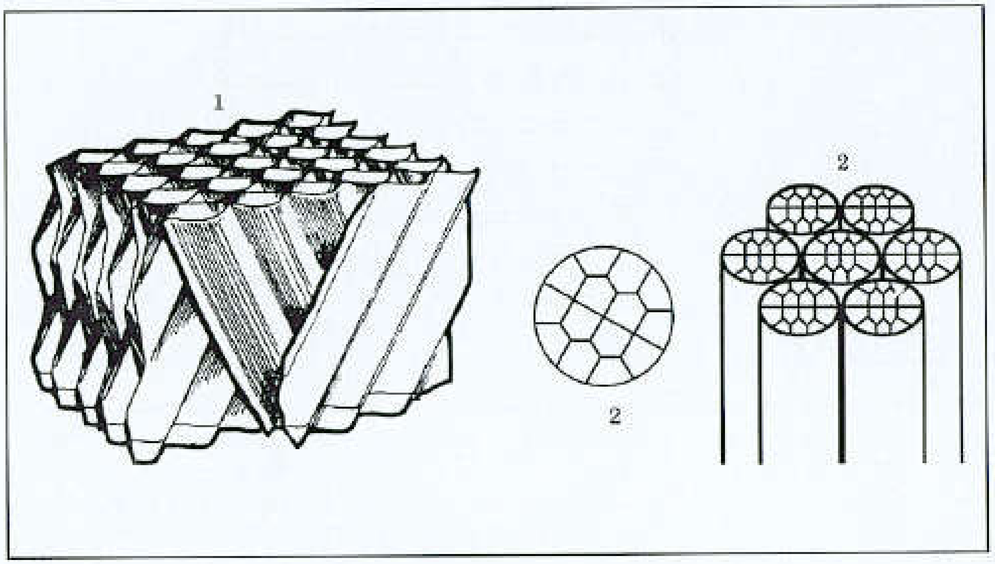


Figure 403. Examples of ordered plastic packing for trickling filter.
1 – Plasdek. 2 – Cloisonyle.

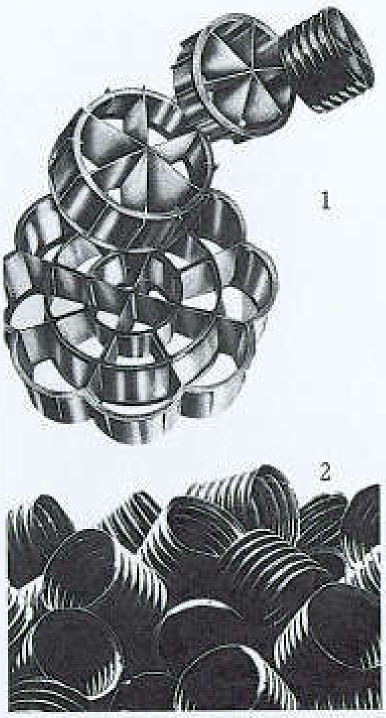


Figure 404. Examples of random plastic fill for trickling filter.
1 – Mass Transfer. 2 – Flocor R.

2.1.2.3. Purification efficiency

(a) Equation for sizing

where:

$S°$ = BOD$_5$ of the raw water, after settling (mg.l^{-1}),

S_f = BOD$_5$ of the water leaving the trickling filter, after settling (mg.l^{-1}),

A_S = specific area of the plastic media in question ($m^2.m^{-3}$),

H = filling depth (metres),

Q = hydraulic load expressed in $m^3.d^{-1}$ per m^2 of cross-section of the bed. This loading does not take the recycling into account and is thus only calculated on the flow treated,

n = experimental coefficient. The following relation is the most satisfactory:

K = biodegradability constant depending on the nature of the pollution to be handled, and on the temperature.

The following table gives the values of the constant K for some wastewaters.

Effluent type	Value of K
Slaughterhouses	0.0082
Poultry slaughterhouses	0.0189
Dairy farms	0.0108
Fruit and vegetable canneries	0.0153
Breweries	0.0101
Edible oils (olives)	0.0140
MWW	0.0226

By way of example, figure 405 gives, for these various types of wastewater, the volume of the material Cloisonyle (specific area 130 $m^2.m^{-3}$) to be used for a 7 m filling depth, according to the desired pollution removal efficiency.

The preceding equation needs some qualifications:

(1) Below 10-12°C in the trickling water, the efficiency drops considerably, and it is necessary to take this into account in cold regions. On the other hand, for greater values, the favourable influence of temperature is less obvious.

(2) To obtain a given efficiency, it is better to work with a great depth of material and a smaller bed cross-section than with limited depth and greater cross-section.

(3) For a given hydraulic load, the So/Sf relation is practically independent of the concentration of the influent. This is only true in a certain concentration range (roughly from 200 to 1,000 g.m^3 of BOD_5.

(4) Experience shows that the influence of the recycle rate is practically insignificant on the efficiency of a trickling filter with plastic media. But this recycle is nevertheless absolutely necessary to maintain the minimum hydraulic load below which there would be no sloughing.

(b) Role of the clarifier downstream

The stated purification efficiencies generally correspond to a settled, even filtered wastewater; yet in the case of a trickling filter used for pretreatment of an industrial wastewater before discharge into the municipal sewer, the downstream clarifier is often eliminated so as to free the industry of the sludge problem. The true purification efficiency can then be clearly lower.

If a trickling filter used for pretreatment is incorporated in the treatment plant unit upstream of an activated sludge stage, an intermediate settling tank makes it possible to extract the sloughed off excess sludge, which is highly fermentable and non-mineralized. This sludge would considerably increase the oxygen demands of the second treatment stage. The quantities of excess sludge produced by the trickling filter are particularly significant if the raw wastewater has a high concentration of suspended solids and is not settled beforehand.

The sludge (fragments of biological film) released by a pretreatment trickling filter can settle very well, but the interstitial water is quite turbid.

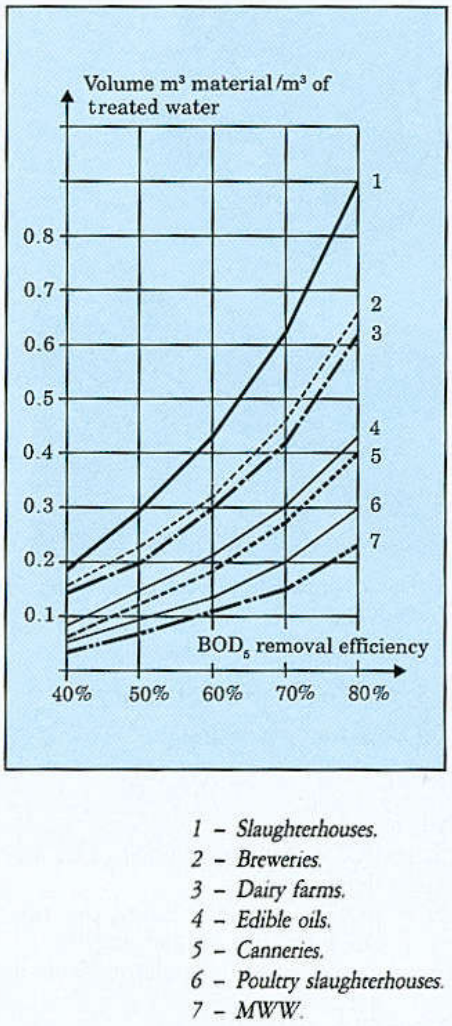


Figure 405. BOD_5 removal efficiencies on Cloisonyle bed.

Figure 406. San Miguel brewery, Philippines. Capacity: 14 t BOD_5 per day. Trickling filter for pretreatment.

2.2.
FIXED GRANULAR BEDS

Degrémont implemented these techniques in France at La-Barre-de-Monts in 1973 on MWW, and for Mobil Oil at Notre-Dame-de-Gravenchon, in 1980 on IWW.

The result of progress made is that now, biofiltration has become a particularly advantageous treatment process. In MWW treatment, it makes it possible to carry out secondary biological purification (removal of carbon and nitrogen) and retention of the SS at the same time. In the treatment of drinking water, these processes are particularly suited for nitrification and denitrification.

The term "biofiltration" is often used to cover all processes that combine biological purification with SS retention. According to the characteristics of the support material, the clarification effect can vary considerably. Initially, the English term "biofilter" was given to low rate bacteria beds filled with coarse materials of several centimetres size range, and often operating without secondary settling tank. The SS content of the wastewater treated then exceeded 50 $mg.l^{-1}$. The old process of slow filtration of drinking water, on fine sand (less than 1 mm ES), is another type of biofiltration of much more lightly loaded water leading to treated water with low turbidity. The term biofiltration, used in treating MWW, usually covers processes leading to the production of treated water that complies with usual discharge standards, i.e., with an SS content of a few dozen $mg.l^{-1}$.

These techniques use biomass of greater concentration and, above all, of greater activity than activated sludge and have the following advantages:

- savings in land space, particularly due to elimination of the wastewater clarification stage. This compactness makes it easier to cover units, control harmful effects (smell and sound) and produce aesthetic units,
- no risk of leaching since the biomass is attached to a support such that flow variations can be readily handled,
- easy adaptation to dilute wastewaters,
- quick restarting, even after stopping for several months,
- modular construction and easy automation

Oxygenation can be carried out by prior dissolution of atmospheric oxygen or pure oxygen, or by direct transfer of air into the reactor. In the latter case, the respective flow directions of air and water are particularly significant. The practice of filtration of drinking water has led, as an initial approach, to the development of downflow reactors with countercurrent air flow; this technique leads to the slowing down and the coalescence of the injected air bubbles, hence the formation of gas pockets in the granular mass. This is the phenomenon of **air binding** which involves the following disadvantages:

- increase in the head loss leading to reduction of the treated water flow and an increase in the washing frequency,
- need to continuously (and uselessly) increase the process air flow: this no longer becomes necessary because of the biological needs, but because of the mechanical and hydraulic needs,
- this excessive injection of air causes turbulence reducing the SS retention capacity.

These different reasons led Degrémont in the case of direct transfer, to select air-water cocurrent techniques, either in **upflow (Biofor), or in downflow (Biodrof).** There is one exception, however: nitrification of drinking water in which clear treated water is also desired. The negligible concentrations of SS in the effluent to be treated, together with the low growth rate of the nitrifying bacteria, considerably limit clogging and, consequently, the risks of air binding. In this case it is possible to use an air-water countercurrent (Nitrazur process).

Each biofiltration technique, by virtue of its particular characteristics, has a very precise application.

2.2.1. Filter media: Biolite

The filter media has a dual role:

- support of microorganisms,
- filtering effect.

The choice of a suitable support is fundamental and depends on the type of reactor being considered and the nature of the wastewater to be treated (drinking water, MWW or IWW, after pretreatment, primary settling or secondary biological treatment).

Degrémont developed a family of materials called Biolite (L, P, F) whose ES can vary from 1 to 4 mm and granular density from 1.4 to 1.8 $g.cm^{-3}$. They have the following common characteristics:

- surface conditions favourable to bacterial development,
-low friability and low loss in acid.

2.2.2. Biofor (Biological Filtration Oxygenated Reactor)

2.2.2.1. Description

This is a system of **aerobic biological filtration with air and water upflows** (Figure 407). Oxygenation is thus carried out by introduction of air cocurrent with the water.

A Biofor installation mainly comprises (Figure 408):
- a battery of identical reactors generally made of concrete (1), operating in parallel (or possibly two batteries in series, in the case of combined removal of carbonaceous pollution with nitrification),
- a unit for distributing the water to be treated (2),
- an access gallery to the automatic valves and pipework, to the filter bottoms, drains, etc. (3),
- an adjoining bay for the backwash pumps (4),
- a bay for the various air blowers and compressors (5),
- a treated water tank for wash water (6).
- possibly a tank for recovery of the waste wash water, with drainage pumps (7).

Each reactor, comprised of a rectangular, concrete pit, includes:
- a feed well for water to be treated, equipped with a protecting screen,
- a support floor for the granular media, made of prefabricated slabs,
- two front-mounted weirs, with surface sloping upstream for collecting the treated water and the wash water. These weirs are protected by a material trap comprised of a stilling picket fence eliminating turbulence, particularly in the air scour + water washing sequence of the washing cycle (Figure 409),
- a front-mounted treated water collecting trough for each reactor, and a part of the waste water collecting channel shared with the battery of reactors.

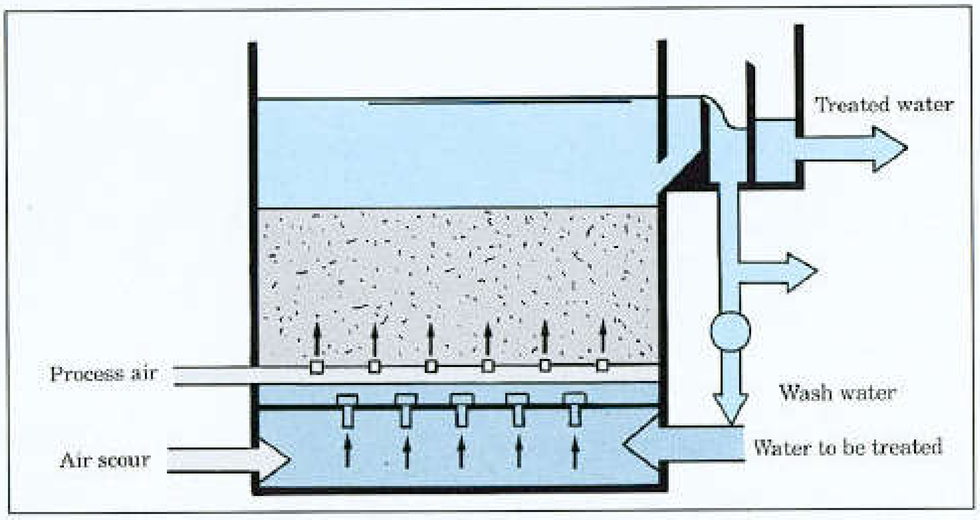


Figure 407. The principle of the Biofor.

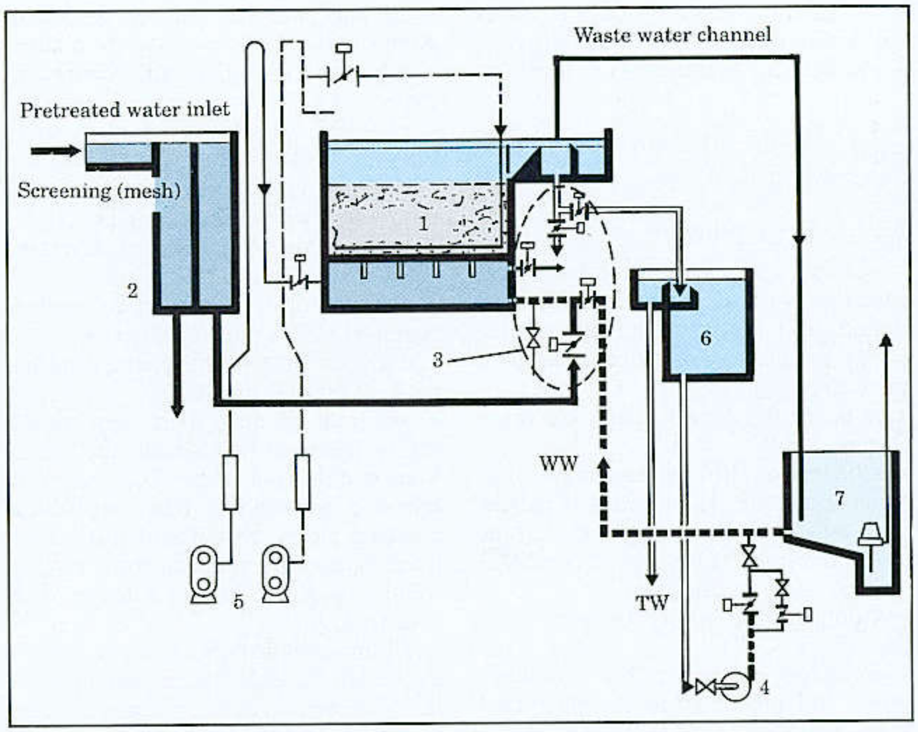


Figure 408. Diagram of a Biofor installation.

