Type of Pond or Pond System	Common Name	Identifying Characteristic	Application
Aerobic (0.5–2 ft) (0.2–0.6 m)	High-rate aerobic pond		Nutrient removal, treatment of soluble organic wastes, conversion of wastes.
Aerobic (2–5 ft) (0.6–1.5 m)	Low-rate aerobic pond	Designed to maintain aerobic conditions throughout the liquid depth.	Treatment of soluble organic wastes and secondary effluents.
	Maturation or tertiary pond	Similar to low-rate aerobic ponds but very lightly loaded.	Used for polishing (upgrading) effluents from conventional secondary treatment processes, such as trickling filter or activated sludge.
Aerobic–anaerobic	Facultative pond	Deeper than a high-rate pond. Photosynthesis and surface reaeration provide oxygen for aerobic stabilization in upper layers. Lower layers are facultative. Bottom layer of solids undergoes anaerobic digestion.	Treatment of screened or primary settled effluent and industrial wastes. Secondary effluent polishing
Aerobic–anaerobic	Facultative pond with mechanical surface aeration	As above, but small mechanical aerators are used to provide oxygen for aerobic stabilization.	Treatment of screened or primary settled effluent and industrial wastes. Secondary effluent polishing

TABLE 23.10 Types and Applications of Stabilization Ponds

Stabilization ponds have been used singly or in various combinations to treat both domestic and industrial wastes. Aerobic ponds are used primarily for treatment of soluble organic wastes and effluents from effluent treatment plants. Aerobic–anaerobic ponds (facultative) are the most common type and have been used to treat domestic effluent and a wide variety of industrial wastes. Anaerobic ponds are especially effective in bringing about the rapid stabilization of strong organic wastes. Usually, anaerobic ponds are used in series with aerobic–anaerobic ponds to provide complete treatment.

Rotating Biological Contactors

A RBC, also known as bio-disc, uses a biological slime of microorganisms, which grow on a series of thin discs mounted side-by-side on a shaft (Fig. 23.8).

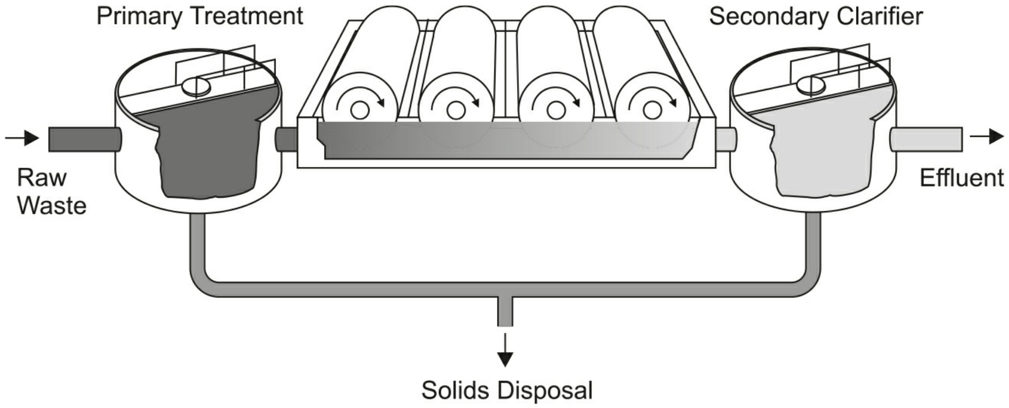


FIGURE 23.8 Schematic of RBC process.

This is considered an attached growth biological process. Discs are rotated slowly and are partially submerged in effluent. Discs are usually made of lightweight plastic. The RBC may be covered to protect the process from low temperatures and to reduce odors. When the process is first started, microbes in the effluent begin to stick to disc surfaces and grow there until all discs are covered with a 1/16 to 1/8 inch (1.6–3.2 mm) layer of biological slime. A thin film of effluent and the organisms on the disc get oxygen from air as the disc rotates. This film of effluent then mixes with the rest of the effluent, adding oxygen to the treated and partially treated effluent. Excess growth of microbes breaks off from the discs and flows to the clarifier to be separated from the effluent. Rotation of the discs provides fresh media surface for buildup of attached microbial growth, brings growth into contact with effluent, and aerates effluent and growths in the effluent reservoir. The attached growth is like the growth in a trickling filter, except that microbes are passed through effluent rather than effluent passing over microbes. The process can achieve secondary effluent quality or better. By placing several sets of discs in series, it is possible to achieve even higher degrees of treatment, including biological conversion of ammonia to nitrate (nitrification).

The RBC system design is based on disc surface area and percent BOD and ammonia removal efficiency. Common loading rates for secondary treatment of municipal effluents are 2 to 4 gpd/ft^2 [0.08–0.16 m^3/(d · m^2)] of effective media area. At temperatures above 59°F (15°C), 90% nitrification can be obtained at loadings of 1.5 gpd/ft^2 [0.06 m^3/(d · m^2)].

Trickling Filters

A trickling filter consists of a bed of coarse material, such as stones, slats, or plastic, over which effluent is discharged from moving spray distributors or fixed nozzles. A secondary clarifier usually follows a trickling filter to reduce effluent suspended solids. Sometimes, trickling or high-rate filters are used as a first stage treatment for high BOD effluents, followed by an activated sludge system. Figure 23.9 shows a trickling filter and its principal components, which include:

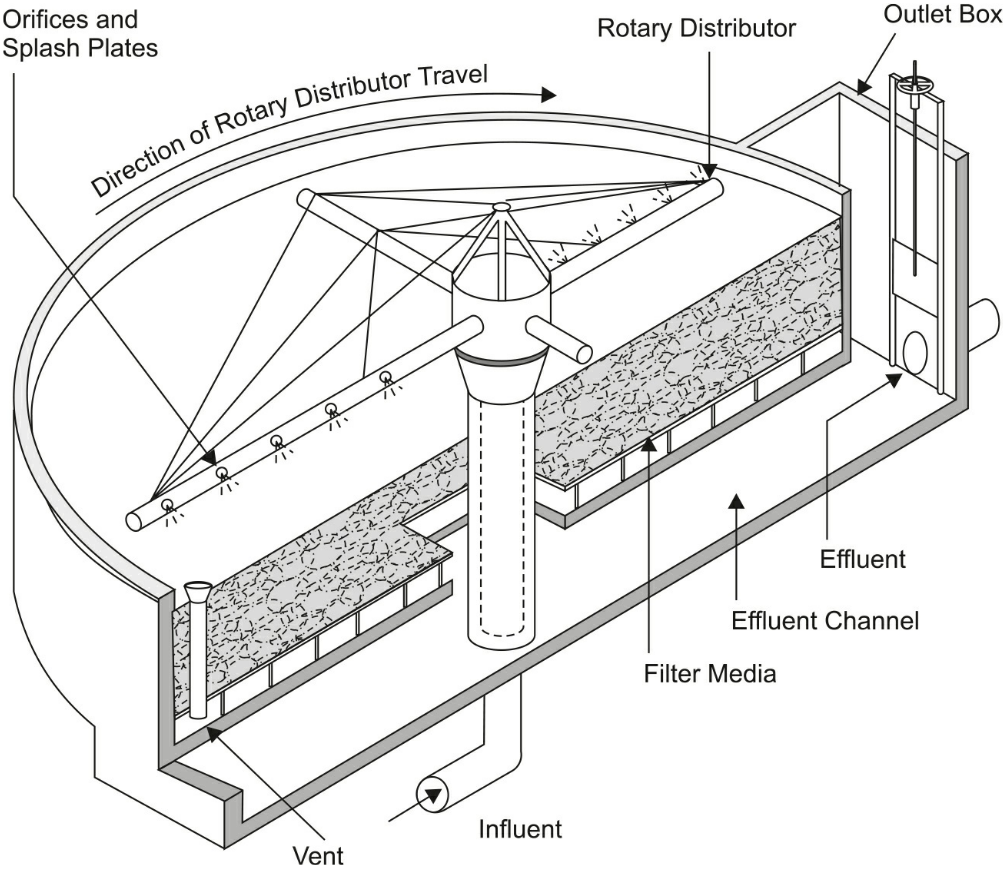


FIGURE 23.9 Trickling filter cross section.

- Distribution system, which applies effluent to filter media
- Filter media, which provides surface area for microorganisms to grow
- Under drain system, which supports the media and provides drainage of waste flow to a collection channel, while permitting air circulation up through the media to supply oxygen to microorganisms

The rotary distributor is used to prevent growth of flies that were common in older designs using pipe headers and nozzles. Distributors are rotated by reaction of the discharge of water through orifices on the distributor arms.

Principles of Operation

Trickling filters are not a filtering or straining process as the name implies. The rocks in a rock filter are 1 to 4 inch (25–102 mm) in diameter, too large to strain solids (Fig. 23.9). Filters provide large amounts of surface area where microorganisms cling and grow in slime on rocks as they feed on organic matter. Excess growths of microorganisms wash from the rock media and would cause high levels of suspended solids in the plant effluent if not removed. Thus, flow from the filter is passed through a secondary clarifier to allow these solids to settle.

There are several ways to prevent biological slimes from drying out and dying when effluent flows are too low to keep the filter wet. One method is to recycle filter effluent. Recirculation reduces odor potential and improves filter efficiency as it provides another opportunity for microbes to consume organics that escaped the first pass through the filter. Another approach to improve performance or handle strong effluents is to use two filters in series, referred to as a two-stage trickling filter system.

Synthetic media for trickling filters have recently become popular. These materials include modules of corrugated plastic sheets, redwood slats, and plastic rings. These media offer larger surface areas for slime growths, typically 27 ft^2 (2.5 m^2) surface area per cubic foot (0.028 m^3) as compared to 12 to 18 ft^2 (1.1–1.7 m^2) per cubic foot (0.028 m^3) for 3 inch (76 mm) rocks, and greatly increase void ratios for increased airflow. The materials are also much lighter than rock (by a factor of about 30), and trickling filters can be much taller without structural problems. While rock in filters is usually not more than 10 ft (3 m) deep, synthetic media depths are often 20 ft (6.1 m) or more, reducing overall space requirements for the trickling portion of the treatment plant. Molded plastic media use pieces of interlocking corrugated sheets of plastic that look like a honeycomb. Sheets are stacked so that they interlock and fit inside the filter structure.

Sludge Reduction Process

Biological effluent treatment processes always result in generation of a considerable amount of excess sludge that has to be wasted. In general, 0.5 to 0.6 lb (kg) dry sludge is produced when 1 lb (kg) BOD is treated. The expense for excess sludge treatment has been estimated at 40 to 60% of the total expense of effluent treatment. Moreover, the conventional disposal method of landfilling may cause secondary pollution problems. In areas where landfilling of sludge is restricted, sludge disintegration methods have an economic benefit and fit in the market. However, in areas where sludge disposal options are still relatively inexpensive, sludge disintegration techniques are not readily employed due to additional costs of equipment and operation.

Overall process efficiency can be measured by the ratio of soluble COD divided by total COD. Another way to measure efficiency is to determine the amount of disintegrated solids divided by total sludge solids. At the time of this writing, there are different methods used for this calculation, and there is no apparent universally accepted method as different authors use different calculations.

Sludge reduction can be achieved by inserting sludge disintegration devices in most biological effluent treatment processes as shown in Fig. 23.10. In this process, some part of return sludge thickened in the clarifier is sent to a sludge disintegrator to solubilize the sludge. Solubilized sludge that contains soluble BOD and cell debris is sent back to the bioreactors, where live microorganisms consume the BOD and cell debris. Since only about 60% of carbon contained in disintegrated sludge is converted to new microorganisms while about 40% turns to carbon dioxide, net sludge reduction can be readily achieved.

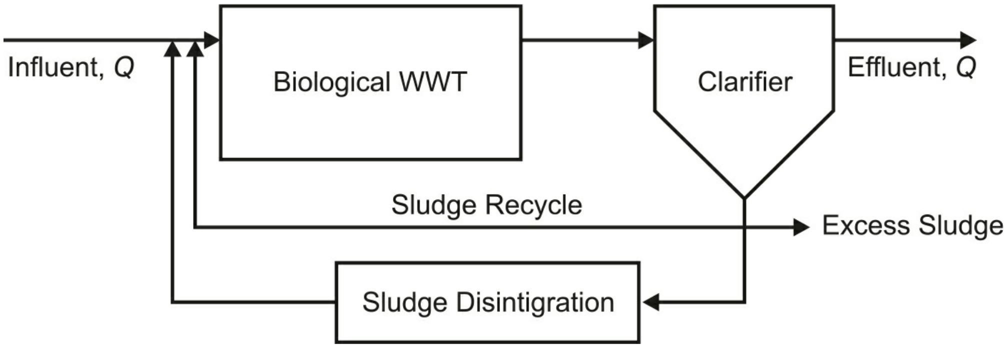


FIGURE 23.10 Schematic of basic concept of sludge reduction process.

In principle, all kinds of chemical, mechanical, and biological methods that kill microorganisms can be used for sludge disintegration. While ozone is most commonly used at a dosage of 0.02 to 0.10 g O_3/g TSS, ball mill, microwave, ultrasound, electrolysis, and alkaline/acid treatments can be also used for sludge disintegration. In some commercial processes, biological methods such as thermophilic reactors and anoxic selectors are used for sludge disintegration. In thermophilic processes, part of return sludge is sent to a high-temperature aerobic reactor that is operated at 140 to 158°F (60–70°C). In this high-temperature condition, the majority of microorganisms contained in return sludge die, and the debris is used to grow thermophilic microorganisms, which die again after recycled to the aeration basin. An identical logic is used for an anoxic selector.

Accumulation of inert materials in sludge can affect overall efficiency significantly. Since about 8% of cell mass is nonbiodegradable in aeration basin conditions, inert material can accumulate, if the sludge disintegrator does not convert it to biodegradable materials. In this case, the portion of biologically active solids in MLVSS increases and the actual F/M ratio goes up. To maintain proper biological activity in sludge, some excess sludge removal is inevitable. However, if the disintegration process is efficient in converting nonbiodegradable materials to biodegradable materials, excess sludge removal can be minimized. In general, chemical sludge disintegration methods have an advantage over mechanical methods in terms of inert material accumulation.

It is known that nitrogen removal is hardly affected by sludge disintegrators, if anoxic reactors are simultaneously used with the aeration basin and disintegrated sludge is supplied to the anoxic tank. It is because the denitrification rate is boosted by additional BOD supplied from the sludge disintegrator. However, phosphorous removal efficiency decreases, since phosphorous removal relies solely on the amount of sludge removal.

Anaerobic Systems

Most of the discussions so far have been about aerobic biological treatment processes. This section addresses anaerobic treatment processes.

Anaerobic Sludge Digestion

Anaerobic digestion is one of the oldest processes used for stabilization and reduction of domestic primary and biological sludges. Typically, it is not used in industrial effluent treatment systems. In the process, organic material in sludge is converted biologically to a variety of end products, including methane (CH_4) and carbon dioxide (CO_2), under anaerobic conditions.

The process is carried out in an airtight reactor with sludge introduced and removed on an intermittent basis. There are two basic types of sludge digestion systems: standard rate and high rate. In the standard rate system, reactor contents are unmixed and unheated. The detention time is 60 to 90 days.

The reactor for the high-rate process is completely mixed and heated to 85 to 100°F (29–38°C), resulting in a typical detention time of 15 days or less.

The most common configuration is the two-stage system, in which the first stage is heated and mixed. The second stage reactor is not mixed or heated and is allowed to stratify to remove concentrated digested sludge, supernatant liquor, and methane gas. Generally, a scum layer develops on the surface of the liquor in domestic systems. The resulting sludge is well stabilized, and total solids are reduced 45 to 50% by weight. Methane produced is used to heat the digester, heat buildings, generate electricity, or drive mechanical equipment such as pumps and blowers.

Anaerobic Treatment

The anaerobic treatment process involves decomposition of organics in effluent to methane and carbon dioxide in the absence of oxygen. Process kinetics and material balances are similar to aerobic systems, but there are certain basic differences that require consideration. Conversion of organics to methane gas yields little energy, so that the rate of cell growth is slow and the quantity of organic growth is low. Thus, the rate of treatment and sludge solids yield are both considerably less than in the activated sludge process.

The anaerobic treatment process is used for treating effluents that have high organic content. Among these industries are meatpacking, breweries, alcohol production, pharmaceutical, various types of food processing, pulp and paper, and oilfield produced water. Influent BOD and COD in some effluents being treated are very high, such as alcohol stillage with 40 g/L BOD and 120 g/L COD. The anaerobic process may be the sole treatment, or it may be ahead of an aerobic treatment system, depending on treated water discharge requirements. Typical organic removals are 75 to 95%, depending on design and application. Table 23.11 illustrates the BOD/COD characteristics from anaerobic treatment of various effluents.

Effluent Source	BOD, mg/L	COD, mg/L
Sugar	50–500	250–1500
Dairy	150–500	250–1200
Maize starch	—	500–1500
Potato	200–300	250–1500
Vegetable	100	700
Wine	3500	—
Pulp	350–900	1400–8000
Fiber board	2500–5500	8800–14 900
Paper mill	100–200	280–300
Landfill leachate	—	500–4000
Brewery	—	200–350
Distillery	—	320–400

TABLE 23.11 BOD and COD in Anaerobic Treatment Effluents

Advantages and disadvantages of the anaerobic treatment process as compared to aerobic systems relate directly to the slow growth rate of organisms in anaerobic systems. Slow growth rates mean that reactor detention times have to be relatively long for high efficiency. Slow growth also means that only a small portion of organic material is synthesized into new cells. This means there is a minimal amount of sludge for disposal. A sufficient amount of nutrients must be present, just as in aerobic systems. The amount of nutrients is substantially less than in aerobic systems due to the low growth rate. Most organics are converted to methane that is a useful, combustible product.

Process

Four groups of microorganisms sequentially degrade organic matter in anaerobic fermentation. Hydrolytic microorganisms degrade polymer-type material such as polysaccharides and proteins to monomers. This reaction results in no COD reduction.

Monomers are then converted into fatty acids by acid-forming bacteria with a small amount of hydrogen (H_2). Principal acids are acetic, propionic, and butyric. In the acidification stage, there is minimal reduction of COD. Should a large amount of H_2 occur some COD reduction occurs? This seldom exceeds 10%.

All acids higher than acetic acid are converted to acetic and H_2 by acetogenic microorganisms. The conversion of propionic acid is:

$$C_3H_6O_2 + 2H_2O \rightarrow C_2H_4O_2 + CO_2 + 3H_2 \tag{23.18}$$

In this reaction, COD reduction does occur in the form of H_2.

Acetic acid and H_2 are converted to methane by methanogenic organisms (methane formers):

Acetic acid:

$$C_2H_4O_2 \rightarrow CO_2 + CH_4 \tag{23.19}$$

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \tag{23.20}$$

Hydrogen:

$$HCO_3^- + 4H_2 \rightarrow CH_4 + OH^- + 2H_2O \tag{23.21}$$

The kinetic relationship commonly employed for anaerobic degradation is the Monod relationship:

$$\mathrm{ds/dt} = K_{\max} SX/(K_S + S) \tag{23.22}$$

where $\mathrm{ds/dt}$ = substrate (COD) utilization rate, mg/(L·d)
$K_{\max}$ = maximum specific substrate utilization rate, g COD/(g VSS·d)
S = effluent COD concentration, mg/L
X = biomass concentration, mg/L
K_S = half saturation concentration, mg/L

One pound (0.45 kg) of COD or ultimate BOD_L removed in the process yields 5.62 ft^3 (0.16 m^3) of methane at standard conditions [32°F (0°C) and one atmosphere] and 6.3 ft^3 (0.18 m^3) at 35°F (1.7°C). Low BOD and COD effluents may not produce enough gas to heat the reactor. Conversely, high strength wastes produce excess gas that is used as a source of energy such as heat and electricity. Coefficients for Eq. (23.22) are shown in Table 23.12.

Temperature, °F (°C)	K_{max}, d^{-1}	K_s, mg/L
95 (35)	6.67	164
77 (25)	4.65	930
68 (20)	3.85	2130

TABLE 23.12 Typical Coefficient Values for Monod Relationship

Actual organic loading to the reactor depends on reactor design and type of waste. Bench and pilot tests have to be conducted, if the supplier of the anaerobic system has not had prior experience on the type of waste. Startup of an anaerobic system can take anywhere from a few months to nine months or more, depending again on the type of organic waste. Seed sludge taken from a similar application reduces startup time.

Membrane Bioreactors

Use of MBR has expanded considerably, from a few systems in the 1980s to several thousand in 2005. In these systems, ultrafiltration (UF) or microfiltration (MF) membranes replace sedimentation basins for separation of biomass from water.

MBR Process

The membrane can be installed in the bioreactor tank or in an external tank, where biomass is continuously separated from water. Since solids–liquid separation is performed by a membrane, lower effluent TSS can be achieved compared to a conventional settling basin. More importantly, MBR decouples the biological process from the process of settling biomass. This allows operation of the biological process at conditions that would be untenable in a conventional system, including high MLSS of 8 to 15 g/L, long SRT, and low hydraulic retention time. In conventional systems, such conditions could lead to sludge bulking and poor settleability.

The MBR process replaces the conventional clarifier with membranes, which can be submerged directly in the aeration basin or reside in an external tank. These microporous membranes have a pore size range between 0.04 and 0.4 μm and allow for almost complete particle separation from mixed liquor.

MBR have the following benefits:

- MLSS can be increased to 8 to 15 g/L (versus 1.5–8 g/L for conventional systems)
- Higher MLSS can reduce HRT
- Lower sludge production
- Lower effluent TSS
- Lower effluent BOD
- Up to 50% footprint reduction
- Higher SRT can produce good nitrification

A conventional system is shown in Fig. 23.11, while the MBR system is shown in Fig. 23.12. Membranes serve as the separation device for solids–liquid separation instead of a clarifier or dissolved air flotation (DAF) unit. Membranes are used in this submerged configuration and operated under vacuum, or they are used external to the aeration basin and operated under pressure. In a submerged MBR (sMBR), a suction pump is used to pull clean water through the membrane, while excluding passage of particles. In an external MBR (eMBR), a recirculating pump is used to deliver mixed liquor under pressure to the membranes and then back to the aeration basin.

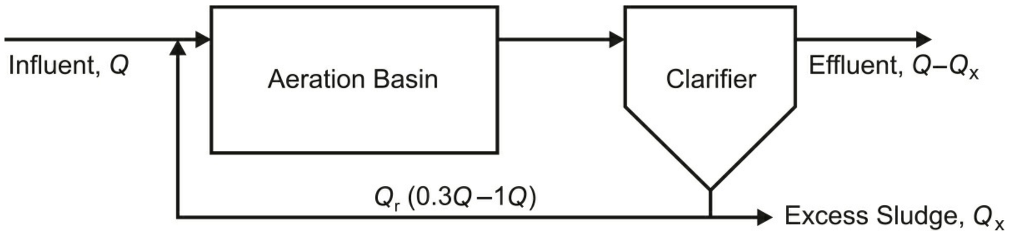


FIGURE 23.11 Conventional activated sludge process.

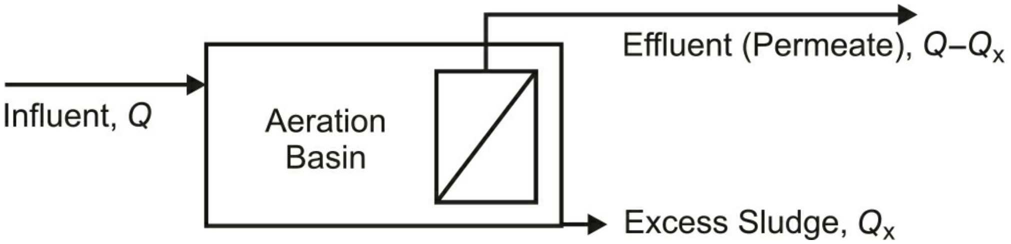


FIGURE 23.12 MBR process.

In sMBR, air bubbles are released directly underneath the membranes, and this provides the shear forces necessary to minimize solid particle build-up on the membrane surface. The main operating variables used to maintain flow across the membrane surface (flux) are the aeration rate and suction pressure, which is the driving force that controls the amount of water transported across the membranes, and is directly related to flux. Cross-flow velocity is the main operating variable that controls flux in eMBR.

In addition, to further maintain flux, both systems depend on intermittent operation. During the off cycle, the membrane surface continues to be scoured by water and air, and solid debris is loosened and removed. In some membrane systems using hollow fibers, a periodic back pulse of permeate is used to help remove accumulated solids. Membranes can be taken out of service and cleaned chemically with sodium hypochlorite, caustic, or organic acids.

Membranes are constructed of polymeric or ceramic materials. The vast majority of membrane systems are made from polymeric materials such as polyvinylidine difluoride, polyethylene, and chlorinated polyethylene. Membrane geometry is usually either hollow fiber or flat sheet (Figs. 23.13 and 23.14).

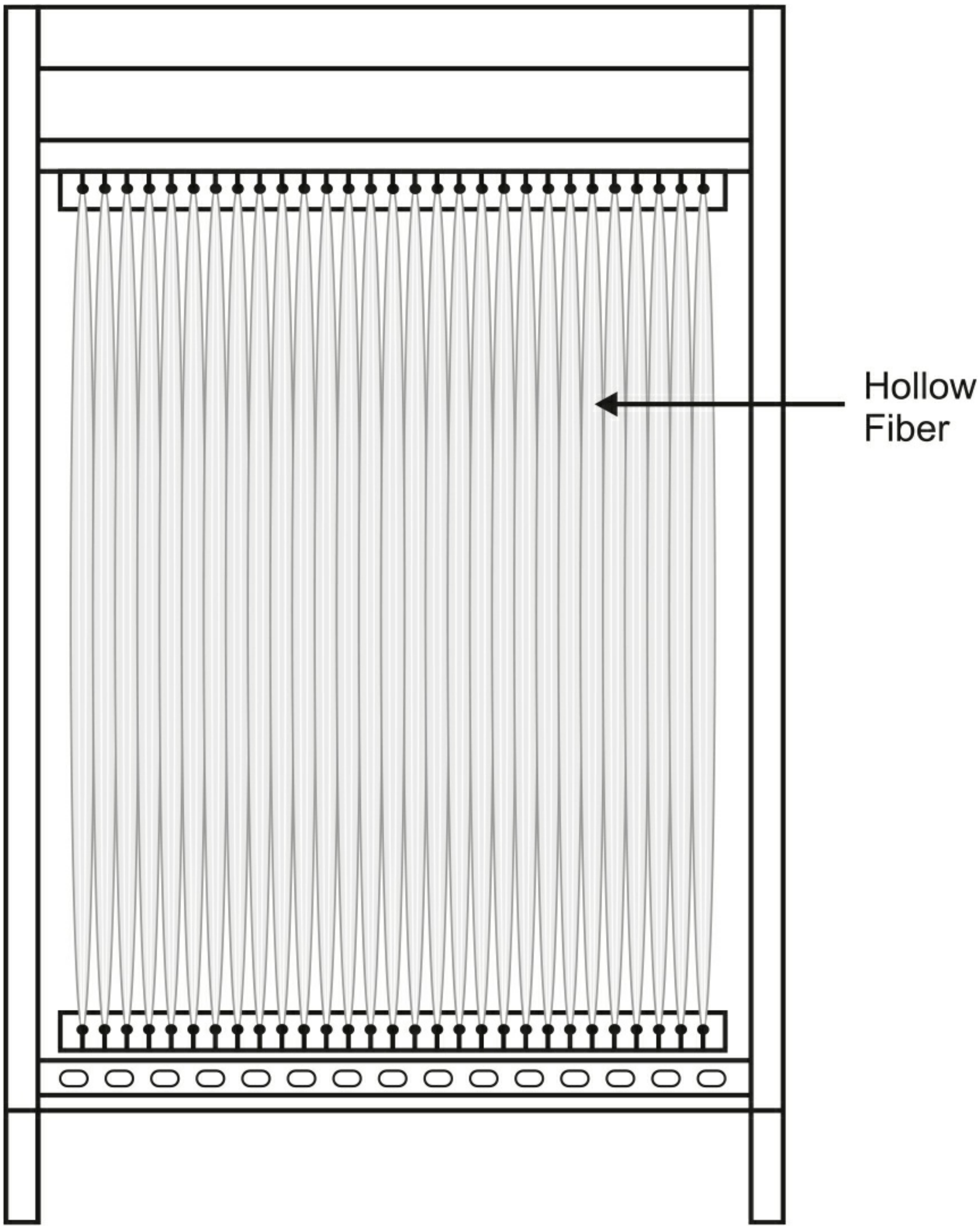


FIGURE 23.13 Hollow fiber MBR membrane configuration.

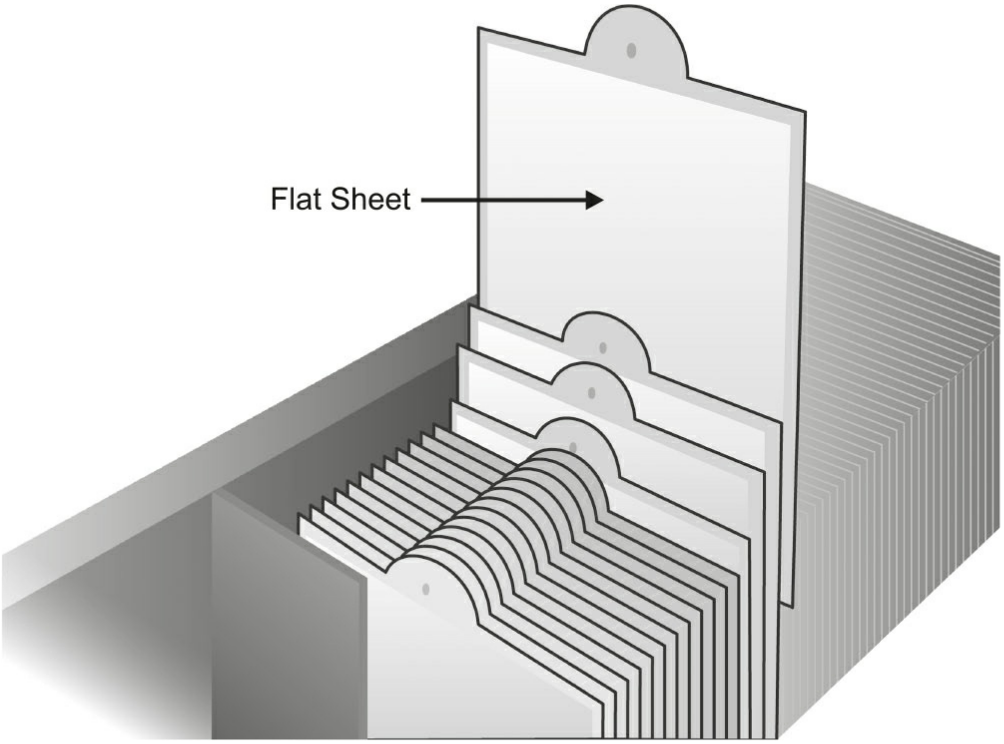


FIGURE 23.14 Flat sheet membrane configurations.

In hollow fiber and flat sheet membranes, water flow is from the outside to the inside. Pore openings can range from the UF to the MF size. Key operational variables are flux, transmembrane pressure (TMP), and membrane aeration rate.

Gross flux is calculated from Eq. (23.23):

$$\text{Flux}_G = F/A \tag{23.23}$$

where Flux_G = gross flux, $\text{gal}/(\text{h}\cdot\text{ft}^2)$ $[\text{L}/(\text{h}\cdot\text{m}^2)]$
F = flow rate, gph (L/h)
A = membrane area, ft^2 (m^2)

The net flux is the gross flux minus the time required for relaxation, during which there is no water flow and is given by Eq. (23.24):

$$\text{Flux}_N = \text{Flux}_G(100 - \text{Relax}\%)/100 \tag{23.24}$$

where Flux_N = net flux, gal/(h · ft^2) [L/(h · m^2)]
Relax% = time required for relaxation, %

MBR Limitations

Use of MBR is growing worldwide at a rate of 25 to 30% per year. Driving this growth rate is the many advantages of MBR over conventional effluent treatment processes. However, membrane fouling is the one problem that is limiting even greater expansion, and is causing many operational issues at existing MBR plants. Various approaches have been tried to reduce membrane fouling, such as intermittent suction, back flushing, module design improvement, and optimization of aeration. Combinations of these methods have reduced costs of MBR significantly, but further improvements are possible.

Membrane fouling is directly related to condition of the biomass. Although MBR do not have to operate under conditions to form settleable floc such as in a waste activated sludge system, certain operating conditions tend to generate more foulants and make membranes more susceptible to fouling and flux loss. Reasons why these foulants form are complex and not completely understood. However, frequent changes in influent feed water quality, lack of equalization, frequent peak flow events, insufficient DO, and poor control of MLSS concentration are contributing factors that tend to generate more foulants and increase membrane fouling. These factors are all interlinked to the operating parameters of the MBR such as HRT, SRT, and percent MLSS. The main objective of any MBR is to obtain long-term sustainable flux and good water quality under normal and peak flow conditions, and to accomplish this at minimum cost.

Microbial Foulants

Soluble microbial products (SMP) are major membrane foulants in the MBR processes. SMP consist of soluble polysaccharides and protein biopolymers that are produced by microbial organisms. This material is released when microbial cells lyse. SMP material along with other submicron particles can deposit on membrane surfaces and restrict flow of water through the membrane. If particles are smaller than the membrane pore size, this material can block the pores and irreversibly foul the membrane surface. Irreversible foulants cannot be removed by the techniques described above, but instead, membranes must be taken off-line and cleaned by submersion and soaking in various cleaning solutions, such as bleach, acids, and caustic. Even this aggressive cleaning sometimes fails to remove foulants. Irreversible fouling is the most significant contributor to reduced membrane life.

SMP material that is larger than the membrane pore size can coat the surface of the membrane and form a gel layer. This layer can actually help prevent particles that are smaller than membrane pores such as viruses from passing through the membrane into the effluent water. However, if this gel layer becomes too thick, there is often increased resistance that reduces membrane flux.

After membranes are cleaned using cleaning methods recommended by the supplier of the membranes, filtration rate and membrane pump pressures are monitored to determine the extent of membrane filtration improvement. The cleaning process should have brought the membrane performance back to design conditions. If not, then significant fouling has occurred, and either additional cleaning or replacement of membranes could be required.

CHAPTER 24

Tertiary Effluent Treatment

The main objective of tertiary effluent treatment is removal of ammonia, phosphorous, and suspended solids, and the purification of secondary effluent to a level sufficient for discharge into the environment. Secondary effluent treatment processes typically remove over 90% of the biochemical oxygen demand (BOD), suspended solids, and a variety of other pollutants. Sometimes, additional removal of excess ammonia, phosphorus, and organics is required to meet discharge permits.

Requirements for water discharge vary by location and by industry. Thus, industry-specific requirements may require special treatments to address specific issues. However, many industries have similar issues with effluent ammonia, phosphate, and solids. For example, excess ammonia nitrogen can cause toxicity issues, while excess phosphate can cause algae blooms in receiving waters. Algae blooms can consume dissolved oxygen in the receiving water and result in fish kills. Excess BOD can cause bacterial blooms as well. Thus, tertiary treatment processes are specifically designed to follow a secondary (biological) waste treatment system, and ensure reduction in ammonia, phosphate, and other pollutants to meet permit requirements, and ensure protection of the environment.

Specific operations and processes applicable to tertiary effluent treatment can be classified as physical or chemical, and the actual treatment is often a combination of both. Selection of a given operation or process depends on end use of treated effluent, nature of the effluent, and suitability of the various operations and processes to achieving the goals.

The most common tertiary effluent treatment goals are as follows:

- Disinfection through chemical or mechanical means
- Dechlorination for water discharge

- Solids removal
- Ammonia reduction
- Phosphate reduction
- Organics removal

Disinfection

Disinfection of effluent can be achieved through chemical and mechanical means. The disinfection process has the goal of killing microorganisms in water to ensure suitability of the water for entry into the environment. The disinfection process not only must provide a sufficient kill of microorganisms but also provide a residual effect to maintain control over the microbial population. A disinfection process should control and prevent pathogenic bacteria from growing and recontaminating the water.

Mechanical or physical disinfection processes include ultraviolet light, radiation, and heat. While these treatments can kill bacteria, none have a residual effect, and the bacteria can recontaminate water after treatment. Thus, mechanical treatment is often followed by chemical treatment that has disinfection persistence in water. The more common chemical treatments include chloramines, bromine, iodine, hydrogen peroxide, chlorination with chlorine gas or bleach (sodium hypochlorite), and in some cases ozone and chlorine dioxide. Use of ozone and chlorine dioxide is less common because as a gas they tend to flash off and do not provide long-term microbial control. Chlorination is the most common disinfection practice due to the extensive knowledge of how it works, industry wide acceptance of the practice, and overall lower cost.

In some special cases, ozone combined with ultraviolet light is used to maintain bacterial control in critical process waters where halogens are undesirable. In these systems, ozone provides bacterial control, and ultraviolet light is used to destroy the ozone before the water is used. While this is not an extremely common effluent treatment practice, ultraviolet light is being used to disinfect effluent, and developments are being made in ultraviolet light technology that may promote further use in the future.

Chlorination

Chlorination is widely practiced in municipal effluent treatment because of regulations requiring disinfection of effluent effluents. Chlorination can be used to disinfect effluent treatment effluents, convert ammonia in the waste flow to other nitrogen compounds, stabilize sludge (chlorine oxidation), and oxidize some heavy metals to an insoluble form. For disinfection, chlorine concentration and contact time dictate the process for achieving acceptable results. The range of typical chlorine dosages for various types of effluents is shown in Table 24.1. Contact time can vary depending on the situation. For example, at least 1 mg/L residual needs to be maintained for at least 15 minutes for disinfecting sand filter effluent. Higher dosage and longer contact time are required for disinfecting raw sewage.

Waste	Chlorine Dosage, mg/L
Raw sewage	6–12
Raw sewage (septic)	12–25
Settled sewage	5–10
Settled sewage (septic)	12–40
Chemical precipitation effluent	3–10
Trickling filter effluent	3–10
Activated sludge effluent	2–8
Sand filter effluent	1–5

TABLE 24.1 Typical Effluent Chlorination Dosage Ranges

Chlorination Processes in Effluent Treatment

In biological treatment processes, chlorination is probably the most widely applied process unit operation encountered involving chemical addition. In the United States, chlorination processes are readily instrumented with dosage dependent on the objective. Facilities required for this process are usually simple. Effluent from a treatment plant flows into a mixing tank and contacts chlorine as a solution or gas. Chlorine reacts with water according to the two-step reaction:

1. Hydrolysis:

$$Cl_2 + H_2O \rightarrow HCl + HOCl \tag{24.1}$$

2. Dissociation:

$$HOCl \rightarrow H^+ + OCl^- \tag{24.2}$$

Generation of hydrogen ions (H^+) can lower the pH of water treated with gaseous chlorine, when water alkalinity is too low to buffer the acidity created. In processes where removal of ammonia is intended (breakpoint chlorination), the dosage of gaseous chlorine is usually high enough to require some form of caustic addition.