The floor supports:

- two intermediate support layers,
- about 3 metres of the specific media.

The equal distribution of the fluids introduced under the filter floor (raw water, wash water, air scour) is ensured by approximately 55 nozzles per m^2. These nozzles are specially adapted for wastewater use.

Introduction and equal distribution of the process air is ensured by a grid collector assembly on the filter floor. Equal distribution of the air in the mass of support material is ensured by **Oxazur diffusers** (page 710).

Two types of materials are currently used:

- Biolite 2.7 with an ES between 2.5 and 2.9 mm,
- Biolite 3.5 with an ES between 3.2 and 3.8 mm.

In the case of lightly loaded wastewaters that must comply with strict SS standards, sand with an ES of 1.35 mm is used: this can be the case for nitrification on a Biofor, downstream of a first Biofor removing the carbonaceous pollution.

2.2.2.2. Operation - Automation

(a) Treatment cycle: the raw water is introduced under the floor of the reactor. The number of units in use may be related to the flow to be treated.

The introduction of process air is continuous on the reactors in service. Each of them is equipped with a blower of its own, in such a way as to overcome the variations in head loss from one reactor to the other.

The treated water, collected by the front-mounted weir, drains by gravity at the outlet after filling the treated water reservoir.

(b) Washing cycle: this is automatically initiated by a time switch, or possibly earlier if the maximum allowable head loss is reached. The entire washing cycle is automatic and lasts 30 to 40 minutes; it includes an actual washing phase (with air and water) and a rinsing phase. The techniques used are quite similar to those described on page.775

The air is supplied by a blower common to all the Biofors. The wash water represents 5 to 10% of the volume of the filtered water.

(c) Automation: management of the washing cycles and control of the rotating machinery and automatic valves are ensured by a programmable controller.

2.2.2.3. Application and operating results

The Biofor is normally used after primary settling or flotation (these steps can be preceded by flocculation). The application of this technique is:

Figure 409. Gréoux-les-Bains facility in southern France.
Flow: 4,000 $m^3.d^{-1}$. MWW purification.
View of one of the 4 Biofor reactors with 14.1 m^2 unit surface area.

Figure 410. Métabief facility, France. Maximum flow: 2,300 $m^3.d^{-1}$. MW purification. 4 Biofor reactors with 10.5 m^2 unit surface area.

- removal of the BOD_5 from wastewaters having a concentration below 300 $mg.l^{-1}$,
-retention of the SS from wastewaters having a concentration below 150 $mg.l^{-1}$,
- removal of the ammonia by oxidation to nitrates (it should be pointed out that ammonification is limited due to the short retention time),
- denitrification of nitrified water without the addition of process air.

(a) Excess sludge production

Excess sludge production is greater than with low rate activated sludge. The shorter retention times of the water, the limited degradation and greater retention of the SS explain this phenomenon.

Wash water, whose SS concentration is in the 2 and 3 ($g.l^{-1}$) range, is either returned downstream of the pretreatment stage if the plant has a settling or flotation unit, or treated separately by settling or flotation before discharge into the environment.

(b) Results

Process air - Oxygenation capacity Energy consumption: the injected air flow can vary, depending on the treatment conditions, between 4 and 15 $Nm^3.m^{-2}$ of reactor area per hour. As the oxygen transfer efficiency in actual treatment conditions is about 20%, the oxygenation capacity can vary from 0.3 to 0.9 kg of $O_2/m^2.h$. The energy consumption of oxygenation can be as low as 0.75 kWh per kg of removed BOD_5 (at full load). The energy consumed by the periodic washing of the media (air and water) must be added to this energy consumption: it is roughly 0.1 kWh per kg of BOD_5 removed.

Removal of SS: the performance of the Biofor depends on the choice of media, the hydraulic load on the reactors and the

SS concentration of the raw water. In MWW treatment, the SS removal efficiency of raw water having an initial SS content of about 100 mg.l^{-1}, varies from 85 to 70% at velocities of from 2 to 6 m.h^{-1}.

The SS retention capacity between washes is between 1.5 and 2 kg.m^{-3} of material.

Removal of BOD$_5$ (Figure 411): unlike the SS, the removal of the BOD$_5$ is little affected by the ES of the media used. On settled MWW of average concentration, the BOD loadings adopted are between 2 and 6 kg BOD$_5$/m .d for which the BOD$_5$ removal efficiencies vary between 85 and 75%.

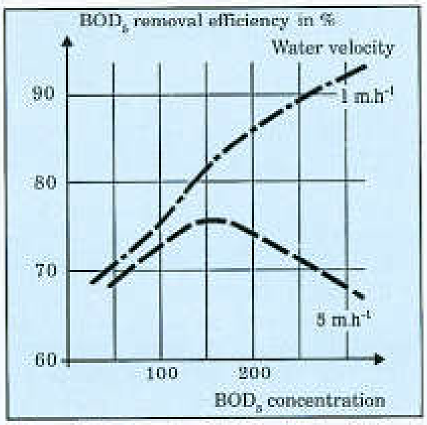


Figure 411. Removal of BOD5 with the Biofor.

Oxidation of ammonia to nitrates (Figure 412): on MWW, after removal of the carbonaceous pollution, it is possible to nitrify 1 kg of N-NH$_4$/m^3.d at 20°C. At 12°C, this figure is only 0.45 kg N-NH$_4$/m^3.d.

The curves of Figures 411 and 412 were developed on MWW.

2.2.3. Biodrof (Biological Dry Oxygenated Filter)

2.2.3.1. Description

In this process (Figure 413), the wastewater to be treated trickles through the granular bed. This allows the transfer of oxygen within the active mass without having recourse to direct injection of air into the reactor. The air circulates in cocurrent with the water, creating a low pressure zone at the base of the reactor.

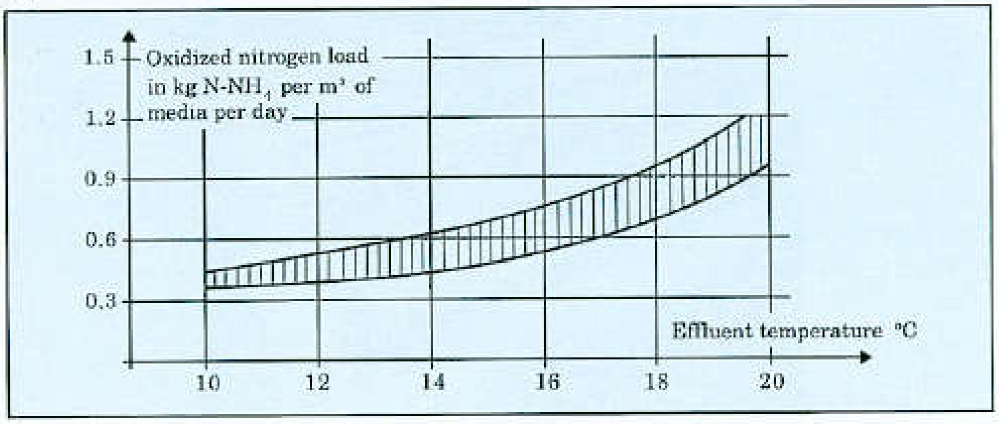
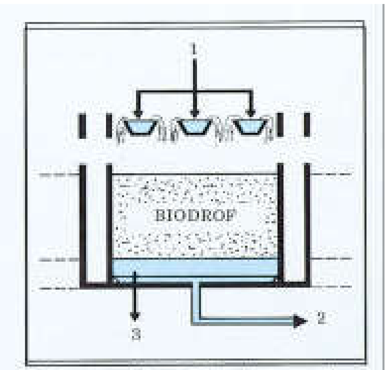


Figure 412. Oxidation of ammonia to nitrates with the Biofor (raw water having a BOD5 of less than 60 mg.l^{-1}).

The water is evenly distributed at the surface of the bed by a system of troughs or by rotary or travelling distributors. It trickles through a preliminary dispersion layer, into the bed, then through the floor where it drains into a collector or a bottom channel.

A water seal makes it possible to maintain the low pressure under the floor. This low pressure varies from 0 to 150 cm WC. The velocity of the air must be high enough to ensure good penetration of the SS into the media and to promote oxygenation of the biomass.

The layer depth is of the order of 2 m.



1 Raw water inlet. – 2 Treated water outlet. – 3 Low pressure.

Figure 413. Principle of the Biodrof.

2.2.3.2. Operation

The Biodrof is used for simultaneously removing the carbonaceous pollution and SS, on MWW or on certain IWW, either directly after primary treatment or as polishing treatment after an existing facility.

The media is washed as soon as the internal low pressure or the cycle duration reaches a predetermined value. After filling the biofilter, this washing includes the standard washing phases of a filter with water and air.

The total duration of these operations, including drainage and emptying, is about 45 minutes. As in the case of the Biofor, the volume of wash water represents 5 to 10% of the volume of filtered water. This wash water follows the circuit described earlier for the Biofor.

Figure 414. Mannheim facility, Germany. Polishing treatment for purification of municipal wastewater. Maximum flow: 14,000 $m^3.h^{-1}$. 32 Biodrof reactors (unit surface area: 87 m^2).

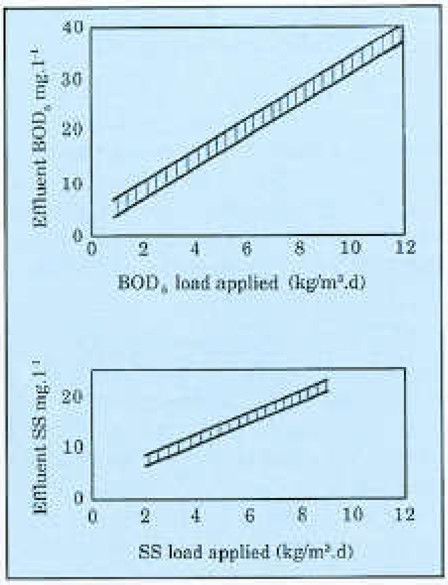
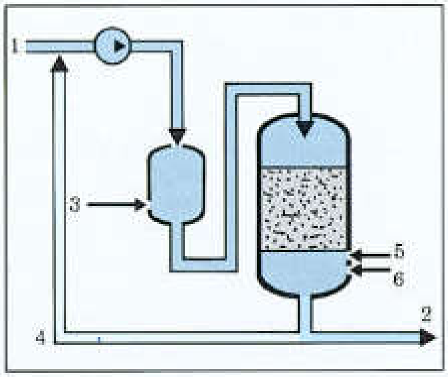


Figure 415. Removal of BOD$_5$ and SS with the Biodrof.

2.2.3.3. Conditions of use and results

The Biodrof process is advantageous in tertiary treatment or on highly dilute wastewaters.



1 – Effluent to be treated.
2 – Treated effluent.
3 – Process air or pure oxygen.
4 – Possible recycling.
5 – Air scour.
6 – Wash water.

Figure 416. Filtration with predissolution of pure oxygen or air.

The curves of Figure 415 show the results obtained on Canadian MWW containing an average of 65 mg.l^{-1} SS and 75 mg.l^{-1} BOD$_5$

Figure 417. Obernai facility for the Kronenbourg brewery in eastern France. Flow: 15,000 m^3.d^{-1}. Tertiary treatment by filtration ow Biolite with predissolution of air.

2.2.4. Filtration with predissolution of air or oxygen (Oxyazur)

The **predissolution of air** under pressure makes it possible to work in a twophase system in the biofilter. The filtering effect of the media (in general Biolite) is not disturbed by the presence of air bubbles, making it possible to obtain high **SS removal** efficiency. The filters used are of the downflow type. This technique is used especially in polishing, for removing the suspended solids, when the residual BOD of the water to be treated is low. On more polluted water, the capabilities of removal of the organic pollution are enhanced by recycling the treated water, although this has the disadvantage of increasing the filtration rate, or better by using **pure oxygen** under pressure (see Figure 416).

2.2.5. Nitrazur

The Nitrazur process covers the techniques for removal of nitrogen in drinking water treatment. The process is applicable either for nitrification (oxidation of ammonium to nitrates), or in denitrification (removal of nitrates in nitrogen form).

2.2.5.1. Nitrazur N (Nitrification)

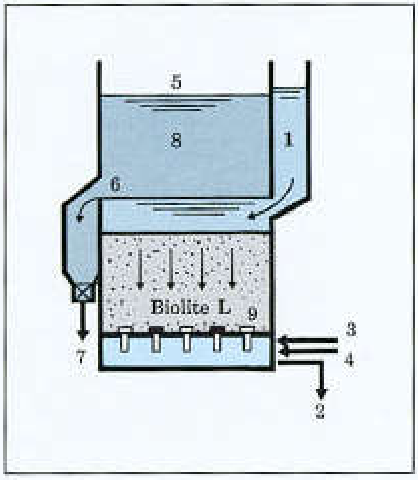
The ammonium concentration after treatment must be much lower than the values desired in MW (0.05 mgl^{-1} according to EEC standards). Moreover, the medium is very poor in nutrients.

The support material used is Biolite L, which was recognized as being the most effective for nitration (transformation of nitrites into nitrates); this reaction has slower kinetics than nitrite production ($NH_4 \rightarrow NO_2$)and it is the limiting factor of nitrification.

The Nitrazur N can be used either in upflow, where its effectiveness will be at maximum, or in downflow: in this case, the benefit is a greater filtering effect which makes it possible to retain a greater quantity of SS. This is illustrated in Figure 418. The support floor (9) is equipped with two types of nozzles one of which is reserved for introducing the process air. This process air makes it possible to maintain a sufficient oxygen concentration throughout the depth of the media. It is thus possible to nitrify water containing more than 2 $mg.l^{-1}$ of NH_4. During washing, the two types of nozzles are used to simultaneously inject the air and the wash water. In order to keep the light material from being washed out, zone (8) is used to store the waste wash water during the air scour and water wash phase; this wash water is then drained via the channel and the valve (7). During rinsing, the water level is maintained at the level of the wash weir (6); this phase is shortened due to sweeping by the water to be nitrified.

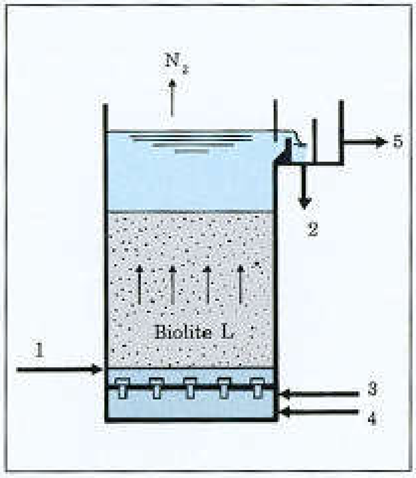
2.2.5.2. Nitrazur D (denitrification)

In this process, the reactor (Figure 419) uses bacteria that are not strictly aerobic and that use the oxygen present in the nitrates for their metabolism; the reactor operates in an anoxic condition. The support material is Biolite L. The operating direction is **upflow**: this direction of flow promotes the removal of the nitrogen gas, which is the final product of the denitrification reaction. Downflow operation would result in the accumulation of the nitrogen in the midst of the reactor, thus significantly increasing head loss. The water to be denitrified is introduced, with its reagents, at the base of the reactor (1). The denitrified water is collected at the surface (2). The floor is equipped with a single type of nozzle.



1 – Inlet of water to be nitrified and sweeping water.
2 – Nitrified water outlet.
3 – Process air.
4 – Air scour and wash water.
5 – Normal operating level.
6 – Rinsing level.
7 – Wash water outlet.
8 – Storage of waste wash water.
9 – Nozzle-fitted floor.

Figure 418. Nitrazur N in nitrification.



1 – Inlet of water to be treated.
2 – Denitrified water outlet.
3 – Air scour.
4 – Wash water.
5 – Wash water outlet.

Figure 419. Nitrazur D in denitrification.

2.2.6. Choice of treatment technique with fixed granular beds

The following table shows the applications of the various aerobic attached growth processes in wastewater treatment.

13

FILTERS

The enormous variety of ways in which granular or precoat filtering media can be used, means that a large number of filters have been designed accordingly. The major groups are as follows:

- for **granular media,** depending on hydraulic conditions during use:

- pressure filters,
- (open) gravity filters, made of concrete or metal,
- special filters.

- for **precoat filters,** depending on the support:

- candle filters,
- frame filters.

1. FILTERS USING GRANULAR MEDIA

The technical considerations common to the various types of filters which use granular media are summarised below;these relate to:

- operating conditions; and
- internal arrangements for backwashing.

1.1. OPERATING CONDITIONS

- **Cycles**

Almost all filters using granular media operate in cycles which include a final backwashing.

The essential parameter which limits the duration of these cycles is head loss, but in addition to a maximum acceptable head loss, it is also possible to use other parameters, such as:

- filtered volume or time (8 hours, 24 hours, 48 hours, etc.),
- turbidity, which can be monitored by a turbidimeter.

Maximum head loss is determined by:

- the available hydraulic head (gravity feed head or pump curves, which in turn are selected on the basis of an acceptable energy consumption value),
- maintaining the **quality of the filtered water** over the entire cycle, with varying levels of suspended solids depending on the intended use of the water. This is essential for make-up water or drinking water. For certain grades of industrial water, this condition may not be imposed, and pressure filters can be used with high head losses (0.5 to 1.5 bar); all that is then important is the average quality of the water.

Resuming production

In a filter battery, a backwashed filter must not be subjected to excessive flow when it is brought back on line. The risk becomes greater, the smaller the number of filters; equal distribution ensures the best filtered water quality.

In some cases, it is advisable to discard the first bed volumes of filtered water that are too highly loaded (very rapid filtration, no prior clarification of the water, etc.).

1.2. SUPPORTS FOR THE MEDIA

Since the effective size of the media can, in practice, vary from 0.35 mm (garnet) to 2 mm (sand) or 5 mm (anthracite), it can be supported:

- either by a floor fitted with nozzles perforated with slots much smaller than the size of the media; or
- by a support layer (gravel, garnet, etc.), especially if the dimensions of the filtering media and the slots in the nozzles are not compatible. This support

layer, between 5 and 40 cm deep, can consist of two to four sublayers of intermediate grain sizes, depending on the media and the distribution system (laterals or nozzles).

1.3.
BACKWASHING DENSE MEDIA FILTERS

These filters are always washed in up-flow, using one or two fluids (see page 192).

1.3.1. Distributing the washing fluids

A system to distribute one or both of these fluids must therefore be provided beneath the filtering media; air requires special arrangements. There are two possible types of device:

- simple distribution mains for water backwash alone,
- air cushion devices placed beneath the floors or in special headers.

1.3.1.1. Devices for water backwash alone

These can consist of laterals connected to a central box, or a transverse distribution main. The laterals are fitted with orifices or nozzles which distribute the water.

1.3.1.2. Air cushion devices

Stemmed nozzles are used to maintain the air cushion that is needed to distribute this fluid. Figure 430 shows a section of a long-stem nozzle fastened to a concrete floor during the water and air washing stage.

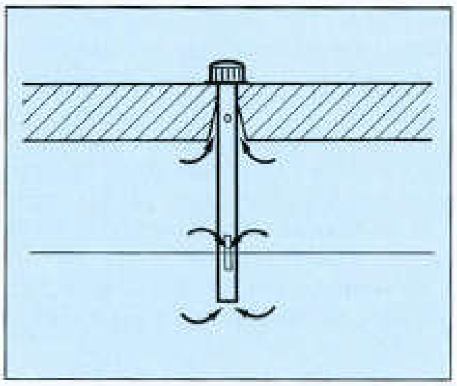


Figure 430. Nozzle during the air and water filter washing stage.

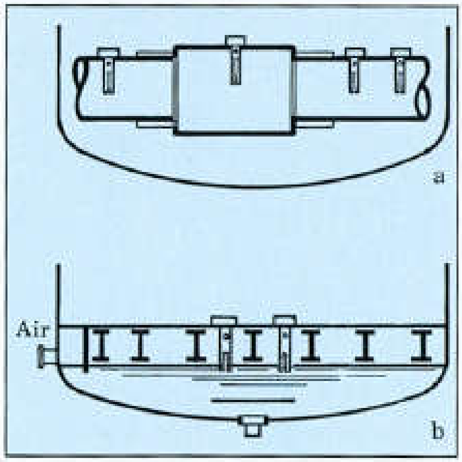


Figure 431. Air cushion devices for metal filters. (a) header type; (b) under-floor type.

This nozzle has a head with fine slots which block passage of the filtering media, and a stem consisting of a tube which has a hole at the top and a slot at the bottom.

Air injected under the floor forms a cushion which, once it has been formed, supplies the holes and slots of the nozzles, providing an air/water mixture which is thus distributed over the entire surface of the filter. This particularly efficient washing system helps to conserve water.

To prevent the formation of mud balls, approximately 55 nozzles must be provided for each square metre of floor, with a countercurrent air flow of 1 m3.h-1 per nozzle.

Air scour is therefore implemented in two ways for metal filters (Figure 431).

1.3.1.3. Nozzles

Two types of nozzles can be used, depending on the washing method:

-nozzles for washing with water alone (Figures 432 a and b). These differ in terms of shape, the width of the slot, and the construction material.

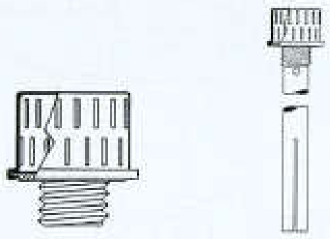


Figure 432 a.
D 50 metal nozzle.

Figure 432 b.
D 50 metal nozzle.

Figure 432. Degrémont nozzles for washing with water alone.

Figure 433 a.
D 28 long-stem plastic nozzle.

Figure 433 b.
D 25 plastic nozzle with sealing ring for steel floors.

Figure 433. Degrémont nozzles for air and water washing.

Figure 434 a.
D 22 plastic nozzle with sealing ring for concrete floors.

Figure 434 b.
D 15 plastic nozzle for steel floors with threaded hole.

Figure 434. Degrémont nozzles for air and water washing.

Figure 433 a.   Figure 433
b.
D 28 long-stem plastic   D 25 plastic
nozzle nozzle   with sealing
ring
forsteel floors.

-nozzles for water and air washing: air is distributed via an air cushion, and the long-stem nozzles (Figures 433 and 434), specially designed for this application, ensure the equal distribution of air and water.

Experience gained at Degrémont has led to the development of various types of nozzles that are adapted for different filtration techniques, and are made of materials that can withstand a variety of aggressive environments.

1.3.2. Wash water consumption versus filtered volume

Consumption is highly dependent on SS concentration and on the nature of the solids. For clarified water filtration, however, it is possible to indicate some comparative orders of magnitude:

- 1-2% for "air and water" washing of single-media filters (Aquazur),
- 3-5% for "air then water" washing of dual-media filters (Mediazur).

1.4
DEGREMONT FILTER TYPES

Washing type	**Gravity filters**	**Pressure filters**	**Special filters**
Water alone Single layer of sand or anthracite		FC Hydrazur	Self-washing
Air and water Single sand layer	FV1 Aquazur T, V,	FV2 FH FP FECM	Colexer
Separate air scour, then water washing Dual-media (sand/anthracite) or single-media (Biolite)	Mediazur T, G V, BV, B, GH	Mediazur FECB FPB	

2. PRESSURE FILTERS

These filters are constructed with coatings suitable for their applications. Provisions for discharging backwash water must be particularly well-designed, to ensure uniform water collection.

These filters readily lend themselves to completely automatic operation. Degrémont has produced units in diameters of up to 8 metres.

2.1. FILTERS WASHED WITH WATER ALONE

In most cases these filters are filled with a single filtration layer, either sand or anthracite. The maximum head loss reached at the end of the cycle can vary between 0.2 and 2 bar, depending essentially on the fineness of the filtration layer and the filtration rate.

Washing is achieved exclusively by water backflow, the velocity of which must be adjusted to the grain size of the media. The table below indicates velocities for sand and a temperature of 1525°C:

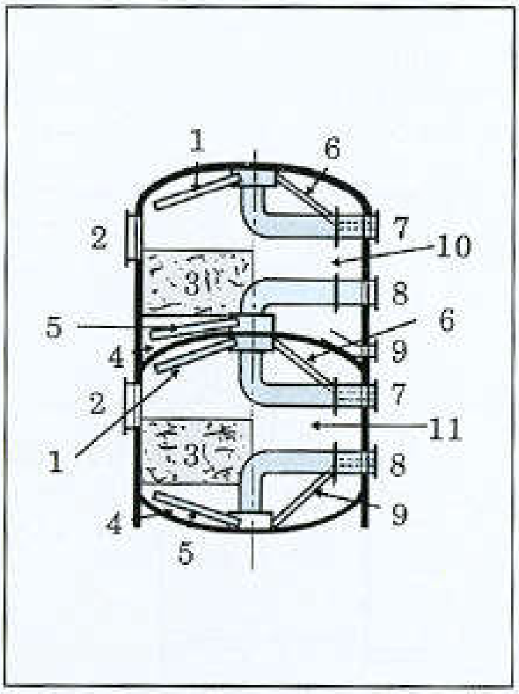
Effective size (mm)	0.35	0.55	0.75	0.95
Rate ($m.h^{-1}$)	25-35	40-50	55-70	70-90

Control of washing velocity is essential, and can easily be provided by equipping the waste wash water sump with a calibration threshold. At the same time, the change in quality of the discharged water can be monitored as a way of regulating washing time. This time varies between 5 and 8 minutes, depending on sand depth and the kinds of matter retained.

Possible configurations

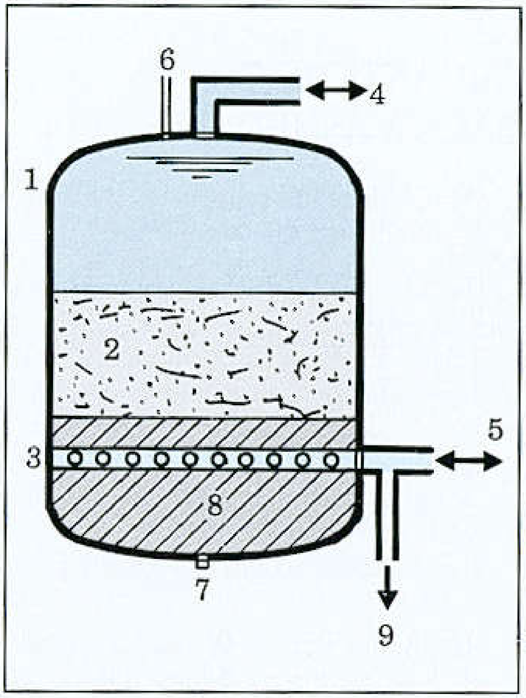
Lined steel **Hydrazur filters** for high filtration rates, which can consist of a dual column (Figure 435): - layer depth 0.6 m, - diameter 1.4 to 3 m, - usable for swimming pool water. **FC filters** (Figure 436):

- layer depth 0.6 m,
- diameter 0.65 to 3 m,
- usable for neutralisation operations and filtration over activated carbon or anthracite.



1 – Upper manifold.
2 – Access manhole.
3 – Filtering layer.
4 – Support bed.
5 – Lower manifold.
6 – Air blowdown.
7 – Raw water inlet.
Wash water outlet.
8 – Wash water inlet.
Filtered water outlet.
9 – Drain.
10 – Upper filter.
11 – Lower filter.

Figure 435. Dual column Hydrazur filter.



1 – Filter body.
2 – Filtering media.
3 – Manifold.
4 – Raw water inlet.
Wash water outlet.
5 – Filtered water outlet.
Wash water inlet.
6 – Air vent blowdown.
7 – Drain.
8 – Support bed.
9 – To rewash (if necessary).

Figure 436. FC filter, backwashed with water.

2.2.

AIR AND WATER BACKWASHED FILTERS

These filters have a single layer, and are backwashed with air and water simultaneously.

The filter bed, which is homogeneous over its entire depth, is supported by a steel floor or a manifold, onto which rings are fastened and into which nozzles (metal or plastic, depending on the nature and temperature of the liquid being filtered), are screwed. These filters are generally filled with sand.

The usual characteristics of this type of filter are as follows:

-particle size (ES)……………. 0.7 to 1.35 mm

-air flow ………………………….. 55 m^3/h.m^2

-water flow during air scour ….. 5 to 7 m^3/h.m^2

-rinsing water flow ………... 15 to 25 m^3 /h.m^2

-pressure drop at end of cycle …. 0.2 to 1.5 bar

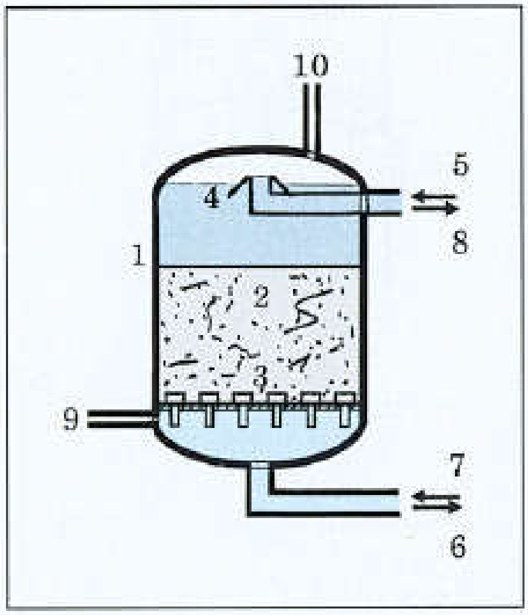
The; layer depth is essentially determined by the filtration rate and the mass of solids that needs to be retained. Filtration rates are usually in the range of 4 to 20 m.h^{-1}. In industrial applications, this filter can be used with layer depths of 1 to 2 m, and sand grain sizes of between 0.65 and 2 mm. Filtration rates can be as high as:

- 20-40 m.h^{-1} for rough pressure filtration of oxide-laden water,
- 30-50 m.h^{-1} for fine filtration of deep sea water.

These filters, which are highly suitable for use in batteries of large-diameter units, have some significant advantages: ease of use; completely safe operation; and low instantaneous wash water rate, which reduces water consumption.

Possible configurations FV 2 filters (Figure 437):

- Standard vertical filters for boiler water and process water, drinking water, etc.
- Layer depth about one metre.
- Diameter 0.95 to 3.2 m.



1 – Filter body.
2 – Filter media.
3 – Floor with nozzles.
4 – Feed basin.
5 – Raw water inlet.
6 – Filtered water outlet.
7 – Wash water inlet.
8 – Wash water outlet.
9 – Air scour inlet.
10 – Air blowdown.

Figure 437. FV 2 filter.

FP filters:

-Tall cylindrical vertical filters (Figure 438).

-Layer depth 1.8 to 2 m. -Diameter 2.5 to 6 m.

-Specific applications: steel industry, wastewater,biological iron removal.

FECM filters

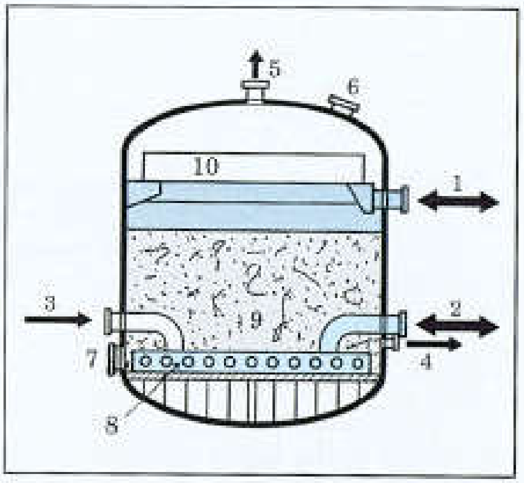
- Compact, high-rate vertical filters for corrosive water (figure 439).
- Layer depth of about one metre.

-Diameter 1.6 to 3.5 m.

-Applications: brines, sea water injection.