Dechlorination

Dechlorination of chlorinated effluent is required in many places to protect aquatic biota in the receiving stream. Dechlorination is a very fast reaction and easily accomplished using:

- Activated carbon
- Sodium metabisulfite ($Na_2S_2O_5$)
- Sodium thiosulfate (hyposulfite) ($Na_2S_2O_3$)
- Sulfur dioxide (SO_2)
- Sodium sulfite (Na_2SO_3)

Sulfite (SO_3^{-2}), from either gaseous SO_2, or solid or liquid sodium salts (sulfite, metabisulfite, or thiosulfate), is the most common reducing agent for dechlorination of effluent plant effluents. These reducing agents also work for destroying other oxidizers such as peroxide. Design of gaseous SO_2 equipment and facilities is essentially the same as that of gaseous chlorine facilities, the exception being that special attention must be given to the SO_2 supply system, because of its low vapor pressure. As with all chemical additions, complete mixing with the effluent before discharge must be assured.

Disinfection By-products

Disinfection by-products are formed from the reaction of an oxidant such as chlorine with organic matter in water. Identification of these compounds is very difficult because of the wide variety of naturally occurring organics and extremely low concentration at which they are present. Several chlorinated organics have been identified because of chlorinating water: chloroform and trihalomethanes. Formation of these chlorinated organics appears to be related to the type of disinfectant chemical used, dosage, and reaction time. Chlorinated by-products may be formed directly or because of the breakdown of other disinfection by-products. Control of chloroform and trihalomethanes can be accomplished by controlling the type of disinfectant chemical used, dosage, and reaction conditions. Often, chlorinated organics do not pose an issue with effluent discharge due to very low concentrations. However, if effluent is to be reused or recycled, there may be a concern depending on the end use of the water.

Solids Removal

Excess suspended solids can require additional treatment by settling and filtration. These processes are the same as those used for primary and secondary effluent treatment. See Chap. 6 for detailed descriptions of clarification and filtration processes.

Ammonia Reduction

Nitrogen in its many forms has long played a fundamental role in the aquatic environment. In certain forms, ammonia nitrogen is one of the major nutrients supporting blooms of green and blue-green algae in surface waters. Ammonia not only has microorganism nutrient value, but can represent as much as 70% of the total oxygen demand of conventionally treated municipal effluent.

During conventional biological effluent treatment, almost all nitrogen contained in effluent is converted into ammonia nitrogen. Although ammonia has very little toxicity to humans, treated effluent containing ammonia has several undesirable features:

- Ammonia consumes dissolved oxygen in the receiving water.
- Ammonia can be toxic to fish life.
- Ammonia increases the amount of chlorine required for disinfection.

Ammonia nitrogen levels can be reduced or removed from effluent by either biological or physical–chemical methods. Biological treatment processes are discussed in Chap. 23. The physical–chemical category can be further divided into: ammonia stripping, selective ion exchange, and breakpoint chlorination.

Ammonia Stripping

Alkaline effluent can be pumped to the top of a cooling tower and distributed over the fill. Air is drawn through media to extract ammonia from water droplets. The simplicity of the process makes it the least expensive method of removing ammonia; however, ammonia is simply transferred to air, where there could be issues with air quality. During warm weather, air stripping can achieve 95% removal of ammonia at pH 11.5 by using 400 ft^3 of air per gallon of effluent (3 m^3 of air per liter of effluent). Cold weather adversely affects performance, and prolonged periods of freezing weather render the process inefficient and often inoperable.

Scale formation is a serious operating problem in full-scale ammonia stripping towers. If soft scale formation is anticipated, a water spray system can be installed to keep soft scale from accumulating. If scaling results in hard deposits, spraying is not likely to eliminate the problem. Scale inhibitors and threshold treatments can be effective in preventing hard scale formation.

Selective Ion Exchange

In this process, ammonium ions in solution are exchanged for sodium or calcium ions displaced from an insoluble exchange material. The process operation resembles that of a water softener, except that the material being removed is ammonium ion rather than water hardness. Both are ion exchange processes.

The selective ion exchange process derives its name from use of ion exchange material that selectively removes ammonia. The process is very efficient and can remove 95 to 97% of the ammonia. However, it is not particularly effective at removing other forms of nitrogen that might be present. Regeneration waste contains ammonia and needs to be handled further before disposal.

Breakpoint Chlorination

In this process, chlorine is added to effluent to satisfy the chlorine demand, so that further addition of chlorine results in directly proportional chlorine residual. Breakpoint chlorination is used for ammonia removal because chlorine, when added to effluent containing ammonia, reacts to form compounds that are oxidized to nitrogen gas. To achieve conversion, about 10 mg/L of chlorine must be added per mg/L of ammonia. Actual dosages are higher due to other compounds in water, which consume some of the chlorine. The overall reaction is:

$$3Cl_2 + 2NH_3 \rightarrow N_2 + 6HCl \tag{24.3}$$

A typical secondary effluent ammonia concentration of 20 mg/L requires about 1700 pounds of chlorine per million gallons treated (200 kg/1000 m^3)—about 40 to 50 times more than normally used in an effluent plant for disinfection only. Reducing organics and solids in effluent reduces the amount of chlorine needed to reach breakpoint. The breakpoint process can result in over 99% removal of ammonia, reducing concentrations to less than 0.1 mg/L (as N). Breakpoint chlorination is typically a very expensive method of ammonia removal, and for this reason, biological treatment processes are typically used instead.

Phosphate Removal

Phosphate is required in secondary effluent treatment plants to maintain healthy biomass for efficient BOD reduction. Typically, 0.5 mg/L phosphate residual in the aeration basin effluent is required to ensure biomass health. Although this level is sufficiently low for most surface water discharge requirements, there is a general trend in regulations to require lower levels. Thus, tertiary treatment for phosphate removal involves precipitation of orthophosphate with metallic ions such as aluminum, iron, and calcium. Polyphosphates and organic phosphates do not readily react with metallic ions, and are removed only after conversion to orthophosphate by biological treatment and hydrolysis, followed then by chemical precipitation. However, small amounts of polyphosphates and organic phosphates may be removed through absorption on floc solids formed by precipitation products of metal ions.

Aluminum Treatment

Aluminum compounds for phosphate precipitation include alum, sodium aluminate, and the various polyaluminum chloride (sulfate) products available in the marketplace. Aluminum ions combine with orthophosphate ions to form aluminum phosphate, which precipitates as follows:

$$Al^{+3} + PO_4^{-3} \rightarrow AlPO_4 \qquad (24.4)$$

The solubility of aluminum phosphate compounds is shown as a function of pH in Fig. 24.1. This solubility curve applies to the use of aluminum sulfate (alum) as well as sodium aluminate.

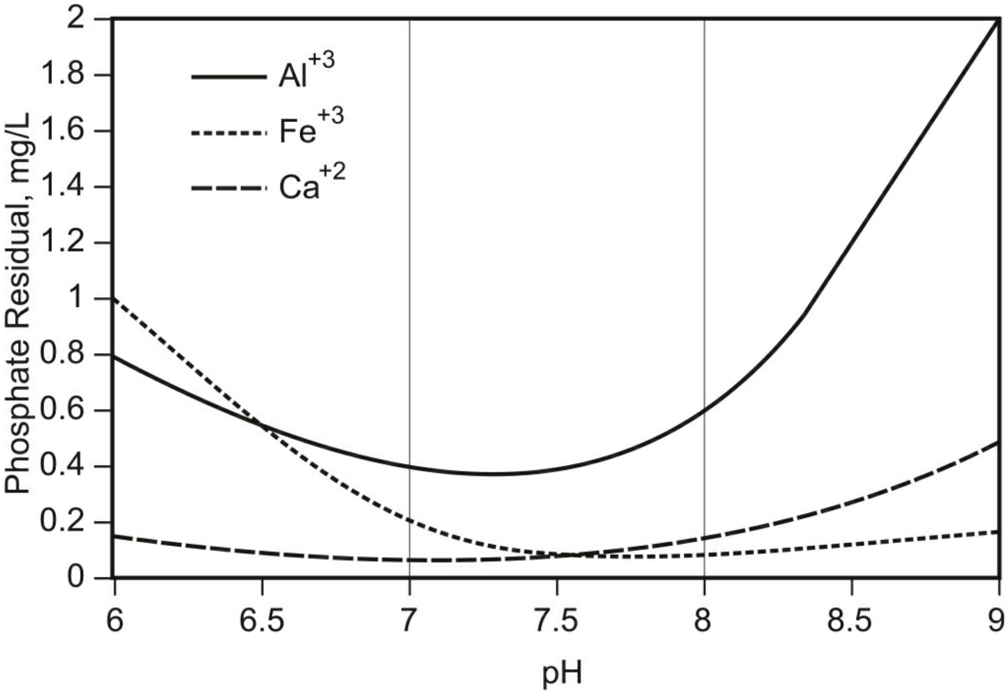


FIGURE 24.1 Solubility of metal phosphates versus pH.

Main factors that affect the actual quantity of alum required to attain a specific orthophosphate concentration include, alkalinity and final pH of effluent. In addition, ionic constituents such as sulfate, fluoride, and sodium, quantity and nature of suspended solids, microorganisms, intensity of mixing, and other physical conditions in the treatment facility may affect overall efficiency of phosphate removal. Optimum pH for precipitation of metal phosphate using alum ranges from 5.5 to 6.5, with 6.0 being best. When running tests or in the full-scale application, it is best to adjust water pH to a value where once the chemical treatment is added, final pH is as close to 6.0 as possible. This reduces formation of aluminum hydroxide and maximizes aluminum phosphate formation and precipitation.

Iron Treatment

Both ferrous (Fe^{+2}) and ferric (Fe^{+3}) ions can be used in precipitation of orthophosphate. Common sources of iron are ferric chloride ($FeCl_3$), ferrous chloride ($FeCl_2$), ferric sulfate [$Fe_2(SO_4)_3$], ferrous sulfate ($FeSO_4$), and pickle liquors (a waste product from metal finishing mills). Ferric is typically most effective in removing orthophosphate when the pH ranges from 4.5 to 6, while ferrous is typically more effective in a pH range of 7 to 8. When testing or in the actual application, it is best to adjust the water pH to a point where once treatment chemical is added, the desired final pH is obtained. This helps maximize precipitation of ferric phosphate and minimize formation of ferric hydroxide.

Iron precipitates phosphate as follows:

$$Fe^{+3} + PO_4^{-3} \rightarrow FePO_4 \tag{24.5}$$

$$3Fe^{+2} + 2PO_4^{-3} \rightarrow Fe_3(PO_4)_2 \tag{24.6}$$

Calcium Treatment

Calcium ions react with orthophosphate ions in the presence of hydroxyl ions to form hydroxyapatite, a form of calcium phosphate. Calculating an approximate dosage for phosphorus removal is possible using mass balance, as was done for alum. However, it is generally not necessary because lime dose is largely determined by alkalinity reactions, similar to those in lime softening that take place when pH is increased.

Reaction of lime with phosphate is pH dependent, and the largest fraction of phosphate can be removed where solubility of hydroxyapatite is lowest (pH about 7). In lime treatment of effluent, operating pH is often determined by the pH required to obtain good suspended solids removal, and as long as the pH does not exceed 9.0, good phosphate removal generally follows.

The total amount of lime sludge generated is more than 2.25 times the amount when sodium aluminate is used for phosphate removal.

Organics Removal

The principal uses of activated carbon as a tertiary treatment process are removal of objectionable organics from effluent and removal of chlorine residual. Both granular activated carbon (GAC) and powdered activated carbon (PAC) can be used. Activated carbon removes organics that are not degraded in conventional biological treatment systems. These refractory organics can be herbicides, lignins, tannins, ethers, or other such compounds. Partitioning of these organics between the water and activated carbon is based on their water solubility. Very soluble organics such as methanol are not removed by activated carbon. In addition, insoluble organics that are in water as an emulsion are difficult to remove.

There are currently two approaches for the use of activated carbon in effluent treatment. One approach is to use GAC in a tertiary treatment sequence following conventional primary and biological secondary treatment. This involves treating secondary effluent by contacting with GAC in fixed beds (columns). Adsorption of residual organics and further BOD and chemical oxygen demand (COD) removal takes place. GAC may be regenerated off site with a loss of about 5% per cycle. Regenerated GAC usually costs about half as much as virgin GAC, and is more generally used in effluent treatment.

The second approach utilizes PAC in a physical–chemical treatment (PCT) process, in which PAC is added directly to the secondary clarifier or biological treatment unit. Although exact mechanisms are not fully understood, bench tests and pilot studies have shown that PAC has positive effects in biological systems. By adsorbing toxic substances and by concentrating feeding sites for bacteria, activated sludge solids retention times tend to increase, thereby effectively reducing treatment costs and counterbalancing the otherwise increased cost for PAC. Regeneration of the dewatered PAC-biosolids mixture is not economically justifiable, and it is typically disposed of by landfilling or incineration.

Addition of PAC to a biological system does not necessarily involve large capital expenditures for equipment, and may solve many problems. Use of PAC may allow a plant to meet effluent standards and reduce costs. Among the possible benefits are as follows:

- Improved organic pollutant removals [BOD, COD, and total organic carbon (TOC)]

- More uniform operation and effluent quality, particularly during periods of widely varying organic and hydraulic loads
- Adsorption of organics, such as detergents, oils, and dyes that are refractory and nonbiodegradable
- Protection of the biological system from toxic waste components
- More effective removal of organically bound phosphorus and nitrogen
- Increased effective plant capacity at little or no additional capital investment
- Savings on operating costs resulting from reduced defoamer, coagulant, and power requirements
- Greater treatment flexibility since carbon dosages can be varied to match waste strengths and flow rates
- Increased solids retention times in biological processes

Many pollutants, not otherwise biologically degraded, may be removed when adsorbed by carbon added to the mixed liquor. Contact time is extended from hours to days, and pollutants are adsorbed by carbon thoroughly intermixed with biological solids.

CHAPTER 25

Heavy Metal Removal

Metals are among the oldest known toxins to humans. Lead and arsenic have been recognized for many years as agents responsible for illnesses and death in people. Metals differ from organic toxins inasmuch as they cannot be created nor destroyed. Further, a heavy metal may have a half-life in a human organ of several years. This means that it can take years for the body to cleanse itself of one half of any toxic metals that enter. Because of this long residence time, metals are said to bioaccumulate when introduced into a target organism.

The biochemical mechanism responsible for metal toxicity differs with the metal and the type of organism it enters. The most commonly held mechanism for toxicity involves the bonding of metals to biomolecules in a manner that alters the normal function of the biomolecule. For example, many enzymes require a metal ion to activate catalytic activity. However, it is possible to inhibit normal activity of enzymes through bonding of a foreign metal to the enzyme. This disrupts normal metabolism, resulting in an alteration in the normal life functions of the organism.

Metals are present in the earth's landmass and are naturally introduced to the groundwater and surface waterways at low concentration. Some metals are essential for life when present in trace amounts, but act as toxins if present in higher amounts.

In some facilities, industrial processes produce effluent that is high in the concentration of heavy metals. In order to ensure that aquatic life and food sources are protected from exposure to toxic levels of metals, removal of various metals from effluent to meet safe standards is necessary.

Regulatory Issues

Many industrial countries have implemented regulations on the discharge of pollutants into the environment. Chemicals that have been proven or are suspected as being toxic to the environment are regulated.

Local laws generally specify discharge limits for heavy metals. A daily maximum level or a maximum monthly average may regulate a given metal. Allowable discharge limits are established by an environmental agency based upon impact of the metal on the environment. Metals such as mercury, arsenic, and more recently selenium that carry serious environmental impact, generally receive low discharge limits (in the µg/L range), while other less toxic metals such as iron and nickel, usually have maximum allowable limits in the mg/L range.

Most local regulatory agencies have separate guidelines for direct dischargers and those that send effluent to a public treatment plant. Discharge to a sewer (indirect discharge) is subject to further treatment before water enters the environment, and limits tend to be less severe than for discharge directly to a waterway.

Sources of Metals

Metals are the raw materials used in many industrial processes, and they may concentrate in water through water reuse. Because of the inherent nature of these processes, metals are introduced into effluent from normal operations. Some examples of industrial sources of heavy metals are as follows:

- Spent baths from plating and etching operations
- Rinse water from plating baths
- Air scrubbers from refineries
- Ore process waters
- Waters from casting operations
- Dissolution of metal-containing catalysts

Metals occurring in waste streams, which are listed as hazardous and likely to be subject to discharge limits, are shown in Table 25.1.

Antimony	Chromium	Nickel
Arsenic	Cobalt	Silver
Barium	Copper	Selenium
Beryllium	Lead	Vanadium
Cadmium	Mercury	Zinc

TABLE 25.1 Common Hazardous Metals in Waste Streams

Chemistry of Metals

Many heavy metals of interest are members of a group known as transition metals. The first series of transition metals are common targets for removal from effluent. This series consists of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc. Metals such as these are often utilized in industry because they exhibit properties that make them desirable in a variety of applications. In their elemental state, they are hard, strong, high melting, conduct heat and electricity, and in some cases show low corrosion rates.

Metal ions are always surrounded by groups of atoms or molecules that stabilize the ion when it is in a dissolved state. Surrounding groups are referred to as ligands, while the metal ion along with its surrounding groups is referred to as a complex ion or simply a metal complex. Most heavy metals form complexes in solution as a means of forming the most stable configuration for the metallic ion. Ligands can be very simple single atomic species such as chloride (Cl^-) or fluoride (F^-) or more complex ions such as cyanide (CN^-). Neutral molecules like ammonia (NH_3) or water (H_2O) may act as ligands, giving rise to complexes such as $Cu(H_2O)_4^{+2}$ and $Cu(NH_3)_4^{+2}$. A metal always seeks the most stable molecular arrangement.

Ligands may also be organic molecules such as an amine or carboxylic acid. Examples of an amine and carboxylic acid that can complex with a metal are ethanolamine and acetic acid, respectively.

First row transition metals are characterized by bond formation that typically involves the 3d orbital on the metal atom. Ligands are able to donate or share electrons with the metal in the complex.

The 3d orbitals that participate in metal-ligand bonding are spatially arranged in such a manner as to most commonly give rise to octahedral or tetrahedral complex geometries. The most stable configurations are to have the electronic orbital empty, half filled, or completely filled. This is one of the reasons why aluminum (Al^{+3}) does not form precipitate complexes with ethylenediaminetetraacetic acid (EDTA), carbamate, and other chelating agents. The structure of an octahedral and tetrahedral complex for a metal (M) with ligand (L) is shown in Fig. 25.1.

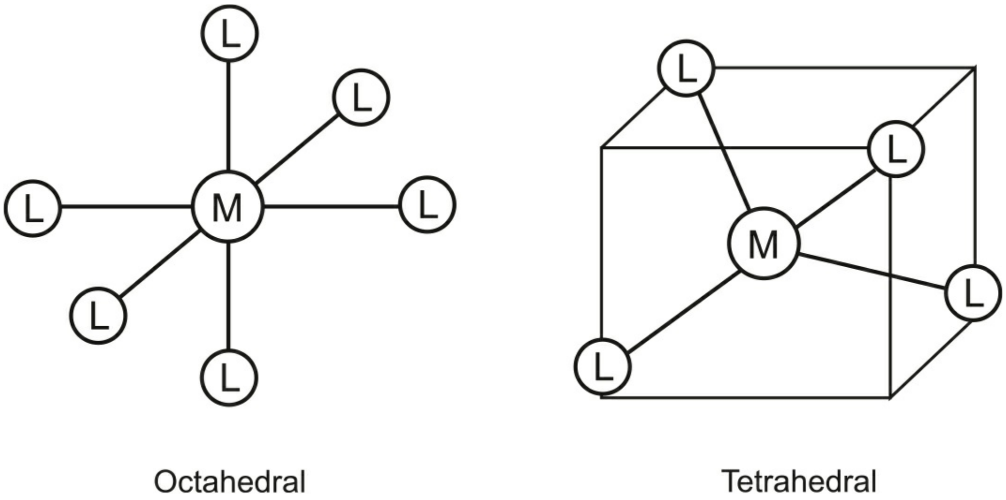


FIGURE 25.1 Tetrahedral and octahedral metal–ligand complexes.

Metals may be coordinated with a number of anions and neutral molecules. This number is called the coordination number of the metal in the complex. The most common coordination numbers for transition metals are four and six. Molecules of these coordination numbers often show the tetrahedral and octahedral geometries shown in Fig. 25.1. Examples of complexes with a coordination number of four include $Zn(CN)_4^{-2}$, $FeCl_4^{-}$, and $CoBr_4^{-2}$, while examples of complexes with a coordination number of six are $Co(NH_3)_6^{+2}$ and $Cu(NH_3)_5 \cdot H_2O^{+2}$.

The most common chemical means for removal of a metal ion from effluent is through reaction with a precipitating agent to form an insoluble complex or precipitate. Various precipitation agents used for metal removal in industrial effluent treatment are discussed under Chemical Methods later in this chapter. Equation (25.1) shows the reaction of ferric ion with hydroxide to form insoluble ferric hydroxide.

$$Fe^{+3} + 3OH^- \rightleftharpoons Fe(OH)_3 \tag{25.1}$$

This precipitation is shown as an equilibrium reaction indicating that if ferric hydroxide is added to water, some of the solid dissolves, resulting in a mixture of solid ferric hydroxide, ferric ion, and hydroxide ion. Likewise, if caustic is added to a solution of ferric ion, the same mixture results.

An equilibrium constant can be written for any chemical reaction as a ratio of the concentrations of products divided by the concentrations of reactants after equilibrium is reached. For dissolution of ferric hydroxide [reverse of Eq. (25.1)], the products are Fe^{+3} and OH^-, and the equilibrium constant (K_{eq}) can be expressed as the ratio shown in Eq. (25.2).

$$K_{eq} = [Fe^{+3}][OH^-]^3/[Fe(OH)_3] \tag{25.2}$$

Concentrations need to be raised to the appropriate power as Eq. (25.2) shows for the $[OH^-]$ raised to the power 3. The larger the equilibrium constant for a reaction, the more the reaction favors formation of the products in the reaction as written.

In dissolving ferric hydroxide in water, the concentration of solid ferric hydroxide does not change significantly, and it remains a constant that can be combined with K_{eq} to define the solubility product (K_{sp}).

$$K_{sp} = [Fe^{+3}][OH^-]^3 \tag{25.3}$$

K_{sp}, as defined in Eq. (25.3), is the solubility product for ferric hydroxide in water. Since temperature affects solubility of all solids, the value of K_{sp} is reported for a specific temperature. The solubility product is a measure of the tendency of metals to precipitate when the appropriate anion is added to a solution of the metal. In general, the smaller the solubility product (K_{sp}), the less soluble the compound and the more effectively a metal can be removed from solution. Ferric hydroxide is among the least soluble metal hydroxides (MOHs) ($K_{sp} = 1.1 \cdot 10^{-36}$), and ferric ion is very effectively removed from solution by addition of caustic.

Table 25.2 shows solubility products for some common MOHs, carbonates, and sulfides in pure water. Their low K_{sp} makes hydroxide, sulfide, and carbonate effective precipitation agents for metal removal.

Compound	**Chemical Formula**	**K_{sp} at Room Temperature**
Copper (II) carbonate	$CuCO_3$	10^{-10}
Copper (II) hydroxide	$Cu(OH)_2$	10^{-20}
Copper (II) sulfide	CuS	10^{-36}
Lead (II) carbonate	$PbCO_3$	10^{-13}
Lead (II) hydroxide	$Pb(OH)_2$	10^{-15}
Lead (II) sulfide	PbS	10^{-26}
Manganese (II) carbonate	$MnCO_3$	10^{-11}
Manganese (II) hydroxide	$Mn(OH)_2$	10^{-13}
Manganese (II) sulfide	MnS	10^{-13}
Mercury (II) sulfide	HgS	10^{-50}
Nickel (II) carbonate	$NiCO_3$	10^{-9}
Nickel (II) hydroxide	$Ni(OH)_2$	10^{-15}
Nickel (II) sulfide	NiS	10^{-22}
Zinc (II) carbonate	$ZnCO_3$	10^{-11}
Zinc (II) hydroxide	$Zn(OH)_2$	10^{-17}
Zinc (II) sulfide	ZnS	10^{-24}

TABLE 25.2 Solubility Products for Various Metal Salts in Pure Water

Ionic Strength

Solubility of a precipitate is affected by ionic strength of the medium in which it dissolves. Ionic strength is simply a measure of all dissolved ions in solution and is therefore related to conductivity of the water. Waste streams often have numerous dissolved salts that produce water with significantly higher ionic strength than that of pure water. Though the solubility products given in Table 25.2 offer a measure of the effectiveness of a precipitation agent, added ionic strength can offer enhanced solubility for precipitates.

The reason for this greater solubility lies in the attraction that precipitate ions have for other ions in solution. In general, high ionic strength (high conductivity) solutions can enhance solubility of a precipitate by two to threefold over that observed for pure water. Figure 25.2 shows the effect of a dissolved salt (sodium sulfate) on the solubility of zinc at pH 9.2. Salts other than sodium sulfate show similar effects.

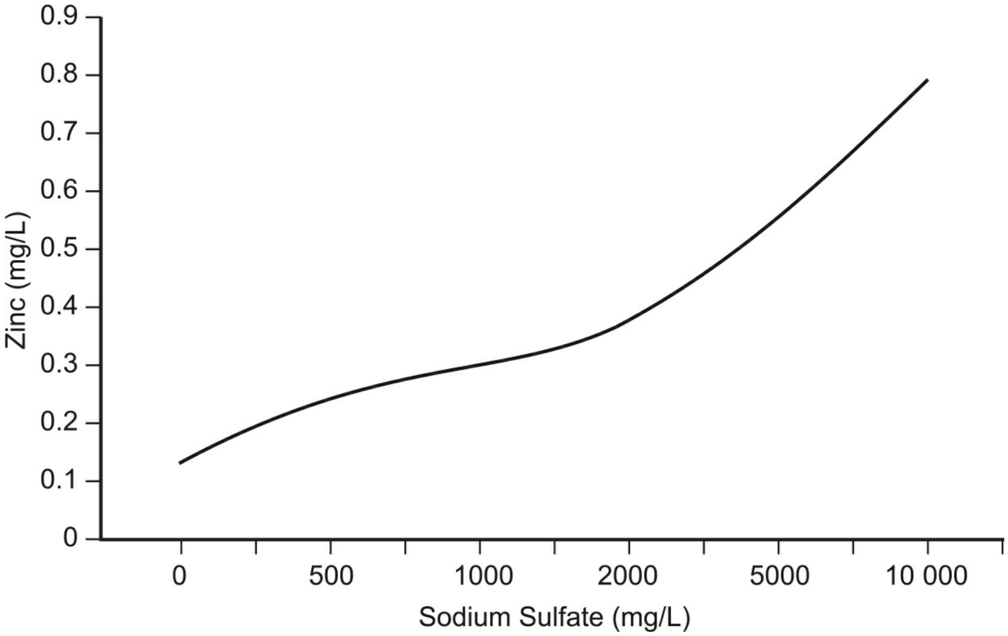


FIGURE 25.2 Effect of sodium sulfate on solubility of zinc hydroxide.

Since ionic effects are determined by interactions between charged species, higher valence ions generally show greater solubility increases than is seen for monovalent metal salts.

One of the unfortunate consequences of employing recycling practices in a plant is to produce a process water with higher dissolved salts that reduces performance of precipitation processes.

Chelation Effects

Chelating agents or chelants are ligands that possess two or more donor groups capable of simultaneously bonding to a metal. Chelating agents are often found in industrial products such as cleaners and therefore make their way into effluent. Examples of two of the most common chelating agents, EDTA and nitrilotriacetic acid (NTA), are shown in Figs. 25.3 and 25.4. Figure 25.5 shows the structure of the octahedral complex that is formed when a metal (M) is coordinated with the chelant (EDTA). A general feature of the chelant-metal structure is the formation of five and six member rings that leads to enhanced stability of the metal–chelant complex.

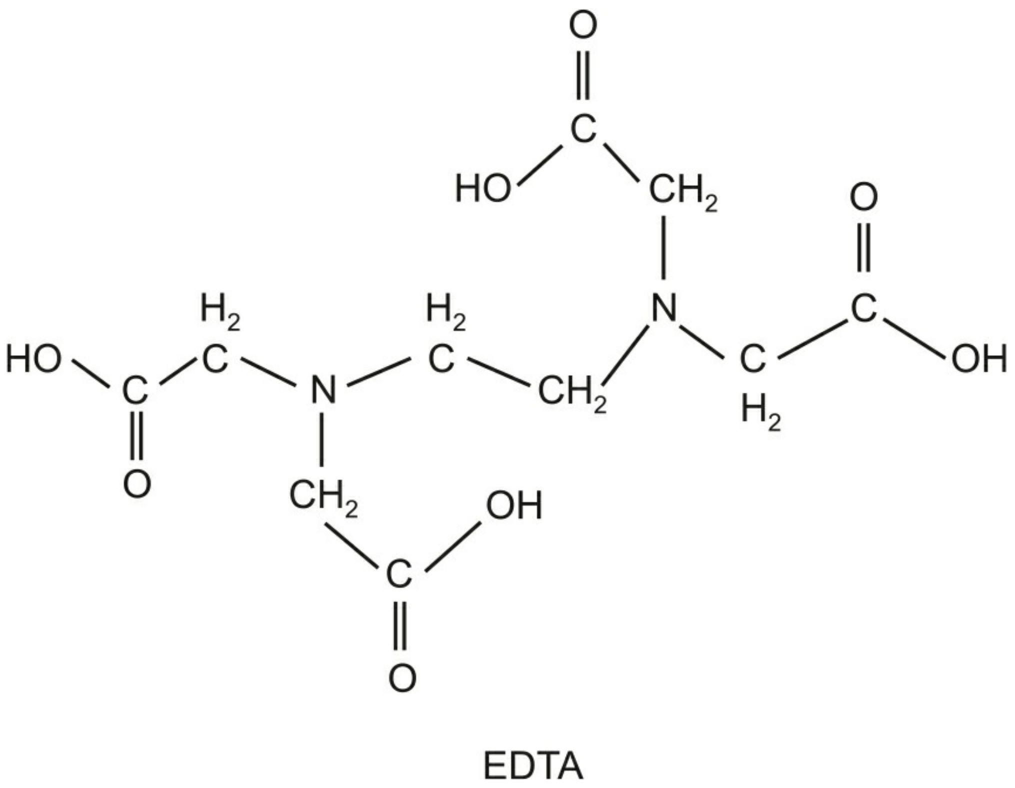


FIGURE 25.3 Chemical structure for EDTA.

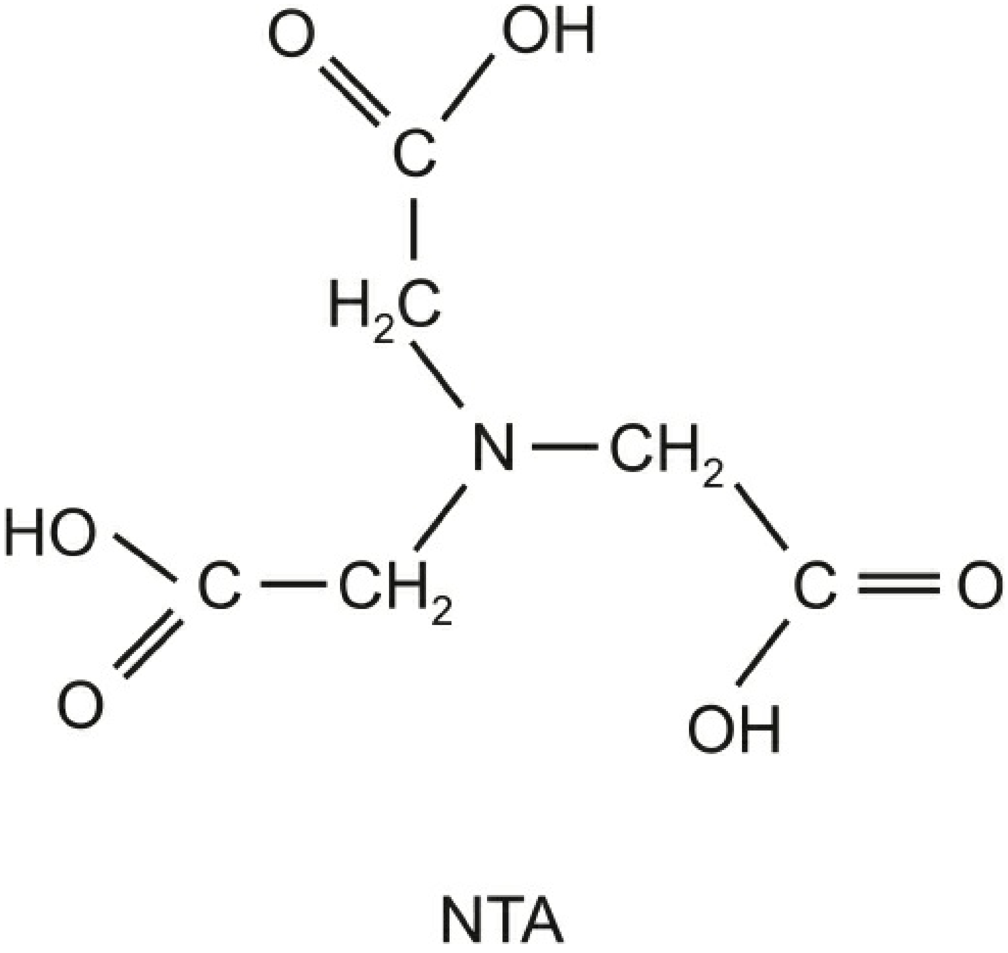


FIGURE 25.4 Chemical structure for NTA.

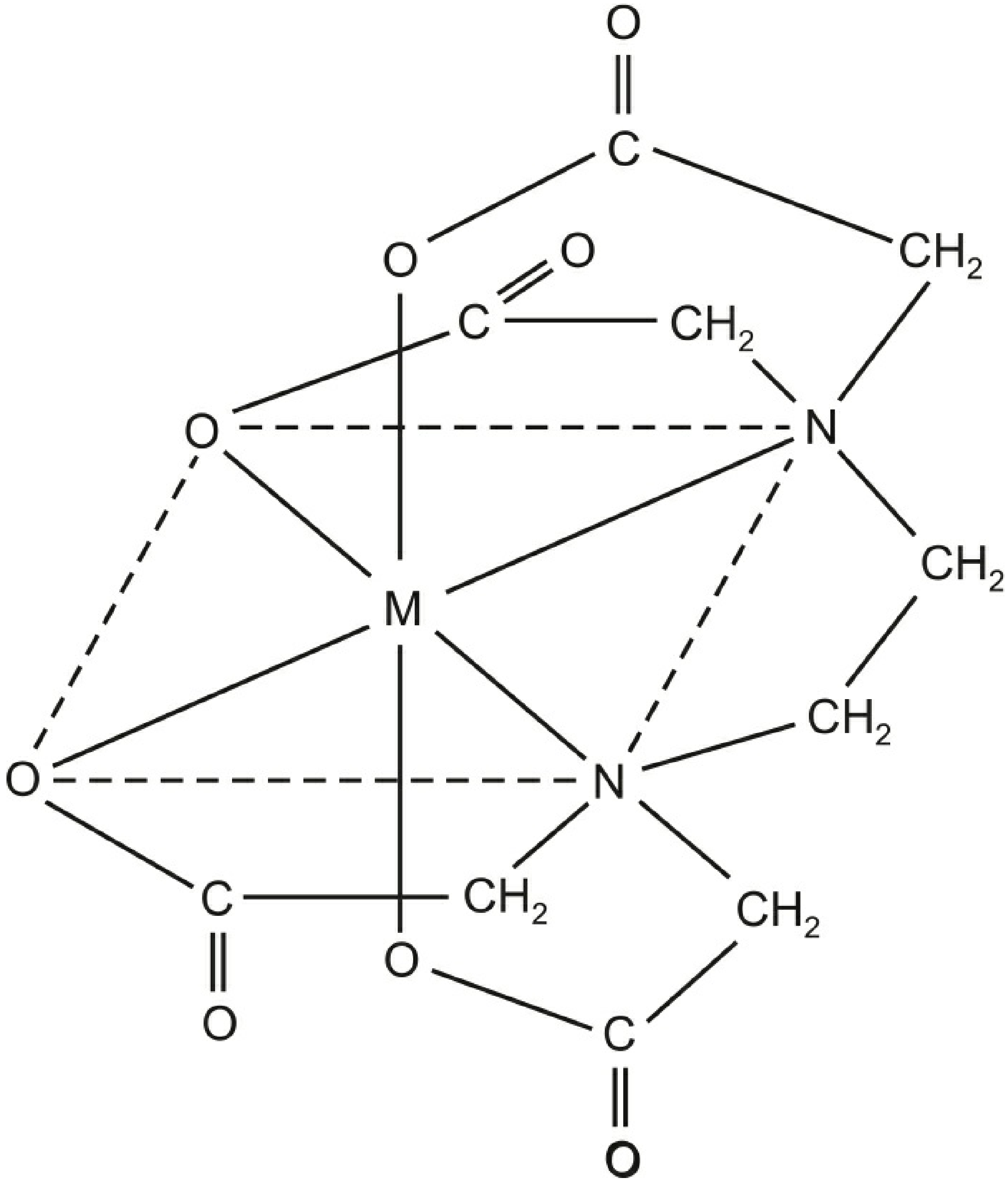


FIGURE 25.5 Chemical structure for metal–EDTA complex.

Presence of chelating agents in metal bearing effluent can make removal of metal ions by precipitation much more challenging. Chelated metals are bonded in stable water-soluble complexes that must be disrupted in order to be removed through chemical treatment such as precipitation.

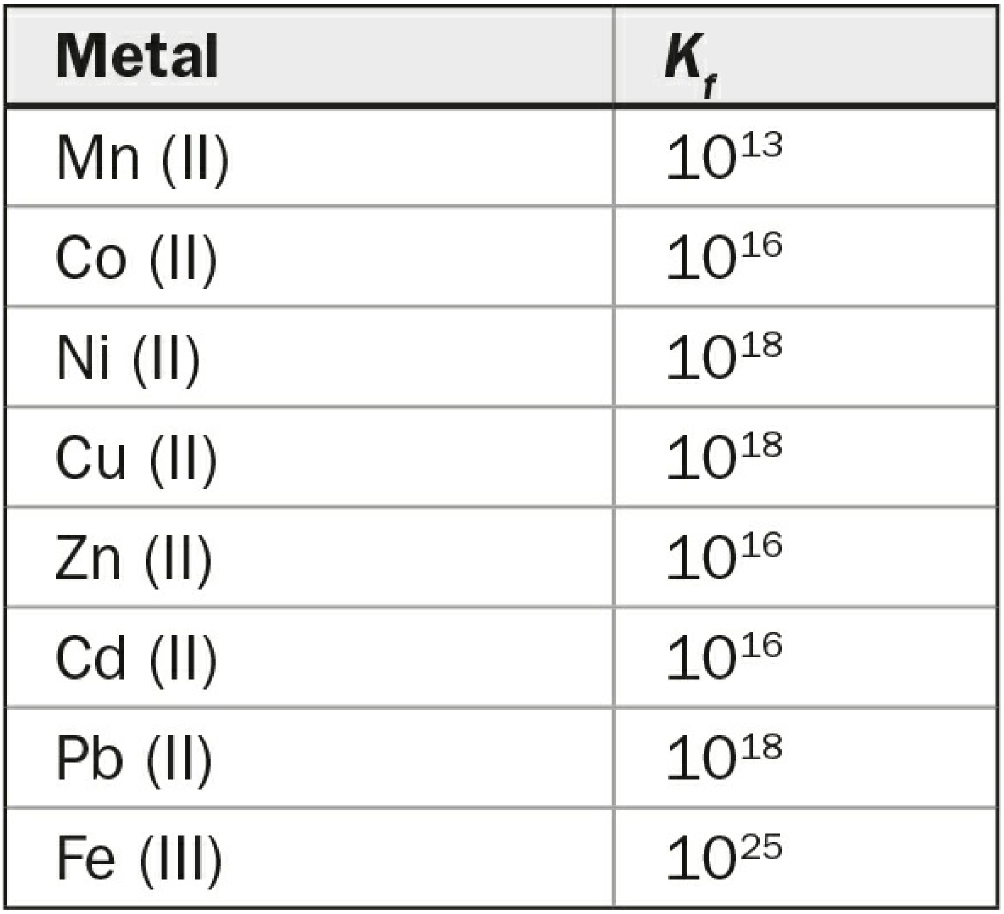
Chelating agents (C) react with metals (M) in a manner that is schematically represented by Eq. (25.4).

$$M + C \rightleftharpoons MC \tag{25.4}$$

The equilibrium constant (called the formation constant K_f) for this reaction is expressed in Eq. (25.5).

$$K_f = [MC]/[M][C] \tag{25.5}$$

In practice, more than one chelant molecule can react with a single metal, resulting in a second equilibrium expression. Formation constants for metal–EDTA complexes are given in Table 25.3.



Metal	K_f
Mn (II)	10^{13}
Co (II)	10^{16}
Ni (II)	10^{18}
Cu (II)	10^{18}
Zn (II)	10^{16}
Cd (II)	10^{16}
Pb (II)	10^{18}
Fe (III)	10^{25}

TABLE 25.3 Formation Constants (K_f) for Various Metal–EDTA Complexes

Chelants present a competing equilibrium problem when a metal is treated with a precipitation agent in a chelant-metal effluent. The metal has an opportunity to complex with the chelant remaining in solution or reacting with the precipitant to form an insoluble salt. This situation can be expressed in the chemical equilibrium reaction shown in Eq. (25.6).

$$\mathrm{MC} + \mathrm{OH} \rightleftharpoons \mathrm{MOH} + \mathrm{C} \tag{25.6}$$

In this reaction, hydroxide ion must compete with chelant (C) for formation of insoluble MOH. The equilibrium constant for this reaction is shown in Eq. (25.7).

$$K_{\mathrm{eq}} = [\mathrm{MOH}][\mathrm{C}]/[\mathrm{MC}][\mathrm{OH}] \tag{25.7}$$

This equilibrium constant can be written as a ratio of the solubility product (K_{sp}) and the formation constant (K_f) as shown in Eq. (25.8).

$$K_{\mathrm{eq}} = (1/K_{\mathrm{sp}})(1/K_{\mathrm{f}}) \tag{25.8}$$

Therefore, the solubility product (K_{sp}) for precipitation and the chelant-metal formation constant (K_f) give an idea whether a metal that is chelated can be precipitated with a chemical precipitation agent. The larger the product of the inverse of K_{sp} and K_f, the more likely Eq. (25.6) will favor precipitation. In the reaction of Fe (III)-EDTA with hydroxide, $K_{sp} = 10^{-36}$ while $K_f = 10^{25}$. Therefore, K_{eq} defined in Eq. (25.8) is 10^{11}. In this case, the precipitation reaction wins out over the chelation reaction, and ferric iron can be removed from effluent containing EDTA. For many precipitation reactions, the K_{sp} and K_f product defined in Eq. (25.8) is not as large as this example, indicating that chelants have a strong influence on the ability of precipitation agents to remove metals through formation of a precipitate. An example is EDTA chelated zinc, which does not precipitate with hydroxide or sulfide precipitation chemistries.

Metal Removal

The best approach to heavy metal pollution control is a comprehensive program of prevention practices and point source treatment. This may include production modifications, operational changes, material substitution, materials and water conservation, recycling, and end-of-pipe chemical and equipment treatment. In other words, a successful environmental management system requires a mechanical, operational, and chemical (MOC) approach in order to meet regulatory compliance.

Operational Factors

Several operational factors can contribute to successful environmental management. These include training and supervision, production planning, raw material substitution, waste segregation and separation, loss prevention and housekeeping, and closed loop recycling.

> ***Training and Supervision***—Training of employees ensures that all are aware of the company goals in meeting regulatory guidelines. It also emphasizes that equipment must be operated as designed in order to minimize waste.
>
> ***Production Planning***—Production planning can eliminate unnecessary steps such as cleaning operations that contribute to overall waste generated.
>
> ***Raw Material Substitution***—Where possible, toxic raw materials and products should be replaced with less hazardous substitutes. For example, replacement of hexavalent chromium and cyanide in plating and metal finishing operations reduces toxicity of waste generated.
>
> ***Waste Segregation and Separation***—Facilities need to develop treatment plans that handle hazardous and nonhazardous waste separately. Mixing wastes complicates removal of hazardous components. For example, cyanide-bearing effluent should be pretreated before mixing with other waste streams.
>
> ***Loss Prevention and Housekeeping***—Maintenance of equipment to minimize spills and leaks are a necessary part of an environmental management system. Use of chemical analysis, rather than elapsed time or production numbers, to determine when process solutions need replacement can reduce waste.
>
> ***Closed Loop Recycling***—Closed loop recycling is often linked to mechanical or equipment methods in waste treatment. Any equipment treatment process [e.g., ion exchange and reverse osmosis (RO)] that is capable of separating or concentrating metals so that they can be returned to the process is of great value in reducing the amount of metals that are treated in an end-of-pipe treatment. Separation and concentration methods that form a recycle loop are discussed below.

Equipment Methods

Most mechanical options discussed in this section fall into the category of physical separation techniques and are therefore mainly equipment related processes. Most of these processes generate concentrated solutions of the metal, which still may require chemical treatment for disposal or reuse.

Production mechanical changes should be implemented where possible to affect overall success of the pollution control program. Whenever possible, equipment should be evaluated for modifications that minimize the amount of metal-bearing effluent generated. For example, changing the rack configuration in a plating process may be able to reduce drag-out and lower overall metal in effluent.

Ion Exchange

Ion exchange is a reversible chemical reaction where ions in a feed stream are exchanged for similarly charged ions on the surface of a solid ion exchange resin. Ion exchange resins vary widely in composition, but all resins contain charged groups that attract ions of opposite charge. Ion exchange resins are classified as anion or cation, depending upon the type of charged species they exchange. Typically, cation exchange resins exchange hydrogen (H^+) for other cations such as metals. This resin is the most widely used in effluent applications, since removal of cations is a common goal in effluent treatment. Anion exchange resins often exchange hydroxide (OH^-) for anions in a feed water stream.

Once capacity of the resin is reached (most ions of the resin are exchanged), the resin is taken out of service for regeneration. Cation resins are most often regenerated using a mineral acid, while anion resins are regenerated using caustic. In the regeneration process for cation resin, a concentrated metal-bearing stream is produced that can be recycled, if possible, or further treated for metal removal.

Ion exchange can be used as an in-process treatment for closed loop recycling or an end-of-pipe treatment for removal of toxic ions to meet regulatory compliance.

In treatment facilities where divalent metal ions are targeted for removal, selective resins are sometimes employed. This process is referred to as scavenging. The regeneration process produces a highly concentrated metal containing regenerant that is suitable for recovery of the metal.

Membrane Filtration

Membrane filtration techniques utilize a membrane and a driving force to separate dissolved species and finely divided particles from liquids. The most common membrane filtration methods used in treatment of effluent are electrodialysis (ED), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and RO. A comparison of these techniques is shown in Table 25.4. Figure 25.6 shows separation characteristics for these processes.

Membrane Process	Driving Force	Membrane Type	Size Limit	Application
ED	Electric field gradient	Anion and cation specific	Dissolved ions	Electroplating waste streams
MF	Pressure gradient	Ceramic and polymeric	0.1–10 μm particles	Removal of suspended solids and oil/water
UF	Pressure gradient	Ceramic and polymeric	10–100 nm	Removal of colloidal material, dissolved oils, bacteria, high MW organics
NF	Pressure gradient	Polymeric	1–10 nm	Removal of dissolved salts
RO	Pressure gradient	Polymeric	<1 nm	Removal of dissolved salts

TABLE 25.4 Comparison of Membrane Filtration Methods

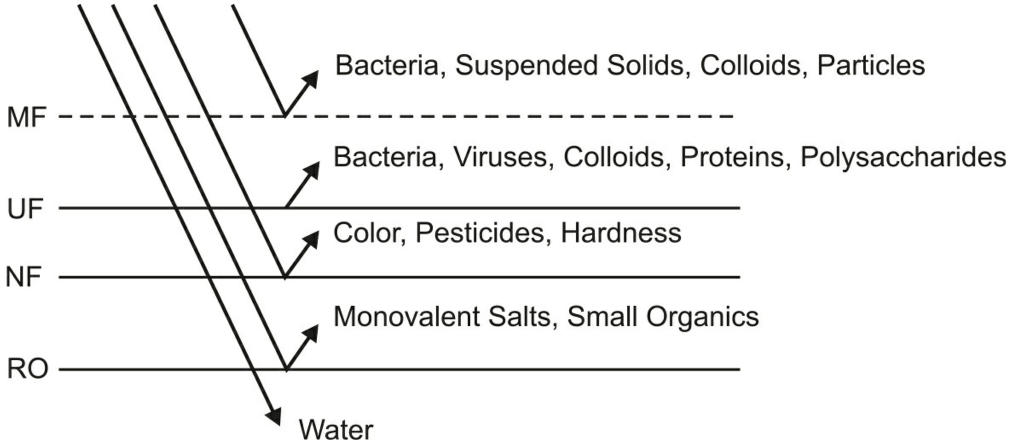


FIGURE 25.6 Separation characteristics of MF, UF, NF, and RO processes.

Electrodialysis ED uses a set of anion and cation specific membranes to form a set of compartments. A static electric field is applied across the membrane assembly to generate an electric field gradient. The unit consists of a membrane stack and a rectifier, which converts alternating current (AC) to direct current (DC), so that a static electric field can be applied.

The waste stream enters parallel to the membrane stack perpendicular to the field direction. Anions and cations are attracted to the anode and cathode, respectively. The ion selective membranes are semipermeable. The cathode transport membrane allows passage of only cations migrating toward the cathode, while the anion transport membrane allows anions to pass toward the anode. Ions pass to an adjacent compartment before becoming trapped by an opposing type of membrane that does not allow passage. The net result is the production of a series of alternating concentrated and depleted ionic compartments (see Fig. 25.7). Facilities typically use ED to remove metal ions from electroplating effluent.

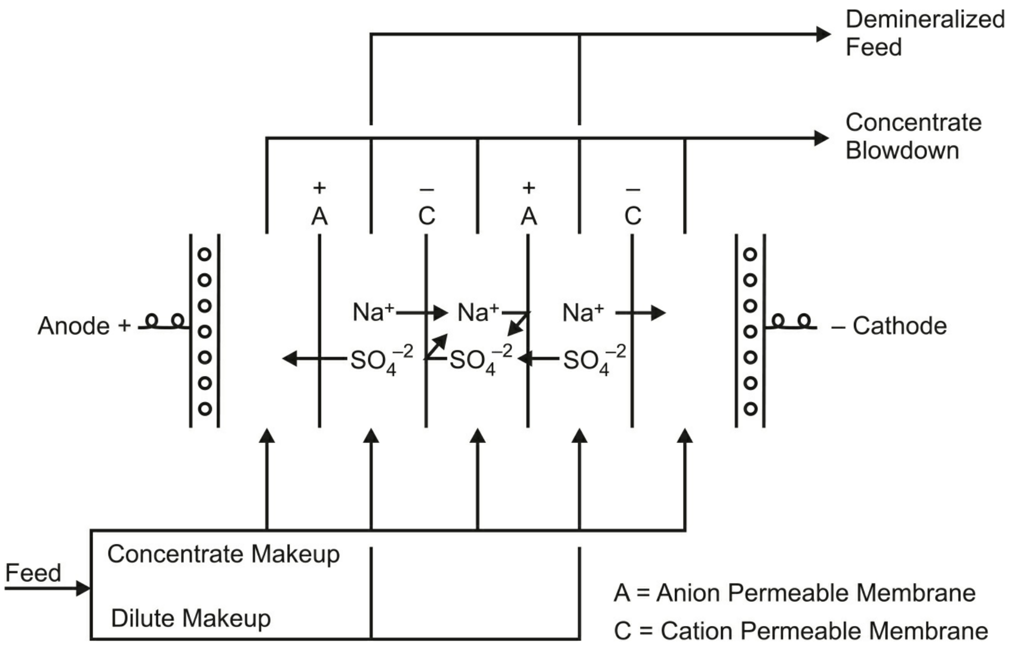


FIGURE 25.7 ED process.

Microfiltration, Ultrafiltration, and Nanofiltration MF, UF, and NF all separate particulate, colloidal, or dissolved species by passage of solute through a membrane. All of these methods rely on separation based on the size and shape of the particulate or solvent species. The major difference between MF, UF, and NF lies in the membrane construction and resulting pore size of the membrane used. This dictates the effective size separation range of the various filtration methods (see Fig. 25.8).

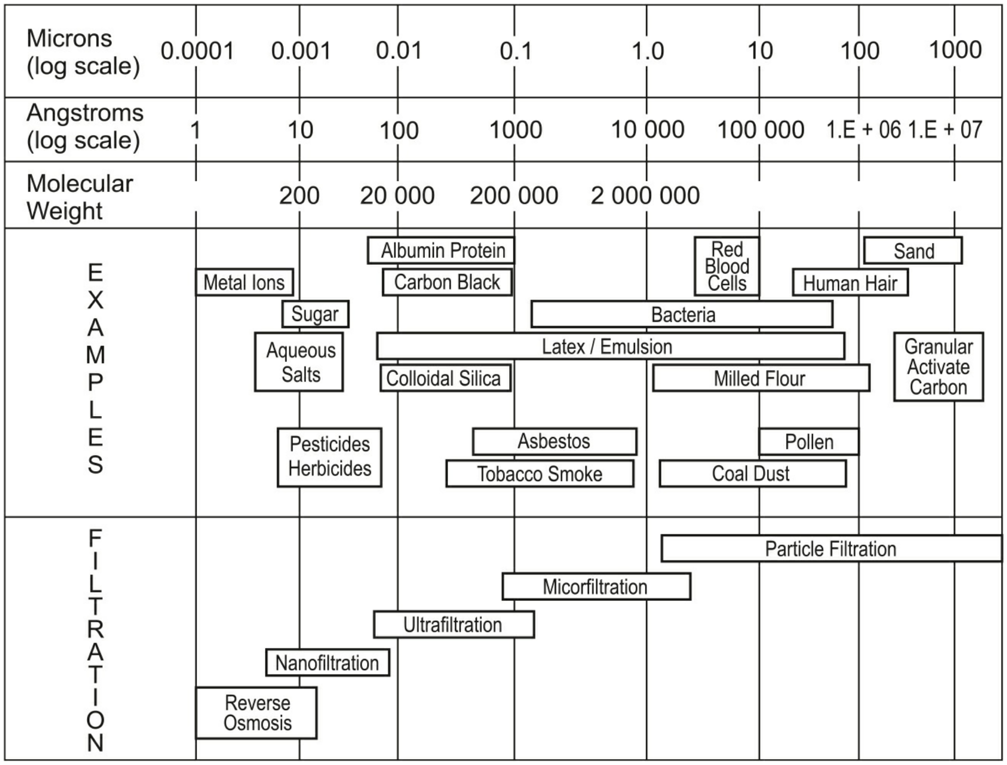


FIGURE 25.8 Filtration methods and particle size relationships.

Table 25.4 shows the effective separation range associated with MF units. Separation limits of the MF process (0.1–10 µm) make it most useful in separation of finely dispersed particulate or in separation of oil from water. In heavy metal removal, MF may be used in conjunction with various precipitation techniques to reach low levels of metals in treated effluent. In cases where soluble metals are reduced below the discharge target range, achieving the discharge target becomes a solid–liquid separation issue. Gravity clarifiers may not produce effluent where total heavy metal (soluble plus particulate) meets discharge limits. In these cases, removal of finely dispersed metal precipitate with MF should be considered.

Reverse Osmosis RO is the most widely used membrane filtration process in treatment of waste and raw water. Osmosis is the tendency of a liquid to pass spontaneously from a dilute to a concentrated salt solution, when the solutions are joined by a semipermeable membrane. If pressure greater than the osmotic pressure is applied to the concentrated solution, liquid (and some small ions) passes through the membrane to the dilute liquid. This pressure driven osmosis process is termed RO. It is easily seen that this process is capable of producing a concentrated dissolved salt stream and a clean stream when effluent is fed to an RO unit.

Table 25.4 shows the working range of size separation that can be achieved with RO membranes. The effective size range for RO makes the technique applicable for removal of atomic sized species. In fact, RO has the capability of retaining 99% of multivalent ions and about 95% of monovalent ions in the concentrated (reject) stream.

RO membranes are constructed of organic materials and may be configured in a variety of designs, similar to designs used in other membrane filtration processes. Operating pressures are significantly higher in RO than other membrane filtration systems and range from 400 to 1000 psig (2.8–6.9 MPag). Capacity of an RO unit is determined by operating pressure and surface area of the membrane. Higher operating pressure and surface area generally increase throughput volume (flux). Reject stream concentration increases with pressure and decreases with flow volume (effective residence time). The maximum achievable concentration in a reject stream is usually between 20 and 30 g/L of total dissolved solids (TDS). Refer to Chap. 8 for more information on RO systems.

This technique is most applicable for concentrating a heavy metal for recycling, or coupling with other methods such as electrolytic recovery or evaporation to recover the metal. RO has been used effectively in electroplating rinse waters. If the reject stream is acceptable for return to the plating bath, a closed loop can be created where permeate is also returned to a rinse bath. Often, however, reject stream concentration is not suitable for recycling, and metals must be further treated for removal.

RO has higher capital costs than ion exchange, if both processes are coupled with electrolytic recovery. Both methods are equally effective in removal of heavy metals, but RO can handle higher feed stream concentrations. Both methods produce about the same concentration factors in the reject and regenerant streams.

For most operations, membrane life is usually five years, if proper precautions and maintenance are observed. Flux rates should be monitored as a means of determining when membrane cleaning is needed.

Electrolytic Recovery

Electrolytic recovery is an electrochemical process for removal of metals from a waste stream. A metal-bearing solution is processed in an electrolytic cell that consists of a pair of closely spaced electrodes that receive an applied potential. Current is applied across the cell, and metal ions are reduced to their elemental state at the cathode of the cell. The overall unit is made up of one or more cells, a transfer pump, and a rectifier to supply the potential.

Capacity of the equipment depends on total surface area of the cathode, with surface areas that range from 1 to 10 ft^2 (0.09–0.9 m^2). The reduction process is governed by Faraday's Law, which states that the amount of chemical reduction (recovery) is proportional to the electric current applied. Flat electrodes are used to recover metals from solutions that contain 1 to 20 g/L of dissolved metal. Reticulate cathodes having a woven fiber design possess significantly higher surface area than flat electrodes and are used for metal recovery from solutions containing less than 100 mg/L dissolved metal.

Chemical Methods

Chemical methods of metal removal are often the most cost-effective processes to meet regulatory discharge limits. However, as discharge limits are lowered, chemical removal methods likely need to be coupled with other techniques to produce effluent that satisfies government regulations. In general, chemical precipitation works best on more concentrated metal solutions. Low concentration solutions (50–250 μg/L) are very difficult to treat, as contact between the metal and precipitating chemical is greatly reduced. To overcome this issue, higher dosages of precipitating chemical are used, and if not very accurately controlled, can lead to redispersion of metal precipitate.

The most widely used end-of-pipe treatment for removal of heavy metals is chemical precipitation and flocculation followed, by separation of resulting floc. When properly monitored and controlled, chemical precipitation is a very effective means of metal removal in many waste streams. It currently is by far the most cost-effective means of reducing metal concentration to meet local environmental regulations. Several agents are used to form insoluble salts with heavy metals. The most common precipitants are hydroxide, sulfide, carbonate, small organic molecules, natural molecules, iron hydroxide (iron co-precipitation), and synthetic polymers.

The rate at which precipitate forms is an important practical consideration in removal of metal ions through precipitation techniques. Unfortunately, no conclusions can be reached about the rate that precipitate forms from the magnitude of the solubility product. Some precipitates with very small K_{sp} proceed to equilibrium at very slow rates. Precipitates can be slow to form, requiring contact times of minutes or even hours. This may complicate removal by limiting throughput in a treatment plant.

Hydroxide Precipitation

Hydroxide precipitation is the most common chemical method of heavy metal removal. Reaction of a divalent metal with sodium hydroxide to form the MOH is shown in Eq. (25.9).

$$\mathrm{M^{+2} + 2NaOH \rightleftharpoons M(OH)_2 + 2Na^+} \tag{25.9}$$

Table 25.2 shows that some MOHs have limited solubility (small K_{sp}) in water, making this method very effective in removing metals from solution. Figure 25.9 shows metal solubility as related to pH through the precipitation reaction shown in Eq. (25.9).

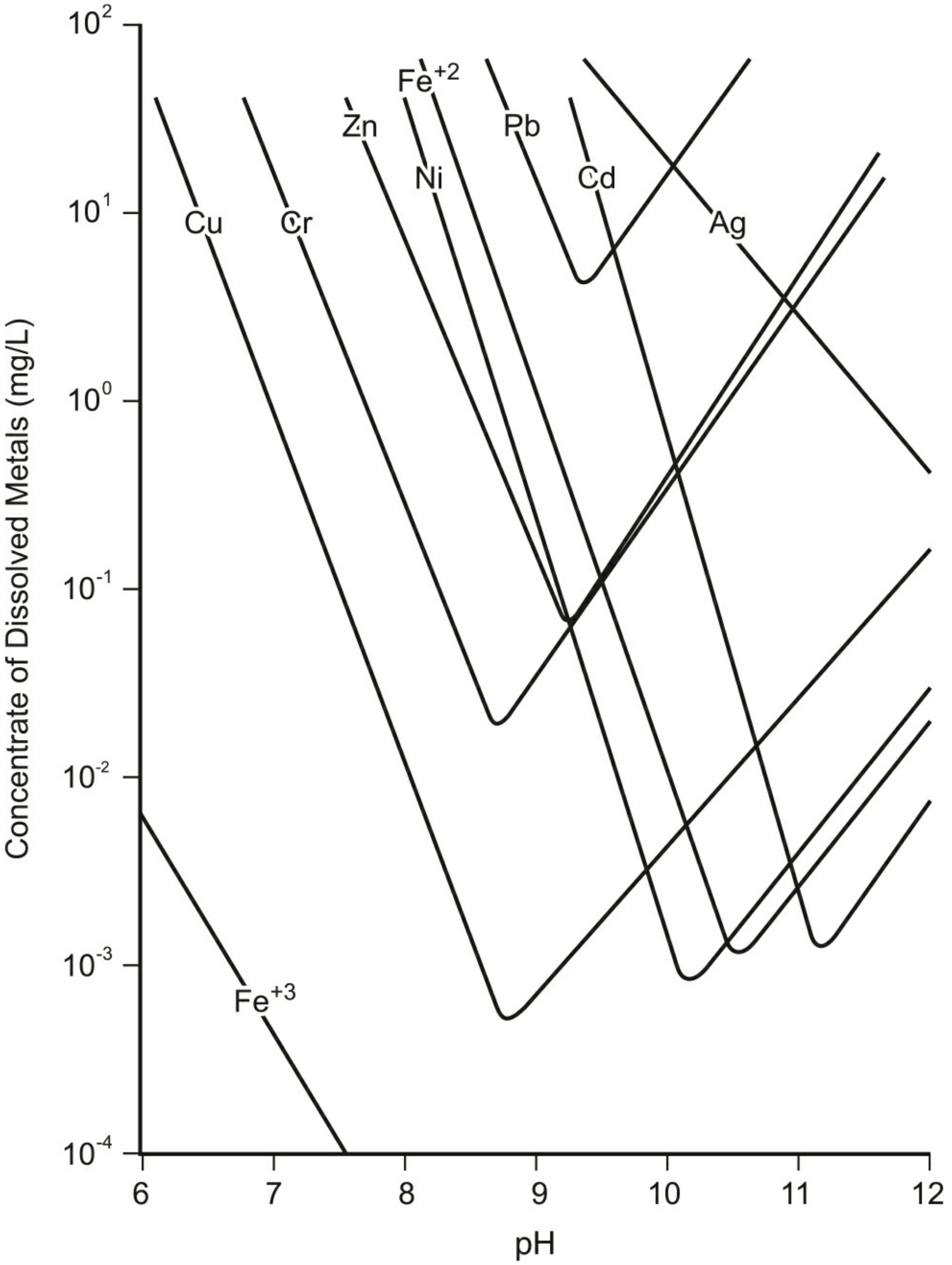


FIGURE 25.9 Solubility of various metals versus pH.

By examining the solubility curves in Fig. 25.9, we can make two important observations. MOHs of several heavy metals have very small solubility products, (K_{sp}), and the equilibrium reaction shown in Eq. (25.9) greatly favors the insoluble hydroxide. Secondly, solubility is influenced by pH, suggesting that MOHs, in some cases, form complexes with excess hydroxide with increased solubility. Equation (25.10) shows the reaction of zinc hydroxide with excess caustic to form the more soluble zincate ion [$Zn(OH)_3^-$]. Just as chelants interfere with precipitation equilibrium, the reaction shown in Eq. (25.10) presents another competing process.

$$Zn(OH)_2 + OH^- \rightleftharpoons Zn(OH)_3^- \qquad (25.10)$$

This type of chemistry is observed for several heavy metals shown in Fig. 25.9 and indicates that proper pH control is critical in removal of these metals from solution.

Metals that can be effectively removed through hydroxide precipitation include arsenic, cadmium, chromium III, copper, iron, manganese, nickel, lead, and zinc.

For economic reasons, the preferred reagent used to furnish hydroxide ion for precipitation is quick lime (CaO) or hydrated lime [$Ca(OH)_2$]. Other precipitants such as sodium hydroxide (NaOH) and magnesium hydroxide [$Mg(OH)_2$] are also used. Though lime is often used, it is more difficult to control addition of a solid or slurry than feed of a liquid such as sodium hydroxide. In addition to application benefits with sodium hydroxide, sodium salts are generally very soluble, and unlike lime, caustic does not produce as much sludge due to insoluble by-products.

Hydroxide precipitation offers the most cost-effective method of heavy metal removal. It can produce, in many cases, effluent that meets regulatory discharge requirements for the metal. However, there are problems associated with this technique that may make it difficult to apply as a sole treatment scheme.

- In mixed metal wastes, it may be difficult to find a single pH that is effective for precipitation of all regulated metals. Multiple precipitation steps at different pH may be effective but in practice can be impractical.
- Hydroxide precipitation can be ineffective, if effluents contain chelants or complexing agents.
- In systems that process large volumes of water, this technique may be impractical.
- Sludge that is produced can be voluminous and difficult to filter,

resulting in high handling costs.

Sulfide Precipitation

This process is similar to hydroxide precipitation; inasmuch as soluble metal is reacted with a reagent (sulfide) to form an insoluble metal sulfide complex. Equation (25.11) shows the reaction of a divalent metal ion (M^{+2}) with sulfide ion (S^{-2}) to form insoluble metal sulfide (MS).

$$M^{+2} + S^{-2} \rightleftharpoons MS \tag{25.11}$$

Sulfide precipitation is often a more effective alternative to hydroxide, since metal sulfides generally have lower solubility and much higher binding constants. Thus, sulfides can displace chelants better than hydroxides and force reaction toward the insoluble precipitate. Very low levels of metals can be achieved with sulfide precipitation compared to corresponding hydroxide precipitation. Copper, cadmium, zinc, and mercury can be effectively precipitated with short contact time.

Sulfide precipitation uses either soluble sulfide or insoluble sulfide as the source of the sulfide reagent. In soluble sulfide precipitation (SSP), water soluble sulfides such as hydrogen sulfide (H_2S), sodium sulfide (Na_2S), or sodium hydrogen sulfide (NaHS) serve as the source of sulfide. In insoluble sulfide precipitation (ISP), insoluble sulfide salts [e.g., ferrous sulfide (FeS)] are used.

Sulfide precipitation has both advantages and disadvantages compared to hydroxide precipitation. Advantages include:

- Lower residual dissolved metal concentration is achieved, since sulfides are less soluble than hydroxides.
- Sulfide can be effective in precipitating metal even in the presence of chelating agents.
- Sludge is less subject to leaching than hydroxide sludge.
- Sludge tends to be easier to filter and dewater.
- Dichromate and chromate can be removed without reduction to the trivalent state.

- Mixed metal streams can be treated at the same pH.
- Disadvantages associated with sulfide precipitation include:
- Higher cost compared to hydroxide.
- Potential for generation of H_2S gas (highly toxic) if contact is made with acidic effluent.
- Residual sulfide ion is toxic, and care must be taken to insure its discharge limit is not exceeded.
- Optimization of the solid–liquid separation with coagulation and flocculation can be difficult.

Carbonate Precipitation

Carbonate precipitation uses addition of carbonate ion (CO_3^{-2}) to effluent to remove metals as insoluble metal carbonates. The reaction of a divalent metal (M^{+2}) with carbonate ion to form an insoluble carbonate salt is shown in Eq. (25.12).

$$M^{+2} + CO_3^{-2} \rightleftharpoons MCO_3 \qquad (25.12)$$

Solubility of metal carbonate salts generally falls between MOHs and metal sulfides, though some metals are not removed effectively in a carbonate precipitation process. Metals such as cadmium can be effectively removed at neutral pH, if sufficient carbonate is available to drive the reaction shown in Eq. (25.12). Lead can be removed more efficiently with carbonate than hydroxide, since lead carbonate lends itself to easier filtration.

Sodium carbonate, calcium carbonate, and carbon dioxide are all used as carbonate sources. When introduced into water, carbon dioxide dissolves to form carbonic acid, which upon pH adjustment forms carbonate.

Advantages that carbonate precipitation can provide over other methods include:

- Process for specific metals (cadmium and lead) is more effective than hydroxide precipitation.
- Metal carbonates are denser than hydroxides, offering easier

separation.

- Disadvantages encountered with carbonate precipitation systems are as follows:
- Higher cost than hydroxide systems.
- Long retention times necessary (greater than 45 minutes).
- Release of carbon dioxide can result in foaming and floating sludge.

Small Organic Molecule Precipitation

Small organic molecule precipitants are low molecular weight (less than 500) organic sulfides that have strong affinity for metals. Figure 25.10 shows the chemical structure for dimethyldithiocarbamate (DTC), trithiocarbamate (TTC), and trimercaptotriazine (TMT), three of the more commonly used organic precipitants.

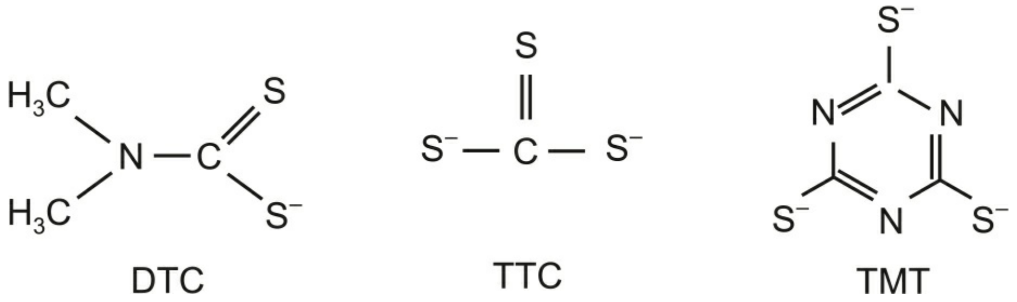


FIGURE 25.10 Chemical structure for common organic sulfide precipitants.

Molecules of this type react with metals in a stoichiometric manner to form complexes that, like inorganic sulfides, have limited water solubility. Equation (25.13) shows the reaction of DTC with a divalent metal to illustrate stoichiometry of the reaction. Two moles of DTC are required to precipitate each mole of divalent metal (M^{+2}).

$$2DTC^{-} + M^{+2} \rightleftharpoons M(DTC)_2 \tag{25.13}$$

Advantages of organic precipitants are as follows:

- DTC is a very effective precipitant, and low residual metal can be achieved.

- Moderate cost for DTC.
- TMT is nontoxic.
- Disadvantages are as follows:
- DTC has very high aquatic toxicity.
- TMT is relatively high cost.
- All require coagulation and flocculation.
- Optimization of precipitation and solid–liquid separation can be difficult.
- Overfeed leads to high cost and effluent toxicity.

Iron Hydroxide (Iron Co-precipitation)

Iron co-precipitation is a common variation of the hydroxide precipitation process. It is very effective at reducing the concentration of metals such as arsenic, beryllium, cadmium, copper, lead, nickel, and zinc to levels below that achieved with hydroxide precipitation. Iron co-precipitation involves adding an iron source (ferric sulfate or ferric chloride) to effluent at the pH adjustment stage. As pH increases, iron hydroxide precipitates along with the target heavy metals. The target metals may be incorporated as impurities into the iron hydroxide matrix or physically entrapped within iron hydroxide precipitate. MOHs can also be adsorbed onto the surface of iron hydroxide precipitate.

Factors that affect effectiveness of this technique include iron dosage, pH, initial concentration of target metals, and competition for adsorption sites from other species. The process requires some effort to optimize.

Synthetic Polymer Precipitation

A synthetic polymer has been developed that reacts with metals to form insoluble complexes. A schematic structure of this polymer is shown in Fig. 25.11.

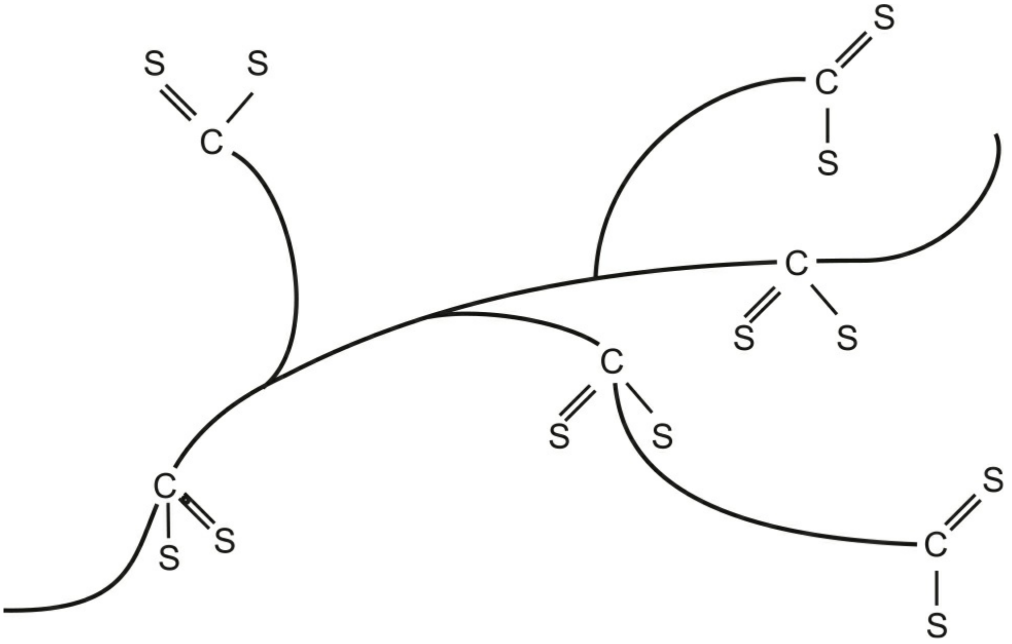


FIGURE 25.11 Chemical picture of synthetic polymer precipitant.

This polymer incorporates the metal binding structural feature into a polymer structure. The main advantage of the polymeric sulfide is that simultaneous precipitation and clarification take place in a single step. This means that good solid–liquid separation can be achieved without optimization of a second chemical.

A second important advantage with the polymeric precipitant is reduced aquatic toxicity compared to small organic sulfides. This factor becomes important in a situation where precipitant is overdosed or where there is concern for chemical toxicity on secondary biological systems.

Monovalent ions form stronger complexes with this polymer than divalent ions. Metals are therefore removed from the system in the order:

Hg>Ag>Cd>Cu>Pb>Zn>Co>Ni>Fe>Mn

The polymer works best at neutral pH, though zinc removal is more effective at lower pH. At elevated pH, it is possible to benefit from hydroxide precipitation and polymer co-precipitation.

Metallic Replacement/Cementation

Metallic replacement or cementation is a process in which dissolved metal ions are spontaneously displaced from solution by another metal. An example of this process is shown in Eq. (25.14) where dissolved copper is replaced by iron.

$$Cu^{+2} + Fe^{0} \rightarrow Cu^{0} + Fe^{+2} \tag{25.14}$$

This type of reaction does not proceed spontaneously for all pairs of metals, and this process has limited application. It has its widest application for recovery of copper, but it can be applied to recovery of silver paired with iron metal and mercury paired with iron or zinc metal.

The main advantage of the method is that it utilizes scrap metal to recover a higher value metal. In addition, no energy costs are involved in the recovery.

The main disadvantage is that the target metal [copper in Eq. (25.14)] is replaced by another metal (iron) that needs to be removed from the waste stream.

Chemical Reduction

In any reduction reaction, electrons flow from the reducing agent to the species that is reduced. In the removal of metal ions from solution, reducing agents such as sodium borohydride, hydrazine, and sodium bisulfite furnish electrons to the metal ions. Upon reduction, the metal in its neutral metallic state forms an insoluble precipitate that can be removed through standard separation methods.

Ionic mercury can be effectively converted to metallic form through use of reducing agents such as hydrazine, stannous chloride, and sodium borohydride.

Chemical reduction works well even when metals are chelated with agents that make chemical precipitation difficult. This characteristic is one of the main advantages with all electrolytic and chemical reduction processes.

Associated Pretreatment

There are varieties of effluent compositions that require pretreatment or special processing before implementation of metal removal techniques.

Chromium Reduction

Chromium is commonly found in effluent from processes such as anodizing, conversion coating, and electroplating. Hexavalent chromium poses significant environmental concerns due to its toxicity to humans. This toxicity has prompted its removal as a corrosion inhibitor in applications such as open cooling water systems. However, despite its toxicity, it remains popular in the plating industry due to the corrosion resistant nature and brightness of chromium surfaces.