FH filters:

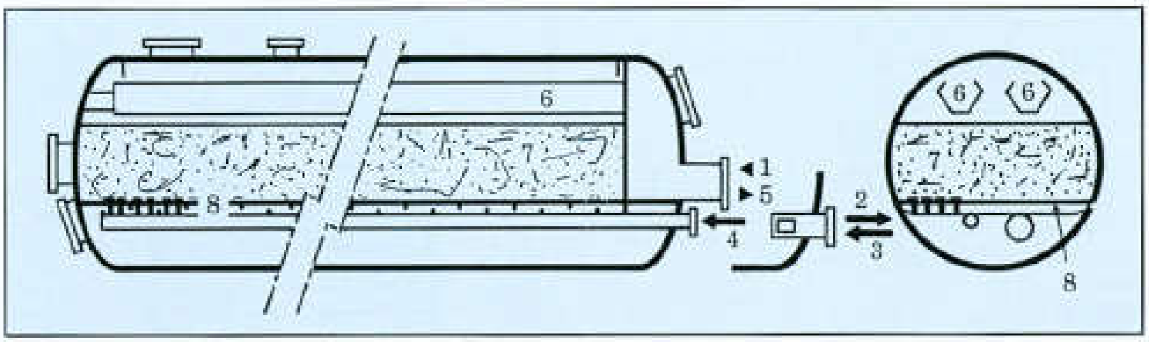
- Horizontal filters, with one or two troughs, with special provision for collecting wash water (figure 440).
- Layer depth of about one metre.
- Diameters 2.5 to 3.4 m, length up to 12 m.
- Applications: filtration of large volumes of industrial water (lime softening, rolling mills, sea water).



1 – Raw water inlet (wash water outlet).
2 – Filtered water outlet (wash water inlet).
3 – Air inlet.
4 – Drain.
5 – Vent.
6 – Access hole.
7 – Manhole.
8 – Nozzles on manifold.
9 – Filter media.
10 – Wash water collection trough.

Figure 439. FECM filter.

Figure 438. Sea water filtration skid for injection purposes. Shell installation at Fulmar (North Sea). Capacity: 1400 $m^3.h^{-1}$.

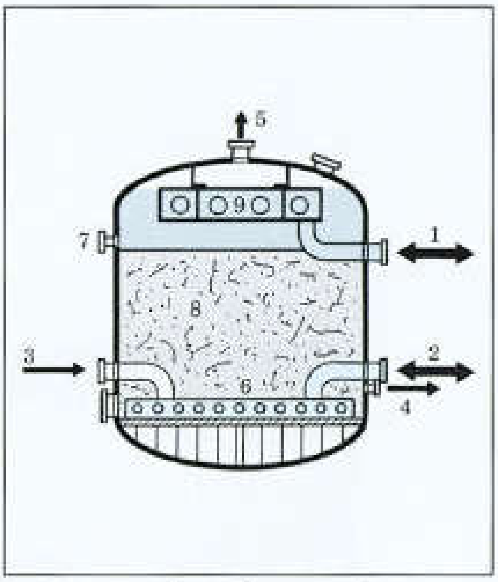


1 – Raw water inlet.
2 – Filtered water outlet.
3 – Wash water inlet.
4 – Air scour.
5 – Wash effluent.
6 – Wash effluent collection troughs.
7 – Filtering media.
8 – Floor with nozzles.

Figure 440. FH two-trough filter.

2.3.

FILTERS FEATURING SUCCESSIVE AIR SCOUR AND WATER WASHING



1 – Raw water inlet (wash water outlet).
2 – Filtered water outlet (wash water inlet).
3 – Air inlet.
4 – Drain.
5 – Vent.
6 – Manifold with nozzles.
7 – Level detector.
8 – Filter media.
9 – Wash water collection system.

Figure 441. FECB filter

The filters just discussed can also be filled with a layer of lightweight media (anthracite, activated carbon, Biolite), or with two layers of different media (dualmedia filters). Washing these filters requires two successive phases (see page 194).

Before air scour, the water level must be lowered.

When the fine media of the dualmedia consists of sand, the backwash water rates that must be provided are those shown in the table for filter backwash water alone, for the same sand size. These flow rates are higher than those used for single-media filters: the piping, valves and wash water pump must be sized accordingly. Moreover, expansion of the filter bed means that the collection system for the wash water must be elevated.

- **Possible configurations**

FECB filters:

- Compact vertical filters for corrosive water or sea water (figure 441).

- Layer depth of about one metre.

- Diameter 1.6 to 3.5 m.

- Applications: in-line coagulation, iron removal, lime softening.

FPB filters:

- Vertical filters with a deep layer of large-grain media, for water from rolling mills and oily waste water (figure 442).

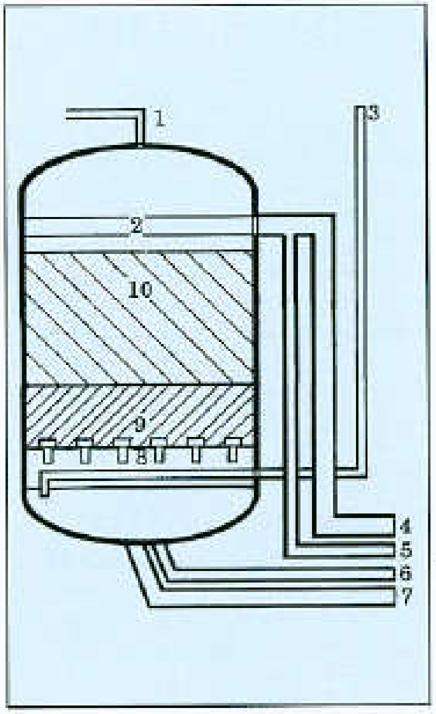
- Layer depth 2 m.

- Diameter 2.5 to 6 m.

- Applications: rolling-mill water, oily waste water.

The characteristics of dual-media filter beds are as follows:

	FECB filters		FPB filters	
Combination	1	2	3	4
Sand, NES (mm)	0.55	0.7	1.35	1.8
Anthracite, NES (mm)	1	1.6	2.6	4



1 – Vent.
2 – Wash water collection trough.
3 – Air scour inlet.
4 – Wash water outlet.
5 – Raw water inlet.
6 – Filtered water outlet.
7 – Wash water inlet.
8 – Floor with nozzles.
9 – Sand.
10 – Anthracite.

Figure 442. FPB filter.

3. GRAVITY FILTERS

Most filtration plants designed to supply drinking water, as well as many highflow rate installations for clarifying industrial or wastewater, use (open) gravity filters, generally made of concrete.

Depending on the particular case, the water being filtered is either fed with no reagent, or it is simply coagulated with no settling phase, or it is coagulated, flocculated, and settled. The last process is the most often used. The treatment method influences the technological design of the filters, and especially the overall design of the filter battery.

Gravity filters operate at filtration rates between 5 and 20 $m.h^{-1}$, and can be washed either with air and water simultaneously, or with air followed by water.

3.1.

FILTERS BACKWASHED BY AIR AND WATER

These filters are backwashed by a simultaneous high air flow and a reduced flow rate of water, followed by a rinse at a moderate flow rate that does not cause the filter bed to expand.

The major types are:

- Aquazur T filters, used at filtration rates between approximately 5 and 10 $m.h^{-1}$,
- Aquazur V filters, used at rates between 7 and 20 $m.h^{-1}$,
- FV 1 filters,
- Greenleaf filters.

3.1.1. Aquazur T filters

These are characterised by:

- a filter bed, with a homogeneous particle size that remains homogeneous after

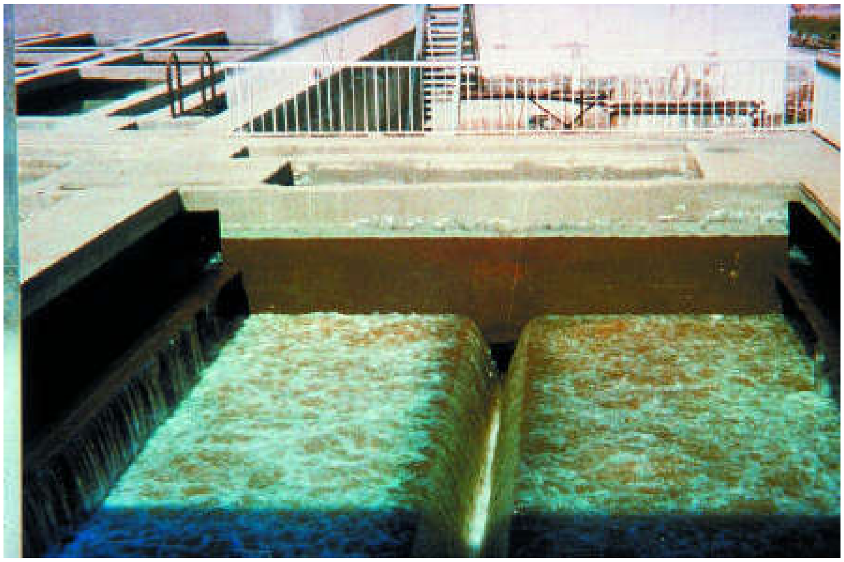


Figure 443. Aquazur filter. Air and water backwash phase.

washing and a depth generally between 0.80 m and 1 m,

- an effective media size between 0.7 and 1.35 mm,
- a shallow water depth above the sand (0.50 m),
- a reduced available head, generally 2 metres, which prevents excessive clogging from causing significant gas release.

Depending on the nature of the water being treated, and its tendency to release gases, the maximum filtration rate can be between 5 and 10 m.h^{-1}.

Aquazur T filters are equipped with type D20 long-stem nozzles screwed into a floor that can consist of:

- slabs of reinforced polyester (figure 444),
- slabs of prefabricated concrete (figure 445), or
- a monolithic slab.

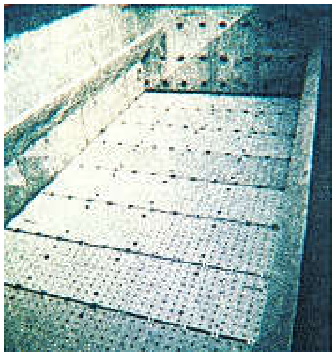


Figure 444. Reinforced polyester plate; its length is the same as the width of the filter cell

The third type is constructed using the precast slab method; it has the advantage of simplified design and absence of joints.

In T filters with a low surface area, air is distributed beneath the floor by a manifold of air pipes (figure 446).

In larger filters, air is distributed by a concrete channel located under one of the wash water drainage troughs (figure 447).

In both cases, this air is distributed equally over the entire surface of the filter due to formation of an air cushion by the long-stem nozzles.

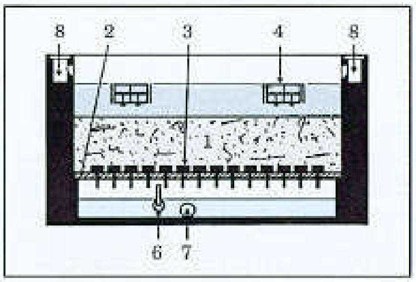
T filters have three main valves, for filtered water, wash water, and air scour.

The raw water inlet is controlled by a clack valve which closes automatically during washing when the water level in the filter rises above the level in the inlet trough (figures 448 and 449).

Wash water is discharged by overflow into the longitudinal troughs.

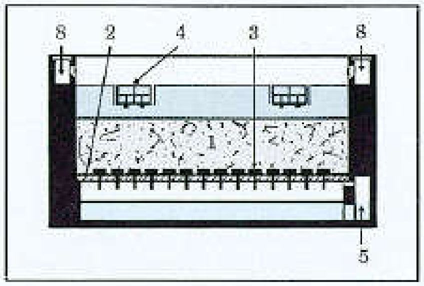
Level control in these filters is pro-

Figure 445. Aquazur V filters under construction: view of the filter floor with the nozzles, the V-shaped sweeping trough, and the wash water discharge trough.



1 – Sand. 2 – Concrete floor. 3 – Nozzles. 4 – Water inlet clack valve. 5 – Air/wash water distribution channel. Filtered water outlet.

Figure 446. Aquazur T filter, with concrete floor and air header.



6 – Air header. 7 – Wash water inlet. Filtered water outlet. 8 – Sludge discharge trough.

Figure 447. Aquazur T filter, with concrete floor and air/water channel.

Figure 448. Water inlet clack valve in open position (filtration)

Figure 449. Water inlet clack valve in closed position (Flier washing)

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vided either by a partialised siphon or by single filters valve.

The shallow water depth above the sand (0.50 m) is an important operating advantage: it allows very rapid rinsing, since the impurities being discharged are not diluted in a large volume of water. This saves both time and wash water. This type of filter is extremely simple to operate, and can be run by non-specialised personnel.

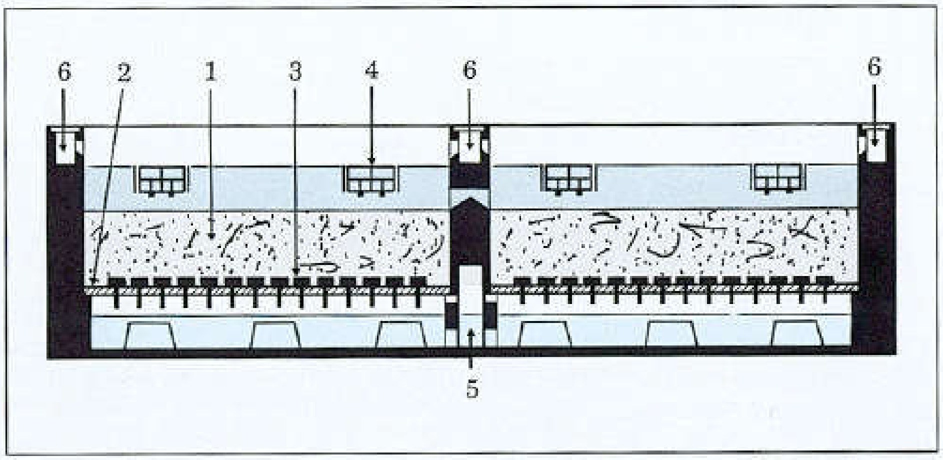
The filters can be arranged either as single filters(including one controller per a filtration element) or as double-cell filters. In the latter case, the two filter elements communicate at the top and bottom, with a single controller (figure 450).

Washing Aquazur T filters

These filters can be washed either manually, semi-automatically, or completely automatically.

The washing cycle is as follows:

-setting up the air cushion,



1 – Sand.
2 – Concrete floor.
3 – Nozzles.
4 – Water inlet flap valve.
5 – Air/wash water distribution channel. Filtered water outlet.
6 – Waste wash water discharge troughs.

Figure 450. Double Aquazur T filter, with concrete floor and air/water channel.

- injecting air and water for a period of 5 to 10 minutes,
- rinsing with a large flow of water until the water discharged to the trough is clear.

The flow rates used are as follows:

-wash water flow rate during air scour ….5 to 7 m^3/h.m^2
-air scour flow rate ………………….. 50 to 60 m^3/h.m^2
-rinse water flow rate ……………………… 20 m^3/h.m^2

The instantaneous power needed during washing (blower and pump) is about 1.5 kW per m^2;washing takes approximately 15 minutes, excluding idle time. Wash water consumption depends essentially on the type of water being treated, and generally varies between 1 and 2% of the volume filtered.

Standard dimensions

-for air header filters:

Width (m)	Surface area (m^2)
2.46	From 6.5 to 25
3.07	From 23.5 to 33.5

- for filters with air and water channels:

Width (m)	Surface area (m^2)
3	from 24.5 to 38.5
3.5	from 28 to 52.5
4	from 46.5 to 70

These dimensions refer to single-cell filters with prefabricated concrete slabs. For double-cell filters, surface areas range between 49 and 140 m^2.

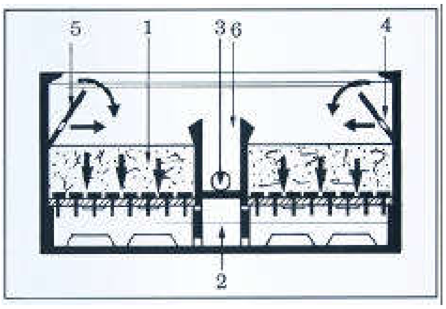
3.1.2. Aquazur V filters

A high filtration rate (between 7 and 20 m.h^{-1}), imposes certain specific technical choices, particularly with regard to:

- selection of the filter media and its depth,
- washing method,
- general hydraulics.