Hexavalent chromium (Cr^{+6}) exists in aqueous solution as the chromate ion (CrO_4^{-2}) and does not form insoluble precipitate with hydroxide. Therefore, in order to precipitate chromium as chromium hydroxide, Cr^{+6} must first be reduced to trivalent chromium (Cr^{+3}). Reduction simply means that electrons flow to the hexavalent chromium, and the valence state is reduced from plus 6 to plus 3. Electrons in a reduction reaction can be supplied through an electrode (cathode) as in electrolytic reduction, or can be furnished chemically through a compound that is termed a reducing agent. Chemical reduction is the industrial process used in the reduction of chromium. Sodium metabisulfite, sodium bisulfite, and sulfur dioxide are the most commonly used reducing agents in industrial chromium pretreatment. In practice, the solution must be reduced to pH 2 for the chemical reduction to proceed at a significant rate. At pH levels above 5, the reduction rate is slow, and oxidizing agents such as dissolved oxygen and ferric ion consume the reducing agent. Equation (25.15) shows the reaction of chromate (chromic acid) with sulfur dioxide.

$$2H_2CrO_4 + 3SO_2 \rightarrow Cr(SO_4)_3 + 2H_2O \tag{25.15}$$

Figure 25.12 shows a typical chrome treatment system. Pretreatment takes place in the initial tank where pH is adjusted to approximately 2 followed by addition of a chemical reducing agent. Addition of reductant is controlled by a probe that measures oxidation–reduction potential (ORP), so that the proper stoichiometric amount is added. Typical reaction time is 15 to 45 minutes for this pretreatment step. After conversion of hexavalent chromium to trivalent chromium has been accomplished, precipitation, and removal of the insoluble hydroxide takes place in the neutralization and settling tanks. Equation (25.16) shows the neutralization step that results in formation of insoluble chromium hydroxide [$Cr(OH)_3$].

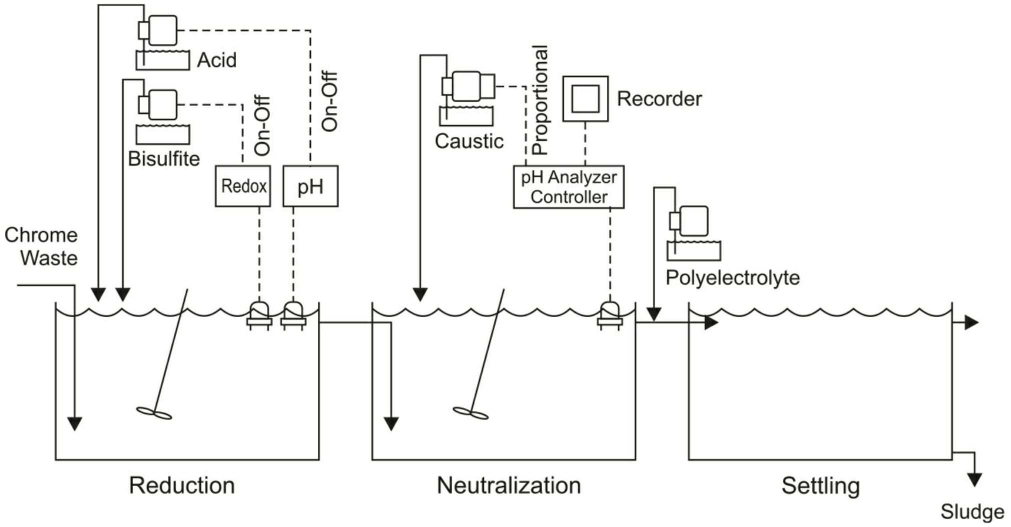


FIGURE 25.12 Typical chromium treatment system.

$$Cr_2(SO_4)_3 + 6NaOH \rightarrow 3Na_2SO_4 + 2Cr(OH)_3 \tag{25.16}$$

The pH is adjusted to 7.5 to 8.5, which is effective in precipitation of Cr^{+3} and meets pH discharge limits. The graph in Fig. 25.9 shows that Cr^{+3} solubility reaches a minimum at about pH 8.5.

The process can be semi-automated, so that a pH controller and ORP probe control pH adjustments and reducing agent addition. Though ORP is sensitive in the control of reducing agent to ensure that a sufficient amount of reductant is added, analytical testing needs to be done to determine chromium levels in the treated water accurately.

Cyanide

Cyanide (CN^-) solutions are used in plating processes for zinc, cadmium, copper, brass, silver, and gold. In addition to its toxicity, cyanide forms soluble complexes with metals that hinder subsequent removal with precipitation agents. The plating industry is moving toward replacing cyanide with more environmentally friendly agents, but cyanide is still used in many plating operations. In fact, in the United States alone, there are over 1100 plating facilities that have the need to remove cyanide.

Cyanide must be removed from rinse waters in a pretreatment process that typically reduces the level of cyanide below 1 mg/L. The most frequently practiced pretreatment process involves destruction of cyanide in a two-stage alkaline chlorination process. Figure 25.13 shows a typical diagram of a two-stage cyanide treatment system.

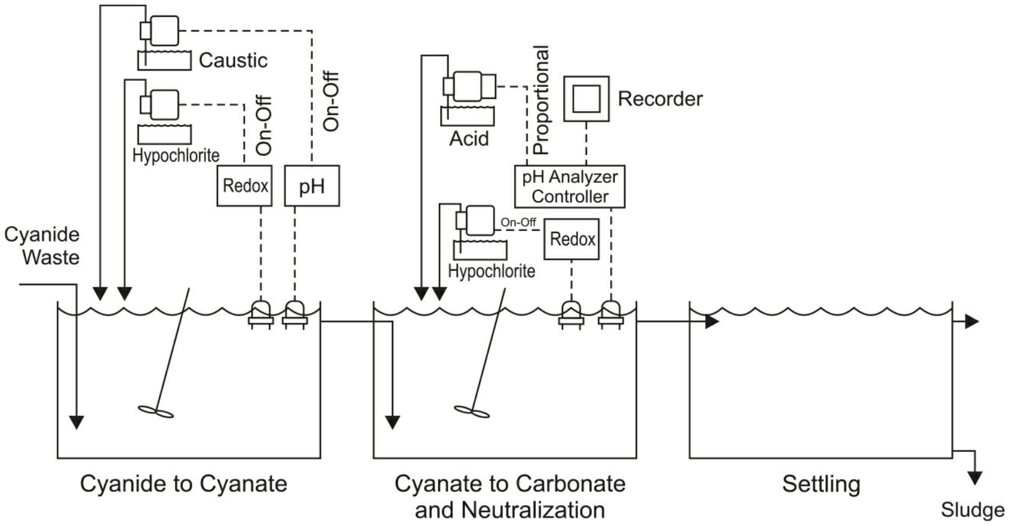


FIGURE 25.13 Typical cyanide treatment system.

In the first stage, pH is adjusted to approximately 11, and chlorine gas or sodium hypochlorite is added to oxidize cyanide to cyanate (CNO^-). Reaction of sodium cyanide with chlorine is shown in Eq. (25.17).

$$Cl_2 + NaCN + 2NaOH \rightarrow NaCNO + 2NaCl + H_2O \qquad (25.17)$$

In the second stage, pH is lowered to 8 to 9, and more oxidant is added to further oxidize cyanate to carbon dioxide and nitrogen. Oxidation of sodium cyanate with chlorine is shown in Eq. (25.18).

$$3Cl_2 + 4NaOH + 2NaCNO \rightarrow 2CO_2 + N_2 + 6NaCl + 2H_2O \qquad (25.18)$$

The first stage reaction is monitored and controlled by two independent loops. Caustic addition is controlled by a pH controller, which is set to deliver caustic when the pH is below set point. Chlorine addition is controlled with an ORP probe that calls for oxidant to maintain a specified ORP in the tank.

In the second stage, pH is lowered to about 8.5 through addition of sulfuric acid. This pH promotes the second oxidation reaction and produces effluent with a pH suitable for discharge. Acid addition must be done with care so that pH does not fall below 7, since that promotes formation of highly toxic hydrogen cyanide fumes. Chlorine addition is controlled by ORP or is added in proportion to the addition in the first stage.

A final step in pretreatment involves use of a settling tank, clarifier, or filter to remove suspended MOHs that may have precipitated. Further treatment may be necessary to reduce metal concentrations to a level below the discharge limit.

A less common treatment method for cyanide destruction involves oxidation by ozone (O_3). Ozone is a powerful oxidizing agent but must be generated on-site and delivered directly to the treatment tank. Equations 25.19 and 25.20 show the two-step oxidation of cyanide by ozone.

$$CN^- + O_3 \rightarrow CNO^- + O_2 \tag{25.19}$$

$$2CNO^- + 3O_3 + H_2O \rightarrow 2HCO_3^- + N_2 + 3O_2 \tag{25.20}$$

One advantage that ozone provides over chlorine lies in the type of by-products that are formed in the process. Chlorine has the potential to react with organics present in effluent to form chlorinated organic compounds. Chlorinated organics have been monitored and controlled in discharge due to the potential negative environmental impact they present. By-products of ozone with organic compounds produce less toxic short chain acids, ketones, and aldehydes.

The major disadvantages of the ozone oxidation process are capital cost, operating cost, maintenance, and operator training. Ozone generators are costly, and facilities must purchase closed reaction vessels to handle ozone gas that might be released from solution.

Oil-Bearing Waste

Some effluents contain significant amounts of oil and grease. Oil-bearing water, in most cases, needs pretreatment before treatment for heavy metal removal. Oil/water separation requires breaking of any oil/water emulsion produced by oil and grease that is dispersed in the effluent. Oil/water separation can be accomplished by chemical emulsion breaking and separation of the oil component by skimming or techniques such as dissolved air flotation (DAF) and membrane filtration. Removal of oil also removes organic compounds that may be present in the effluent that are soluble in the oil phase.

Concentrated Metal-Bearing Effluent

Concentrated metal-bearing waste can be handled in one of three ways:

1. It can be slowly metered into dilute effluent and treated in the normal manner that dilute metal-bearing waste is handled.
2. It can be treated in batch at the source with precipitation or separation techniques such as RO or ion exchange.
3. It can be shipped off-site for treatment.

Option 2 allows treatment in the most effective manner and offers possibility for recycling the metal back into the process.

Chelated Metal-Bearing Effluent

Chelating agents can offer special challenges for reducing metal concentrations to meet discharge limits. They present the most significant problems when conventional precipitation methods are used in end-of-pipe operations. There are three options for effective treatment of chelant-metal effluent:

1. Reduction of metal to elemental form by either electrochemical or chemical reduction
2. Precipitation using an agent that can overcome the chelant-metal bonding
3. Physical separation with ion exchange or RO

A comparison of the K_{sp} and the K_f for metal-chelant formation allows the best opportunity to determine whether precipitation presents a viable option. Selecting the agent with the smallest K_{sp} gives the best hope for formation of an insoluble metal salt. Table 25.2 shows that sulfide precipitation generally provides the best choice among hydroxide, carbonate, and sulfide precipitants. In addition, polymeric precipitating agents can act as effective precipitants for metals in the presence of chelants.

Presence of chelating agents may present problems for some metal removal techniques, especially those involving formation of insoluble precipitate. Formation of metal–chelant complexes presents a stable and soluble species that needs to be broken for precipitants to act.

If chelants are suspected in effluent, it is important to measure chelant content in order to assess potential problems they may present for conventional chemical treatment methods. A total chelant test can be used for measurement of chelant content of a water sample.

Chelant concentration may be variable in effluent, and frequent testing may be required in plants that produce effluent containing both metals and chelating agents.

CHAPTER 26

Sludge Manipulation

When effluent is treated by mechanical, chemical, or biological means, solids are formed as a by-product. These solids must be removed from the water and ultimately disposed in an appropriate manner. Cost of disposal can be quite high, and removal of water through thickening and dewatering reduces disposal costs. Thus, thickening and dewatering are two common operations in effluent treatment plants.

Sludge thickening and dewatering are related, equipment-intensive operations designed to separate water from solids. Separation serves to reduce volume and weight, while increasing percent solids in the final sludge. The major difference between thickening and dewatering is the amount of water separation achieved in each process. Thickening removes only a fraction of water present in sludge, while dewatering removes as much water as possible from sludge.

The amount of water removed from sludge depends on the type of solids being treated. Water in sludge can be classified into three basic categories: free water/floc water, capillary water (bound water), and intracellular water. Each water type has a different susceptibility to removal. Free water is in the bulk fluid phase, while floc water surrounds the floc but is not attached to the solids. Free water and floc water are not constrained by adhesive or capillary forces, and are easily removed during thickening and dewatering. Capillary water is held onto the solids by capillary action and is not easily removed from sludge without chemical treatment. Use of coagulants and flocculants causes an increase in sludge particle size, and converts a portion of capillary water into free water/floc water. This release of water causes sludge to become dewaterable. Intracellular water is that portion of water that resided inside bacterial cells. This water is not dewaterable unless the cell walls are lysed or broken. Therefore, the amount of intracellular water sets the theoretical upper limit for sludge cake dryness.

For example, in a typical waste activated sludge, approximately 70% of the volume is free water, 25% is floc water, 2% is capillary water, 2% is intracellular water, and about 1% is solids. If all water except intracellular water is removed, the maximum solids achievable are only 33%. If none of the capillary water is removed, then the maximum solids attainable drop to 20%.

Common thickening and dewatering alternatives are shown in Fig. 26.1. Selection of the thickening and dewatering process depends on the type and characteristics of the sludge, and the dewatered cake disposal method employed. For example, waste activated sludge is more effectively thickened by floatation then by gravity thickening, while a belt filter press (BFP) dewaters this biological sludge more successfully than a screw press. A dewatered cake solids content that supports its own combustion is best for the most economical final sludge disposal by incineration. In some cases, the dewatering device is apparent from experience with similar sludges, or by economic or geographical constraints. In other cases, an experimental pilot program needs to be conducted, to ascertain the most economical solution to a particular sludge manipulation problem. Physical and chemical characteristics of sludge along with local considerations dictate the most technically and economically effective means for thickening and dewatering. Generally, primary or inorganic sludges produce higher concentrations in both thickening and dewatering, while gelatinous sludges such as aluminum hydroxide precipitate or waste activated sludge, produce lower concentrations in each process sequence. A sludge blending tank is typically installed ahead of thickening or dewatering machines to provide consistent sludge characteristics, when two or more different types of sludges are processed together.

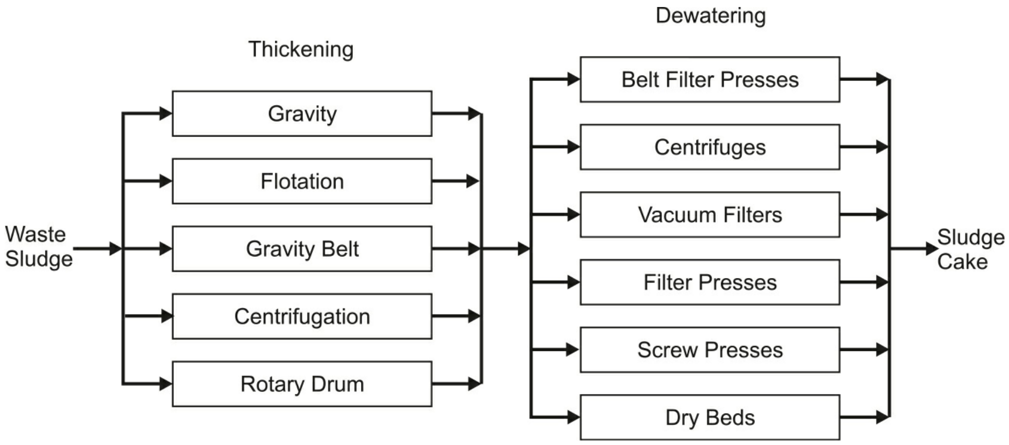


FIGURE 26.1 Conventional sludge manipulation alternatives.

Sludge Thickening

Sludge thickening removes free water from a slurry to reduce volume. For example, increasing the sludge solids concentration from 1% dry solids by weight to 2% reduces sludge volume by 50%, while increasing the concentration from 1 to 10% reduces sludge volume by 90% (Fig. 26.2). Thickening reduces capital and operating costs of subsequent sludge processing such as digestion, dewatering, or liquid transport (pipeline or truck), since these process costs are sensitive to the amount of water that has to be handled. In addition, other benefits including sludge flow and concentration equalization can be realized.

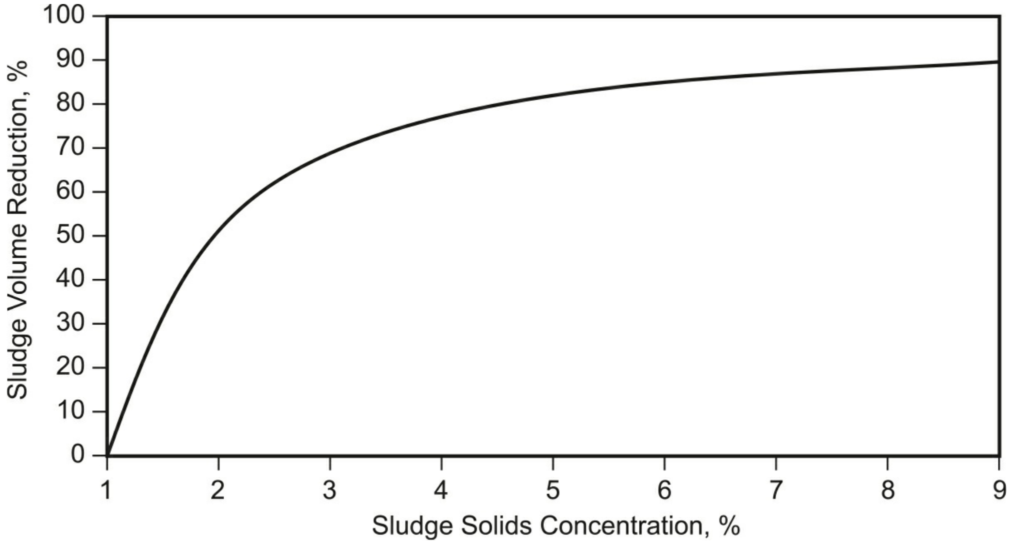


FIGURE 26.2 Sludge volume reduction by thickening.

Primary clarifiers, flotation clarification, sludge digestion processes, and specially designed thickening units, all achieve sludge thickening in effluent treatment plants. Separate thickening is seldom practiced in treatment plants with less than about 1 mgd capacity (158 m^3/h). In this case, gravity thickening is accomplished in the primary clarifier, sludge digestion units, or both. Additional costs for separate sludge thickening in larger treatment facilities are generally justified by improved control of the thickening process and the higher concentrations attained. Higher sludge concentrations reduce capital and operational costs for subsequent sludge handling facilities to such a degree, that installation of separate thickening units is economically viable.

Gravity Thickening

Gravity thickening involves separation of solid particles from the liquid phase by gravity, just like clarification. Thickening is treating slurries having a relatively high solids concentration, and processing them to a higher solids concentration. Clarity of the water removed is of secondary importance. Clarification by sedimentation processes dilute slurries to produce clear liquor, with sludge thickening being of secondary importance. The gravity separation device should be called a clarifier-thickener, when a high effluent clarity in conjunction with maximum underflow sludge solids concentration are of equal importance, such as the secondary clarifier in the activated sludge process.

The gravity sedimentation process takes place in four basic classifications, depending on the characteristics and concentration of solids in the initial suspension. These classifications are discrete particle settling, flocculant settling, hindered (also called zone) settling, and compression settling. In continuous gravity thickeners, all four settling classifications commonly occur simultaneously, and in these cases, the thickener should be called a clarifier-thickener. For example, thickeners treating blast furnace scrubber water in the steel industry, and pulp and paper mill primary clarifiers, are actually clarifier-thickeners. The gravity thickening process works well where the specific gravity of the solids is significantly greater than that of the liquid. A typical clarifier-thickener operation in a steel mill typically more than doubles the solids concentration.

Chemical Treatment

Chemicals may aid gravity thickening. Salts of iron and aluminum have little effect on concentrating sludge or increasing dry solids flux. In some cases, these salts may improve effluent clarity. Polymer flocculants are effective aids to gravity thickening, forming larger, heavier floc particles, which settle faster and increase underflow sludge concentration. Polymers can have cationic, anionic, or nonionic surface charges, depending on characteristics of the solids involved. Effective dosages are generally in the range of 0.5 to 10 lb/ton (0.25–5 kg/tonne) of sludge solids on a dry weight basis. Two test methods are used to arrive at the best chemical program. These are the stirred thickening test, and the simple cylinder settling test. Chemical is mixed with sludge, which is placed in the cylinder and allowed to settle. Measuring the concentration of a sludge sample removed from the bottom of the cylinder and comparing it to the concentration of an untreated sample determines effectiveness of treatment.

The chemical addition point and the postdilution water rate are very important to a successful chemical application program. Suitable feed points can be after the thickener feed pumps, into the feed line immediately outside of the thickener basin, or into the center feed well. Postdilution is the addition of clean (tap) water to polymer solution after the solution has been prepared. The quantity of dilution water used has to be adjusted, so that optimum dispersion of polymer throughout the sludge volume is attained.

Flotation Thickening

Thickening by flotation is usually more effective than gravity thickening, when solids have specific gravity close to the liquid from which they are being removed, and are gelatinous, such as biological sludges from the waste activated sludge process. Dissolved air flotation (DAF) is the process used for flotation thickening and not the induced air system, which is not capable of thickening due to its turbulent surface and limited float removal capabilities. The principles and systems used for DAF thickening are the same as those for DAF clarification.

Thickening of sludges from suspended growth biological treatment processes, such as the activated sludge and nitrification processes, are efficiently thickened by DAF. Other sludges such as primary sludge, aerobically digested sludge, and sludges containing metal salts from chemical treatment have been flotation thickened, but not as commonly as waste activated sludges. Typical design parameters for DAF thickening of waste activated sludge are as follows:

Solids loading rate (solids flux)	1.5 to 2.0 lb/[h · ft^2] (7.3–9.8 kg/[h · m^2])
Hydraulic loading rate	1.5 to 2.0 gpm/ft^2 (3.7–4.9 m^3/[h · m^2])
Air/solids ratio	0.02 to 0.03 lb/lb (kg/kg)
Recycle ratio	75 to 150%
Dissolving pressure	45 to 70 psig (310–483 kPag)

DAF thickening typically yields activated sludge concentrations greater than 4% by weight and solids capture of 90% or higher.

Quality of the activated sludge has a significant effect on the final solids concentration. For example, a filamentous, bulking activated sludge may not achieve 2% solids; while 4 to 5% thickened sludge is achieved with a well biologically flocculated sludge. Sludge volume index (SVI) indicates the potential final thickened sludge concentration. Best thickening performance occurs with SVI less than 160 mL/g. Float concentration deteriorates as SVI increases beyond 200 mL/g.

DAF thickening is often augmented by addition of chemical aids, such as inorganic aluminum salts and organic polyelectrolytes. Moderate to very high molecular weight polymer flocculants have been found to be the most effective. Cationic flocculants are used in most cases, since they are particularly effective in flocculation of biological solids. Introduction of the polymer into the line at a point where bubbles are forming and contacting the solids normally produces the best results. Use of chemicals can increase float concentration and solids capture, while offsetting adverse effects of poor sludge quality when SVI is above 200 mL/g.

Rotary Drum Thickener

The rotary drum thickener is also known as the rotary sludge thickener (RST), which consists of stainless steel or nonferrous wire mesh cloth, mounted on a cylindrical frame (Fig. 26.3). The drum revolves around its horizontal axis and is equipped with a variable speed drive, so that the rotational speed can be adjusted for the specific application. Chemically conditioned slurry flows into one end of the drum, removed free water flows through the screen, and thickened sludge exits out the opposite end of the drum. The pitch of the flights that move the sludge through the drum along with the drum speed establishes sludge retention time in the machine. Sludge depth is approximately the height of the flights. Spray headers located outside and close to the top of the drum clean the screen with high-pressure jets. Common failure of the RST is due to jets plugging, which causes the screen to blind in those sections and a reduction in thickened sludge concentration.

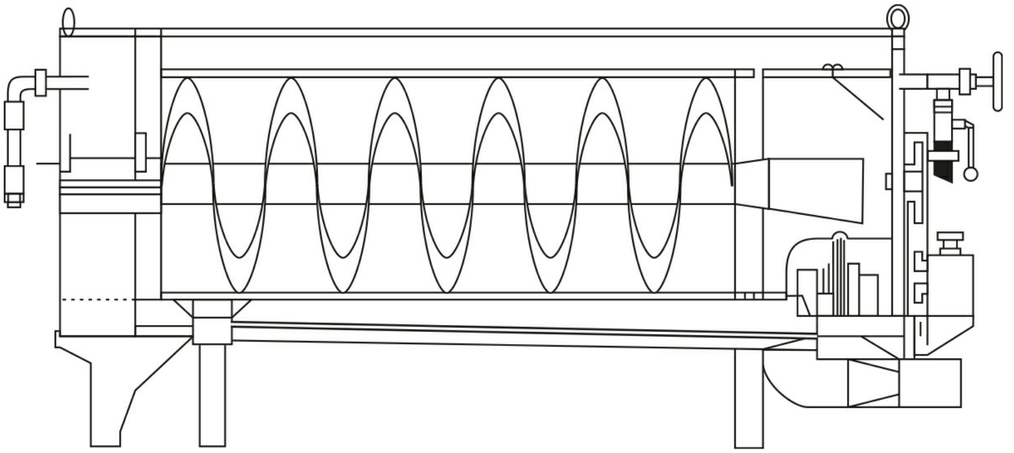


FIGURE 26.3 Rotary sludge thickener (RST).

Organic polymer sludge conditioning is required for thickening. A RST system, therefore, consists of a chemical conditioning system including polymer makeup, chemical feed and polymer/sludge mixing facility, and the rotating drum thickener. Organic flocculants agglomerate fines in the slurry, so that free water can be readily drained through the screen. Moderate to very high molecular weight cationic polymers are used, particularly for conditioning biological sludges. Inorganic or organic coagulants may be used in conjunction with organic flocculants for specific sludges or sludge blends.

The RST system is primary used for thickening biological sludges (waste activated sludges), biological sludge mixtures, and primary sludges. Typical operating results are shown in Table 26.1.

Waste Activated (Biological) Sludge	
Inlet slurry concentration	0.5–1.5%
Thickened sludge concentration	4–10%
Solids capture	95–99%
Polymer dosage	1–25 lb/ton (0.5–13 kg/tonne) dry solids
SVI < 100 produces highest concentration and uses lowest polymer dosage.	
Municipal Primary Sludge	
Inlet slurry concentration	3–4%
Thickened sludge concentration	8–12%
Solids capture	95–99%
Polymer dosage	2–8 lb/ton (1–4 kg/tonne) dry solids
Pulp and Paper Primary plus Waste Activated Sludge (WAS)	
Mixture	30–70% primary, 70–30% WAS
Inlet slurry concentration	1–4%
Thickened sludge concentration	6–10%
Solids capture	95–99%
Polymer dosage	4–20 lb/ton (2–10 kg/tonne) dry solids

TABLE 26.1 Rotating Sludge Thickener Operating Results

Advantages of rotary drum thickeners are low capital cost, energy usage, and maintenance costs along with small space requirements. They are often used to increase capacity of BFPs and screw presses, either for an existing installation or as part of a new dewatering installation.

Gravity Table Thickeners

Gravity table or belt thickeners (Fig. 26.4) are a simple means for thickening sludges. Table thickeners stem from the design of belt presses used for sludge dewatering. In belt press dewatering, effective sludge thickening has to take place in the gravity drainage section of the press, so that remaining sections of the press can successfully dewater the sludge. Chemical treatment of slurry before the belt thickener is required to release the maximum amount of free water from the sludge. The gravity table thickening system therefore includes a chemical conditioning system. The type of organic polymers used is the same as for the rotary drum thickener, and depends on the specific sludge.

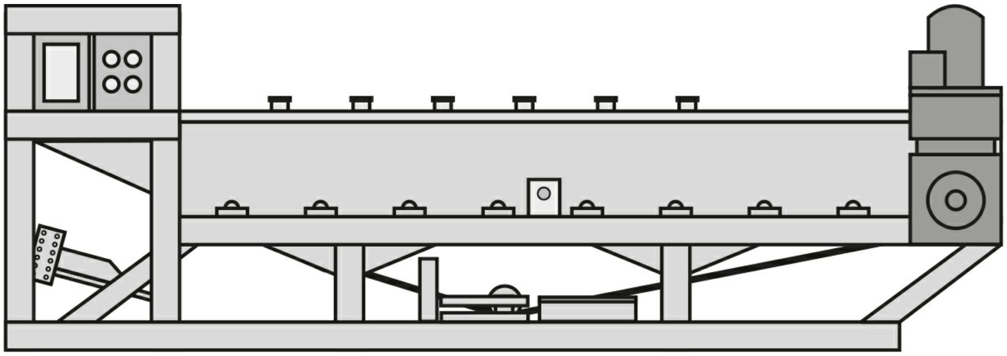


FIGURE 26.4 Gravity table thickener.

Chemically conditioned sludge is distributed across the width of the porous belt media, (right side of Fig. 26.4) running continuously through the machine. Free water drains by gravity into a pan below the moving belt, from where it is returned to the effluent treatment process. Adjustable plows furrow and roll the sludge to prevent ponding, and expose free water to open belt areas. A low-wear grid system supports the belt and shears capillary water from the underside of the belt to increase water drainage through the belt. No pressure or vacuum assistance is needed. Thickened sludge is discharged off the end of the unit. A high-pressure shower assembly washes the belt on its return to the head end of the machine to remove particles trapped in the belt, so that maximum water drainage is accomplished during its next thickening pass. Belt speed adjustment is provided by a variable speed drive for operational optimization.

Table thickeners are used for many types of sludges including primary, biological, and mixtures of the two. Thickening results for table thickeners are similar to those achieved by rotating sludge thickeners. Table thickeners are often coupled with screw presses to increase the press capacity for dewatering dilute slurries.

Centrifugal Thickening

Solids concentration or thickening can also be accomplished by centrifugation. The three types of centrifuges used are the solid bowl (also called decanter), basket, and disk-nozzle. The solid bowl or decanter is the most commonly used type of centrifuge for sludge thickening, while the basket type is used for thickening smaller quantities of sludges.

Solid Bowl (Decanter) Centrifuges

Operating parameters and their interaction in the centrifugal process for liquid/solids separation using solid bowl or decanter centrifuges are discussed in detail later in this chapter. The principal operational variables include characteristics of the feed sludge; SVI for waste activated sludge thickening; bowl rotational speed; slurry feed rate; liquid pool depth in the bowl; differential speed between the bowl and the conveyor; and need to add polymers to improve performance. Interrelationships between these variables are different for each specific installation. Generally, bench scale or onsite pilot plant tests are used to determine appropriate machine size and operating parameters for a specific location.

Solids capture is important when thickening to minimize the amount of solids returned to the treatment process. Many systems are designed with standby polymer systems for use when capture rates have to be increased. Percent capture is calculated by:

$$\text{Percent Solids Capture} = \left[1 - \frac{C_r(C_c - C_s)}{C_s(C_c - C_r)}\right]100 \qquad (26.1)$$

where C_r = concentration of solids in reject liquor (centrate), mg/L or %
C_c = concentration of solids in cake, mg/L or %
C_s = concentration of solids in slurry feed, mg/L or %

Basket Centrifuge

The basket-type centrifuge is a batch operation that limits its application to small flows for thickening and dewatering. The basket centrifuge is more generally used for sludge dewatering, and details of its operation are discussed in the Sludge Dewatering section. Sludge characteristics, slurry feed rate, bowl speed, and duration of sludge removal affect the extent of thickening and solids capture. As with the solid bowl, a standby polymer system is generally included in the installation to increase solids capture when needed.

Disk-Nozzle Centrifuge

The disk-nozzle centrifuge, while primarily a liquid/liquid separation device, can be used to thicken slurries. It is suitable for thickening slurry with very fine, uniform particle size, since it creates greater centrifugal force than a solid bowl or basket centrifuge. It has been used for thickening biological slurries such as waste activated or similar sludges. The disk-nozzle centrifuge effectively thickens waste activated sludge at high feed rates and without polymer addition due to its high gravitational force.

Slurry is introduced into the center of the machine at the top and is distributed between the stacked conical disks (Fig. 26.5). Disks are stacked so that the space between them is 0.1 to 0.25 inches (2.5–6.4 mm) apart. Solids settle to the underside of the disks and slide down the plates to the bowl wall, where compaction takes place due to the gravitational force. Concentrated solids are discharged through nozzles in the periphery of the rotating bowl. Centrate passes under the sludge and discharges from the center of the centrifuge. The disk-nozzle centrifuge is subject to frequent plugging when coarser solids are encountered, due to the close spacing of the disks and the small nozzle size. Slurries containing coarse solids are typically screened before introduction into the machine.

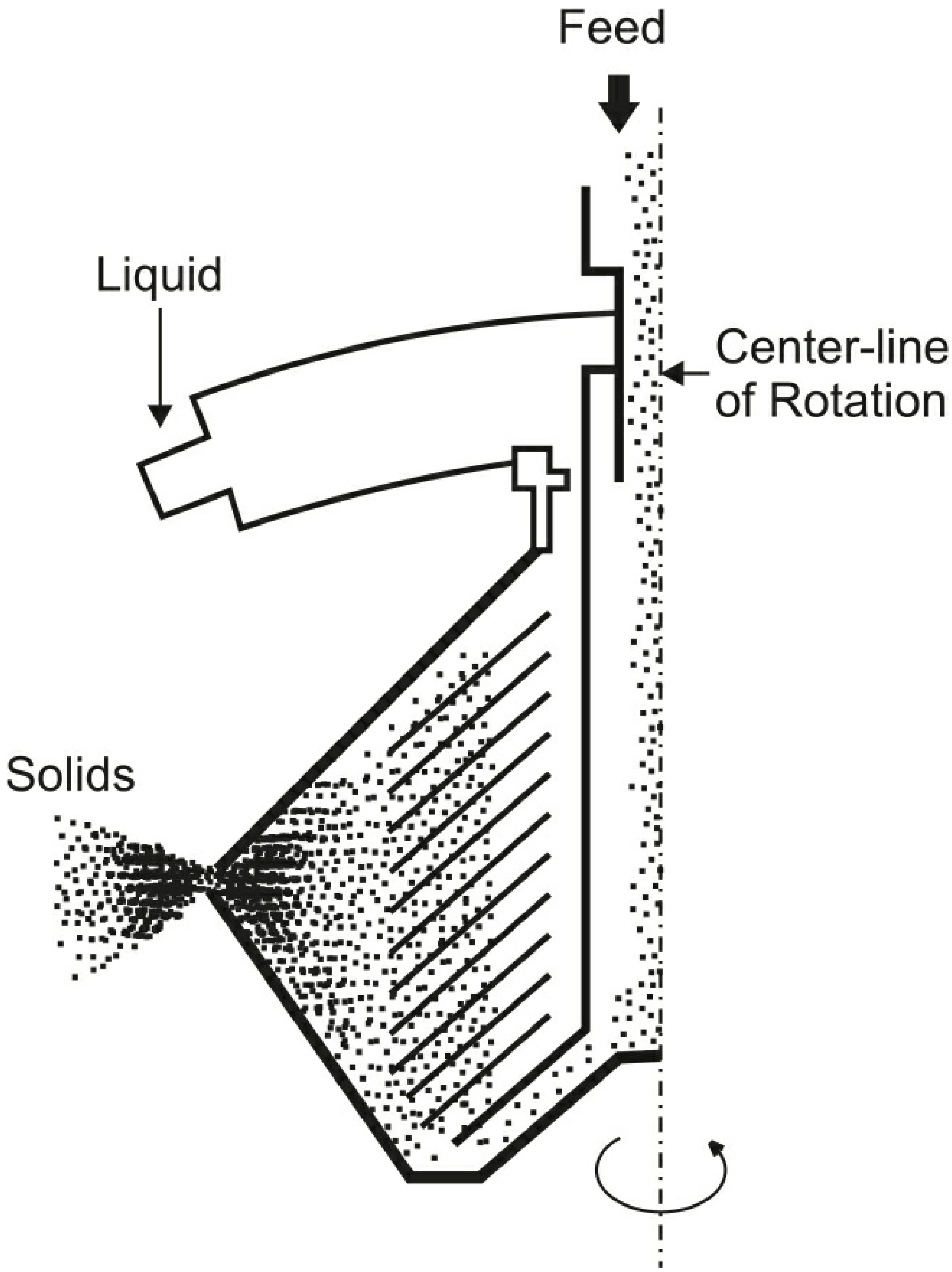


FIGURE 26.5 Disk-nozzle centrifuge.

Sludge Dewatering

Sludge dewatering is normally the final liquid/solids separation step in an effluent treatment process. The dewatering method is often dictated by the nature of solids being dewatered, final method of sludge disposal, and specific local conditions. The goal is to produce a dewatered sludge cake of such density, solids content, and strength, to meet subsequent sludge disposal requirements. For example, maximum water needs to be extracted from sludge if it is going to be incinerated to minimize use of auxiliary fuel. Low cake moisture (high solids concentration) can be required to pass cake drainage tests for landfills and minimize hauling costs. Sludge may not need to be dewatered to such a high extent when cake is used for a land reclamation program.

Nature of Sludge

The nature of sludge refers to both physical and chemical sludge characteristics. Viscosity, volatile (organic) content, compressibility, and particle size, shape, density, and electrical surface charge are included. Typically, some of these are design considerations and out of the effluent treatment plant operational control. Parameters within plant control include feed solids concentration, accumulation of fines, sludge age, and biological health.

Feed Solids Concentration

A change in feed solids concentration can affect solids capture, cake solids, polymer dosage, and sludge throughput of the dewatering device. The primary clarifier operation, upstream sludge thickening facilities, or sludge blending tank, need to be operated so that as consistent a sludge solids concentration is provided to the dewatering device as possible, to avoid continuous adjustment of machine operating parameters and chemical addition.

Accumulation of Fines

The level of fines recycled back to the treatment plant is minimized by a high solids capture by the dewatering machine, and prevents them from accumulating in the plant. The particle size distribution in the sludge changes if fines cycle up in the plant, resulting in increased chemical consumption, wetter cake, and further reduction in solids capture. Fines can also upsetother treatment plant processes such as aeration, clarification, and biochemical oxygen demand (BOD) removal.

Sludge Age

Sludge age in one context refers to the time sludge spends in the effluent treatment plant before dewatering. Prolonged aging periods often alter sludge characteristics through anaerobic decomposition of organic matter or chemical reactions that increase the quantity and sometimes even the type of chemicals needed for conditioning. This aging period needs to be kept as short as possible, so that fresh sludge is always available for dewatering.

In biological treatment processes, sludge age indicates the time sludge is under aeration, which affects sludge dewaterability. Older sludge can result in wetter cake, lower hydraulic and solids throughput, and higher polymer demand. Very young sludge age can also be problematic for dewatering and commonly requires high chemical dosage.

Secondary Sludge Biological Health

One of the first variables that are suspect when problems occur while dewatering secondary treatment sludge is the biological health of the sludge. High SVI for biological sludge indicates difficult sludge to dewater, just as it indicates the sludge is difficult to settle. “Unhealthy” sludge caused by toxins, excessive age, insufficient nutrients, improper dissolved oxygen levels, or imbalanced food to mass ratios dewaters poorly, often increasing polymer requirements, reducing throughput, and producing wetter cake.

Belt Filter Press

The BFP (Fig. 26.6) is also referred to as a twin belt press or a twin wire press, particularly in the pulp and paper industry. The BFP generally employs two moving porous belts to dewater slurries (sludge) to a moist cake.

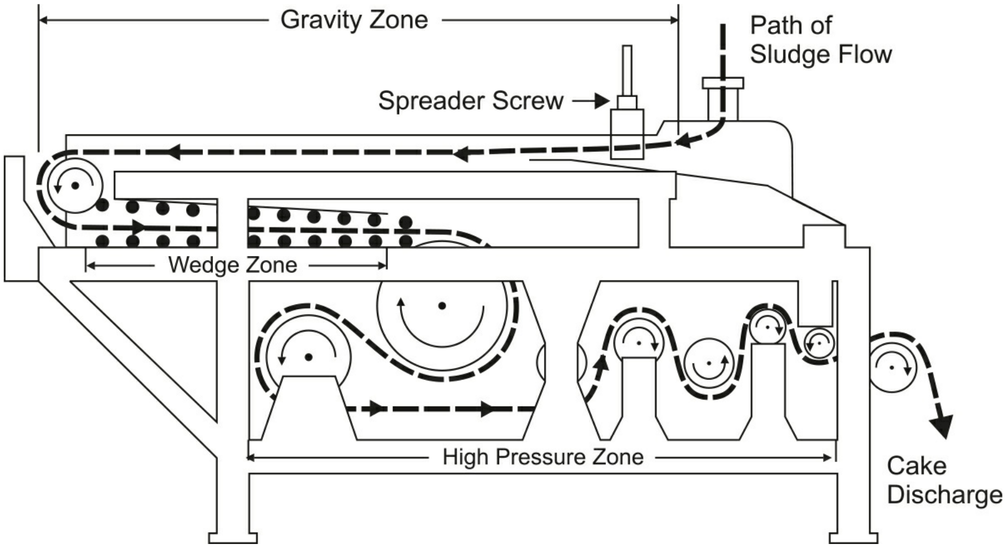


FIGURE 26.6 An illustration of a BFP, Andritz-Ruthner, Model S-7.

Centrifugation

Centrifugation has long been used for dewatering as well as for thickening sludge. Selection of the proper centrifuge is important, since design characteristics can be tailored to meet specific application needs. Several inherent advantages in centrifugation make it attractive for many dewatering applications. Among important advantages are compact design, completely enclosed machine, high throughput, and relative simplicity of operation. They can be installed and operated outdoors in moderate climates.

Vacuum Filters

Rotary vacuum filters have been used for many years by industry and municipalities to dewater waste sludges. They are also used in many process applications such as dewatering slurries in the chemical industry, pulping operations in paper mills, and coal recovery and ore processing in the mining industry to name a few. Solids content of dewatered cake varies considerably, depending on the type of slurry being dewatered and particle size. Slurries of inorganic solids may dewater to 80% solids, whereas a biological sludge may dewater to only a 20% solids level.

The principal component of the continuous vacuum filtration system is the cylindrical filter drum enclosed at both ends. The drum supports a porous medium or cloth and rotates while partially submerged in a slurry vat. The interior surface of the drum is divided into compartments by partitions (seal strips) that are connected by pipes to a valve located at one end of the drum. The valve controls application of vacuum to specific areas of the filtering medium. The valve allows each compartment to function continuously in the following sequence as the drum rotates (Fig. 26.7).

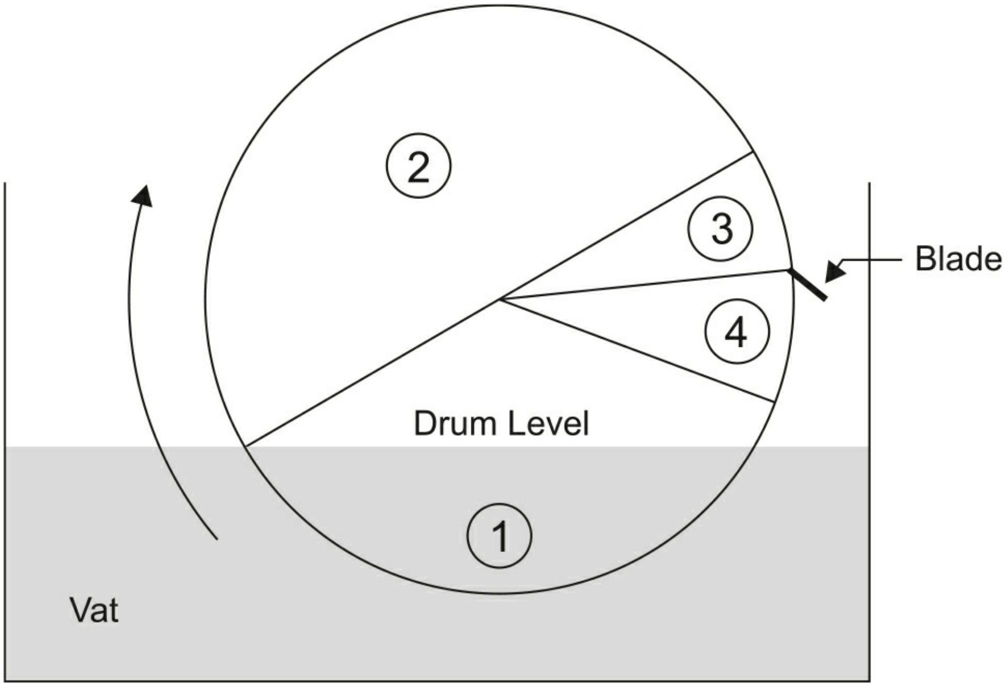


FIGURE 26.7 Operating sequence of rotary drum vacuum filter.

1. *Cake formation*: The drum is submerged in the vat containing slurry, and vacuum is applied during this step. The first solids that collect on the medium act as a filter for subsequent cake formations. For this reason, it is desirable that cake be formed gradually to the optimum thickness.
2. *Liquid extraction or drying*: Vacuum is also applied during the liquid extraction or drying step. Water or liquid is drawn out of the filter cake through the filter media to the inside of the drum, through the valve, and to the receiver through a vacuum line separate from the cake formation vacuum line.
3. *Filter cake removal or discharge*: Removal of filter cake from the drum is accomplished by one of several methods depending on the type of vacuum filter, which will be discussed later.
4. *Media washing*: The final step in the cycle of vacuum filter operation can be accomplished on a continuous or intermittent basis. High-pressure water sprays are normally used to dislodge particles that could buildup and clog the filtering medium. It often becomes necessary to acid wash the filter media on a routine basis, when ferric chloride and lime are used as conditioning chemicals, or if the slurry contains oils or greases.

Screw Presses

Screw presses are used almost exclusively in the pulp and paper industry. The screw press needs compressible solids (like fibers) in the slurry for efficient dewatering performance. Screw presses do not dewater slurries well without some compressible solids in the sludge. Fiber recovery in some mills has improved to a point where screw presses fail to function well due to the lack of fiber in the effluent sludge. In these cases, either some fiber is sent to the dewatering process, or replacing the screw press is required. Addition of sawdust generally does not improve screw press operation, since sawdust is not a good substitute for fiber.

The screw press dewaters pulp and paper mill primary or blended primary, and biological (secondary) sludges to yield cake solids in the 26 to 52% range, depending on the ratio of biological sludge to primary sludge (Fig. 26.8). Operation of screw presses on blended sludges containing as much as 50% biological solids is difficult. The feasibility of using a screw press on blended sludges having 50% or more biological solids is questionable. Other dewatering devices, such as BFPs or decanter centrifuges, are better applications then the screw press for blended sludges with a high percentage of biological solids.

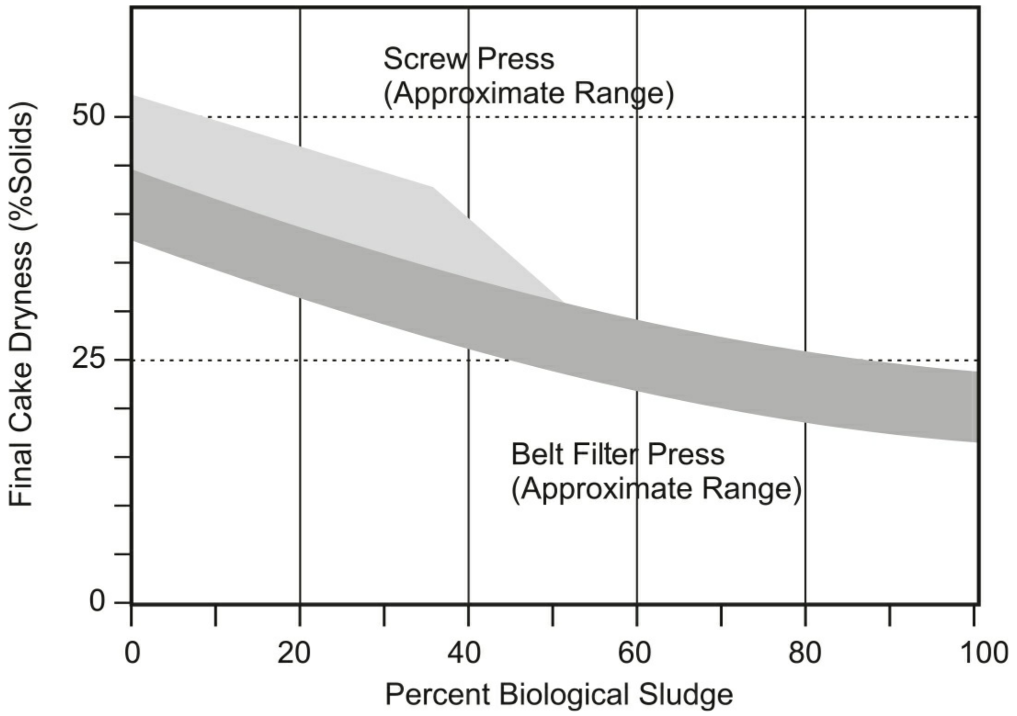


FIGURE 26.8 Application of screw press for blended sludges.

The basic components of the screw press are shown in Fig. 26.9, and include:

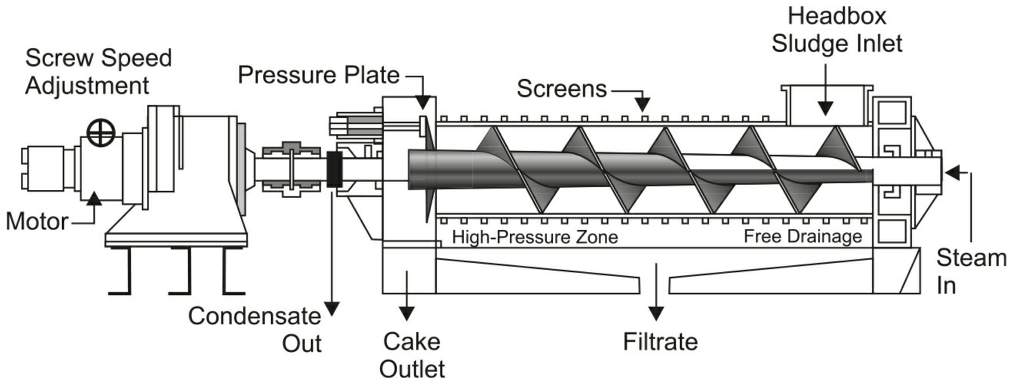


FIGURE 26.9 Cross section of a typical screw press.

- The headbox serves as the sludge inlet to the press. The headbox was only a few feet (about 1 m) high for early presses operating on primary sludge. The headbox for newer presses can be as tall as 10 to 15 feet (3–4.6 m), especially when dewatering blended primary and biological sludges.
- The barrel screen section through which the pressate water flows is divided into four sections along the length of the machine:
    1. Free drainage section immediately below the headbox
    2. Initial- and medium-pressure sections
    3. High-pressure section
    4. Plug section that develops the choke pressure
- A tapered shaft has a small diameter at the inlet end of the machine and increases to a maximum diameter at the cake outlet with helical conveyor flights (helical screw) attached to the shaft. The increasing diameter of the shaft creates a radial pressure on the sludge between the shaft and the barrel screen section as it is moved through the machine by the screw conveyor.
- Low-pressure steam is sometimes introduced into the shaft to reduce water viscosity to improve drainage and heat the sludge to achieve

some evaporative drying after the cake has been discharged from the press. This is not cost-effective unless waste steam is used, even though a dryer cake is achieved.

- The helical flights on the shaft are cylindrical, not tapered, and have a very close clearance to the barrel section to keep the screen openings clear. This clearance is typically about 0.02 to 0.04 inch (0.5–1 mm).
- One or sometimes two of the last helical sections of flights are cut off to create a plug at the end of the screw. This plug creates the necessary high backpressure on the sludge being conveyed forward.
- A pressure plate or spring-loaded doughnut applies final pressure at the press outlet. It pushes against the plug that is being forced out of the press by the rotating screw shaft. It also breaks up cake exiting the machine, so that it does not plug the outlet.
- Cake exits the press into the outlet box.
- A variable speed motor drives the shaft and controls the shaft rotational speed.

Plate-and-Frame Filter Presses

The principle of plate-and-frame press dewatering (Fig. 26.10) is similar to that for vacuum filtration except that pressure, not vacuum, is used to separate the slurry, and batch, not continuous, operation is used. Fluid pressure generated by pumping slurry into the unit provides the driving force. Plate-and-frame presses are also referred to as recessed chamber presses and diaphragm presses. The press consists of vertical plates with recessed chambers held in a frame and pressed together between a fixed and moving end. Each plate is fitted with a medium, normally woven monofilament polypropylene filter cloth because of its resistance to blinding, ease of cleaning, and durability.

FIGURE 26.10 Plate-and-frame press dewatering sewage plant sludge.

Plate-and-frame presses do not close to squeeze or press sludge. Instead, sludge pumps capable of developing pressures up to 225 psig (1.6 MPag), force sludge into the media-lined cavities between vertical plates. Presses for dewatering sludges are generally designed for a maximum pumping pressure of 100 psig (689 kPag). Filtrate flow is initially high as the press fills and then starts decreasing as dewatering progresses. Ultimately, filtrate flow stops or the cycle time (determined by experience) expires, the sludge pump is shut down, the feed line drains, and the press begins to unload. The moving end or the press retracts and separates the plates, allowing filter cake to fall from the plates. Usually, presses are equipped with an automatic gear arrangement to open and separate the plates. After cake has been removed, the moving end pushes the plates against the fixed end for recharging to complete the cycle (Figs. 26.11–26.14). Plates are generally washed between cycles with a high-pressure hose to prevent cloth blinding on succeeding runs. Typical cycle times range from 1 hour to 24 hours, depending on the process and equipment sizing. Presses are commonly installed above floor level, so that a hopper can be placed beneath the press to collect dry cake. Plate-and-frame presses are not as widely used as other mechanical dewatering devices, since they are a batch process while others are a continuous process.

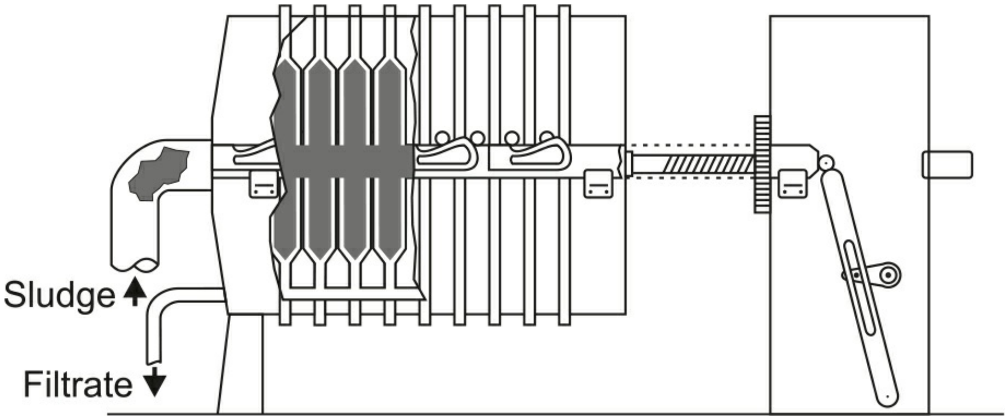


FIGURE 26.11 Plate-and-frame press charging. With plates closed, sludge is pumped into the press. The cake begins to form and becomes the filtering medium. Filtrate flow rate is highest at the start of the cycle.

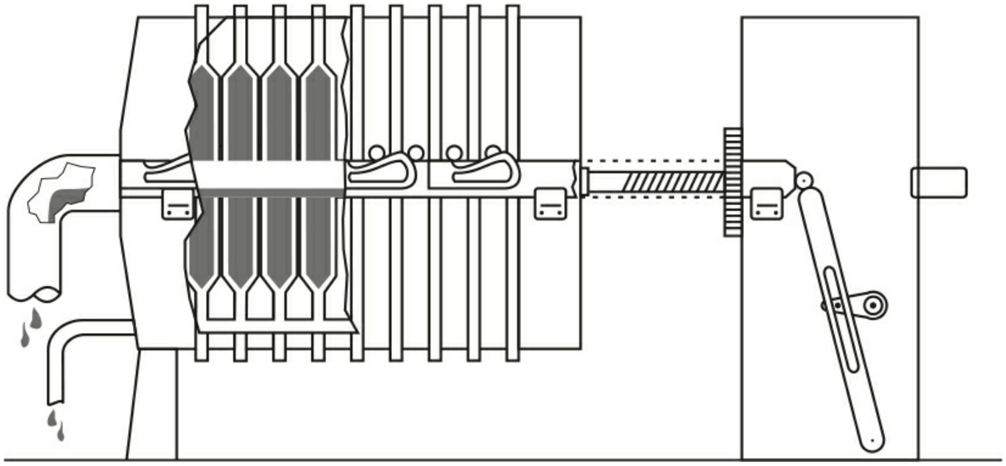


FIGURE 26.12 Plate-and-frame press draining. When cakes are formed and filtrate flow is reduced, the pump is automatically stopped and the inlet line drained.

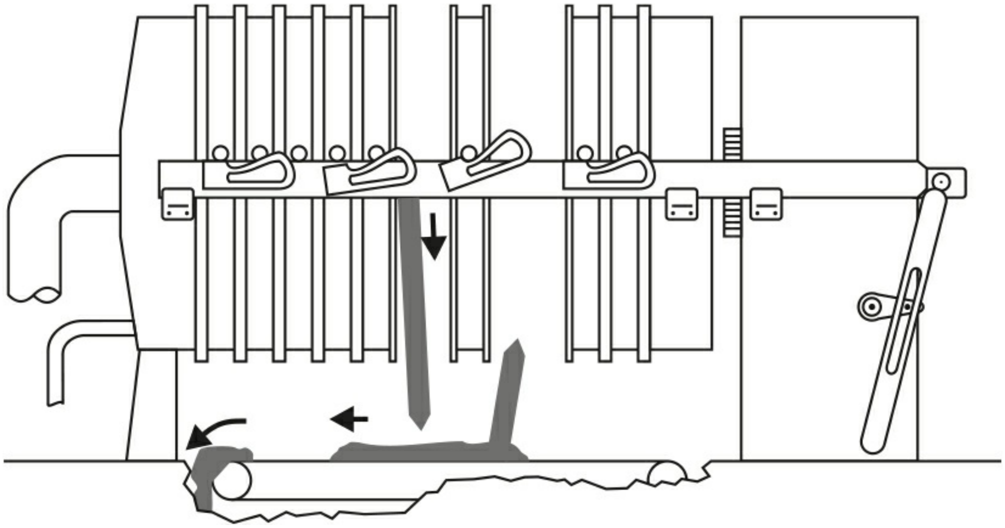


FIGURE 26.13 Plate-and-frame press discharging. The traveling end of the press retracts. A reciprocating mechanism automatically separates plates in sequence. Filter cakes drop and are carried away by a conveyer.

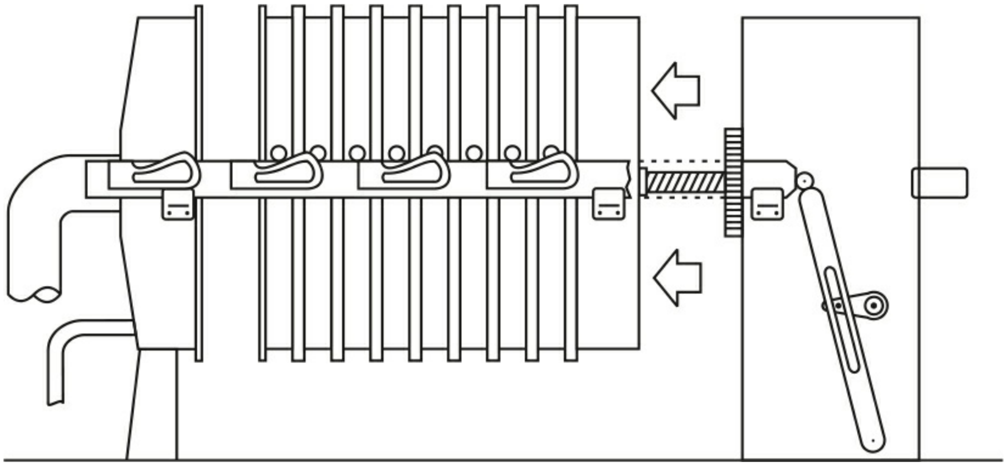


FIGURE 26.14 Plate-and-frame press closing. After the last cake has dropped, the plates are pressed together for another filtering cycle.

The variable volume recessed plate filter press (Fig. 26.15), differs from the fixed volume press, in that it utilizes a flexible membrane or diaphragm to provide a second squeezing phase to sludge within each chamber after filter cake formation. The space between the press plate and its flexible membrane is filled with water to provide additional compression of the sludge at a predetermined filter press feed pump pressure. The variable volume press is generally called a diaphragm press.

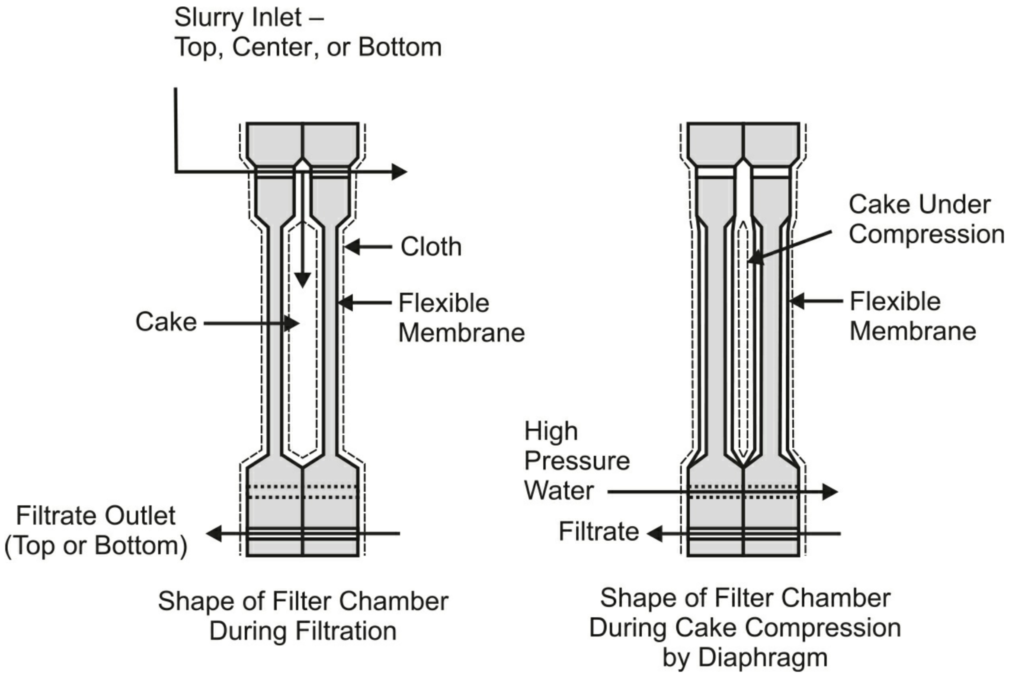


FIGURE 26.15 Variable volume (diaphragm) filter press.

Drying Beds

Drying beds are often used to dewater waste sludges, where land is available and climatic conditions are favorable. In early designs, sand was used as the filtering medium. The typical sand bed has tile underdrains covered by 12 inches (305 mm) of graded gravel, then topped with 6 to 9 inches (152–229 mm) of 0.3 to 1.2 mm sand, with a uniformity coefficient less than 5.0 (Fig. 26.16).

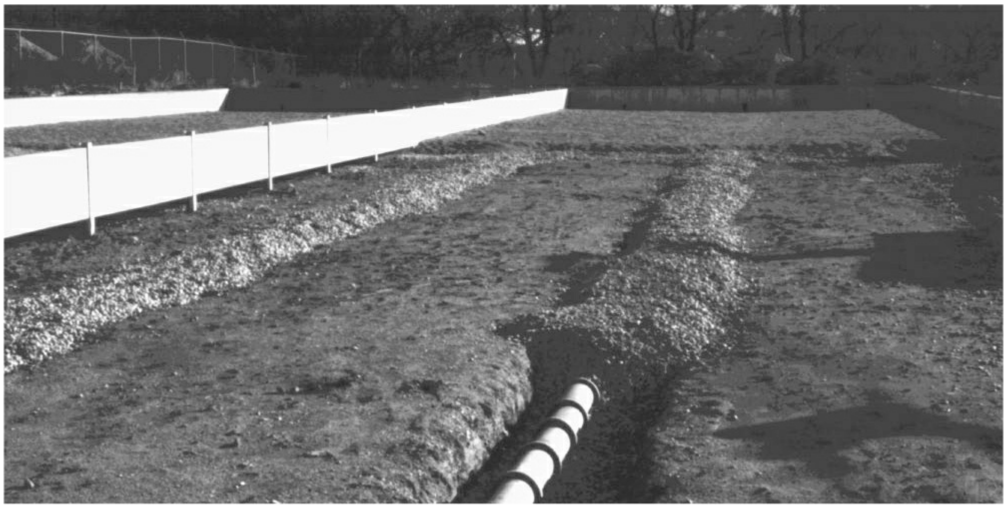


FIGURE 26.16 Conventional sand drying bed with tile underdrain system, shown here during

construction.

Under the right circumstances, the drying bed provides advantages over mechanical dewatering devices such as low operating costs due to low energy requirements, little maintenance, and minimal operator attention. They have the ability to handle variable sludges and to produce drier cakes than most mechanical devices. There are, however, limitations to their use, such as high land requirements and weather dependency. Since drying beds are outdoors, odor may be a problem, if the sludge is high in organic matter.

For effective dewatering on drying beds, sludge must have physical properties that allow drainage of contained water without blinding of the filtering medium. Water drainage should be rapid and relatively complete, reducing to a minimum the residue that must be evaporated. Sludge applied to the drying bed should be as thick as possible to reduce required drying time. Chemicals that improve release of free water have proven effective in speeding drainage and significantly reducing drying time.

Drying beds have been popular for dewatering municipal sewage sludges, including primary, aerobically or anaerobically digested, and mixtures of primary with biological sludges. Many other types of sludges are dewatered on drying beds, including water plant clarification sludges, lime softening sludges, and industrial sludges.

Drying bed designs generally fall into the following categories: impervious bottom beds, impervious bottom with drainage strips, sand beds, and sand beds with multiple cement tracks to provide complete mechanical unloading.

Simple impervious bottom beds and those with drainage strips are relatively easy to install and maintain, but they require longer drying times due to the reduced water drainage. Originally, sand beds were designed with clay tile as the underdrain system. Clay tile tended to break easily, ruling out the use of mechanical equipment for dry sludge removal. In addition, sludge removal with mechanical loaders has caused relatively high sand losses, which can be an important consideration if sand is scarce.

Some plants have been successful with resilient plastic underdrain tile and specially designed buckets to skim off dry sludge from the sand. One bed using alternating sand and cement strips throughout the entire bed, coupled with a drive-down ramp across the full width of the bed, allows a front end loader to make parallel passes when removing dried sludge. Cement strips spaced at tire track distances prevent the bucket from digging into the sand media. This bed appears to offer the advantage of hard surface support along with open sand drainage. The use of polymer significantly increases dewatering speed and therefore reduces the area required.

Where sand beds are already in place, polymer addition allows more complete drying and reduces the volume of dried sludge for disposal. Surface loading rates can often be two or more times as great as on beds not using polymer dewatering chemicals.

Sludge application largely depends on local plant needs and the type of bed used. Normally, sludges are applied from 6 to 10 inches (152–254 mm) deep, depending on local conditions and the amount of sludge available for drying. Addition of new sludge on top of partially dried sludge is not recommended. An exception to this may be thin digester supernate, which is sent to the drying bed first in order to minimize its impact on the primary clarifier. In this case, chemicals must be used in order to prevent blinding of the drying bed by multiple sludge applications.

CHAPTER 27

Emulsion Treatment

Water and oil sometimes combine (emulsify) during industrial processes. Resulting emulsions are either oil-in-water (o/w) or water-in-oil (w/o), depending on which material is dispersed in the other. An o/w emulsion has water as the continuous phase, while the w/o emulsion has oil in the continuous phase. Either type of emulsion may contain other contaminating materials (solids, dirt, metal particles, emulsifiers, cleaners, soaps, solvents, etc.).

Emulsions can be found in a variety of industries and formed by a variety of processes. Since formation of emulsions is so specific to the industry and process, emulsion breaking product selection is somewhat difficult and requires bench testing. Oils themselves vary greatly in composition, ranging from lubricating and machining oils, to soluble oils, rolling oils, animal oils, and occasionally aromatics.

Industries where emulsions are commonly found include:

- Basic metal industries—steel hot strip mills, casting systems, and aluminum
- Automotive and machining industry—metalworking and metal parts manufacturing waste oils such as lubricating oils, cutting oils, lapping compounds, grinding fluids, and specialty fluids
- Petroleum refining industry—slop oils from separator skimmings, tank bottoms, and coke plants
- Petrochemical industry—olefin quenching operations
- Textile mills/synthetic fiber industry—spin finishing mills
- Meat and food processing industry—rendering plants, creameries,

breweries, and canneries

- Paints, surface coatings, and adhesives industries
- Oils, fats, and waxes industries
- Soap and detergents industry including laundries
- Leather industry

Theory of Emulsions

To understand emulsion breaking requires an understanding of emulsion stability. The emulsion is generally stabilized by one or more of three basic mechanisms: ionization, adsorption, and frictional contact.

Ionization is caused by surface-active chemical agents in a system. Surfactant molecules usually carry an ionic charge and seek out the oil–water interface at the surface of the emulsified droplets.

Adsorption stabilization is caused by fine particles adsorbed at the oil–water interface that tend to reinforce the interfacial film. Dispersed droplets thus cannot coalesce because of the interference, or blocking effect, caused by the solids. Electrostatic charges may also be present and play a significant role in emulsion stabilization.

Frictional contact stability occurs when oil and water phases mix with each other. Vigorous agitation is required to form the emulsion. In this case, coalescence of oil is hindered due to the inability of the oil or water to drain with sufficient speed to allow for the collision of two particles. Electrostatic charges can arise from this mechanism, and again tend to collect at the oil–water interface. This gives rise to a stable emulsion due to repulsion of charged emulsified droplets.

In emulsion theory, a double layer of electrostatic charge (the Helmholtz layer) is formed around a spherical emulsified droplet. The surface of the emulsified droplet takes on a characteristic charge, while the outer surface of the Helmholtz layer has a concentration of opposite charge. The Helmholtz double layer model is shown in Fig. 27.1. The emulsified spherical particle has attained a characteristic surface charge, causing the layer just outside to acquire an opposite charge. These charges repel other particles having the same charge, giving rise to emulsion stability. In nearly all cases, surface charge on the droplet is negative.

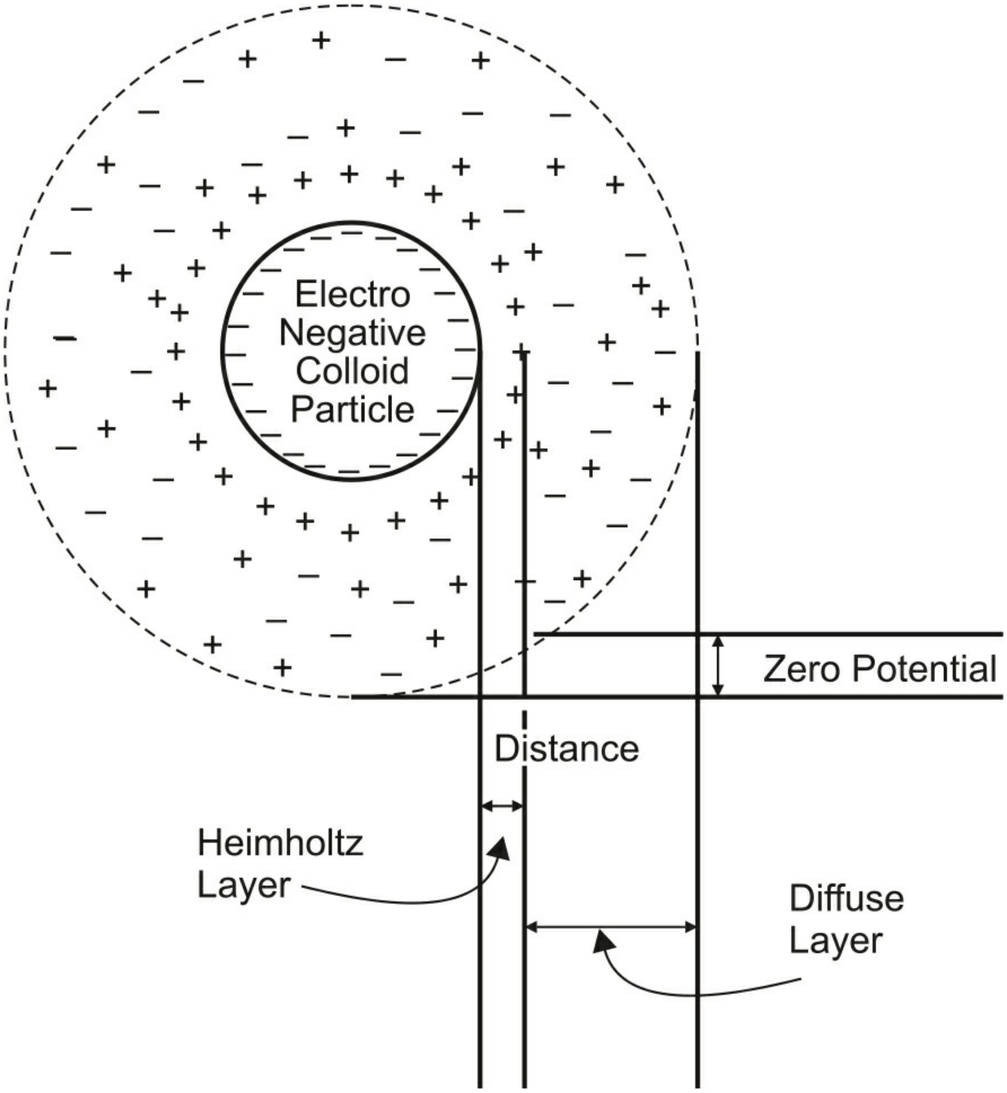


FIGURE 27.1 Electrical charge distribution of emulsified particle.

In destabilizing or breaking emulsions, stabilizing factors must be eliminated or neutralized to allow emulsified droplets to coalesce and the emulsion to resolve. Accumulated electrostatic surface charges associated with an emulsified droplet can be neutralized by introducing an agent having an opposite charge to that of the droplet. Chemical emulsion breakers work on this principle to destabilize and resolve emulsions.

Two types of emulsions occur:

1. Oily waste emulsions—oil dispersed in a continuous water phase
2. Waste oil emulsions—water dispersed in a continuous oil phase

The two types of emulsions can be distinguished by observation. An oily waste emulsion is water continuous, and appears to be oily, dirty water. A drop of oily waste emulsion disperses in a beaker of water upon gentle stirring. A waste oil emulsion is usually thick and viscous, and when a drop of it is placed in water, it remains as a discrete drop (Figs. 27.2 and 27.3).

FIGURE 27.2 A few drops of oily water (o/w emulsion) when added to water will disperse in the water.

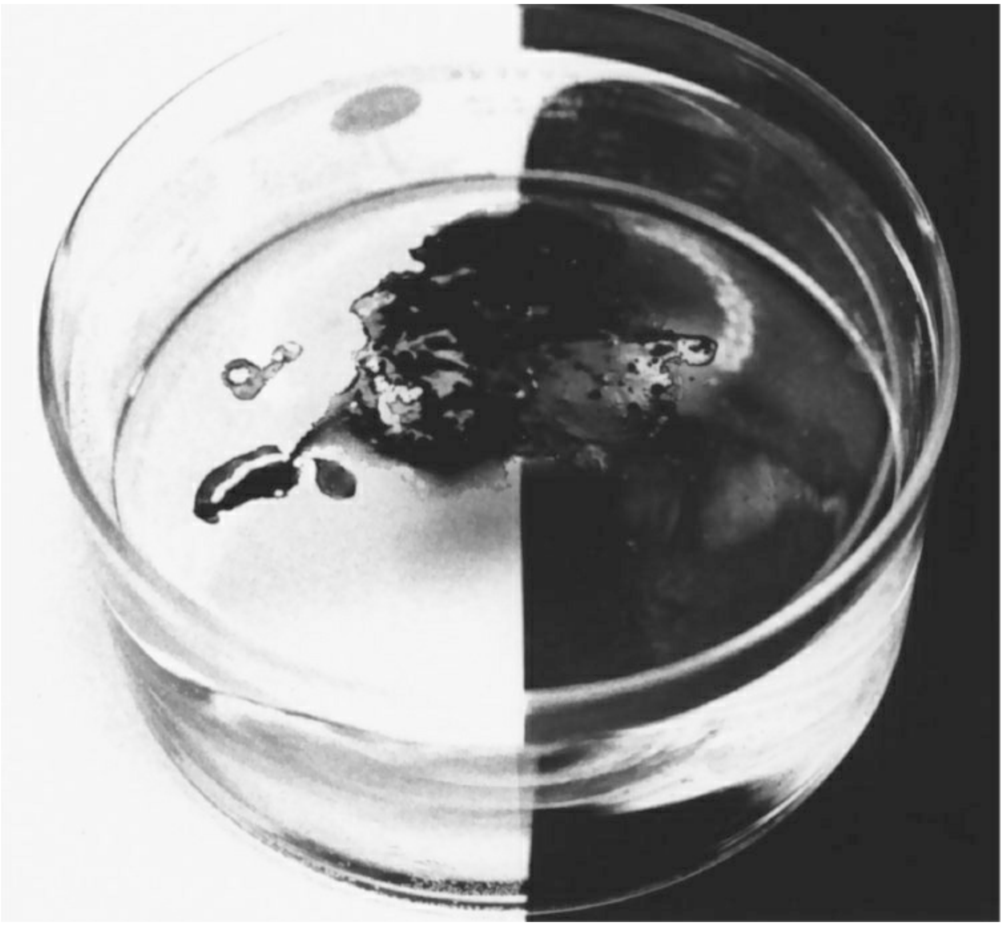


FIGURE 27.3 A few drops of oily water (w/o emulsion) when added to water will remain as a separate phase floating on the surface of the water.

Oily Waste

An oily waste emulsion (o/w) may have an appearance from black to gray, oily, dirty water. Adding an oily waste into water results in the emulsion dispersing into the clean water, forming an oily effluent that is less concentrated than the original emulsion. An oily waste emulsion may contain any of various types of oil in a wide range of concentrations. These oils are defined as substances that can be extracted from water by hexane. In addition to oils, typical contaminants of these emulsions may be solids, silt, metal particles, emulsifiers, cleaners, soaps, solvents, and other residues. The type of oils found in these emulsions depends on the industry. They may be fats, lubricants, cutting fluids, heavy hydrocarbons such as tars, grease, and crude oils and light hydrocarbons such as gasoline, kerosene, and jet fuel. Their concentration in effluent may vary from only a few mg/L to as much as 5–10% by volume. Treating the emulsion is usually accomplished using coagulants dosed at an appropriate level to neutralize the electrostatic charge stabilizing the emulsion.