Aquazur V filters (figure 451) are therefore characterised by:

- a great water depth above the filtering layer - at least 1 m and in most cases 1.20 m,
- a single filter media between 0.8 and 1.5 m deep,
- an effective size for the filter media which is generally 0.95 or 1.35 mm (extreme range: 0.7 and 2 mm),
- simultaneous air and water washing, accompanied by surface sweeping with settled water, followed by water rinsing with no expansion of the filter bed, again with surface sweeping. This sweeping operation allows faster drainage of impurities into the waste trough, which reduces washing time.



1 - Sand.

2 - Channel for filtered water, air and wash water.

3 - Wash water drain valve.

4 - Sweeping water inlet orifice.

5 - V-shaped trough.

6 - Wash water outlet trough.

Figure 451. The Aquazur V filter during the filtration phase.

The various types of floors and control systems are the same for the Aquazur V filter as for the Aquazur T filter.

Aquazur V filters can also be arranged as single filters (with one controller per filtration element) or as double filters (two cells communicating at the top and bottom, and a single controller).

Washing Aquazur V filters

Manual, semi-automatic, or automatic washing is carried out according to the following steps (figure 452):

- lowering the water level to the upper edges of the wash water trough (6) by stopping filtration,
- setting up the air cushion,
- injecting air and water along with a sweeping current,
- rinsing with water, maintaining the sweeping current, until the water discharged into the sewer is clear.

The Flow rates used are as follows:

- backwash with filtered water:7 to 15m^3/h.m^2
- air scour: 50 to 60 m^3/h.m^2
- sweeping: about 5 m^3/h.m^2
- rinsing: 15 m^3/h.m^2.

Including valve actuation times, washing takes 10 to 12 minutes and ends with the filter being filled up to its nor-mal filtration level.

Advantages of the Aquazur V filter

This filter combines all the features that ensure good filtration and efficient washing:

-the water being filtered is continually delivered to the filter, completely or partially, for the entire washing period to provide surface sweeping; during this period, the other filters in the battery do not experience sudden increases in flow rate or filtration rate,

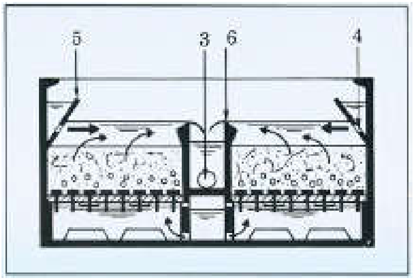


Figure 452. Aquazur V filter. Air/water washing phase with surface sweeping.
3, 4, 5, 6 - See figure 451 opposite.

- it is especially suitable for high filtration rates, for which sand depths of between 1 and 2 m can be used,

-it retains positive pressure over the entire sand depth, and during the entire filtration cycle,

- its washing method, with no expansion, prevents any hydraulic reclassification of the filter bed,

- during washing, the filtered water backflow rate is low, which reduces equipment requirements and energy consumption,

Figure 453. Treatment plant at Pertusillo (Italy). Battery of 14 double Aquazur V filters. Capacity: 16,200 m^3.h^{-1}.

- the washing method, using water backwash during the entire air scour period, is combined with the surface sweeping action. Water loss is the same as with Aquazur T filters,
- filtration is resumed by raising the water level, which produces a gradual restart after washing regardless of the type of control element used. This progressive restart can be extended, if desired, over a period of 15 minutes,
- lastly, the use of constant-flow pump washing eliminates the need for an elevated water tank, with all the drawbacks resulting from such systems.

. **Standard dimensions**

Width (m)	Surface area (m2)
3	from 24.5 to 38.5
3.5	from 28 to 52.5
4	from 46.5 to 70
4.66	from 56 to 79
5	from 70 to 105

These dimensions refer to single-cell filters with prefabricated concrete slabs. For double-cell filters, surface areas range between 45 and 210 m .

3.1.3. FV1 filters

These are (open) gravity vertical metal filters, identical to the Aquazur filters in terms of control system (siphon, butterfly valve) and the water and air wash system.

The depth of the filter media (generally sand) depends essentially on the filtration rate and the solids load that needs to be retained.

The characteristics of these filters (filtration rate, wash water and air flow rates) are identical to those of the Aquazur filter.

3.1.4. Greenleaf filters

The Greenleaf system is used with a battery of gravity filters, washed by water backflow only.

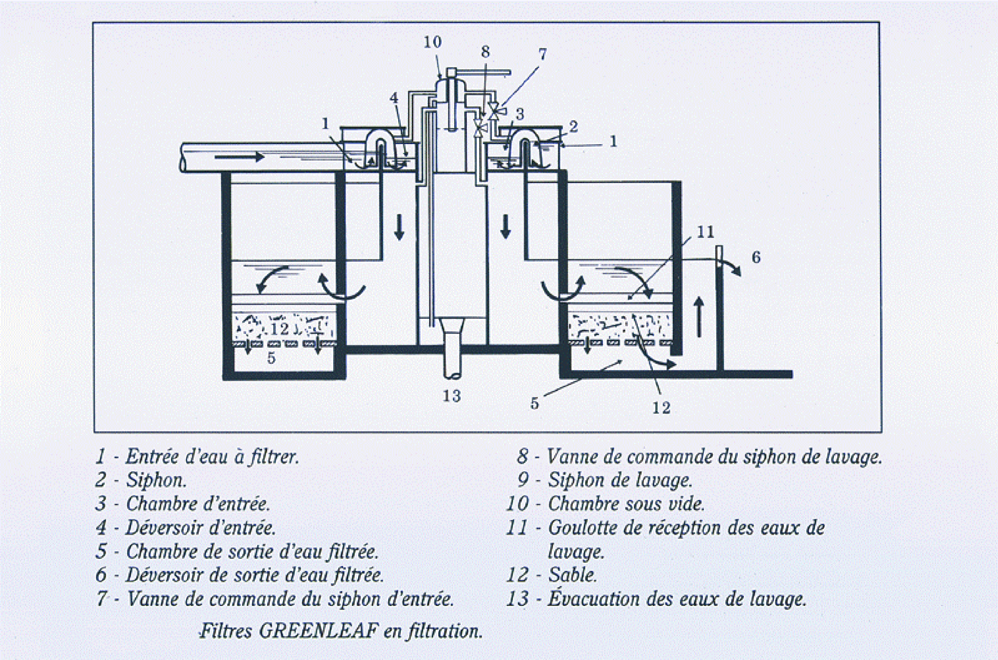
The main element in the Greenleaf system is the central control and distribution unit. This can control four or more filtration cells, which can be circular, square, or rectangular.

Filtration

The water being filtered (figure 454) is brought to the central unit through an annular steel distribution trough (1).

The inlet siphon (2) of each filtration cell brings the water for filtration into the inlet chamber (3) of each cell, which is equipped with a splitting weir (4). These constant-level influent weirs act as flow controllers.

The filtered water is collected in a chamber (5) shared by all the filtration cells, and leaves it over a weir (6) which continually maintains a positive head above the filter media (12).



1 - Raw water.
2 - Siphon.
3 - Inlet chamber.
4 - Inlet weir.
5 - Filtered water outlet chamber.
6 - Filtered water outlet weir.
7 - Inlet siphon control valve.
8 - Washing siphon control valve.
9 - Washing siphon.
10 - Vacuum chamber.
11 - Wash water collection trough.
12 - Sand.
13 - Wash water drain.

Figure 454. Greenleaf filters during filtration.

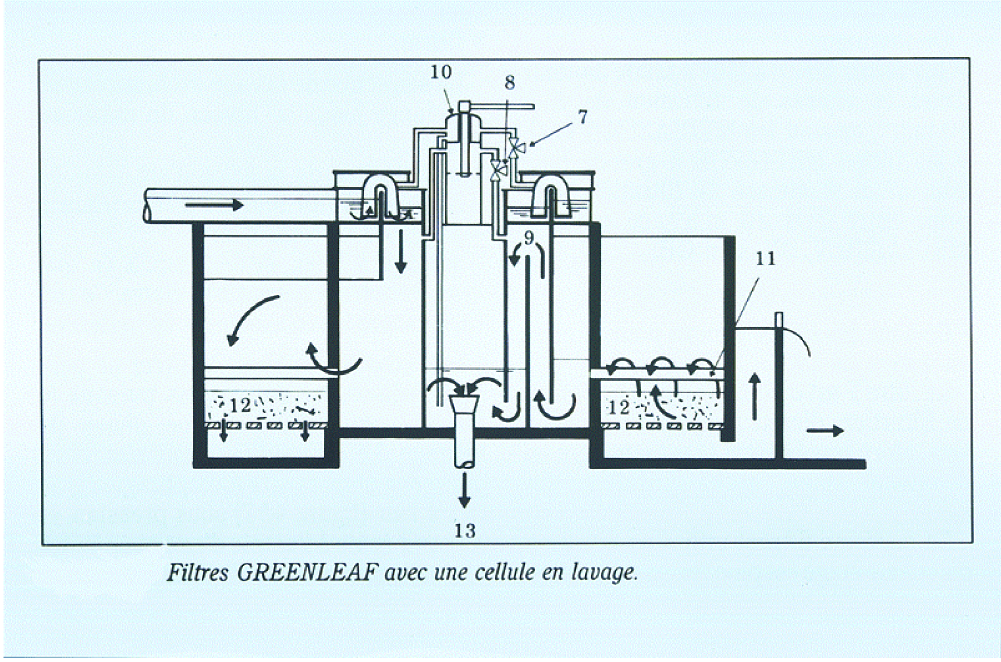


Figure 455. Greenleaf filters with one cell being washed.

Washing

When a cell reaches maximum water level, washing is initiated (figure 455): the inlet siphon (2) for the cell is unprimed by opening the valve (7). The water level then drops down to the weir (6).

The other cells continue to operate.

Closing valve (8) allows the washing siphon (9) to communicate with the vacuum chamber (10). Water then rises in the siphon, from both the wash water discharge tank and the central column of the filter, until priming occurs.

Wash water from the central filtered water reservoir then passes in countercurrent through the filter media, is collected in the trough (11), passes through the siphon (9), and is then discharged through the drain (13).

When the filter media is clean, the siphon (9) is unprimed by opening valve (8). The system is then switched back to filtration mode by closing valve (7) and repriming the inlet siphon (2).

3.2.
FILTERS BACKWASHED SUCCESSIVELY BY AIR AND WATER

These filters are filled with:

- a single layer of lightweight media (anthracite or activated carbon); or
- two layers of different media (e.g., sand-anthracite).

There are two types:

- Mediazur filters with a shallow water media, depth and filtration rates between 5 and 10 m.h^{-1} (Mediazur T and G),
- Mediazur filters with great water depth and filtration rates between 7 and 20 m.h^{-1} (Mediazur V, BV, B and GH).

3.2.1. Mediazur T and G filters

These filters are designed for use with granular activated carbon (GAC).

The T filter is used in the first filtration stage immediately after settling, while the G filter is used in the second stage after sand filtration.

The filter media used for second-stage filtration is finer, with an ES of about 0.55 mm. To prevent this media from being carried over, the wash water must be collected over a considerable length: several transverse troughs are installed in the Mediazur G filter.

These filters are identical in design to Aquazur T filters, differing in terms of washing conditions and raw water admission.

The **washing sequence** is as follows:

- draining down to the level of the filter media
- setting up an air cushion,
- air scour alone (55 to 70 m^3/h.m^2),
- -blowing down the air cushion,
- rinsing with water alone until the water drained to disposal is clear. This rinsing reclassifies the media.

Raw water cannot be admitted through clack valves, since washing begins with a drain down phase. The inlet system comprises an air plug valve that is inflated with pressurised air (figure 457), and a broadcrested weir at the water inlet to prevent any undermining of the filter bed.

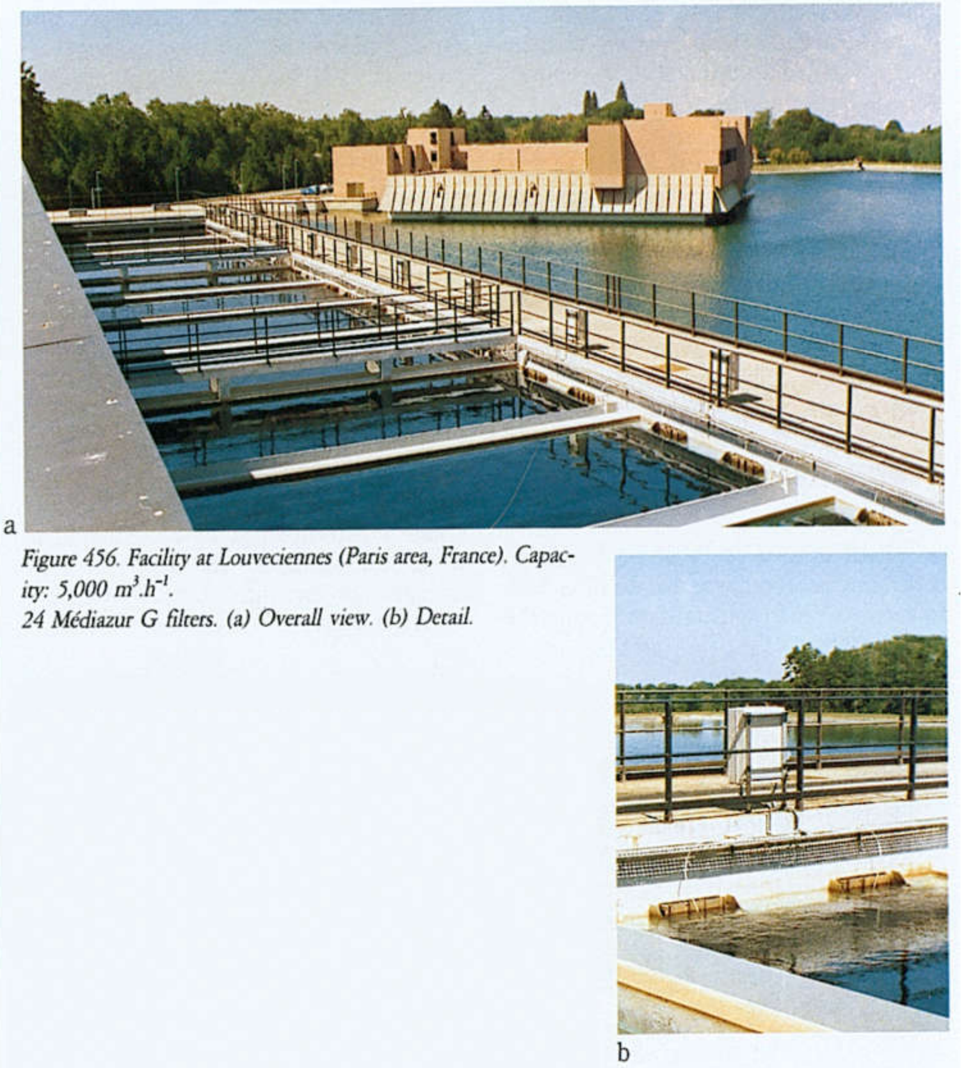
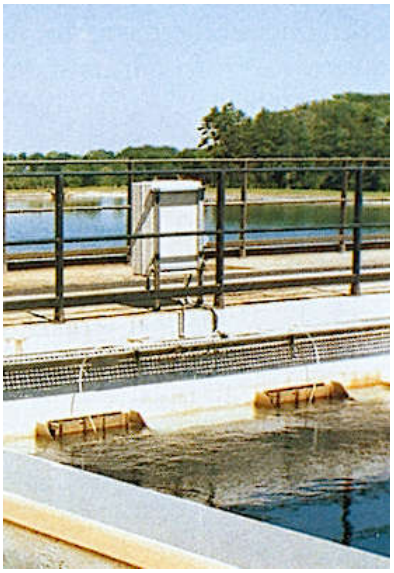


Figure 456. Facility at Louveciennes (Paris area, France). Capacity: 5,000 $m^3.h^{-1}$.
24 Médiazur G filters. (a) Overall view. (b) Detail.

Figure 456. Facility at Louveciennes (Paris area, France). Capacity: 5,000 $m^3.h^{-1}$, 24 MediazurG filters. (a) Overall view. (b) Detail

Figure 457. Inflatable air plug valve.



3.2.2. Mediazur V, BV, B and GH filters

Used with filtration rates of between 7and 20 m.h^{-1}; except for the wash and water inlet method, the design is identical to that of Aquazur V filters

The three types are:

- activated carbon filters used for first-stage filtration (Mediazur V),
- activated carbon filters used for second-stage filtration (Mediazur GH),

- dual-media filters (Mediazur B and BV); Mediazur B is washed without sweeping, Mediazur BV with sweeping.

The following **features** are common to the Mediazur V, BV, B and GH types:

- one or more air plug valves, to completely isolate the flow of raw water during the drainage and air scour phases. In Mediazur BV filters, these air plug valves also partially isolate the feed rate to provide surface sweeping at a restricted velocity,
- an electrode located above the top of the filter bed, to stop drainage of the filter before washing,
- an air scour rate of between 55 and 70 $m^3/h.m^2$,
- a high rate of wash water backflow, depending on the media of the filter bed, to keep its expansion constant during the washing phase.

The Mediazur GH filter is also equipped with multiple transverse troughs.

The **washing sequence** is as follows:

- draining down to the level of the filter layer either by filtration or by dumping to waste,
- setting up the air cushion,
- air scour alone,
- blowing down the air cushion,
- rinsing with water alone, at a high rate, to expand the filter layer, force out impurities dispersed over its entire depth by the air scour process, and reclassify the media.

In Mediazur BV filters, this washing phase is accompanied by readmission of water for filtration through the inlet troughs, to provide surface sweeping which enhances the discharge of impurities

Figure 458. LE-Dumez facility at Moulle (Northern France). Capacity: 2,000 $m^3.h^{-1}$. Battery of seven Mediazur V filters for granular activated carbon filtration.

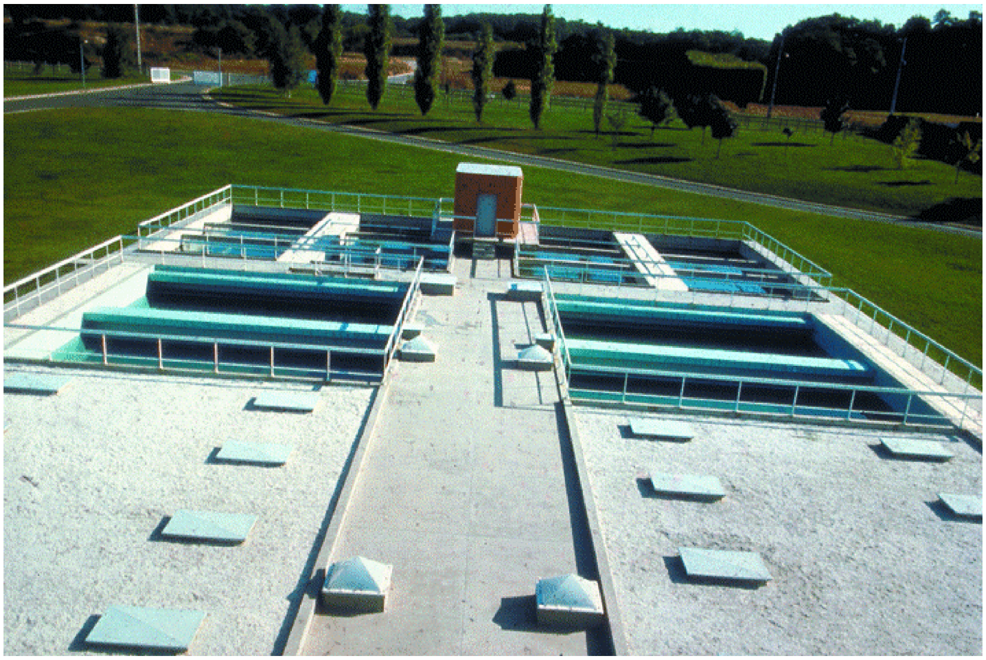


Figure 459. LE-Dumez facility at Morsang-sur-Seine (Paris area, France). Capacity: 3,800 $m^3.h^{-1}$. Phase III extension. 6 covered Médiazur GH filters for granular activated carbon filtration.

4. SPECIAL FILTERS

4.1.
SELF-WASHING VALVELESS FILTERS

These filters operate completely independently and automatically, in both filtration and washing modes. The water for filtration comes from a head tank and, after filtration through a fine grain-size layer, rises back up to the overhead filtered water reservoir. When the reservoir is full, the water exits for use by overflow.

When the filter layer becomes clogged, the level rises in the head tank and in the upstream branch of a siphon. When the maximum head loss is reached, the compressed air contained in the siphon escapes and the siphon is primed. The contents of the filtered water reservoir pass through the filter layer in countercurrent, there by washing it.

This type of filter offers a guarantee that abnormal clogging of the filtration bed will never occur, since washing takes place automatically at a fixed, predetermined head loss value.

These filters are particularly useful where neither compressed air nor electricity are available. They are suitable for water with low to moderate SS levels, in cases where the distribution network will tolerate an interruption during the period when wash water capacity is being re-stored.

Because of the fineness of the sand (NES 0.55 or 0.65 mm) and the shallow depth of the bed, retention capacity is fairly low and filtration rates, which in practice are generally 5 to 7.5 m.h^{-1}, should not exceed 10 m.h^{-1}.

These filters are used:

- for direct filtration with no coagulant or flocculant (except in specific cases), and for water that provokes little clogging (open recirculating cooling systems),
- for filtration of settled water.

They are built for diameters of between 1.6 and 4 m.

Figure 460. Facility at La Casella (Italy) for the Enel-La Casella thermal power plant. Capacity: 300 m^3.h^{-1}.

4.2
THE MEDIAZUR BIFLOW FILTER

4.2.1. Operating principle

The Mediazur biflow filter is a filter specifically designed for use in second stage GAC filtration. It consists (Figure 461) of two filtration cells (1) and (2), housed in the same enclosure (3). Each of these cells has a nozzle floor (4) which supports a layer of activated carbon (AC1 and AC2).

The water to be treated, which has already been clarified and filtered, enters through the pipe (5) equipped with an inlet valve (6); it then flows upward through carbon bed AC1, then passes into cell 2 where it flows downward through carbon bed AC2, then leaves the filter through the filtered water pipe (7), equipped with an outlet valve (8). Located in the centre of the filter is the washing system, comprising a wash water inlet (9) for cell 1, and a wash water and air inlet (10) for cell 2. Cell 2 is equipped with transverse troughs (11) for collecting the wash water, which drains into the main drainage channel (12).

4.2.2. Washing

Cell 1, which operates in upflow, needs only water washing.

The washing sequence is as follows:

- stopping filter operation,
- draining raw water down to the sludge-laden water outlet weir level,
- washing with water in an upflow mode. The flow rate used, which will depend on the type and particle size of the carbon used, must be high enough to produce sufficient expansion and good classification of the adsorbent media.

Cell 2, which operates with downflow, must be washed with air, then water.

The washing sequence is the same as for Mediazur T and G filters.

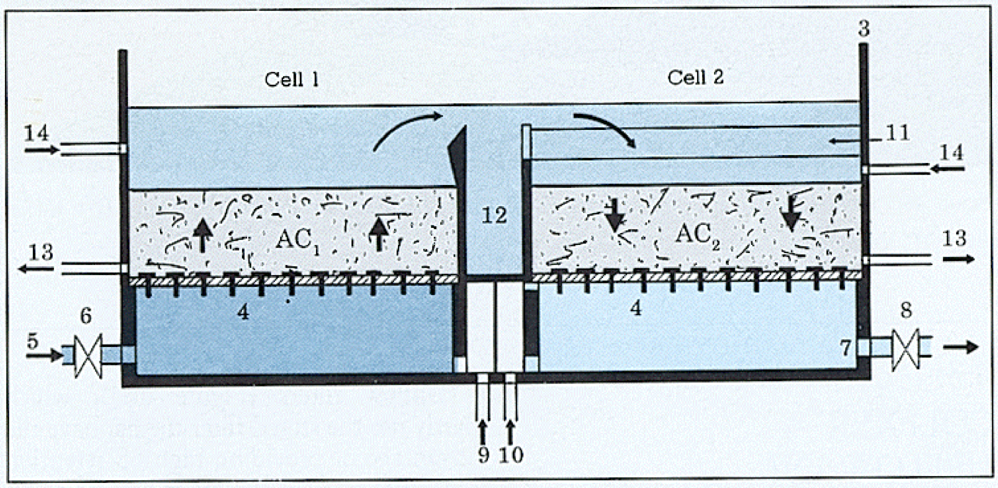


Figure 461. Cross-section of the Médiazur biflow filter.

4.2.3. Operation

When commissioned, cell 1 and cell 2 are filled with activated carbon. When the carbon in cell AC1 is exhausted, it is extracted with a special device (13), and sent for reactivation. Carbon AC is then transferred from cell 2 to cell 1, using the carbon extraction device (13) of cell 2 and the carbon loading device (14) of cell 1. Cell 2 is filled, using its loading device (14), with either new or reactivated carbon.

4.2.4. Advantages

The configuration of this filter, with two cells, allows "countercurrent" contact, which increases the efficiency of the activated carbon: the carbon sent for reactivation is media that is effectively exhausted in terms of the quality of water being treated. In addition, when the filter is used after ozone treatment, residual ozone is destroyed by passing through cell 1; the atmosphere above the filtration cells therefore contains no ozone, and the cover over the filter does not have to be completely sealed.

Figure 462. Mont-Valérien facility (Paris area, France), for CEB. Capacity: 2,000 $m^3.h^{-1}$. Six biflow Média-zur filters using GAC.

Figure 462. Mont-Valerien facility (Paris area, France), for CEB. Capacity 2,000 m3.h-1. Six biflow Mediazur filters using GAC

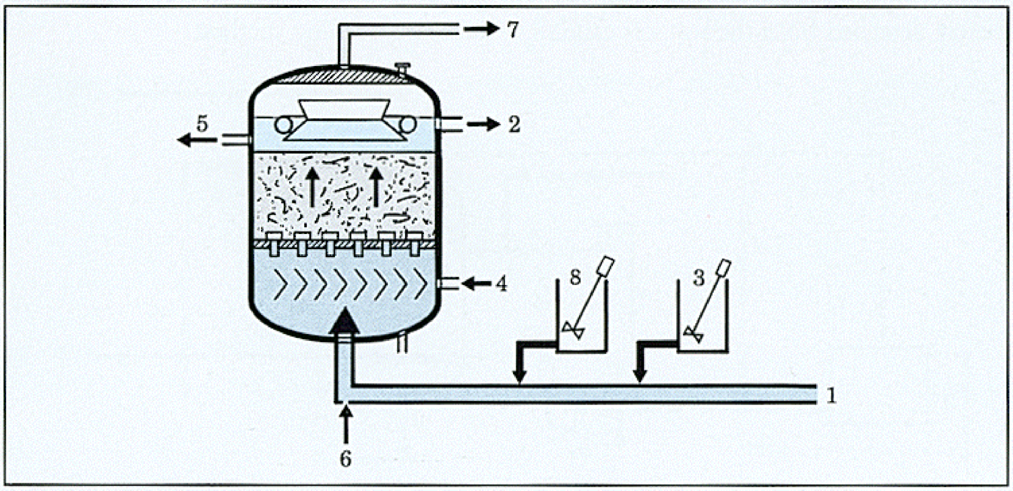
4.3.

COLEXER UPFLOW OIL SEPARATION FILTERS

Upflow filters (Figure 463), which partly use the stored filter media, have the advantage of providing high SS retention capacities but, on the other hand, upflow rates must be low enough to prevent abrupt fluidisation with resulting sludge carry over; in addition, the washing process must provide for sludge removal through all the media. These filters are advantageous in the following applications:

- oil separation for condensates (where the oil coalescence function must take precedence), with continuous oil collection,
- oil separation for "oil-field water" (where the filtration function can be of greater relative importance).

Figure 464. Treating oily condensates. Capacity: 90 m^3.h^{-1}.



1 – Raw water inlet.
2 – Treated water outlet.
3 – Coagulant.
4 – Air scour.
5 – Wash water outlet.
6 – Wash fluids.
7 – Oil recovery.
8 – Polyelectrolyte.

Figure 463. Diagram of the Colexer process.

4.4.
PRECOAT FILTERS - CANNON FILTERS

These units can provide very fine filtration of water with extremely variable SS levels, such as nuclear condensates and yeast suspensions.

They replace candle filters for microfiltration when the water cannot be filtered without a precoat, or when a thick cake forms rapidly and must be discharged with a low quantity of wash water. These installations are therefore characterised by the maximum cake volumes and by the conditions of washing or cake discharge.

4.4.1. Washing

In order for a washing process to be efficient, the retained solids which have attached to the precoat must be completely detached from the support candles.

This can be achieved with hydropneumatic washing. Mechanical cleaning is used especially with filters used for clarification of slurries, in which a dry cake is reused.

A standard hydropneumatic washing sequence operates as follows:

After the filter has been stopped and its upper part is vented to the atmosphere, partial drainage is used to set up an air cushion. The vent valve is closed, and the air cushion is compressed using the pressure from the supply pump. The valve located at the filter base is then opened suddenly; the sudden air release forces the water through the candles from inside to outside, detaching the deposits. The filter is then drained and the candles are rinsed.

4.4.2. Filter design

Filter design is determined by the shape of the support (candles or plates) and the washing method.

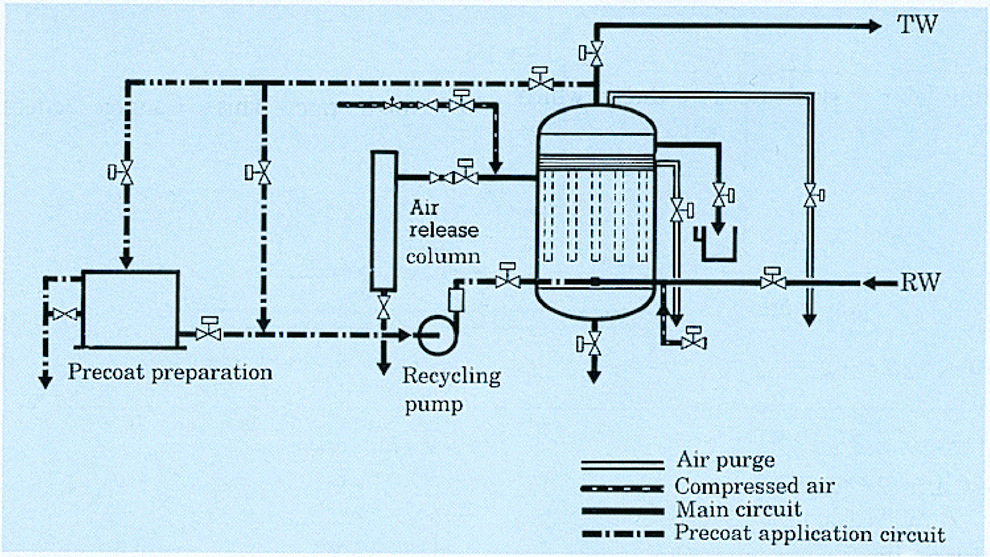


Figure 465. Cannon precoat filter.

Figure 466. Shell Brent facility (North Sea). Flow rare: 1100 $m^3.h^{-1}$. Candle filtration skid.

4.4.2.1. Candle filters

Cannon filters (Figure 465) consist of a sealed cylindrical casing, inside which are located a certain number of vertical candles, fastened onto a support plate. These candles are perforated, hollow stainless steel cylinders, onto which is wound a thin layer of synthetic fibre thread which forms a sleeve: the precoat media is first made into the form of a dilute suspension and then applied onto this sleeve.