Oily waste (o/w) treatment generally uses gravity separation of nonemulsified (free) oil and chemical treatment, and separation of emulsified oil by air flotation processes. However, other more sophisticated methods [reverse osmosis (RO), ultrafiltration (UF), and activated carbon adsorption] are available and can be effective. Gravity separators reduce the amount of suspended particulate matter through settling, and enable nonemulsified oil to rise to the surface. Skimmers in the separator remove free oil for further treatment. Air flotation, using either the dissolved or the induced method of introducing air bubbles into the liquid, helps oil and solids float to the surface as a sludge, where they are skimmed off for further treatment.

Waste Oil

Waste oil emulsions are typically black viscous liquids, where oil is the major component of the emulsion and water is the minor component. When a drop of w/o emulsion is added to water, the emulsion droplet remains intact and does not disperse. Since oil is the major component of the emulsion, emulsion breaking is usually performed for the purpose of oil recovery. W/O emulsions can be broken by chemical or physical methods such as heating or centrifugation. Centrifugation breaks oil emulsions by separating oil and water phases under the influence of centrifugal force. Typically, physical methods alone are not efficient in resolving these emulsions.

Waste oil emulsion terminology varies from industry to industry. Waste oils are also called slop oil, trap oil, floc oil, and skim off. Other forms of w/o emulsions include oily sludge, dissolved air flotation (DAF) sludge, and separator skimmings. Oil skimmings are chemically stabilized emulsions due to coagulants and flocculants needed to remove oil from water.

Waste oil treatment involves recovering oil from an emulsion, using one or more of four common treatment methods: treatment by transfer, pH adjustment, internal mixing, and chemical treatment. Batch processing of the emulsion is common to all four methods. Application of heat and chemicals during processing is often required to reduce viscosity, aid in mixing of treatment chemicals, and neutralize electrostatic charges stabilizing the emulsion. Solids are often a part of the emulsion and need to be addressed during chemical treatment. The emulsion destabilizing chemical plays a key role in separating oil from water and is often chosen based on bench testing.

Emulsion Treatment

Oil separation can be divided into three basic processes: chemical, mechanical, and thermal. Elements of all three are required for efficient emulsion separation.

Chemical Treatment

Chemicals are commonly used for treatment of oily effluents and are used to enhance mechanical treatment and separation. In resolving emulsions, stabilizing factors must be neutralized to allow emulsified droplets to coalesce. Electrostatic charges on emulsified droplets are neutralized by introducing an oppositely charged chemical. Emulsion breakers provide this opposite charge and are most often combined with mechanical and thermal treatments to achieve the best separation.

Oil-in-Water Treatment o/w emulsions are typically treated using cationic coagulants. These coagulants can be organic, inorganic, or blends of both (Fig. 27.4). Since emulsions are highly variable, bench testing is recommended to determine the correct chemical treatment for the emulsion. Surface area of the emulsified particles can be very high, and coagulant dosage is directly dependent on particle size and concentration. Coagulant dosages range from a few mg/L to 1000s of mg/L.

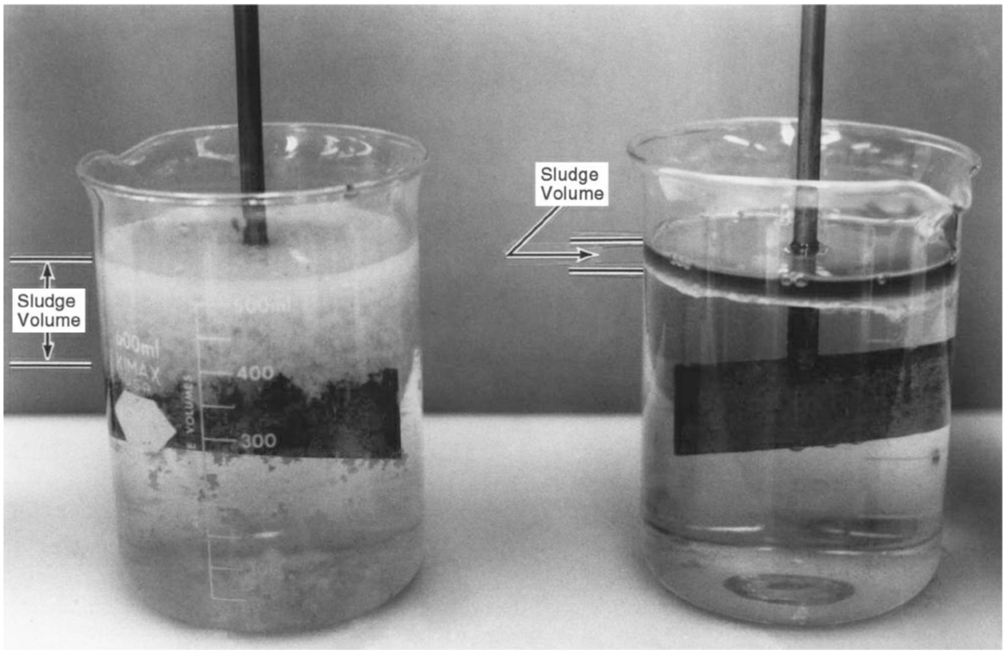


FIGURE 27.4 The use of organic emulsion breakers in place of alum or salts, which form hydrous flocs, greatly reduces sludge volume. The oil can be extracted from the sludge.

While good screening of coagulants is recommended, basic coagulant families are commonly used:

- DADMAC—diallyldimethylammonium chloride
- epi-DMA—epichlorohydrin-dimethylamine
- Aluminum-based chemistries—polyaluminum chloride (PACl)
- Aluminum-DADMAC blends
- Aluminum-epi-DMA blends
- Starch-based coagulants
- Iron-based coagulants

Water-in-Oil Treatment Waste oil emulsions typically require emulsion breakers that are soluble in hydrocarbons. These include ethyleneoxide-proplyeneoxide (EOPO) polymers and oxyalkalated resins and sulfonates. These chemistries neutralize electrostatic charges. Addition of these chemistries is often accompanied with heating waste oil to aid in mixing and the final resolving of water and oil layers. Chemical dosage can range from 100s of mg/L to 1000s of mg/L, depending on the emulsion (Fig. 27.5). Waste oil emulsions may have a significant amount of solids. Flocculating these solids with a medium to high cationic charge flocculant, helps resolve the emulsion into three layers: water, solids, and an oil layer. Chemical programs are normally applied in batch treatment tanks, and these tanks are usually equipped with internal mixing such as electric propeller mixers.

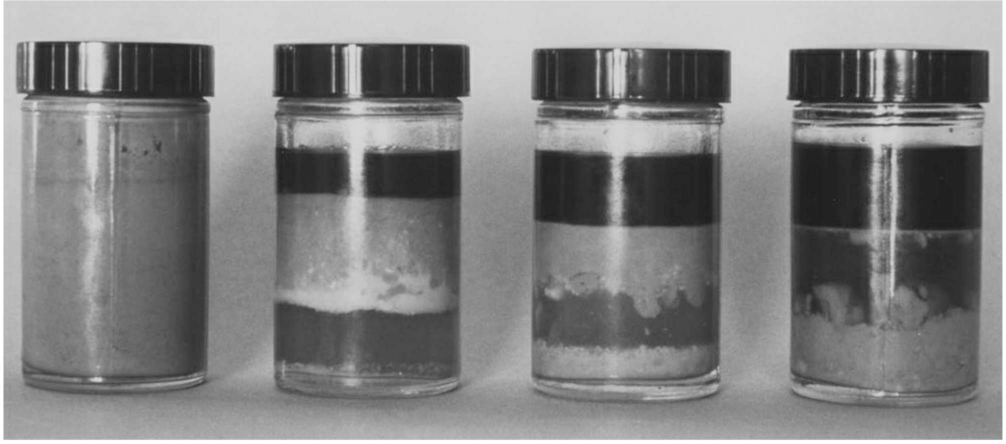


FIGURE 27.5 Breaking a waste oil emulsion with a chemical emulsion breaker showing the effect of increasing chemical dosage on maximizing oil recovery and solids separation.

Mechanical Treatment

Mechanical treatment of emulsions includes DAF, induced air flotation (IAF), and settling in special separators for the refining industry called corrugated plate interceptor (CPI), and American Petroleum Institute (API) separator. Details of the equipment are presented below.

Thermal Treatment

Thermal treatment of emulsions has a twofold purpose. First, increase in temperature reduces viscosity of the mixture, allowing faster film flowing and separation of water from oil. Secondly, increase in temperature allows for better chemical mixing and neutralization of the stabilizing factors of the emulsion. Thus, increasing the temperature of an emulsion does help resolve the emulsion. However, heating an o/w (oily waste) emulsion has less of an effect on emulsion breaking than when a w/o (waste oil) emulsion is heated.

Separation Equipment

Additional equipment information can be found in Chap. 22 on Primary Effluent Treatment.

Oil-in-Water Emulsions

Oil separation and removal can be divided into two basic processes: gravity separation of nonemulsified oil and chemical treatment and separation of emulsified oil.

Equipment for oily waste treatment includes flotation (DAF and IAF), ultrafiltration, activated carbon adsorption, pressure leaf filtration, and RO. These systems are used to break emulsions and separate emulsified oil from the waste flow. They are typically used with some form of chemical treatment.

Gravity Separation

The primary function of gravity separators is to remove free oil from effluents; however, such separators cannot remove soluble impurities or break emulsions. Gravity separators depend on density differences and the resulting buoyant forces, to cause droplets of free oil to rise to the surface. Theoretically, oil droplets rise linearly as predicted by Stokes' law. In practice, turbulence and short-circuiting are common operational challenges with gravity separators.

American Petroleum Institute Separator The API separator consists of a rectangular trough or basin in which effluent flows horizontally, while oil droplets rise vertically to the surface (see Fig. 27.6). Free oil that collects on the surface of the separator is skimmed off and routed to storage.

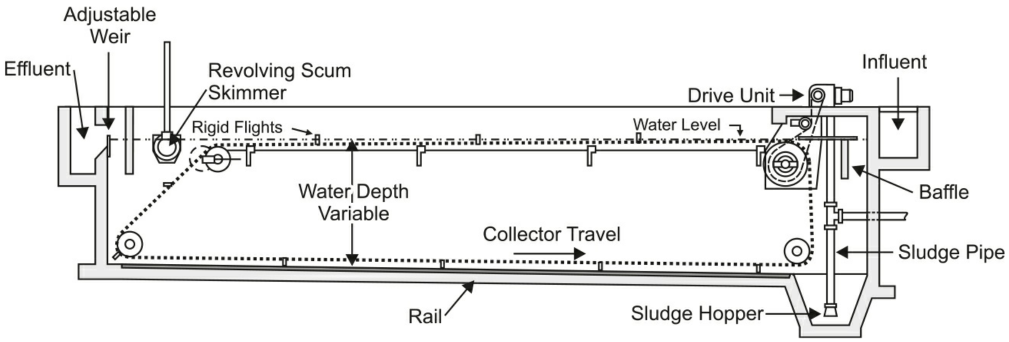


FIGURE 27.6 API separator. (*Courtesy of Envirex Inc., a Rexnord Company*.)

API separators are designed to separate oil droplets of 0.15 mm or larger. Ideally, separators are designed within the following limits:

- Horizontal velocity should not exceed 3 ft/min (0.91 m/min)
- Separator depth between 3 and 8 feet (0.91–2.4 m)
- Depth to width ratio of 0.3–0.5
- Widths should be between 6 and 20 feet (1.8–6.1 m)

Corrugated Plate Interceptor Separator The CPI consists of packs of 12 to 48 corrugated plates mounted parallel to each other at distances of 0.75 to 1.5 inches (19–38 mm). As effluent flows between the plates, lighter oil globules float upward into the corrugation peaks, where they coalesce and move up the plates to the top of the plate pack and then to a floating oil layer at the surface (see Fig. 27.7).

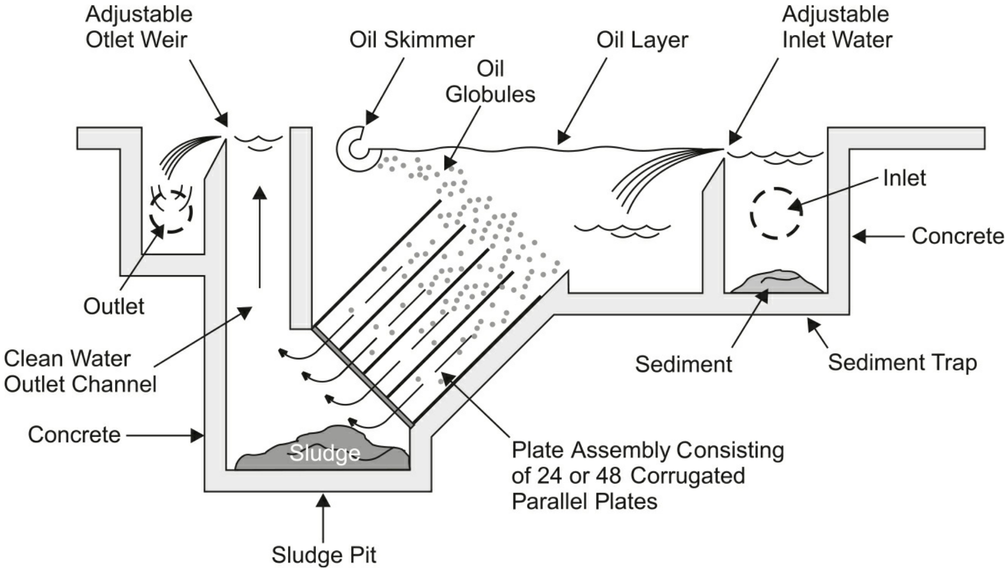


FIGURE 27.7 CPI separator.

Gravity Separator Performance Several factors affect performance of gravity separators, including:

- Flow rate through separator
- Turbulence or short-circuiting
- Temperature
- Effluent pH
- Specific gravity of oil
- Specific gravity of effluent
- Amount of settleable solids present
- Concentration of emulsifying agents

Figure 27.8 illustrates the separation process in an API or CPI separator.

Effluent flows left to right and includes dense grit, dirt, and other insoluble matter, free nonemulsified oil, and stable emulsified oil. Suspended particulate follows a settling gradient depending on specific gravity and flow rate. Free oil similarly follows a rising gradient depending on specific gravity and flow rate. Generally, free oil includes entrapped oil-coated solids and emulsified water. API skimmings, which are generally referred to as slop oil, require treatment before they can be reused since they contain solids and water in excess of 1%, where 1% water is generally considered the acceptable limit for reuse without treatment.

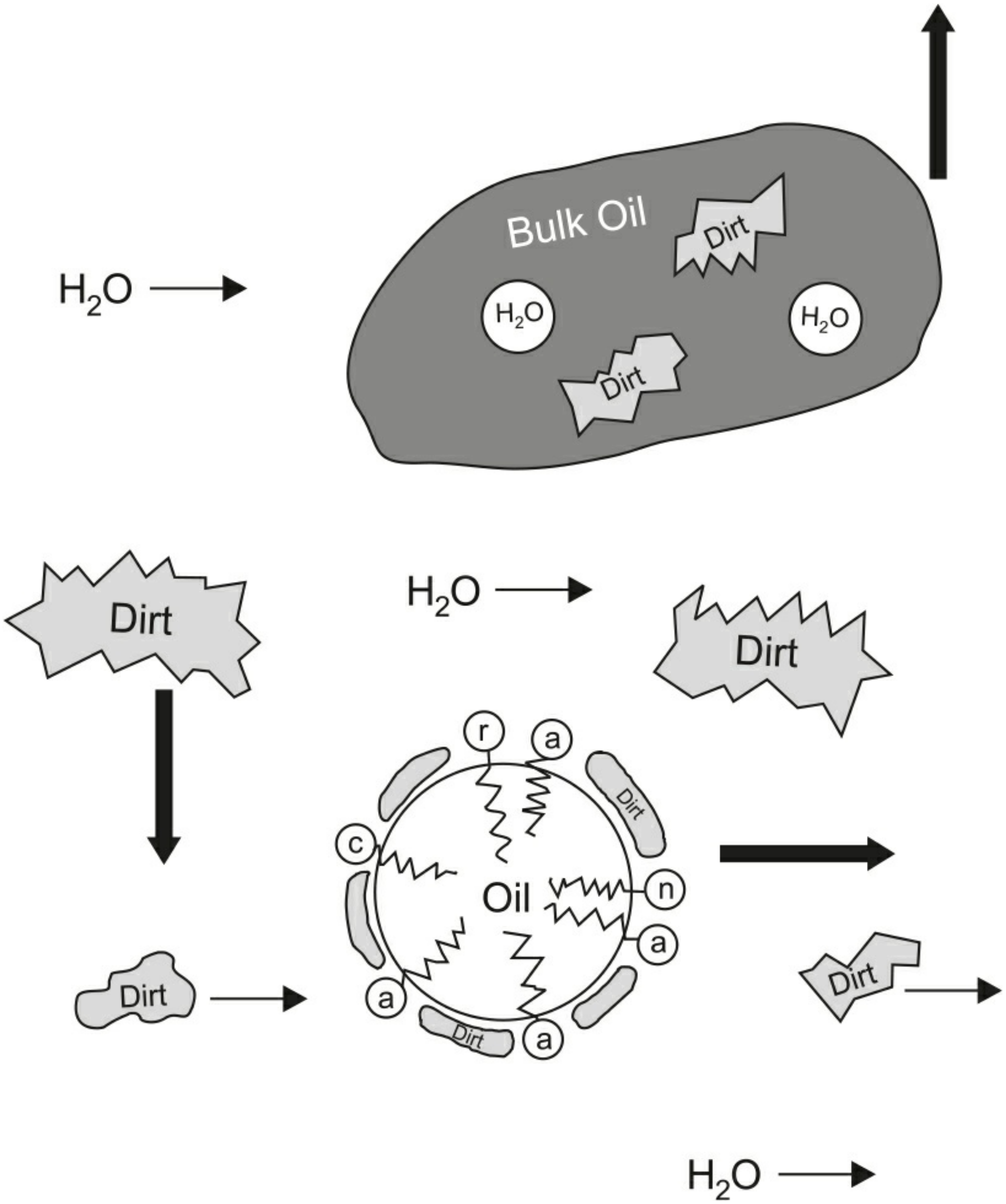


FIGURE 27.8 Action taking place in API and CPI separators.

Table 27.1 illustrates expected effluent concentrations and removal efficiency in a refinery effluent treatment process using an API or CPI separator.

Process	Typical Effluent Concentration, mg/L			
	BOD_5*	COD[†]	TSS[‡]	Oil
API separator	250–350	260–700	50–210	20–100
CPI separator				20–100
	Typical Removal Efficiency, %			
API separator	5–40	5–30	10–50	60–99
CPI separator				60–99

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*Biochemical oxygen demand after five days.

[†] Chemical oxygen demand.

[‡] Total suspended solids.

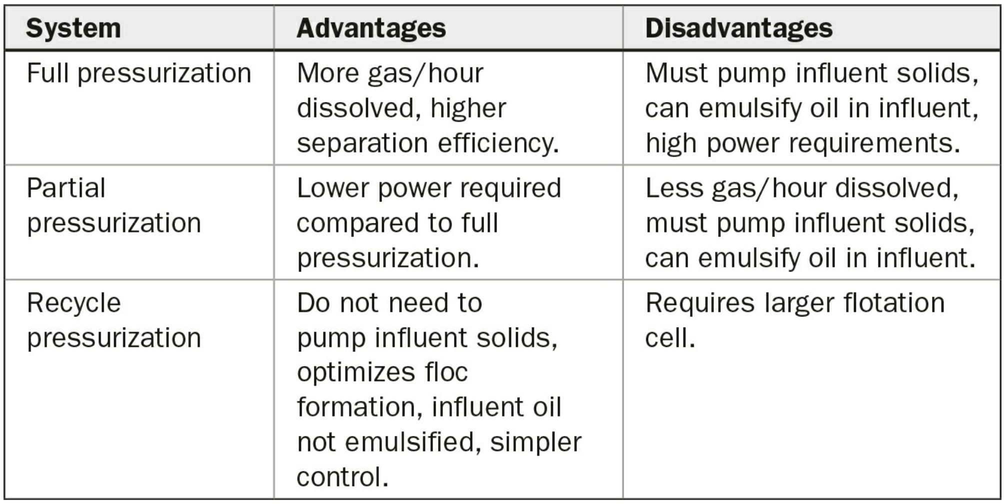
TABLE 27.1 Expected Effluent Results and Removal Efficiency Using Gravity Separation on Refinery Effluent

Air Flotation Separation

Air flotation has been used for many years to treat effluents by separating solids, oils, grease, fibers, and other low-density solids. Air flotation is also used for thickening activated and flocculated chemical sludge. This section deals with flotation for the purpose of clarification of suspended oil and solids.

There are two basic methods of air flotation in use: DAF and IAF. DAF uses water under pressure, which becomes supersaturated in air upon release of the pressure. Bubbles of 30–120 μm are released and promote flotation. In areas where risk of explosion is present, dissolved nitrogen flotation (DNF) is used. Nitrogen flotation is not as efficient as air flotation due to solubility differences between pure nitrogen and air. IAF utilizes mechanical agitation with air either aspirated or pumped into the mixing area. Larger air bubbles, typically 0.5 to 1 mm in size, promote flotation.

Dissolved Air Flotation DAF is used extensively, particularly in the refining industry. Table 27.2 lists the three basic modes of DAF and shows advantages and disadvantages of each.



System	Advantages	Disadvantages
Full pressurization	More gas/hour dissolved, higher separation efficiency.	Must pump influent solids, can emulsify oil in influent, high power requirements.
Partial pressurization	Lower power required compared to full pressurization.	Less gas/hour dissolved, must pump influent solids, can emulsify oil in influent.
Recycle pressurization	Do not need to pump influent solids, optimizes floc formation, influent oil not emulsified, simpler control.	Requires larger flotation cell.

TABLE 27.2 Comparison of DAF Pressurization Methods

DAF functions by altering particulate density through incorporation of air onto or into the floc structure. Bubbles become attached by:

- Adhesion of bubble to particle by collision, or as a condensation site
- Entrapment of bubble in floc structure
- Adsorption of bubble in floc structure

An illustration of oily sludge being formed is presented in Fig. 27.9. Air bubbles are formed in and around suspended solids and emulsified oil droplets. As droplets coalesce, air is trapped within and on the floc structure, producing floc less dense than water. Eventually, the floc becomes a continuous oily sludge.

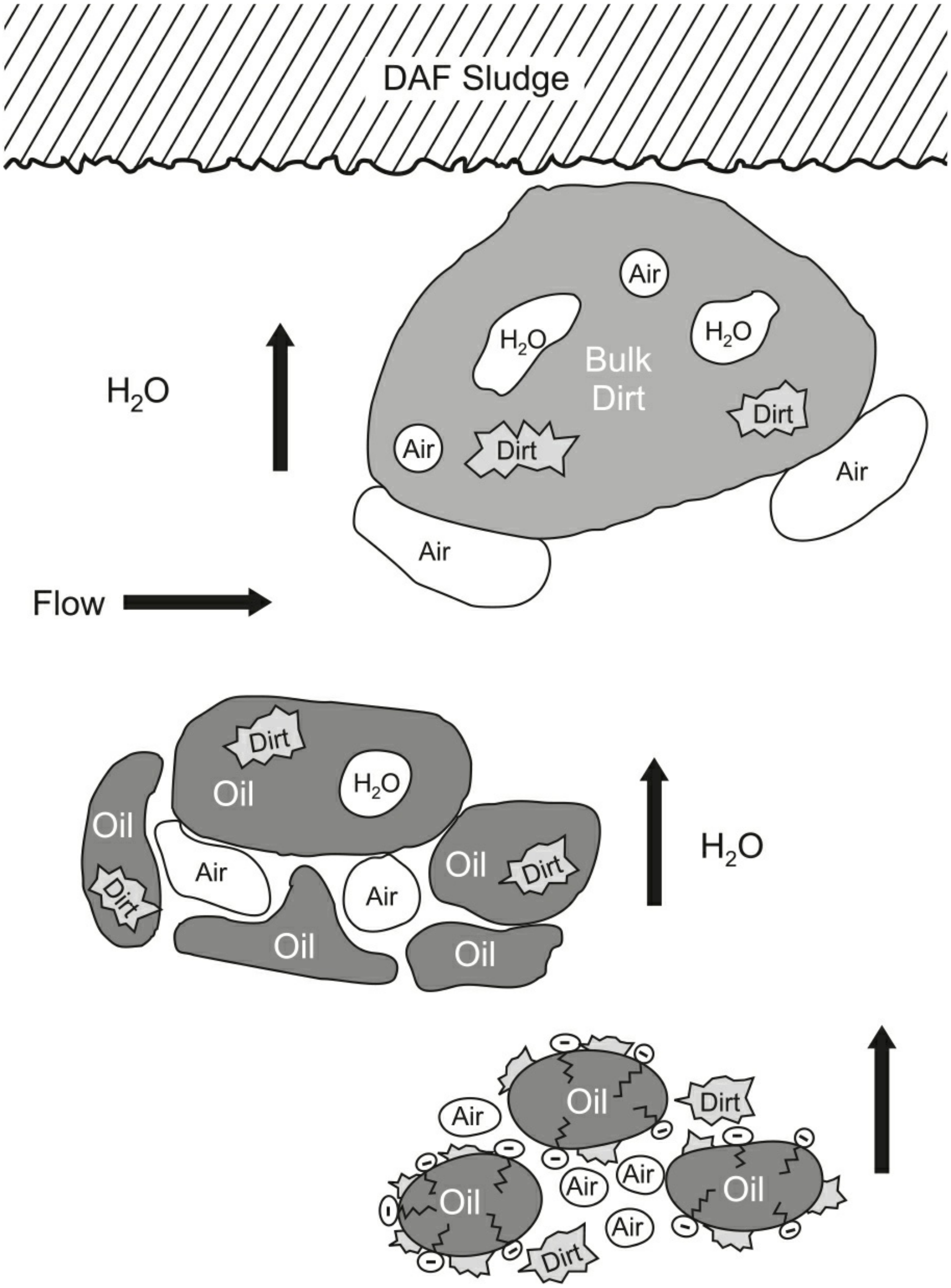


FIGURE 27.9 DAF sludge.

The DAF system typically includes the following hardware:

- DAF float tank (circular or rectangular)
- Air saturation system
- DAF recycle pump (for recycle pressurization system)

- Air compressor or source of high-pressure air
- Rapid mix or flocculator tanks that are either separate or part of the DAF unit

The air saturation system can be described as the heart of the DAF process (Fig. 27.10). In a recycle pressurization system, air is dissolved in the recycle water flow under pressure. This occurs in the air saturation tank, which should be about 50% full of recycle water.

FIGURE 27.10 The float produced by DAF of an oily effluent (o/w) emulsion. (*Courtesy of Infilco Degremont Inc.*)

When evaluating DAF units, the most important operational criteria is hydraulic loading, expressed as gpm/ft^2 (m^3/[h · m^2]) of DAF surface area, and detention time. The hydraulic loading rate is calculated as follows:

$$\mathrm{HLR} = \frac{I + R}{A} \tag{27.1}$$

where HLR = hydraulic loading rate, gpm/ft^2 (m^3/[h · m^2])
I = influent flow rate, gpm (m^3/h)
R = recirculation flow rate, gpm (m^3/h)
A = DAF surface area, ft^2 (m^2)

Typical hydraulic loading rates range from 1 to 2 gpm/ft^2 (2.4–4.9 m^3/[h · m^2]), depending on equipment manufacturer. Hydraulic loading for the average flow condition should be about 1.5 gpm/ft^2 (3.7 m^3/[h · m^2]).

Detention time is calculated as follows:

$$\mathrm{DT} = \frac{V}{I + R} \tag{27.2}$$

where DT = theoretical hydraulic detention time, min (h)
V = tank volume, gal (m^3)
R = recirculation flow rate, gpm (m^3/h)
I = influent flow rate, gpm (m^3/h)

Hydraulic loading and detention time can be checked and compared to design values to determine if the unit is hydraulically overloaded.

DAF performance should be judged on the following factors:

- Effluent quality
- Oil removal efficiency
- Improving throughput or capacity
- Polymer dosage required

Removal efficiency can be determined using Eq. (27.3):

$$R = \frac{100(I_c - E_c)}{I_c} \tag{27.3}$$

where R = removal efficiency, %

I_c = influent oil concentration, mg/L

E_c = effluent oil concentration, mg/L

Table 27.3 shows typical removal efficiency for DAF units.

Process	**Typical Removal Efficiency, %**			
	BOD_5	**COD**	**TSS**	**Oil**
DAF treatment	25–70	10–60	50–85	70–85

TABLE 27.3 Typical DAF Removal Efficiency

For oily waste treatment, skimmings should not be allowed to become more than 2 inches (51 mm) thick, since turbulence might re-emulsify the oil. Skimmers are frequently run constantly to keep oil layers from building up. Skimmer speed and submerged depth may be adjusted to improve formation and removal of oil skimmings. If turbidity levels in subnatant from the unit are rising, increasing skimmer speed to remove skimmings more quickly can help.

Induced Air Flotation IAF units were originally developed for removing fine particles from mineral slurries and concentrating mined material. However, the units found other uses, notably in oilfields for separating oil from water. IAF is used in effluent treatment of oily wastes at refineries, steel mills, railroad yards, shops, and other miscellaneous industries where oils are a problem in waste streams, where the oil more readily separates from water. These units are often used in place of DAF units, since IAF units can be operated at much higher hydraulic loadings (higher flow throughput for equivalent surface area). Therefore, the capital cost for treatment equipment is lower. IAF differs from DAF as shown in Table 27.4.

Induced (Dispersed) Air Flotation	**Dissolved Air Flotation**
Air is mixed with liquid, not dissolved.	Air is dissolved in liquid. Air saturation equipment is required.
Surface interaction between air bubble and oil or solids provides basis for separation.	Flotation of impurities (solids and oil) due to air attachment to solids or oil.
Air bubble size is larger (>100 μm).	Air bubble size is smaller (10–100 μm).
Kinetics of IAF is rapid. Relatively short detention times (loading rates are higher).	Lower loading rates and therefore longer detention times and slower particle rise rates.
Energy and shear turbulence are generally greater.	Turbulence below or at surface should be minimal in well-designed and operated system.
Chemicals are added to cause oil and suspended solids to engulf air bubbles and be floated to the surface.	Chemicals are added to flocculate oil (or break emulsion) and suspended solids to form larger floc so bubbles have greater floc area for attachment.
Clarification only (oil and solids removal).	Clarification and sludge thickening (typically for secondary sludge at municipalities and paper mills).

TABLE 27.4 Induced versus DAF

In general, a DAF unit can be characterized as a quiescent, high retention time device using relatively small quantities of dissolved air, while IAF is a low retention time, less quiescent machine using a relatively large quantity of air. Froth flotation in the IAF is usually enhanced by chemical treatment. Chemical dosage can range from 5 to 15 mg/L in IAF units, but is dependent on loading and oil characteristics.

IAF units consist of a headbox for even distribution of influent flow, four flotation cells in series with skimmer paddles on each side, equipment to induce or disperse air into the waste flow, an effluent box, and a level control mechanism on the discharge pipe or in the effluent box.

Two methods are used to induce air into the waste flow:

- Impeller type device where each cell is equipped with a turbine motor (Fig. 27.11)

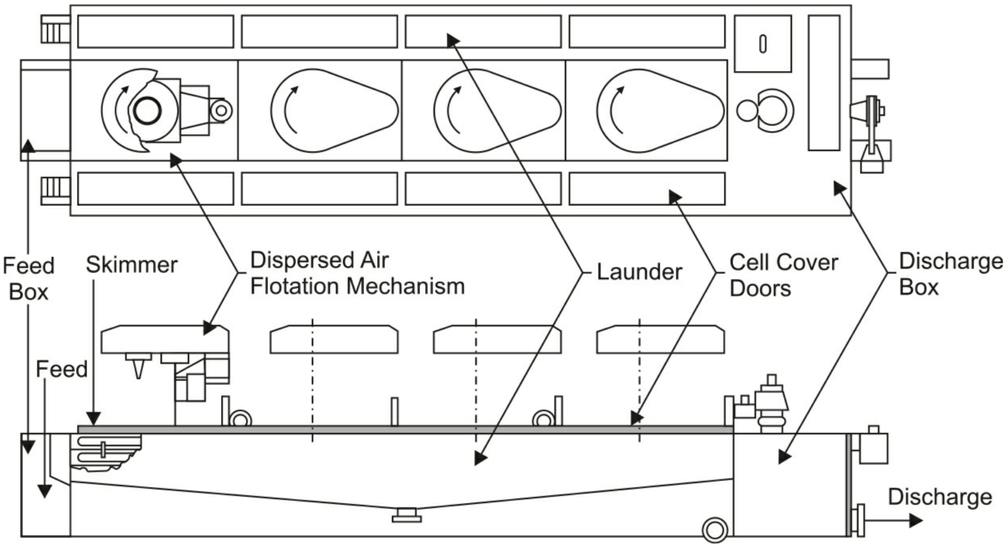


FIGURE 27.11 Impellor-type IAF unit.

- Nozzle air recycle flow flotation unit (Fig. 27.12)

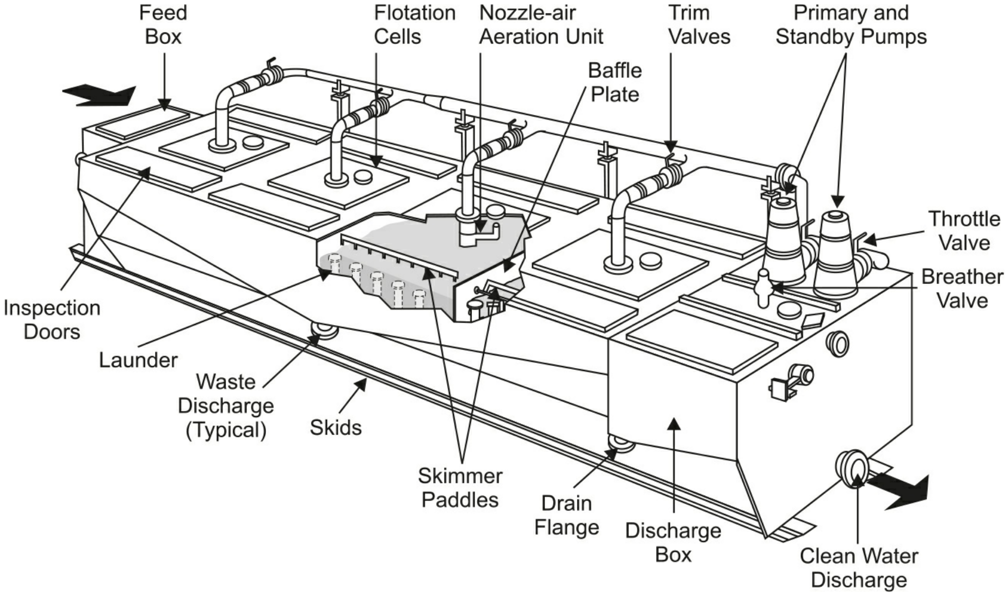


FIGURE 27.12 Nozzle air aeration IAF unit. (*Courtesy of Wemco Division, Envirotech Corporation*.)

The impeller unit consists of a star rotor suspended between a cylindrical standpipe and draft tube. Rotation of the rotor generates a liquid vortex pattern with an air–liquid interface extending from the midpoint of the inner wall of the standpipe, through the interior of the rotor section down to the upper section of the draft tube (Fig. 27.13). This air cavity formed within the vortex serves to induce air from the freeboard of the vessel, through air inlet ducts into the interior of the rotor. Impeller rotation causes liquid to circulate upward from the bottom of the vessel through the draft tube to the rotor, where it mixes with air. This produces an air–water mixture that leaves the impeller section tangentially. By passing the air–water mixture through holes of a disperser that surrounds the impeller, the direction of flow is changed to radial. Contaminant-laden air bubbles then separate by gravity and rise to the liquid surface. The separation region is maintained in a relatively quiescent condition.

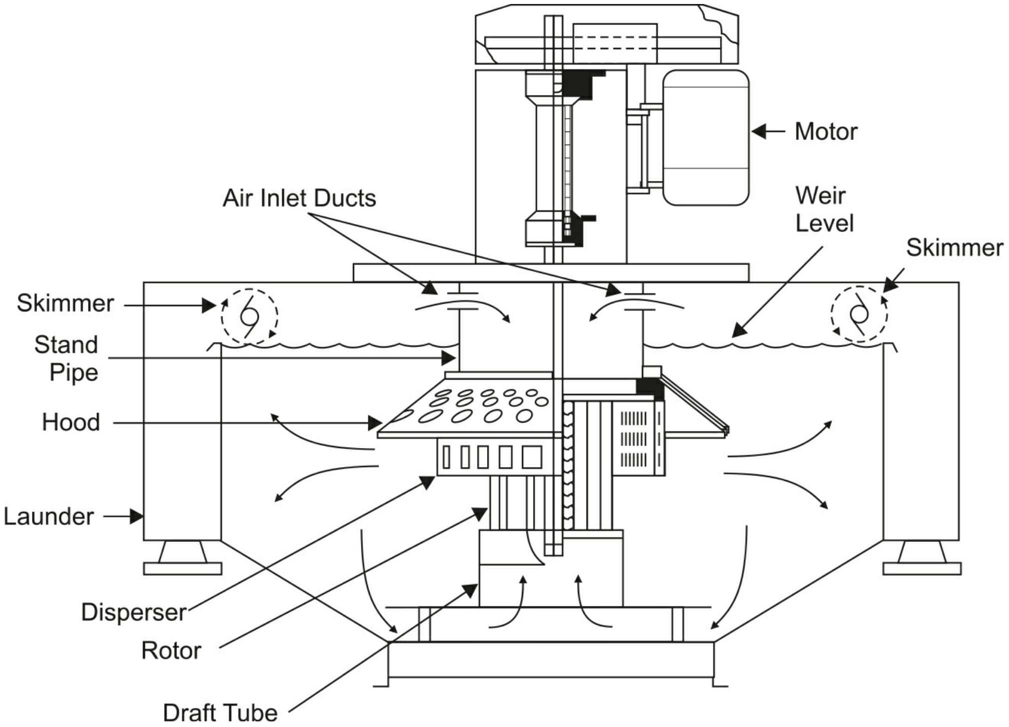


FIGURE 27.13 IAF impellor detail.

Nozzle air flotation units are mechanically simpler than the impeller. Air injection is accomplished hydraulically by recycling a portion of relatively clear liquid effluent to each of the four cells in the unit. As pressurized flow passes by a nozzle opening, air is drawn into the recycle flow by the pressure differential between the ambient air and recycles flow. Manual valves are located on the recycle line to each cell to control or adjust the amount of recycle and air induced into each cell (see Fig. 27.14).