These filters have:

- diameters of between 0.8 and 1.8 m,
- a filtration surface area of 15 to 378 m^2 (120 to 624 candles). Filtration rates are between 2 and 15 $m.h^{-1}$, depending on the composition and concentration of the suspension.

. **Cannon washing**

An air cushion is formed in the upper part of the filter; then, once the filter has been isolated, compressed air is injected under the candle support plate. This air forces a certain volume of water through the candles towards the top of the filter, thus pressurising the air cushion at the top. The air located under the plate is then abruptly released by venting it to the atmosphere: water then passes from the inside to the outside of the candles at a very high rate. This "Cannon" effect abruptly and instantaneously detaches all the deposits, which fall to the bottom of the filter. The process ends with a drainage step.

This type of washing makes it possible to use very long candles, eliminates any danger of irreversible clogging, and requires a minimal quantity of water.

Cannon filters can be used with lowsolids water, and generally feature very long cycle times between washes:

- PWR and thermal power plant condensates (various resins),
- deep sea water injection (diatomaceous earth or perlite),

- recovery of oily condensates (diatoma-shaped plates, aimed at producing homoceous earth),
- final clarification prior to reverse osmosis,
- production of ultrapure water.

4.4.2.2. Frame or disc filters

These filters include fixed or rotating discs or frames, placed horizontally or vertically. These elements are in turn covered with a support cloth. There is a wide variety of types, with simple orgeneous distribution of the deposits. However, the backwash methods, whether or not combined with movement of the filtration supports, are not as effective as hydropneumatic washing, which is desirable for high-rate filtration systems.

These filters are therefore used primarily for slow filtration of suspensions, and with very short cycles: hydrometallurgy, pharmaceutical industry, and AFI.

5. CONTROL AND REGULATION OF FILTERS

A battery of filters can consist of any number of filters, to which water must be supplied as evenly as possible; it is especially important to prevent excessive flow to any one filter. This problem requires particular attention when only two or three filters are being used in parallel.

In pressure filter batteries, is generally high and control methods can be simple: an orifice plate and possibly a regulating valve.

Gravity filters can be classified into three major hydraulic operation types:

-constant rate, variable head type,

-constant rate, with a controller,

-variable flow rate (or declining rate).

The total flow rate treated by the filter the inlet assembly must be equal to the flow rate pressure entering the filter battery.

5.1.

CONSTANT RATE, VARIABLE HEAD FILTERS

These filters have a constant flow rate and variable level (Figure 467).

The total flow being filtered is distributed equally at the filter inlet, where water falls from a height that varies depending on the state of clogging. When the filter is clean, the sand is just covered by water, whose level (1) is kept constant by the height of the filtered water outlet weir. At maximum clogging, the level reaches the height of the inlet water level In general, the elevation of this water level is between 1.50 and 2 m, depending

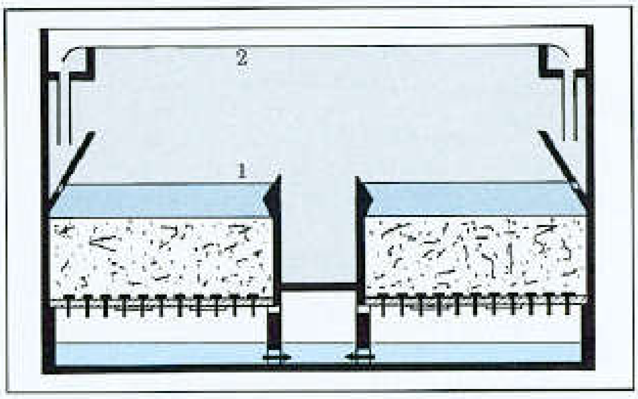


Figure 467. Aquazur V, constant rate, variable head filter

on the particle size of the filter media. which theoretically has no filtering action. This elevation is bwer (0.80 to 1 m) This is the case for Neutralite filters, for when the filter contains, instead of a filter which this variable level operating media, a neutralisation product method is commonly used.

5.2.
CONSTANT RATE, COMPENSATED CLOGGING FILTERS

The water level above the filters is either fixed or changes very little; the filtered water is discharged 2 to 3 m lower down, at a constant flow rate that is equal to the total incoming flow rate divided by the number of filters.

A constant flow rate is maintained, regardless of how clogged the filters are, by a controller located at the outlet of each filter, which acts either as a rate controller or a level controller, and primarily ensures equal distribution. This element creates an auxiliary head loss which is large when the filter is clean and becomes negligible when the filter is completely clogged; the controller compensates for clogging of the filter bed.

5.2.1. Control of a battery of filters

Two types of control are generally used: control with flow measurement; and control to maintain a constant level.

5.2.1.1. Control with flow measurement

Each filter is equipped with a controller located on the filtered water flow rate, the purpose of which is to produce a constant, identical output for all the filters. The filtered water flow rate is measured by a primary negative pressure element (venturi, nozzle pipe, etc.) which sends a signal to the controller, which in turn compares the signal to the current flow rate set point. Depending on the discrepancy, the controller closes or opens the device which controls the rate (butterfly valve, diaphragm valve, siphon) until the measured and set-point values are equal.

This control mode is used both for batteries of pressure filters and for gravity filters.

In the latter case (discussed in more detail below), there is nothing to maintain a certain water level above the filters. An additional controller must therefore be provided to adjust this level depending on the control mode used for the plant as a whole.

. **With upstream control of the overall system** (figure 468), a central element detects the incoming flow rate and adjusts the individual set-point rate of the filters. If the incoming flow rate increases, the level upstream of the filters rises and the central detector increases the set-point rate for the filters until the common upstream level stabilizes, i.e., there is adequacy between the filtered water flow rate and the flow entering the plant.

With this system, the change in water level above the filters can be as much as 30 cm. The flow rate of water for treat-ment can be established either by a program, or on the basis of the level in the filtered water tank.

With downstream control of the overall system (figure 469), a central element detects the level in the filtered water reservoir and adjusts the individual set-point rate of each filter accordingly. Another central controller, located in the filter feed,channel, detects the water level and acts on the actuator controlling the flow rate entering the plant, so as to provide the filters with a flow rate equal to their set-point rate.

The change in water level in the trough and the filters can again be as much as 30 cm.

1 - Pneumatic raw water inlet valve.
2 - Settling tank.
3 - Settled water channel, supplying the filters.
4 - Transmitter to pneumatic controller.
5 - Orifice admitting water to the filter.
6 - Automatic water inlet clack valve.
7 - Filter.
8 - Venturi. 9 - Control valve.
10 - Filter rate controller.
11 - Pneumatic transmitter indicating level in the treated water tank.

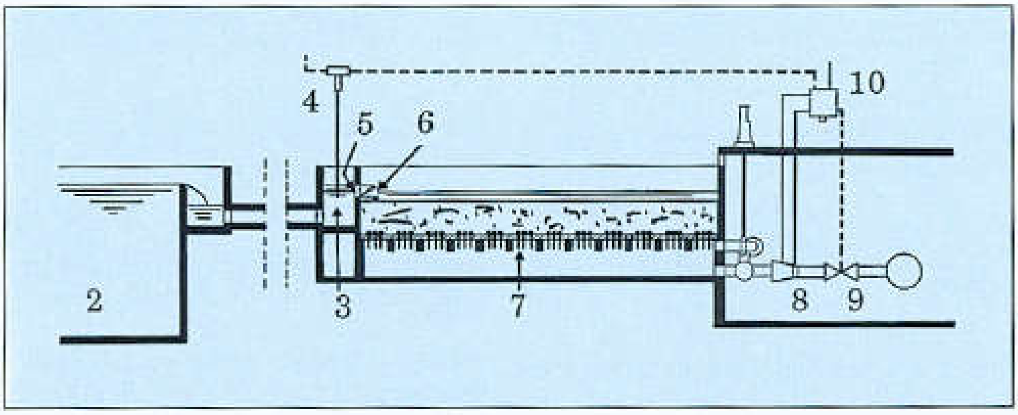


Figure 468. Control with flow measurement. Upstream control.

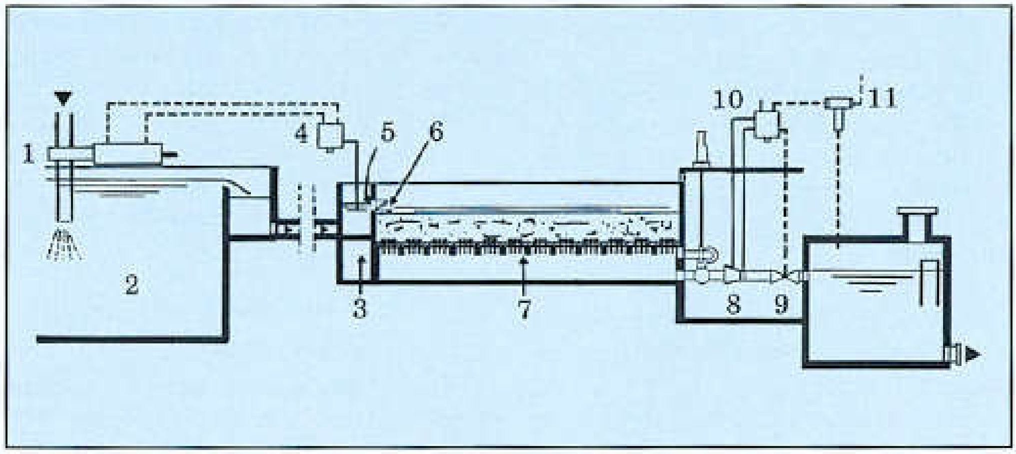
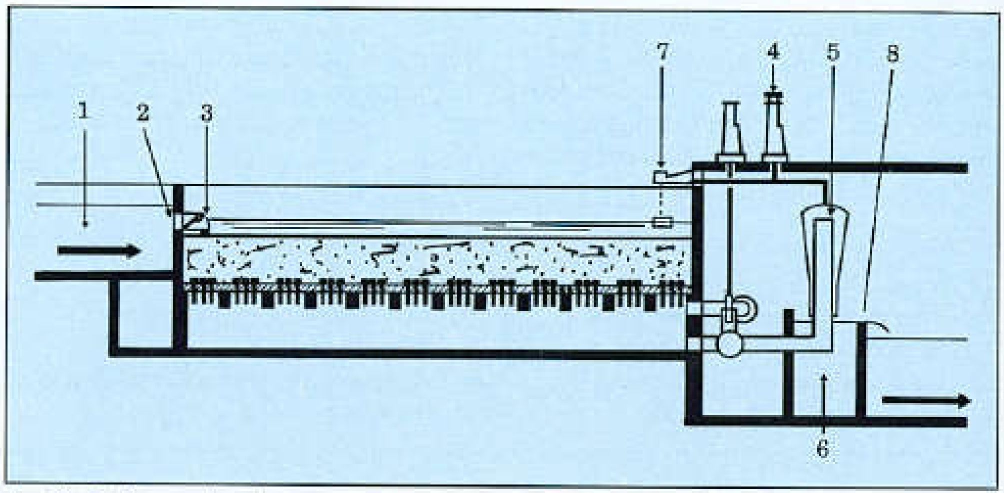


Figure 469. Control with flow measurement. Downstream control.



1 – Clarified water channel.
2 – Orifice plate.
3 – Inlet clack valve for settled water.
4 – Clogging indicator.
5 – Concentric siphon.
6 – Filtered water chamber.
7 – Partialisation box.
8 – Filtered water outlet weir.

Figure 470. Equal distribution and upstream control for Aquazur filters (maintaining a constant level).

5.2.1.2. Control to maintain a constant level

A constant level can be used as a means of producing a constant flow rate from each filter. In this case, the first task is to distribute the total flow equally among the filters, the outlet valves of which are governed by the constant level upstream (or in some cases downstream), which is taken as a reference.

With upstream control (figure 470), the flow rate entering the plant is first distributed equally to the inlet of each filter, which thus receives a flow rate equal to the incoming flow rate divided by the number of filters.

Each filter is equipped with a control element which detects the upstream level, which it keeps constant by acting on the outlet flow controller.

Because the upstream level is kept constant, the outlet flow is equal to the incoming flow and clogging is compensated for until it reaches a maximum level which depends on the available head.

When a filter is shut down, the total incoming flow is automatically distributed over the filters that are still in service (except with surface sweeping filters, where water is continuously supplied to the filter while it is being washed).

With this constant level control mode, equal distribution of the flow is implemented simply and reliably by static devices (orifice plates, weirs, etc.). This eliminates the discrepancies between total filtered flow and incoming flow that can occur with control systems that use flow rate measurements.

5.2.2. Filter controllers

5.2.2.1. Siphon control

The **Degrémont concentric siphon and its partialisation** box (figure 471) can be used as a level control system in which the partialisation box is the detection and control element, and the siphon is the regulating element.

. **Siphon**

The siphon consists of two concentric tubes, in which flow occurs from the internal branch into the external (peripheral) one.

If air is introduced into the upper part of the siphon, this air is carried along by the water into the downstream branch, where the specific gravity of the air/water mixture drops, thus decreasing the vacuum at the neck. With no partialisation air, the vacuum at the neck is equal (disregarding the head loss in the downstream branch) to the head H between the water level in the filter and the water level in the downstream filtered water chamber. With air partialisation, this vacuum is reduced to a height "hi" which is equal to °H" times the specific gravity of the water/air mixture. The difference $H - h_l = h_2$ represents the head loss created by the addition of air (figure 472).

If hl represents the clean filter head loss due to filtration through the bed, the floor, and the filtered water discharge pipe down to the siphon neck, h_2 represents the available clogging head for the filter bed.

When the. filter is clean, one therefore simply introduces enough air to create a head loss h_2 and as the filtration bed becomes dogged, the rate of air is then gradually reduced to zero to bring hl up to **H.**

. Partialisation box (figure 473)

This element (B) introduces air at the top of the siphon to control its flow rate. It can be depicted schematically as a flap valve (C) suspended from a spring (D) attached at a point (F) (figure 472).

As a first approximation, at constant flow, F is fixed. The filter gradually becomes clogged; its output decreases, which causes a decrease in the specific gravity of the water/air mixture and therefore in the vacuum h_l at the neck and in the partialisation box housing. The cross section and therefore the air flow rate are then reduced by the action of the spring; the specific gravity of the water/air mixture increases, producing a height hl which is greater than the height exist-

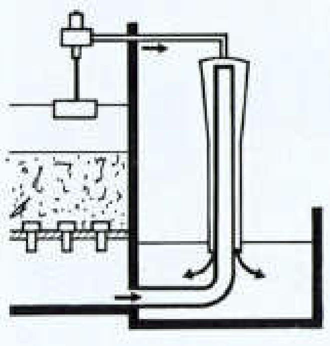


Figure 471

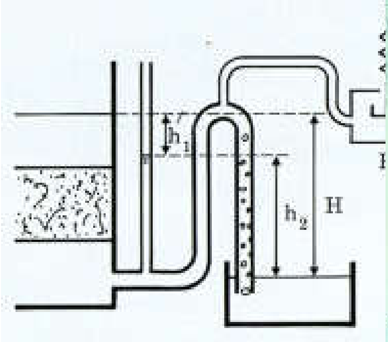


Figure 472.

Figure 473.
Partialisation box

Ing before clogging; the quantity of airintroduced into the siphon decreases.

When the filter is completely clogged, no further air is introduced at all; the filter delivers water at the maximum geometric head H. If it is not washed at this point, its outflow rate will start to decrease.

The partialisation box thus provides automatic clogging compensation. It can also be used to adapt the filter flow rate to the total flow being filtered, simply by linking the height of point F with the box's float level. An increase in flow will correspond to a rise in point F and a decrease in the quantity of air entering the siphon. The head loss h_2 will decrease, causing an increase in the flow rate discharged through the siphon.

Vacuum gauge to indicate head loss

By placing a vacuum gauge at the neck of the siphon, it is possible to measure the vacuum hl which represents the head loss through the filter and its pipework.

Priming the siphon

A simple way of preventing filter re- starts from producing an abrupt increase in flow rate until the water surface (which carries the partialisation box float) reaches its normal level, is to provide for gradual displacement of point F, or for an auxiliary air input which gradually decreases to zero.