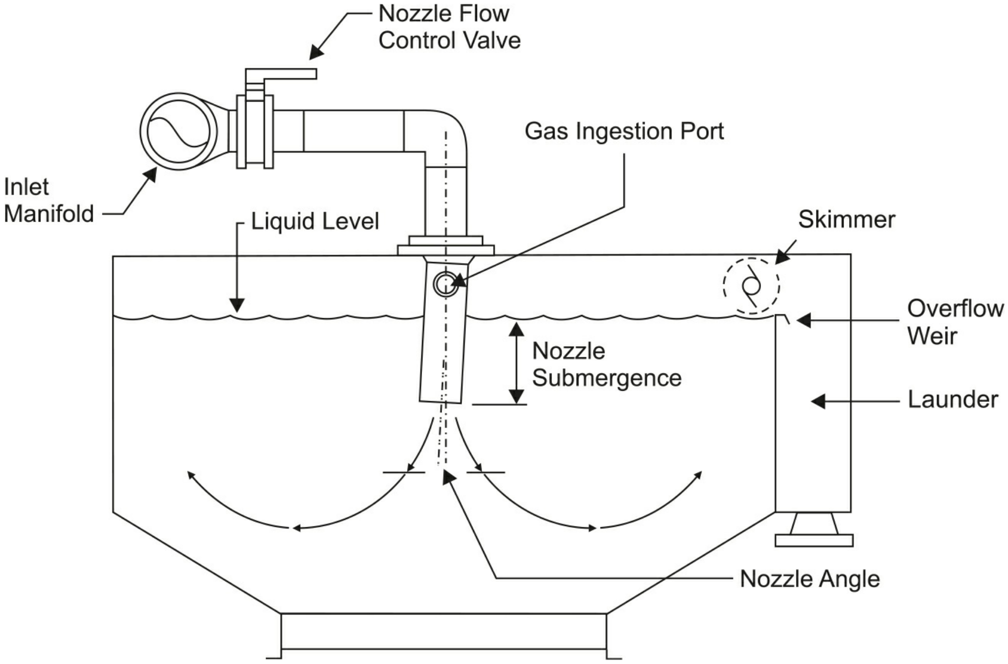


FIGURE 27.14 IAF nozzle air cell detail.

Membrane Filtration

For oily effluent treatment, tubular UF membranes are commonly used. Highly hydrophilic membranes are used in these systems to allow water to pass through and hydrophobic oils to be retained by the membrane. Free oil is usually removed before sending effluent to the membrane system to avoid membrane fouling. Oily effluent is concentrated by UF, significantly reducing its volume.

Water-in-Oil Emulsions

Waste oil (w/o) treatment involves recovering oil from an emulsion, using one or more of three common treatment methods: treatment by transfer, pH adjustment, and internal mixing. Each method includes chemical treatment.

Batch processing of the emulsion is common to all three methods. Application of heat and chemicals during processing is common to all three treatment methods as well.

Treatment by Transfer

The most common method of oil recovery is a batch treatment process, commonly requiring several tanks. Typically, oil skimmings are pumped to one or two holding tanks. Batch treatment is generally limited to 3000 barrels (480

m^3) or less, to permit transfer of the batch in one day. Larger batches tend to suffer from poor mixing and require longer resolution times.

Before any chemical treatment is applied, slop oil is preheated to 150 to 180°F (66–82°C) by means of steam coils in the slop oil holding tank, or a heat exchanger in the transfer line. Heating allows for better mixing of treatment chemicals, lowers viscosity of the emulsion, and speeds up resolution of the emulsion. Without heating, the emulsion may not resolve at all or may need several thousand mg/L of chemical.

Emulsion breaking chemical is added to the slop oil, while it is transferred from the holding tank to the batch treatment tank (see Fig. 27.15). Batch treatment in one tank is possible using recirculation, as long as the temperature is maintained below 180°F (82°C). Once treatment chemical has been added, the recirculation agitation is turned off, and the emulsion is allowed to separate. Often, there is an oil-wet layer of solids that still contains water called the "rag layer." Recirculation does not ensure proper distribution of chemical, and dosage consistency is better achieved by feeding chemical at the required dosage in proportion to the slop oil transfer rate. For example, if the dosage needed is 3000 mg/L (volumetric dosing), and the transfer rate is 100 bbl/h (16 m^3/h), then the chemical feed pump should be calibrated to deliver 12.6 gph (47.7 L/h) or 0.21 gpm (0.8 L/min). Failure to feed proportionately can result in poor resolution.

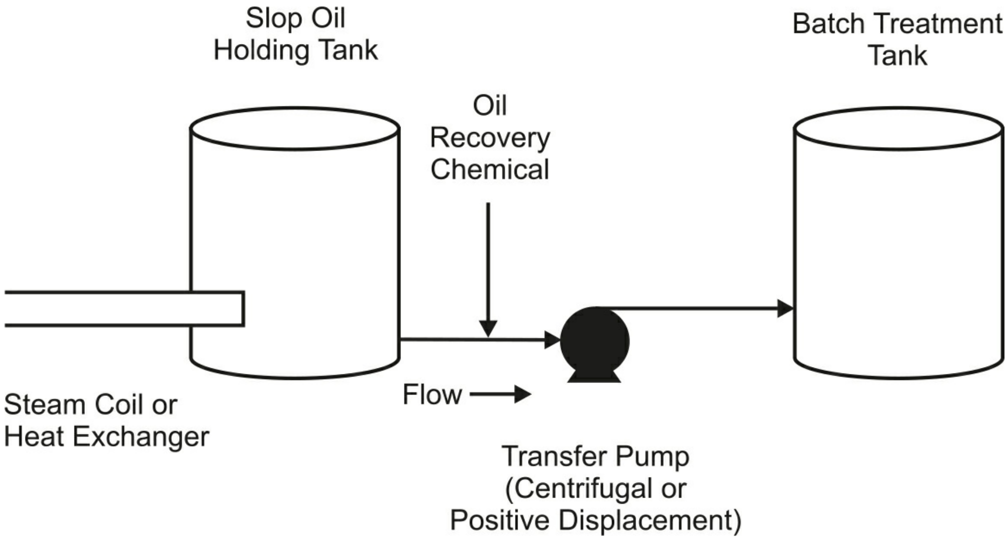


FIGURE 27.15 Typical oil recovery scheme for treatment by transfer.

$$\mathrm{FR} = \frac{(3000\ \mathrm{mg/L})(100\ \mathrm{bbl/h})(42\ \mathrm{gal/bbl})}{10^6} \tag{27.4a}$$
$$= 12.6\ \mathrm{gph\ or}\ 0.21\ \mathrm{gpm}$$

or

$$\mathrm{FR} = \frac{(3000\ \mathrm{mg/L})(100\ \mathrm{bbl/h})(159\ \mathrm{L/bbl})}{10^6} \tag{27.4b}$$
$$= 47.7\ \mathrm{L/h\ or}\ 0.8\ \mathrm{L/min}$$

The treated slop oil emulsion should enter the batch tank at or near the bottom to enhance formation of the free oil layer. Pumping into the top of the tank tends to disrupt and re-emulsify the free oil layer. This can result in a longer resolution time or poor oil recovery.

When the transfer is completed, treated slop oil is allowed to stand for as long as possible, usually 12 to 48 hours. It is not normally necessary to maintain temperature during the resolution period. The emulsion resolves as the tank cools. Shortening the settling time can cause poor oil recovery or poor oil quality.

pH Adjustment

Another approach in waste oil emulsion breaking for oil recovery is pH adjustment. The pH has a significant effect on stability of the emulsion. Lowering pH provides hydrogen (H^+) ions for neutralization of negative charges surrounding water in w/o emulsions.

As with treatment by transfer, slop oil is preheated to 150 to 180°F (66–82°C) by means of steam coils in the slop oil holding tank or a heat exchanger in the transfer line. Heating allows for better mixing of treatment chemicals, lowers viscosity of the emulsion, and speeds up resolution of the emulsion. Without heating, the emulsion may not resolve at all or may need several thousand mg/L of chemical. The traditional method is to lower pH to the 2 to 4 range to increase emulsion breaking efficiency. During bench testing, the effect of pH should always be investigated, both increasing and decreasing the pH level.

Treatment by Internal Mixing

All sludge treatment programs require some heating to usually 180°F (82°C) with thorough agitation in a vessel commonly called a cooking vessel (see Fig. 27.16). Since bubbles of steam collapse immediately and cool quickly, the cooker may vibrate and make noise, but there is little significant motion to the sludge itself. Temperatures greater than 180°F (82°C) should be avoided when cooking DAF sludge, as it may cause foaming and exceed the vessel volume.

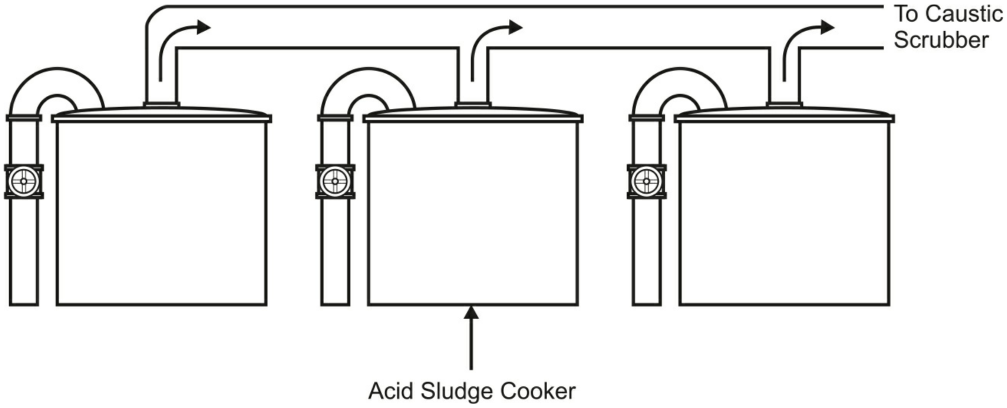


FIGURE 27.16 Acid sludge cookers (vents lead to caustic scrubbers).

Mechanical agitators, such as turbine mixers, work well in cases where the cooker is heated mainly with steam coils or plates. The shaft of the mixer should extend about 2/3 of the working depth into the cooker. Some baffling in the cooker may be needed to achieve proper rolling action. Baffling may be accomplished by hanging plates, coils, or pipes in the cooker.

Foaming may occur during addition of acid. Therefore, concentrated sulfuric acid should be added to a cooker before the temperature reaches 140°F (60°C).

Once the cooker has reached the desired temperature and chemicals have been added, agitation is stopped, and the emulsion is allowed to separate.

Lowering pH to break the emulsion is deemed a last resort method. Low pH with high temperatures causes significant corrosion damage to mild steel tanks, pipes, and pumps.

Water-in-Oil Emulsion Processing

Once waste oil has been treated, it can be separated into water and oil by gravity separation in a tank or processing through either a 2-phase or 3-phase centrifuge. Allowing waste oil to separate in a tank often produces a rag layer (oil wet solids and water), which is often difficult to manage because the oil-wet solids have a tendency to form an emulsion at the oil–water interface.

Processing by centrifuge allows separation of liquid from the solids, and then oil is separated from the water. In a 2-phase centrifuge, liquid and solids are separated, and the liquid (oil and water) then goes to a separation tank to allow for oil–water separation. A 3-phase centrifuge separates solids from the liquid phase, but at the liquid exit port on the centrifuge, a weir separates oil from water. Thus, no separate settling tank is required.

CHAPTER 28

Wet Gas Scrubbers

Wet scrubbers use a liquid to remove solid, liquid, or gaseous contaminants from a gas stream. The scrubbing liquid performs this separation by dissolving, trapping, or chemically reacting with the contaminant.

Scrubbers are used extensively to control air-polluting emissions. So many different scrubber configurations have been used that there is some confusion as to whether they all belong in the same category. In some references, for example, the definition of a scrubber may be restricted to certain design criteria, such as whether the units are open or packed. In this text, any device fitting the definition of the first sentence is a wet scrubber.

Scrubber systems can be designed to remove entrained particulate materials such as dust, fly ash, and metal oxides, or to remove gases such as oxides of sulfur (SO_x) from a flue gas stream to meet air emission standards.

Particle Collection Concepts

In scrubbing particulate matter from gases, the principal concern is usually removal of particles smaller than 10 μm. Larger particles are relatively easy to separate. Successful design and operation of wet scrubbers depend on knowing the size, composition, and derivation of particles to be collected.

Figure 28.1 shows the estimated size for some common pollutants. Just as fine particles in water (colloids) carry a charge of static electricity, so do colloidal particles in fumes and dust, defined as aerosols. If these particles carry no charge, they may be deliberately charged to assist removal in electrostatic precipitators.

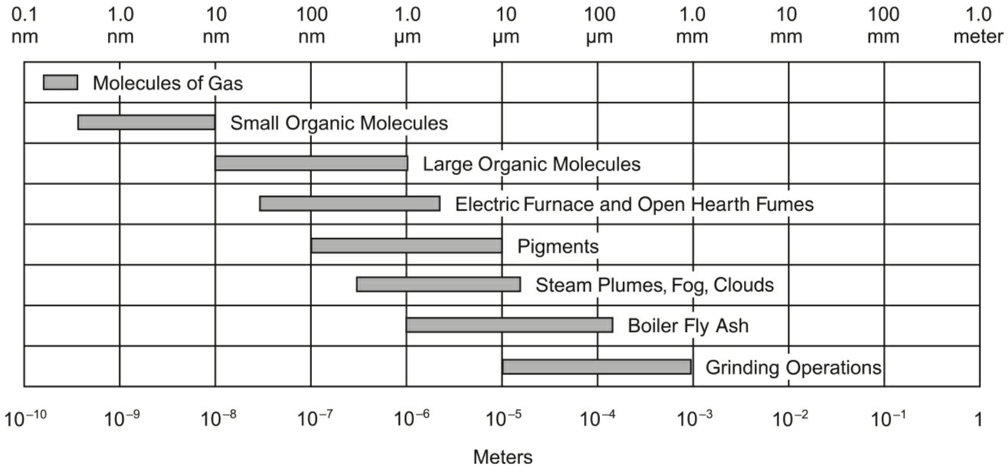


FIGURE 28.1 Comparison of particle sizes in air emissions.

Among particulates (term for suspended solid materials) collected by wet scrubbers are dispersion aerosols from processes such as grinding, solid and liquid atomization, and transport of suspended powders by air currents or vibration. Dispersion aerosols are usually coarse and contain a wide range of particle sizes. Dispersion aerosols consisting of individual or slightly aggregated, irregularly formed particles, are called dusts.

Condensation aerosols are formed when supersaturated vapors condense, or when gases react chemically, forming a nonvolatile product. These aerosols are usually smaller than 1 μm. In condensed aerosols, solid particles are often loose aggregates of a large number of primary particles of crystalline or spherical form. Condensation aerosols with a solid dispersed phase, or a solid–liquid dispersion phase, are classed as smokes or fumes. Aerosols that include a liquid dispersion phase are called mists. This classification usually applies regardless of particle size, and differentiation is sometimes difficult.

In practice, combinations of dispersion and condensation aerosols are encountered. Different size particles behave differently because of physical properties such as light scattering, evaporation rates, and particle movement. The choice of the best device for particle removal from gas is affected by these differences. Microscopic sizing and density estimation may obtain particle sizes, volumes, and weights.

Particulate Emissions

Limits on particulate emissions (smoke, mist, dust) are usually established in four ways:

1. Emission rate: Maximum weight that can be legally emitted in pounds (kilograms) per hour. This may be expressed as the rate for a specific industry in production terms, for example, pounds per hour per ton (kilograms per hour per tonne) of pulp.
2. Maximum concentration: Maximum amount of particulate matter in the gas stream released, for example, g/m^3, grains/ft^3, or lb/1000 lb gas.
3. Maximum opacity: Maximum opacity of the gas stream emitted, usually measured by observation and comparison to empirical standards (Ringlemann numbers).
4. Corrected emission rate: This is tied to an air quality standard by a formula based on atmospheric dispersion considerations.

Often, several particular emission regulations are enforced simultaneously. If all four types of restrictions are employed, a plant might pass on emission rate and concentration, but fail on opacity. This is an understandable situation, since large particles are major contributors to weight, while smaller particles in the 0.1 to 2.0 μm range are major contributors to opacity.

Addition of chemical additives to scrubber water to capture particles in the 0.1 to 2.0 μm range is often an economical way to meet air quality standards, particularly when compared to the cost of process modifications and equipment additions.

Wet scrubbers discussed in this chapter use water to remove particulates, gases, or both from industrial gas streams or stacks. Water chemistry is often extremely complicated in these scrubber systems, because of the variety of operations occurring simultaneously in the scrubber environment, such as;

Heat transfer: The gas and water are often at different temperatures, and heat is transferred in the scrubbing process.

Evaporation/condensation: The gas may be hot and saturated with water vapor. Contact with colder water dehumidifies the gas, and scrubbing water is diluted with condensate. If stack gas is hot and dry, scrubber water evaporates as in a cooling tower and becomes concentrated.

Mass transfer: The gas may contain water-soluble solids or gases that dissolve in scrubber water. Water may transfer gases to the gas stream as well. For example, water may be recycled over a cooling tower becoming saturated with oxygen (O_2) and nitrogen (N_2), later releasing them to the gas stream.

Scaling: As scrubber water is heated or increases in pH, alkalinity, or sulfate–sulfite content, precipitation of calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), or calcium sulfite ($CaSO_3$) may occur, and the scrubber may become scaled.

Corrosion: A common and troublesome problem encountered in most wet scrubbers.

Fouling: Fouling may occur from coagulation of the particulate being removed or from microbial activity. Many industrial gas streams contain organics that supply food to microbes.

Principles of Operation

Scrubber manufacturers offer a bewildering array of products. Scrubbers are available in a wide range of designs, sizes, and performance capabilities. Some are designed primarily for collection of particles and others for mass transfer (gas removal by a chemical reaction). As good liquid–gas contact is needed for both operations, all scrubbers can collect both particles and gases to some extent. The degree to which particle collection and mass transfer characteristics of a scrubber can be utilized, determines applicability of the scrubber for each specific purification problem. Figure 28.2 shows the commonly accepted domain of wet scrubbers based on particle size, relative to other competitive devices. Figure 28.3 shows relative particulate removal efficiency of the more common types.

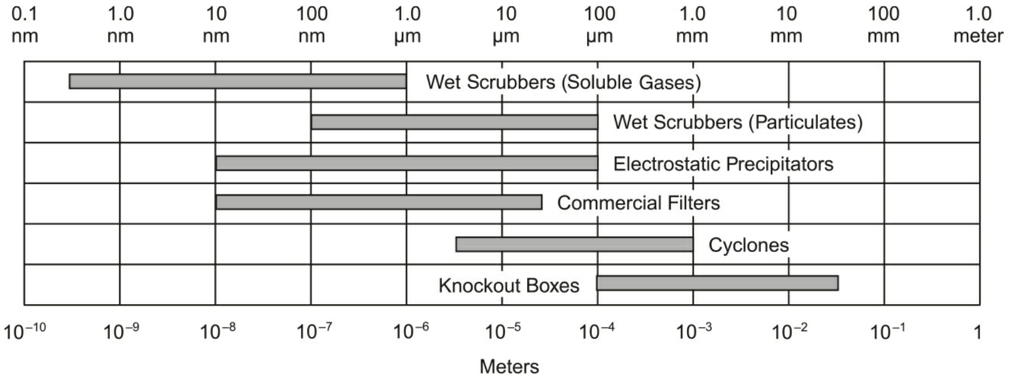


FIGURE 28.2 Application of wet scrubbers compared to competitive devices.

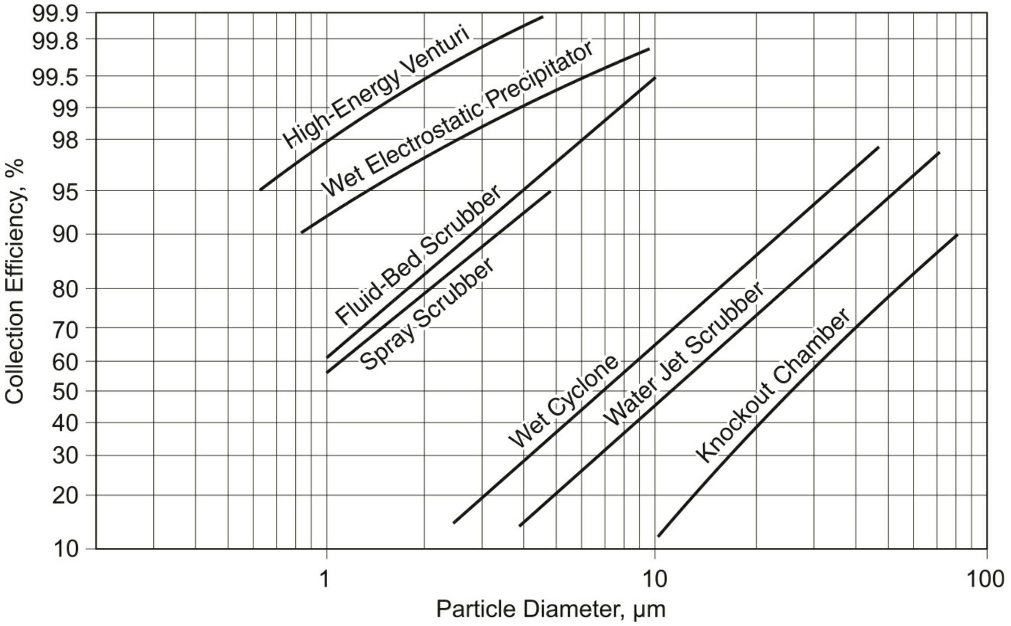


FIGURE 28.3 Performance range of scrubbing devices.

Particle size is one of the most important factors affecting removal efficiency, larger particles being much more easily removed. Submicron particles are the most difficult to remove.

All wet particle scrubbers operate on the same basic aerodynamic principle. A simple analogy: If water droplets of basketball size were projected to collide with gas-stream particles the size of bee bees (BB), statistical chances of collision are small. As the size of the water droplets is reduced to more nearly the size of the particles, chances of collision improve. Studies have shown that a surface film surrounding a water droplet has an approximate thickness of 1/200 of its diameter. A BB (the particle in flight) having a diameter less than 1/200 the diameter of the basketball flows through the streamline film around the basketball without collision (Fig. 28.4). However, if the water droplet were a baseball instead of basketball, collision would occur. A 0.5 µm fume particle requires water droplets smaller than 100 µm for adequate collection. Efficient scrubbing, therefore, requires atomizing the liquid to a fineness that is related to particle size, to afford maximum contact with the particles to be captured.

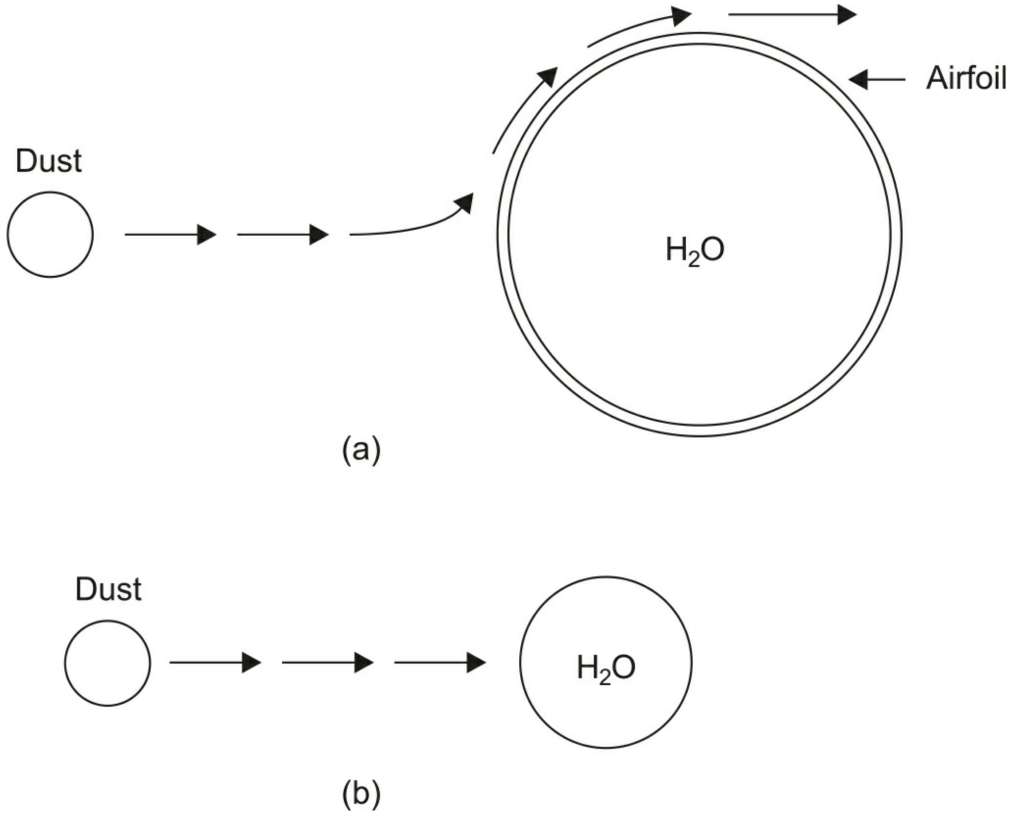


FIGURE 28.4 Effect of relative water droplet size to particle size for capture.

The probability of a droplet hitting the dust particles is proportional to the dust concentration; a ball would be less likely to hit a single BB than a swarm of them. To equalize these factors, scrubbers are regulated as to the volume of gas to be scrubbed (measured by pressure drop of gas stream) and water to be sprayed (measured by hydraulic pressure at the spray nozzles). Scrubbing chamber height and diameter are also tailored to the known characteristics of the gas.

Categorizing Wet Scrubbers

Wet scrubbers differ principally in their methods of effecting contact between the circulating liquid and gas stream. Techniques employed include injecting liquid into collection chambers as a spray, flowing liquid into chambers over weirs, bubbling gas through trays or beds containing liquid, and atomization of liquid by injection into a rapidly moving gas stream.

One way of categorizing wet scrubbers is by energy requirements. Some require high energy while others require very little. Generally, low-energy scrubbers are used for removal of large particulate matter and gaseous contaminants. They rely on high liquid/gas ratios and contact time in the scrubber to increase removal efficiency. High-energy scrubbers are used for removal of very small particulates (1 µm and less). They depend on high gas velocity for atomization to form small liquid droplets, with maximum impact between water droplets and particulate matter.

A second way of categorizing wet scrubbers is based on selectivity toward either gaseous contaminants or particulate matter. Scrubbers designed primarily for removal of gas are called mass transfer scrubbers or gas absorbers; those designed for removal of particulate are called wet particle scrubbers.

Gas Absorption Scrubbers

Gas absorbers are designed to maximize contact time and surface area between the scrubbing liquid and gas. This provides maximum opportunity for liquid–gas chemical reactions to occur. Absorption scrubbers usually have low energy requirements. Types most commonly used are packed bed, moving bed, plate, and impingement scrubbers. Although wet particle scrubbers provide mass transfer removal of some gases, these four types of absorption scrubbers do the job more completely and with greater efficiency.

Mass transfer (gas absorption) reactions require long residence times because contaminants must first be absorbed by scrubbing liquor and then react chemically to form a product that remains in the liquid phase.

Packed Tower

The packed tower (packed bed) consists of a vertical vessel containing packing materials such as rings, saddles, or tellerettes (Fig. 28.5). Water is sprayed across the top of the bed and trickles through the packing material. Gas enters near the bottom, and contaminants are removed as the gas stream moves upward through the water-washed packing.

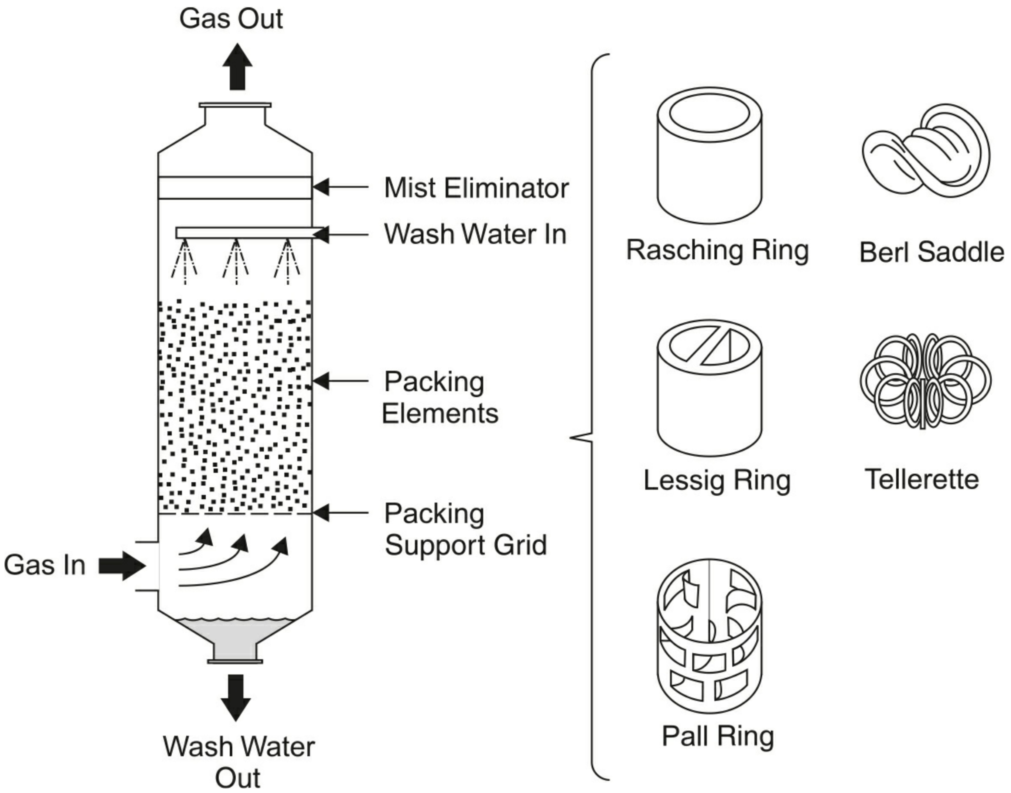


FIGURE 28.5 Packed tower and types of packing.

The cleaned gas stream passes through a mist eliminator near the top, where entrained moisture is removed before discharge. Scrubbing liquor is collected at the bottom. A portion is usually recycled to the inlet, and the balance discarded.

Although flows can also be co-current or crosscurrent, the counter-current type is most widely used. Packed beds have long been used for gas absorption operations, because they are able to reduce odor and pollutant gases to low residual concentrations. The limiting factor is economics. As better separation is needed, beds require greater packing depth and operate with higher pressure drops.

Gases entering a packed bed should not be heavily laden with solid particles, as these cause clogging of the packing material. Pressure drop is typically 0.5 inches of H_2O per foot of packing (3 mm Hg/m).

Typical applications include rendering plants, food processing plants, sewage treatment plants, and metal pickling plants.

Moving Bed Scrubbers

Moving bed wet scrubbers are well suited for high heat and mass transfer rates (Fig. 28.6). They are able to handle viscous liquids and heavy slurries without plugging. They accomplish this by using lightweight sphere packing that is free to move between upper and lower retaining grids. Counter-current gas and liquid flows cause the spheres to move in a random, turbulent motion, creating intimate mixing of liquid and gas. In addition to excellent gas–liquid contact, turbulence provides continuous cleaning of the moving spheres to minimize plugging or channeling of the bed.

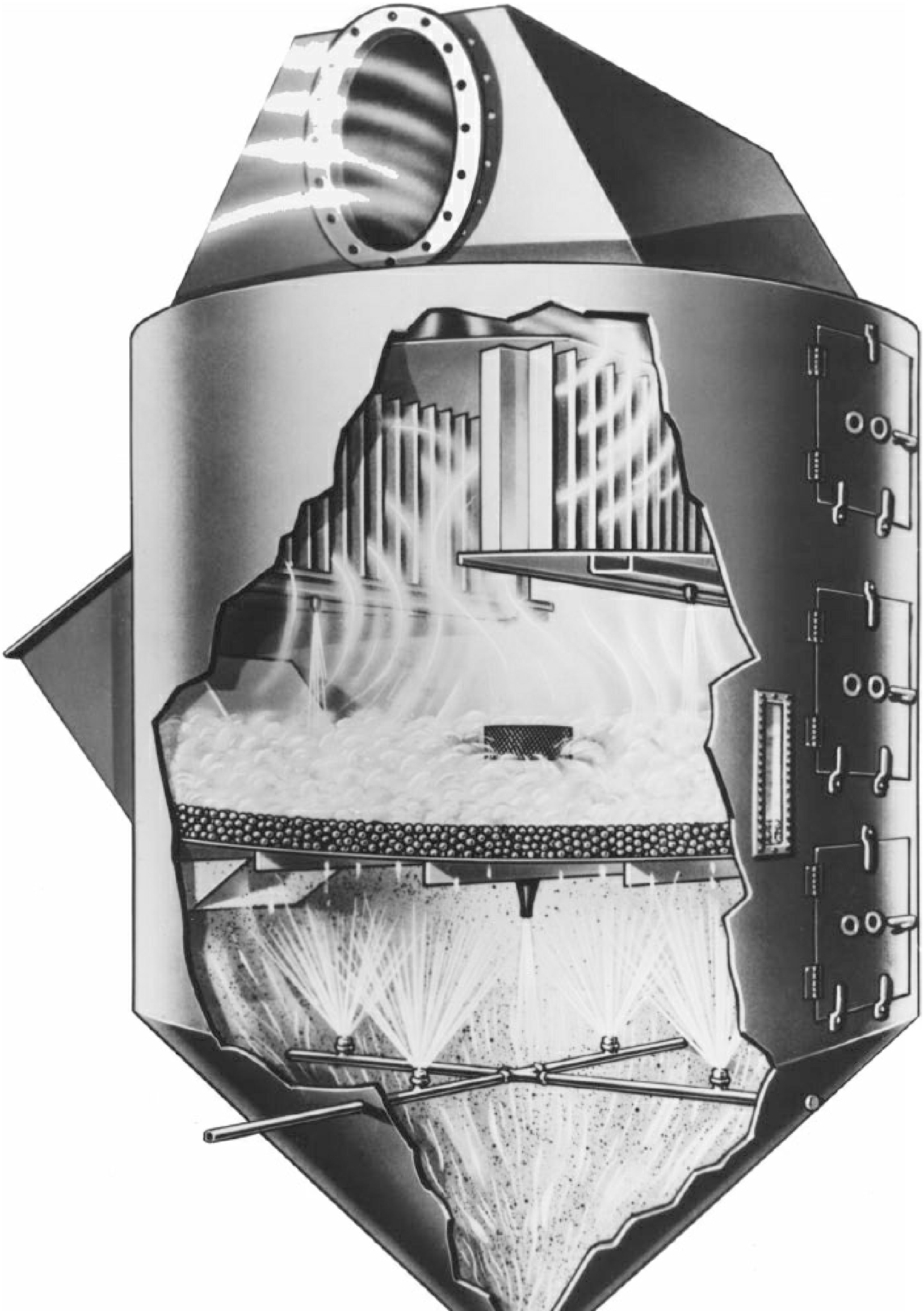


FIGURE 28.6 Moving bed scrubber using lightweight packing of spheres that continually shift, preventing plugging. (*Courtesy of The Ducon Company, Inc.*)

Moving bed scrubbers are useful for absorbing gas and removing particulates simultaneously. This type of scrubber is especially suited for use with gases containing viscous or gummy substances, which would result in plugging of conventional packed bed scrubbers. Efficiency is good for collection of particles larger than 1 µm. Both particle collection and gas absorption efficiency may be increased by employing several stages in series. Pressure drop is typically 0.2 to 0.5 inches H_2O (0.37–0.93 mm Hg) per stage.

Turbulent Contact Absorber The turbulent contact (TCA) absorber was developed as an extension of the moving bed scrubber, the difference being increased turbulence in the TCA unit, resulting from using fewer spheres per unit volume. The TCA enhances beneficial characteristics of the moving bed scrubber and permits high liquid and gas flows.

Plate Scrubbers

A plate scrubber consists of a tower having plates (trays) mounted inside (Fig. 28.7). Liquid introduced at the top flows successively across each plate as it moves downward. Gas passing upward through the openings in each plate mixes with liquid flowing over it. The gas–liquid contact causes gas absorption or particle removal. A plate scrubber is named for the type of plates it contains; if the plates are sieves, it is called a sieve plate scrubber.

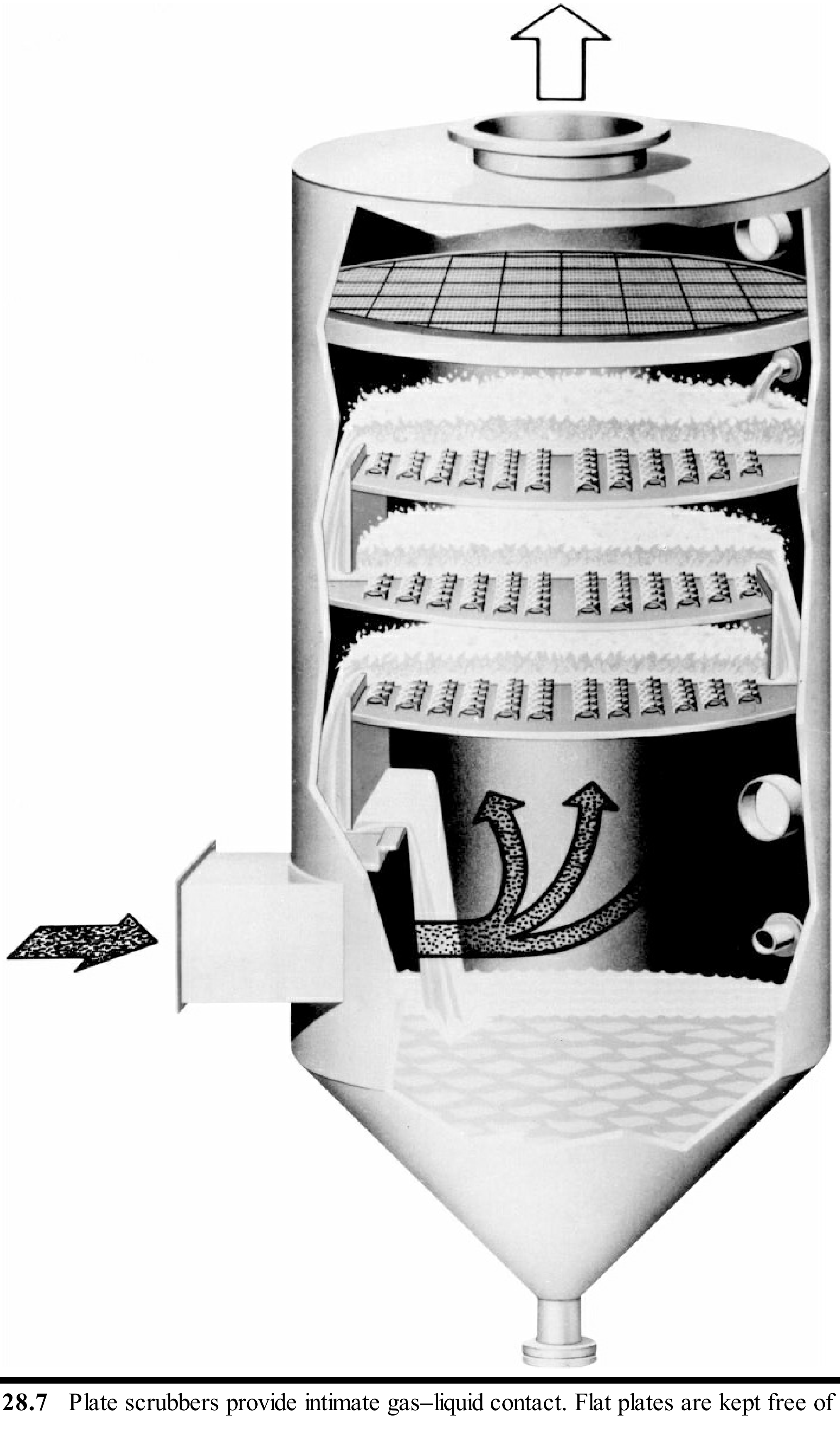


FIGURE 28.7 Plate scrubbers provide intimate gas–liquid contact. Flat plates are kept free of deposits

in most applications by turbulence. (*Courtesy of Koch Engineering Company, Inc.*)

Impingement Scrubbers

In some designs, impingement baffles are placed a short distance above each perforation on a sieve plate forming an impingement plate, to increase turbulence and enhance gas-particle–liquid interaction (Fig. 28.8). Impingement baffles are below the liquid level. Pressure drop is about 1 to 2 inches H_2O (1.9–3.7 mm Hg) for each plate.