When an Aquazur filter with a shallow water level is controlled from upstream, this auxiliary air input is controlled by a clack valve installed on the box.

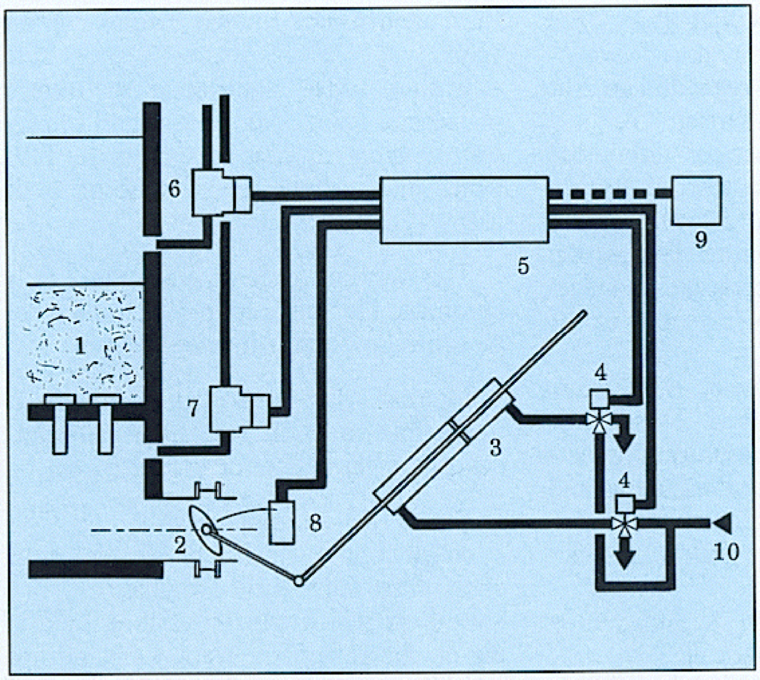
5.2.2.2. Control by valve

The regulated element is a hydraulically or pneumatically actuated valve installed on the filtered water outlet pipe.

Figure 475 shows the operating principle of an electronic control system.

A strain gauge pressure sensor (6) generates an electrical signal proportional to its immersion depth: this signal is compared to a level set-point value which is to be kept constant. Any discrepancy between the measured value and the setpoint value that exceeds the threshold defined for the system is expressed within

Figure 474. Bombay 1 plant (India), Maximum capacity: 87,500 m^3 h^{-1}. Production of drinking water. 72 declining rate Aquazur V filters. Surface area per unit: 151.4 m^2.



1 – Filter bed.
2 – Filtered water outlet valve.
3 – Valve control jack.
4 – Solenoid valve to control jack actuating liquid.
5 – Dégremont controller.
6 – Pressure sensor to measure filter level.
7 – Under-floor pressure sensor.
8 – Potentiometer on valve shaft.
9 – Clogging indicator (optional).
10 – Control fluid supply to jack.

Figure 475. Diagram of the electronic control system for a filter.

the electronic controller (5), after identification of the direction of the discrepancy, by opening of one of the two solenoid valves (4) placed in the line supplying the control jack (3) of the filtered water butterfly valve (2), causing it to open or close until equilibrium has been restored.

A potentiometer (8) coupled to the valve shaft sets up a reset rate reaction in the control loop; this gradually decreases so as to bring the regulated level back to its set-point value without hunting.

This system, which is completely transistorized, includes a number of auxiliary devices to adjust the control band, reaction rate, and amplification gain, and if necessary, to open the system after backwashing for a gradual restart.

Figure 476. Degrémont programmed controller.

5.2.2.3. Programmed controller

The element being regulated is the same as in the previous section.

Progress in microprocessor technology has led to the development of a programmed controller (figure 476). In addition to simple control of filter flow rate, it provides true filter operation management, which can even be extended to the entire battery.

Each filter in the battery is therefore equipped with its own PLC. These PLCs are connected via a communications network which conveys process data and ensures overall operating reliability.

Each unit performs the following functions:

- filter status: off, on, or washing, initiated manually or automatically,
- washing request: by manual initiation or based on predetermined set points (filtration time or head loss),
- constant level control by actuating the pneumatic filtered water outlet valve,
- washing cycle, controlling the filter's pneumatic valves, and pump and blower start or stop commands sent to the PLC which manages the central washing facilities.

This washing cycle can take place fully automatically, be initiated manually, or be controlled manually step by step.

Interlocks are provided to make it impossible to wash two filters simultaneously, regardless of operating mode.

Each PLC is equipped with:

- on-off inputs which indicate the status of the filter valve limit switches,
- outputs which trigger washing by act-ing on the valves, the wash water pumps and blowers, and the control system,
- analogue inputs to measure water level, head loss, and the position of the filtered water outlet valve,

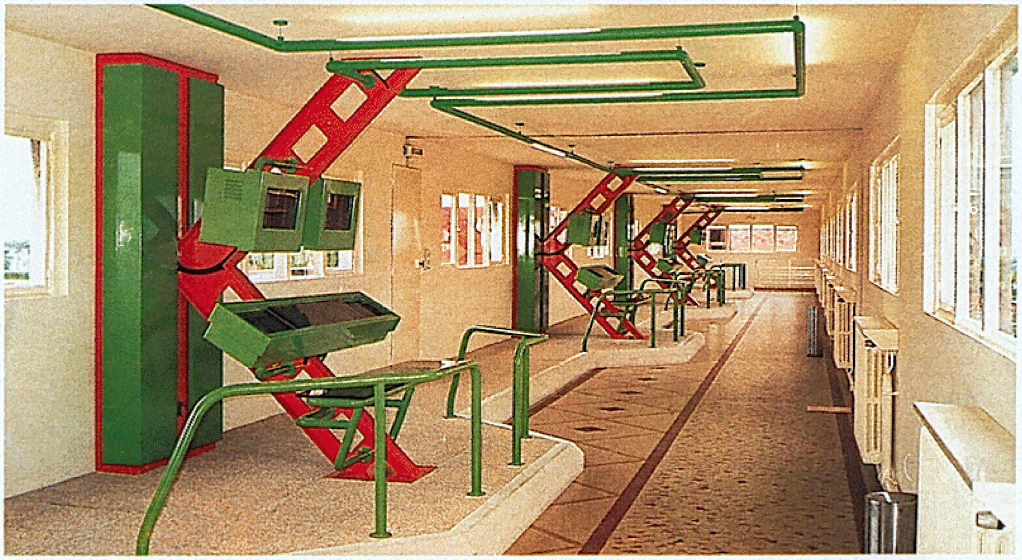


Figure 477. Mont Valérien facility (Paris area, France), for CEB. Clarification of Seine river water. Capacity: 2000 $m^3.h^{-1}$. Filter control gallery for 12 Aquazur filters.

- a microprocessor which manages filter control by opening or closing the filtered water outlet valve as a function of the water level in the filter,
- a microprocessor which manages the washing cycle.

For operator dialogues, each PLC is connected to an intelligent terminal which includes function keys and a character display to store messages.

The battery control installation contains a **common PLC,** equipped with a terminal, which manages the filter washing equipment and the filters themselves, as well as wash water recycling (if used).

All of these PLCs are linked together by a communications network which performs the following principal functions:

- dialogue between the filter PLCs and the common PLC, so that the latter can deal with priority conflicts, decide which filter should be washed or restarted, and manage common washing equipment,
- dialogue among the filter PLCs, to provide interlocks that prevent improper manual operations and to allow washing operations even if the common PLC is shut down,
- dialogue between all the PLCs and the control room, providing plant personnel with remote monitoring capabilities,
- use of a programming console from any of the PLCs, so that adjustment or diagnostic actions can be carried out at any other PLC.

This communications network can be managed by any of the PLCs (called the "master°), in a fashion that is easily understood by the operator.

In addition, this network has a "floating master" feature, meaning that if the master is unavailable (disconnected, shut down, out of service, etc.), the other PLCs that are still operating re-elect a PLC as the master, entirely without human intervention.

This PLC control system ensures consistent filtered water quality by rigorously adhering to the various washing operations. It also relieves personnel work-load

5.3.

DECLINING RATE FILTERS

Some gravity filter batteries can operate in a variable flow mode, with no individual control and no great variation in level (figure 478).

In such cases the filters are supplied with settled water from a single pipe or a single channel, with no head, since there is no need for distribution.

The filtered water flows into individual basins, each of which has a weir (9) that is set so that the filter bed is covered when the filters are shut down or operating at a low flow rate. Each filter outlet is equipped with a filtered water valve (7), open or closed, accompanied by a second valve (8) which creates an auxiliary head loss. The raw water feed (1) is adjusted as a function of the level in the treated water tank (11), by means of a level detector (12) and a main controller (13).

With this type of system, the auxiliary head loss p created by valve (8) is adjusted so that at the maximum flow rate Q treated in the plant:

- the individual flow rate of the filters varies, depending on their degree of clogging, by ± m% of the average flow value Q/N where N is the number of filters in service. The flow rate for a clean filter after washing is therefore (1 + m/100)Q/N’ while the flow rate for a clogged filter before washing is ((1 –m/100)Q/N

Values of m between 20 and 40% are currently used, depending on the particular average rate that has been determined,

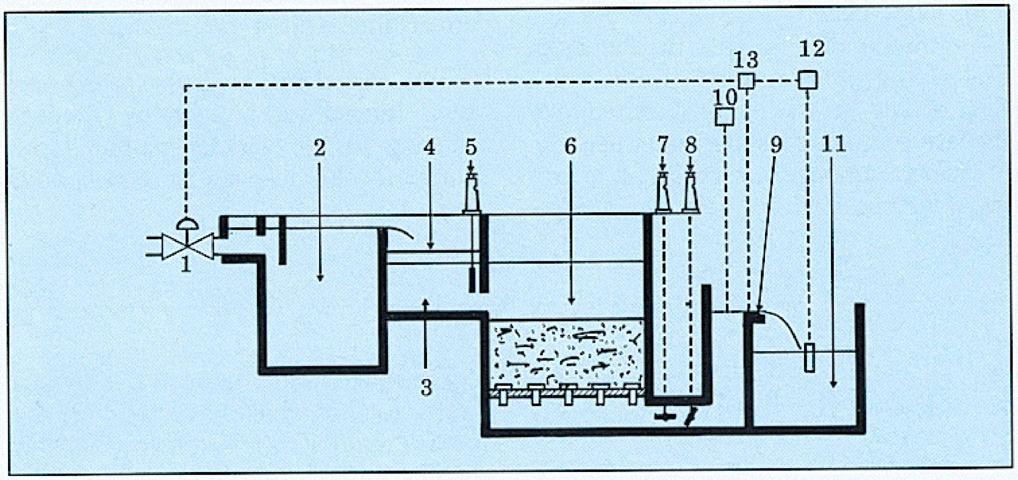
- the head loss due to filter clogging before washing is such that, when brought back to its value for the average filtration rate, it reaches the usual values of 1.75 to 2 m.

These two conditions determine both the auxiliary head loss p and the geometrical head that must be provided on the filters.

In the diagram in figure 478, the raw water flow rate is adjusted on the basis of the level in the tank, resulting in a variable level in the filters. Operation of the declining rate filters requires a knowledge of the individual flow rate of filters, which can be measured, in the same kind of system, by the head over the overflow weir (9).

Characteristics of this type of filter control system include:

- an incoming water inlet valve (5) with a large cross section, to prevent any appreciable head loss,
- a high water depth above the filter bed,



1 – Raw water inlet valve.
2 – Settling tank.
3 – Filter inlet channel.
4 – Overflow weir.
5 – Inlet valve.
6 – Declining rate filter.
7 – Filtered water outlet valve.
8 – Auxiliary head loss regulation valve.
9 – Individual outlet weir for filters.
10 – Individual flowmeter.
11 – Main treated water tank.
12 – Tank level measurement.
13 – Raw water flow controller.

Figure 478. Diagram of a declining rate filter with downstream main control.

- a greater filter height and therefore more extensive civil works than for a filter operating at the same average rate,
- a lower geometric head than with a filter battery operating at a constant rate equal to the average rate of a declining rate filter battery, for the same increase in head loss,
- poorer filtered water quality at the beginning of the cycle due to the high initial rate,
- extended isolation of a filter for washing. The reason is that first a large volume of water above the filter layer must be drained by filtration, then the filter must be washed and progressively brought back on line; these operations can take almost an hour per filter. This means that often two filters must be shut down simultaneously, one being drained and the other under washing, which increases the number of filters per plant compared with a conventional control system,
- relatively easy operation when the overall flow rate and quality of the water being filtered are constant,
- conversely, much more difficult operation when:
  - the overall flow rate being treated in the plant varies; in such cases, each time the overall rate changes, the auxiliary head loss created by valve (8) must also be changed,
  - the quality of the water being filtered suddenly deteriorates; in this case the level in the settled water channel rises rapidly, since the filters cannot be washed fast enough. This leads to the danger of significant losses to the overflow (4) which must be provided upstream from the filters.

Figure 479. Brasilia facility, Brazil. Capacity: 5,000 $m^3.h^{-1}$. Surface water clarification. Siphon gallery.

5.4.

COMPARISON OF THE VARIOUS CONTROL MODES

For a filter to yield the best possible effluent, its instantaneous flow must be as stable as possible, and the changes in its flow must be as slow as possible whenever operating conditions at the plant change.

The best control system will therefore be one with simple, safe and reliable controllers that allow filtration without hunting, and sensors that detect the largest possible water surface areas so that changes in set-point value are slow.

From this point of view upstream control, which refers to the total surface area of the filters, is definitely the method which produces the best results.

Control using programmable logic controllers has a high level of reliability and also integrates backwash control into the system.

5.5.

MONITORING EQUIPMENT

Depending on the type of filters and their control system, it may be useful to know:

- clogging status of the filter bed, by means of a "clogging indicator" which can be either a pressure gauge or a vacuum gauge (in the case of siphon control). This device must be equipped with a remote transmitter when the intention is to combine all signals and, in some cases, records of head loss in a main control room. The device must have an adjustable set point when washing is to be initiated as a function of the degree of clogging of the filter bed;
- opening status of the valves, using limit switches on the filter valves,
- turbidity of the filtered water. This measurement is used to make any necessary corrections to the treatment or the general washing set point, as a result of changes in the characteristics of the raw water. But such measurements are often limited to turbidity at the main filtered water outlet,
- filtered water output of each filter, which is useful for filters operating in flow control mode,
- flow rates of wash water or air; this determination is not always necessary. If a positive displacement blower is used, this ensures the proper air flow rate. As far as water flow measurements are concerned, they are useful only in the case of Mediazur filters, for which it may be necessary to regulate the wash water flow rate needed to expand the filter bed as a function of water temperature.

For Aquazur sand filters, however, in which the main washing action involves simultaneous flow of water and air, selection of the proper type of backwash pump is sufficient. Measurements of the wash water flow rate are still advantageous, however, when the total quantity of wash water consumed for this operation needs to be known.

14

MODERN ION EXCHANGE METHODS

1. COUNTERCURRENT REGENERATION

In conventional cocurrent regeneration methods, the regenerant is not systematically exhausted when brought into contact with layers of decreasingly exhausted ion exchangers. Moreover, ionic contamination of the lower layers by regenerants containing many of the ions to be removed does not provide the high standards of water increasingly required by industry.

Countercurrent regeneration (see page 233) consists in percolating the regenerant solutions against the flow of the liquid being treated. Regeneration takes place either in upflow or downflow, depending on the direction of the percolation flow used during the exhaustion phase.

Upflow usually causes expansion of the resin bed, which presents two major disadvantages:

-disruption of the layers and, consequently, reduction of the exhaustion gradient-and the greater this gradient, the more the ion exchanger is suited to countercurrent regeneration;

-poor distribution of regenerant solutions, resulting from the absence of pressure drop in an expanding granular bed, leading to "channelling" and insufficient contact between the resin and the regenerant.

It is therefore essential to maintain an ion exchange bed fully compacted during the injection of the solution and its displacement by water.

The various "blocking" methods, designed to control resin bed expansion, can be grouped into 3 categories.