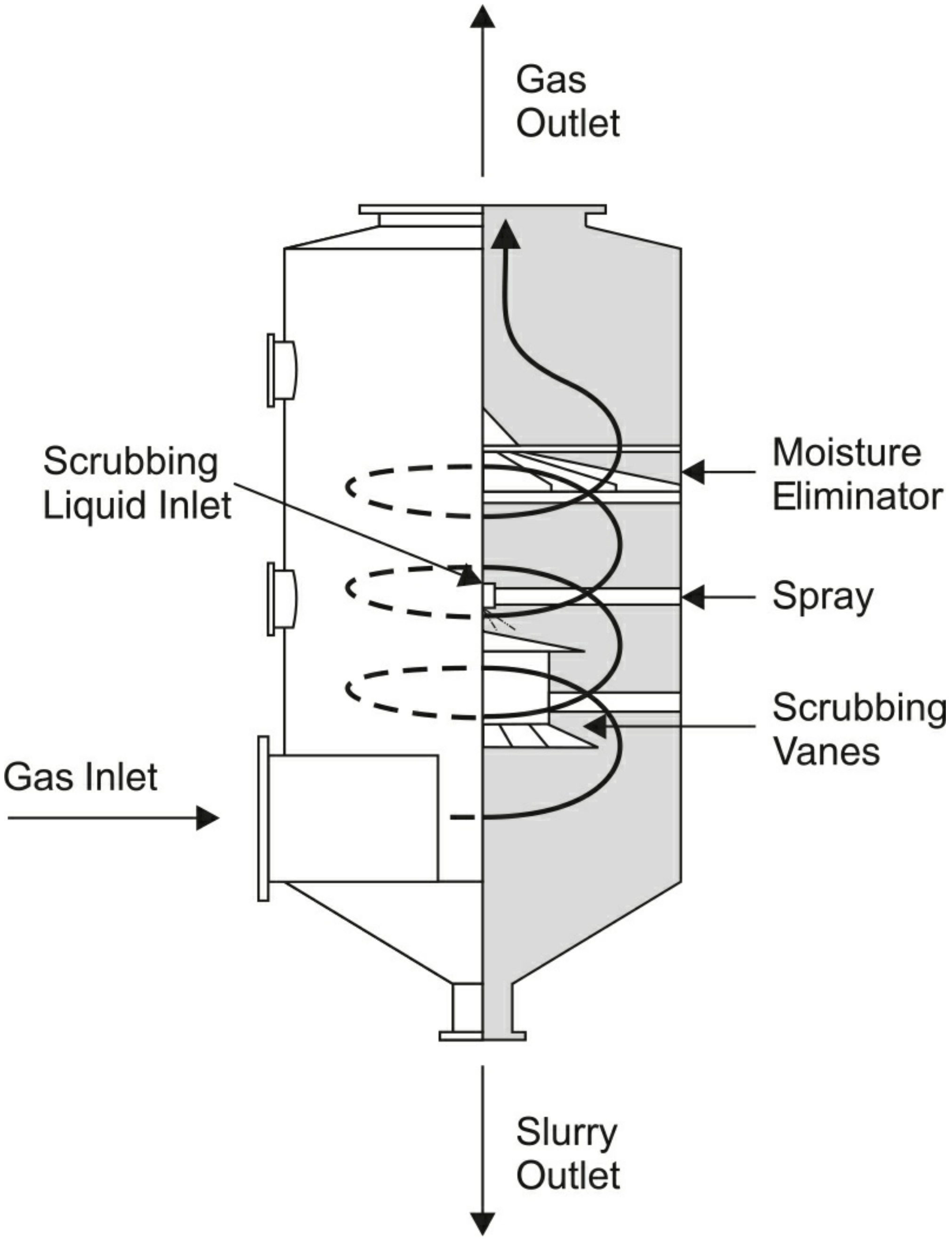


FIGURE 28.8 An impingement scrubber uses a perforated plate to promote gas–liquid contact with impingement baffles over the perforations to atomize water. (*Courtesy of W.W. Sly Manufacturing Company*.)

Wet Particle Scrubbers

The four basic factors that determine the efficiency of wet particle scrubbers are:

1. Water surface area

2. Liquid/gas ratio
3. Particle size and scrubber energy
4. Particulate affinity for water (wettability)

Anything mechanical or chemical that causes water spray nozzles to form smaller water droplets with larger surface area increases the collision rate between particulate in the gas phase and water, resulting in increased particulate removal.

The second way to increase the collision rate is to pump more water through the scrubber. However, increasing the liquid/gas ratio is an inefficient means of increasing the surface area of water. Usually, it is more economical to increase the effective liquid/gas ratio by causing smaller droplets to form mechanically or chemically.

The force, with which particulate matter strikes water, is a third factor in scrubber performance. Since a liquid film barrier separates particulate in the gas phase from water, a particle must have enough energy to force its way into the water droplet to be captured. Smaller particles require more energy than larger ones. They have a lower mass, and strike the barrier with less momentum than larger particles moving at the same velocity. Therefore, higher energy is required for scrubbing small particles than for large particles.

Higher energy must be expended to scrub a particle that is hydrophobic (repelled by water) than a similar size particle that is hydrophilic (attracted to water), and most particulates in the gas stream are hydrophobic. Increasing the mechanical energy of a wet scrubber increases its ability to remove smaller and more hydrophobic particulates.

Another means for increasing removal of these particles is increasing the wetting power of water by chemical reduction of surface tension.

Either a high-energy or a low-energy scrubber may be used for removal of particulates from gas streams, the choice depending on size of the particles. Low-energy scrubbers, such as the spray tower and wet cyclone, may be used for particles over 5 µm. For particles smaller than 5 µm, a high-energy scrubber such as a venturi or a venturi ejector provides more complete removal. Many wet scrubbing systems, such as those cleaning steel mill blast furnace gases, employ a low-energy scrubber followed by a high-energy scrubber. The function of the low-energy scrubber is to cool the gas (reduce volume) and remove large particles, thereby reducing load on the high-energy venturi scrubber. This also reduces size and power of the induced draft fan, because the cooling effect reduces gas volume.

Spray Towers

The spray tower collects particles or gases on liquid droplets produced by spray nozzle atomization. Characteristics of droplets are determined by nozzle design. Sprays are directed into a chamber shaped to conduct gas to the atomized droplets. Spray towers can be used for both mass transfer and particle collection. Low-pressure drop [1–2 inches H_2O (1.9–3.7 mm Hg)] and high water rate make them the least expensive of the mass transfer scrubbers. Spray towers are most applicable for removal of large particles, gas cooling, humidification, dehumidification, and removal of gases with high liquid solubility.

Wet Cyclones

Wet cyclone scrubbers (Fig. 28.9) are effective for removing dusts and liquid aerosols. Finely atomized water spray, contacts the gas stream, which enters tangentially at the bottom to pursue a spiral path upward. Atomized droplets are caught in the spinning gas stream and swept by centrifugal force across to the walls of the cylinder, colliding with, absorbing, and collecting dust or fume particles en route. Scrubbing liquid and particles drain down the wall to the bottom, and clean gas leaves through the top. The higher pressure drop [6–8 inches H_2O (11–15 mm Hg)] increases energy costs over those for a spray tower.

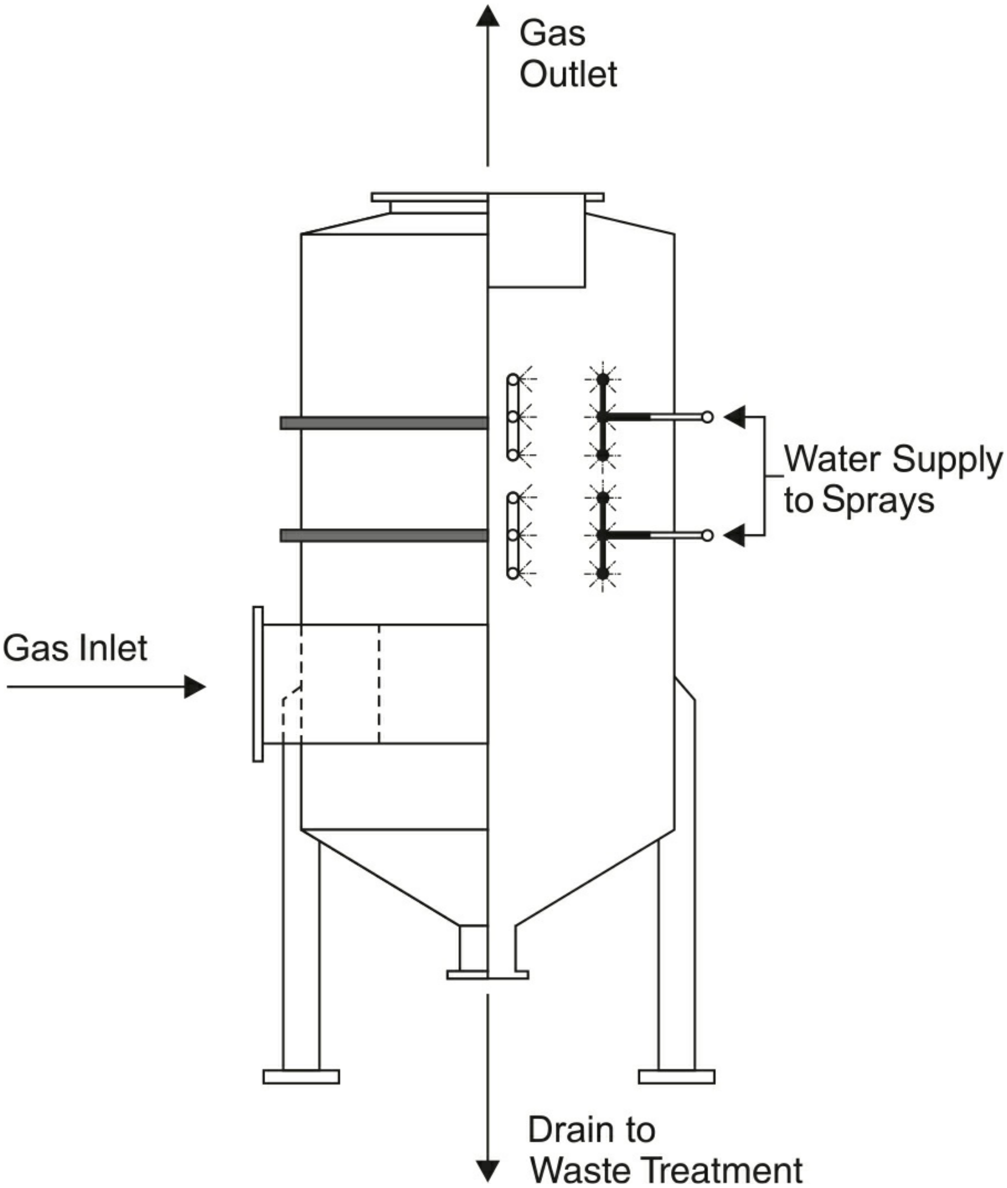


FIGURE 28.9 Wet cyclone scrubber. (*Courtesy of Ceilcote Company, a unit of General Signal.*)

Venturi Scrubbers

Venturi scrubbers (Fig. 28.10) are best suited for removal of 0.05 to 5 µm particulates, such as those created by condensation of a liquid, metallic vapor, or by a chemical reaction forming a mist or fume. Typical examples are ammonium chloride fumes from steel galvanizing, phosphorus pentoxide fumes from phosphoric acid concentration, mists from dry ice plants, and zinc oxide fumes from reverberatory furnaces.

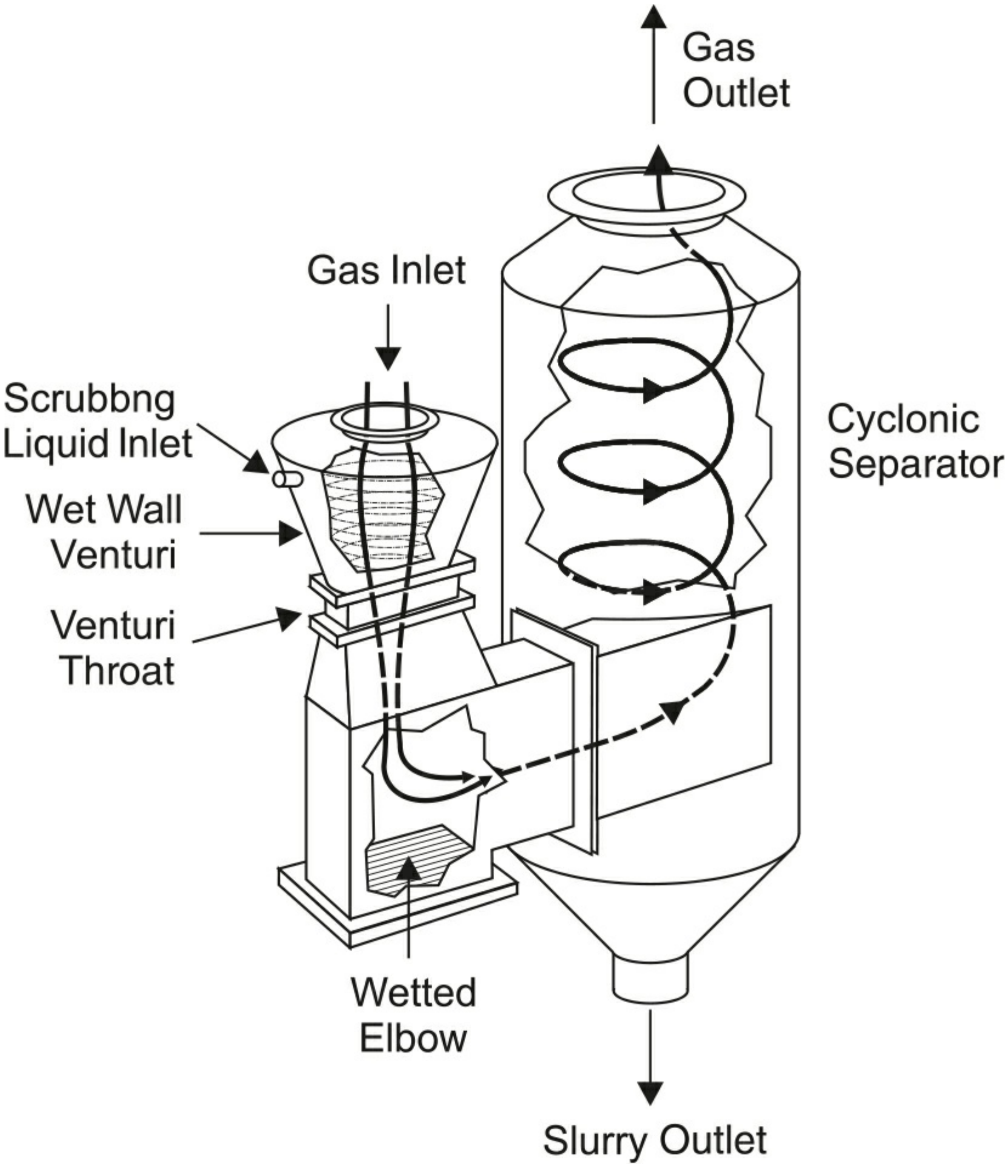


FIGURE 28.10 Venturi scrubber with variable throat to accommodate changes in gas flow. (*Courtesy of FMC Corporation*.)

Passing gas and water streams co-currently through the extremely small throat section of a venturi remove aerosols. As the velocity is accelerated in the throat, the liquid breaks into extremely fine drops. High gas velocities, ranging from 200 to 400 ft/s (61–122 m/s), make the relative velocity between gas and liquid high enough to cause good liquid atomization and particle collection. Liquid drops collide with and remove particles in the gas stream, and then agglomerate for separation from the gas. The cleaned gas stream passes through a separator to eliminate entrained liquid.

Venturi scrubbers require high pressure drops [5–100 inches H_2O (9.3–187 mm Hg)]. Pressure drop must be increased as particle size becomes smaller to ensure adequate removal.

Venturi scrubbers can be used for removing soluble gases. However, such applications are limited to situations where small particulates are also present, since high-energy requirements for operating venturi scrubbers make them costly for controlling gaseous pollutants.

Several modifications of the basic venturi scrubber are available to meet specific requirements of the size and type of particle to be removed. Low, medium, or high-energy venturi scrubbers are available, with energy requirements directly related to the pressure drop needed for removal of submicron particulates.

Many venturi scrubbers have a variable throat to allow for change in load. In addition, as the throat is decreased in size at a fixed load, velocity increases, resulting in increased pressure drop and better efficiency in removing submicron particles.

Venturi scrubbers use several methods to atomize scrubbing water. In the most common, liquid is sprayed through jets across the venturi throat (Fig. 28.10). This provides effective removal of submicron dust, fume, and mist particles and is the first choice for the majority of applications. In another common venturi, the flooded wall type, scrubbing liquid is introduced tangentially at the top, as shown in Fig. 28.11. Liquid spirals down converging walls to the throat in a continuous film. At the entrance of the throat, it forms a curtain of liquid in the gas stream. Impaction of gas into this curtain atomizes the liquid. Further impaction and agglomeration occur in the diverging section.

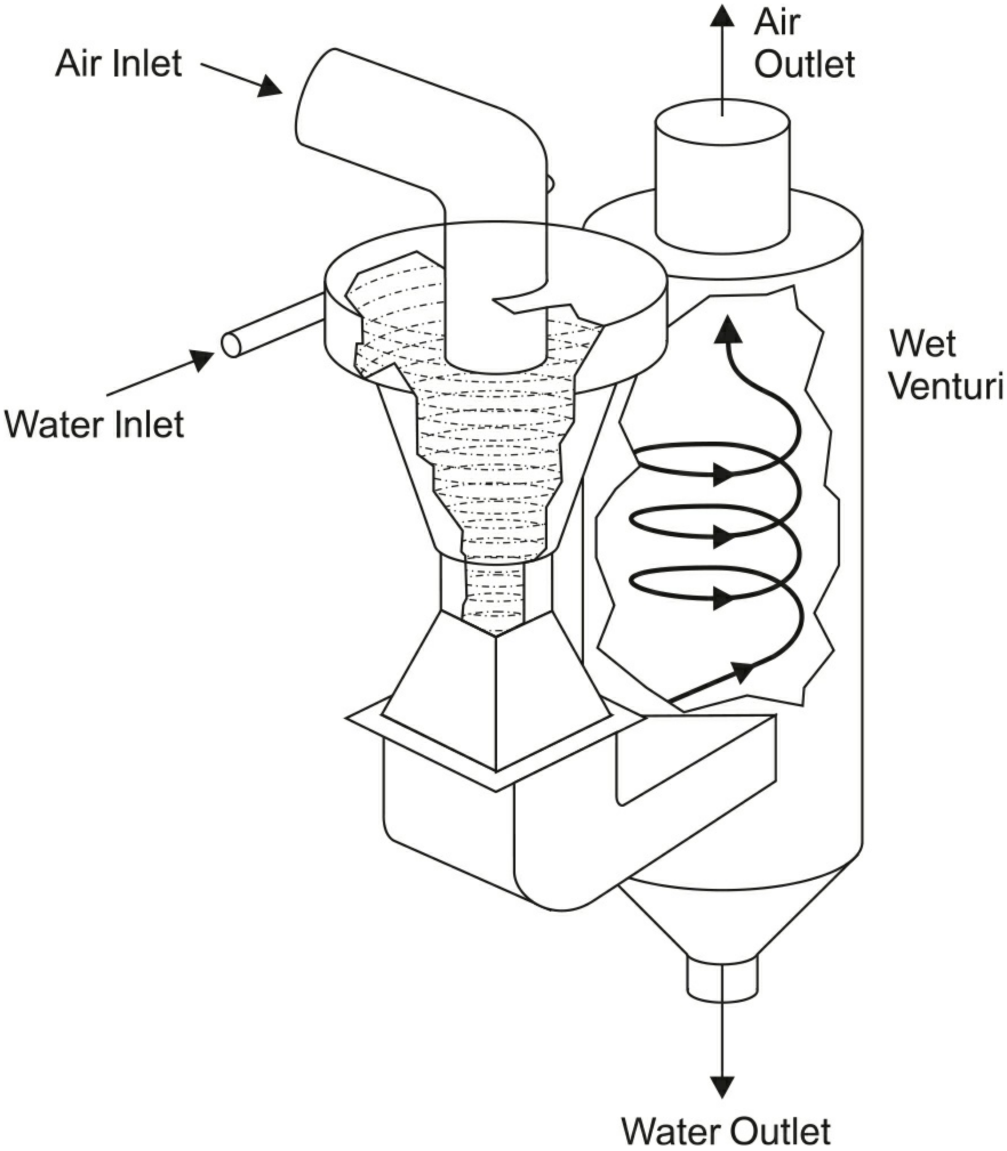


FIGURE 28.11 In this venturi scrubber design, water is atomized and flows down a spiral path toward the venturi throat.

This type of venturi scrubber is recommended for hard-to-handle situations like removal of sticky solids from gases, recycling of dirty water where water supplies are limited, and recovery of process materials in concentrated form.

Another common type is the flooded disk scrubber, in which liquid is introduced to a disk upstream of the venturi throat. Liquid flows to the edge of the disk and is atomized by the high-velocity gas stream.

Figure 28.12 shows an ejector venturi, which uses high-pressure spray nozzles to collect particulates, absorb gases, and move the gas. It derives its energy from high-pressure liquid, while the regular venturi derives most of its energy from high gas velocity produced by the induced draft fan. Depending on the ejector venturi used, an induced draft fan may or may not be required.

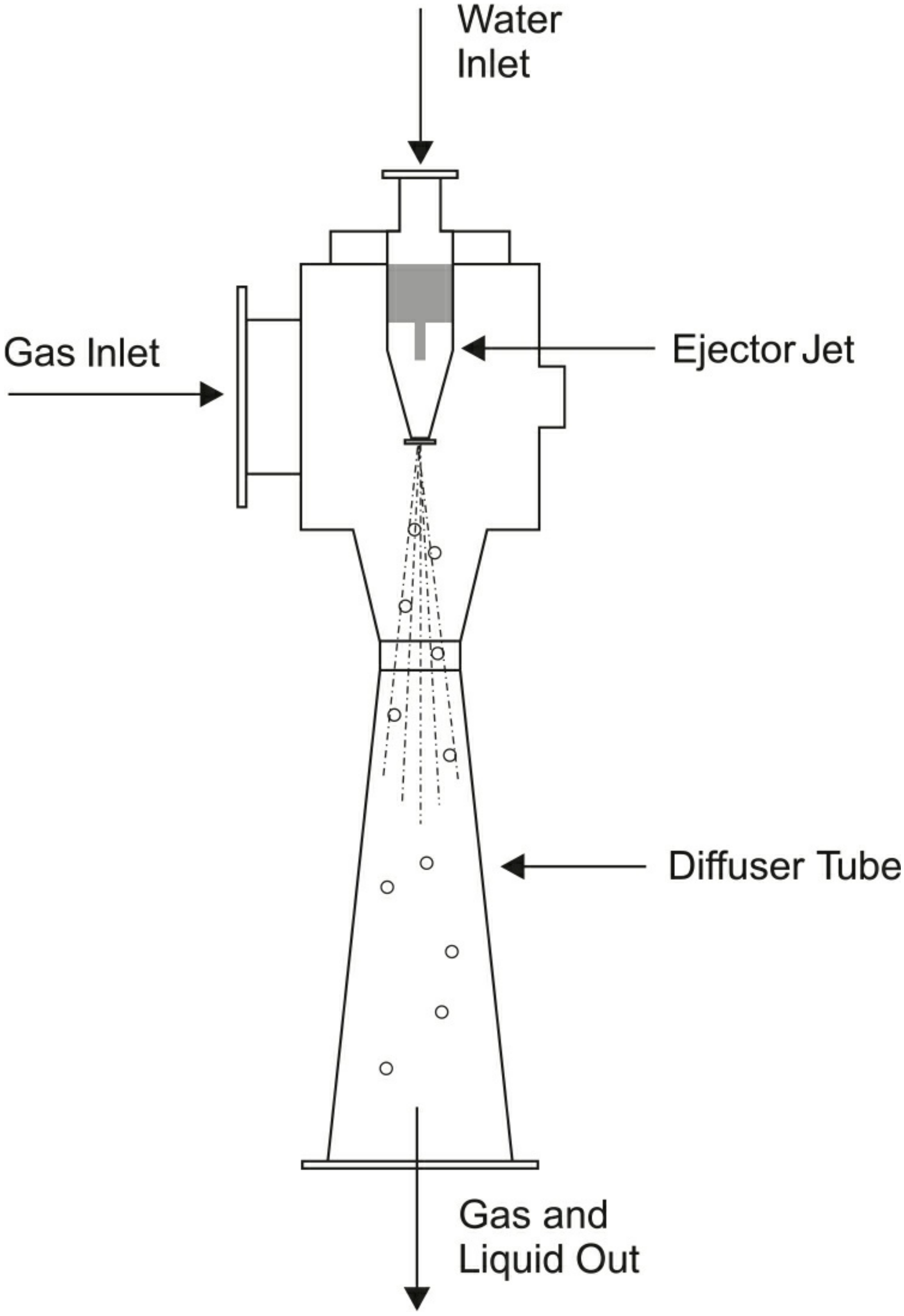


FIGURE 28.12 Water creates the energy for this ejector venturi scrubber.

There is a high velocity difference between the liquid droplets and gas; this affects particle separation. Collection efficiency is generally high for solid particles larger than 1 µm. Mass transfer is affected by the co-current flow of the gas–liquid. Energy consumption is relatively high because of pumping costs.

Ejector venturis may be used alone or as the first stage of a more complex system. The principal collection mechanism in this type of scrubber is inertial impaction, which is effected by liquid drops. Particle adherence upon striking droplets is dependent upon wettability of the particles. Because scrubbing liquid is usually recirculated, nozzles must be capable of handling a high solids concentration.

Wet Electrostatic Precipitators

Water can also be used with electrostatic precipitation to improve removal of particulates. In this type of system, water is continually recirculated over the plates, and discharged to an ash sluice pond or thickener to be clarified for reuse.

Waterside Problems

Operating conditions in the scrubber may produce severely corrosive or scaling water, depending on the gas stream being scrubbed and the nature of chemicals added to the water. Many systems use lime or limestone slurries to react with sulfur dioxide (SO_2), forming insoluble compounds removed in a thickener. Problems encountered in wet scrubber operations parallel those found in an open recirculating cooling water system, but scrubber water is often more saline.

Chemical treatment programs for wet scrubber systems are designed to:

- Maintain clean nozzles and collection surfaces, preventing deposit or scale buildup, thus helping to maintain unit efficiency
- Improve particulate capture or, for gas removal, mass transfer
- Control corrosion in the scrubber and recirculating water systems

Water problems in scrubbers range from scale and deposits to corrosion and waste disposal. Depending on the moisture level or dew point of the gas stream, gas cooling can result in evaporation or condensation, leading to concentration or dilution of scrubber water.

If the gas stream is above the dew point, recycling water for wet scrubbing results in evaporation and concentration of scrubber water, adding to corrosion and scale problems inherent with gases or particulates removed from the gas stream. However, in some systems, the gas contains substantial water vapor, and condensation with resultant dilution of recycle water may occur. This tends to lessen the potential for scale, deposits, and corrosion. Dilution is less common than concentration.

Each scrubbing system must be considered individually because of the wide variety of construction materials available, including mild and stainless steels, copper and nickel alloys, fiberglass, polyvinylchloride (PVC), ceramics, lead, and refractory, to name a few. Many manufacturers construct scrubbers of alloyed metals and nonmetallic materials to avoid corrosion problems but still encounter problems of scale and deposition. The same techniques and principles used for corrosion and deposit control in cooling water systems apply to scrubbers.

Scrubber systems that operate under low pH conditions, usually have deposits that are primarily particulates removed from the gas. Those systems that operate at a pH greater than 7.0 normally yield scale deposits produced from water reactions or scale and suspended solids combined.

However, even high-pH systems sometimes yield deposits that are primarily particulates removed from the gas. It is difficult to generalize regarding composition of deposits, because of the wide variability of scrubber designs, process gases, and water characteristics. The most commonly encountered deposits are calcium carbonate, calcium sulfate, lime [$Ca(OH)_2$], iron oxide, carbon black (soot), oils and greases, aluminosilicates (clays), and metal sulfides. Deposits, like corrosion, can plague virtually every section of the scrubber system from inlet gas ports to induced draft fan and stack. Deposits usually form at the venturi throat, trays, and packing in gas absorbers, liquid recycle lines and pumps, mist eliminators, induced draft fans, and clarifier supply lines.

Chemical treatment for scale and deposit control is effective in controlling the majority of deposits, but it must be individualized for each scrubbing system owing to variation in deposition problems.

Waste Treatment

Since the basic function of the wet scrubber is to remove contaminants from process and combustion gases, once scrubber liquid has done its job, disposal of contaminants transferred to the water must be considered. For the small plant, this may entail merely discharging a bleed-off of recycle water to the sanitary sewer. The larger plant may be required to install an in-plant clarification system.

There are two basic types of clarifier systems. The first is the full-flow, in-line clarifier that clarifies all scrubber water after it has made one pass through the scrubber. Water is recycled from the clarifier to the scrubber for further reuse. Problems are usually less severe with this type of unit, because suspended solids are usually maintained at a low level. This type of system is in many respects comparable to a once-through system.

The second type of clarifier is that used for clarification of a blowdown sidestream from the recycle system before discharge. Problems are normally more severe with this type of system.

Scrubbing liquid that contains high biochemical oxygen demand (BOD), heavy metals, or toxic matter may require additional treatment such as biological oxidation before discharge.

Auxiliary Equipment

Although the wet scrubber is the heart of the gas cleaning system, auxiliary equipment is required to help the scrubber work efficiently. Auxiliary equipment may be categorized as follows:

- Dust catchers remove gross solids to prevent overloading the scrubber.
- Gas quenchers cool high-temperature [over 1000°F (538°C)] gas and reduce evaporation in the scrubber.
- Entrainment separators (demisters) reduce water droplets in exit gas.
- Gas cooling towers reduce plume discharge.
- Cooling towers, cooling ponds, and spray ponds facilitate optimum water recycle and minimize makeup.
- Induced draft fans move gas from the scrubber to the discharge vent or

stack.

- Forced draft fans move gas to the scrubber and through to the vent or stack.
- Gas reheat systems reduce plume discharge by raising the gas dew point.
- Clarifiers, thickeners, and settling ponds facilitate recycle and recover solids for disposal or reuse.
- Sludge dewatering devices consolidate recovered solids.

Selected Gas Scrubbing Systems

This section presents examples of gas scrubbing systems used in the electric utility, steel, and paper industries, including the basic types of scrubbers and auxiliary systems used in these applications and the nature of waterside problems.

SO_X Removal from Flue Gas

Flue gas desulfurization (FGD) is widely practiced to remove sulfur oxides (SO_x) from boiler stack gas, particularly in the electric utility industry. Wet limestone scrubbing is a popular FGD method.

Chemistry of Flue Gas Desulfurization

The FGD process uses alkali (limestone) to react with and neutralize acidic sulfur gases. For this discussion, sulfur dioxide (SO_2) is used.

The first step in the neutralization process is to absorb SO_2 into the spray water as shown in Eq. (28.1):

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (28.1)$$

Sulfurous acid (H_2SO_3) can undergo dissociation as shown in Eq. (28.2):

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{-2} \qquad (28.2)$$

Addition of limestone ($CaCO_3$) slurry neutralizes the acidity of SO_2, producing calcium sulfite ($CaSO_3$):

$$H_2SO_3 + CaCO_3 \rightarrow CaSO_3 + CO_2 + H_2O \tag{28.3}$$

Under conditions maintained in the scrubber, $CaSO_3$ precipitates as the hemihydrate:

$$Ca^{+2} + SO_3^{-2} + 1/2\,H_2O \rightarrow CaSO_3 \cdot 1/2\,H_2O \tag{28.4}$$

Proper pH control in the scrubber is critical for performance. Many FGD scrubbers operate at pH 5.6 to 5.8. If scrubber water pH is too low, SO_2 removal decreases. If scrubber water pH is above 6.0, limestone feed is too high, which affects operational costs.

Generally, flue gas contains excess oxygen to assure complete combustion of fuel. Excess oxygen reacts with bisulfite (HSO_3^-) and sulfite (SO_3^{-2}) to form sulfates:

$$SO_3^{-2} + 1/2\,O_2 \rightarrow SO_4^{-2} \tag{28.5}$$

Experience indicates that the first 15 mole percent of sulfate ions co-precipitate with sulfite to form calcium sulfite–sulfate hemihydrate ($0.85CaSO_3 \cdot 0.15CaSO_4 \cdot ½O$). Sulfate above 15 mole percent precipitates as gypsum:

$$Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{28.6}$$

Chemistry control of scrubber water markedly affects potential scale formation in the spray tower. Experience indicates that scale can be minimized or even prevented when scrubber water is operated in a completely oxidized state (no calcium sulfite–sulfate hemihydrate formation) or in a completely nonoxidized state (no gypsum formation). Therefore, most FGD installations operate in one of these two modes to avoid scale formation and the associated costs of reduced throughput and downtime for cleaning.

The completely oxidized state is more popular because the product (gypsum) is easier to handle and can be sold. Calcium sulfite–sulfate hemihydrate is a soft solid that is difficult to dewater and does not have good market value. Gypsum, on the other hand, can be vacuum filtered to produce a relatively dry cake. Wallboard manufacturers find this gypsum source attractive due to its purity and uniform particle size. Therefore, gypsum production from FGD systems has good market value. Gypsum production can be maximized by installing forced air oxidation systems to convert all sulfite ions to sulfate ions.

Flue Gas Desulfurization Scrubber Design

Design of FGD scrubbers has undergone many changes during evolution of this technology. Originally, FGD scrubbers contained packing, and many installations still do. However, packing is prone to scaling during chemistry upsets. Newer designs reduce the amount of packing or even eliminate packing entirely, by using spray nozzles to create intimate contact between flue gas and scrubber water. Figure 28.13 shows an FGD open spray tower design.

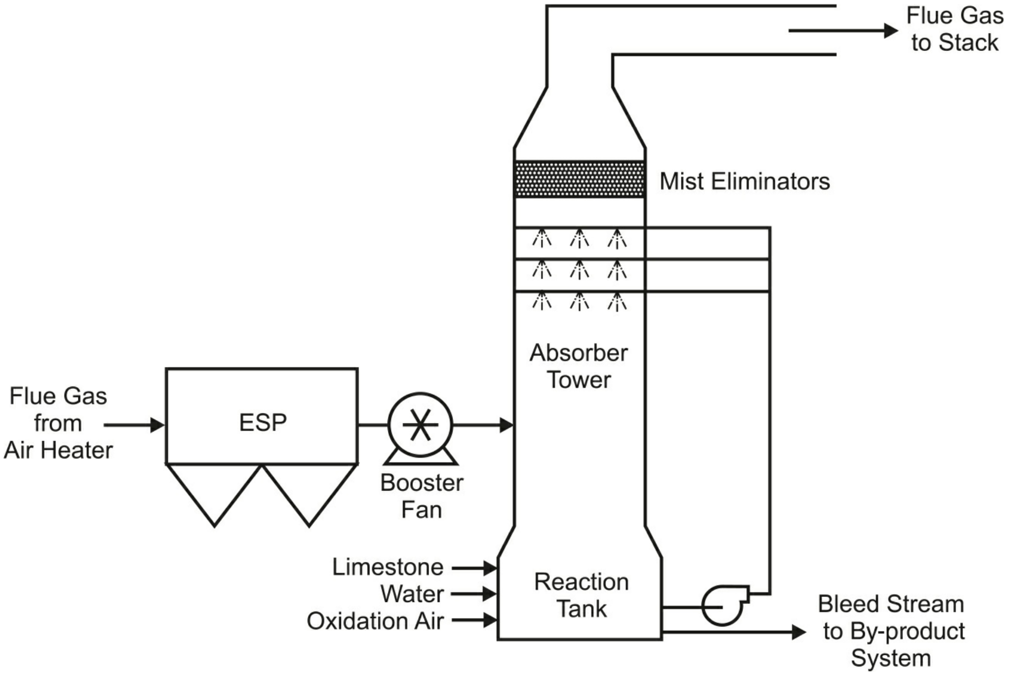


FIGURE 28.13 Utility stack gas scrubbing system.

Even with forced air oxidation to generate only gypsum, a number of operating issues still present challenges:

- Scale formation during chemistry upsets
- Spray nozzle efficiency and plugging
- Mist eliminator performance and maintenance
- Limestone quality, particle size, reactivity, and additives for improved performance
- By-product disposal or sale, including both cake and liquid

Limestone represents a significant operating cost in FGD systems, and optimization of limestone use is a key operating concern. Poor limestone reaction leads to increased limestone feed, which increases operating costs. Some factors that affect limestone reactivity and use include: quality, particle size, residence time, and solids–liquids separation in the scrubber water.

FGD designs continue to evolve. New systems, such as the Chiyoda process, provide new methods to contact flue gas with limestone slurry and attempt to address operating issues of existing FGD systems.

SECTION 4

Energy in Water Systems

CHAPTER 29

Energy Use in Effluent Systems

The U.S. Environmental Protection Agency (EPA) estimates that 0.1 to 0.3% of the nation's total energy usage is consumed in municipal and industrial effluent treatment. Energy costs can account for 30% of the operations and maintenance budget of a typical municipal effluent treatment facility, second only to staffing costs. By comparison, chemicals represent about 4% of the same budget category. Electrical energy accounts for over 90% of the total energy consumed in effluent treatment. Fuels such as oil and natural gas are sometimes used for onsite generation of electricity, but in most instances, electricity is supplied by independent remote generators. Interestingly, effluent treatment can be a producer of energy. Anaerobic digestion, which generates combustible biogas (a combination of methane and carbon dioxide), and even flowing water, typically at the outfall, can be utilized as energy sources. That said, other than a handful of demonstration facilities, no effluent treatment plant is completely self-sustaining with regard to energy, and most are net users of energy and in particular electrical energy.

The focus of this chapter is on primary, secondary, and tertiary effluent treatment with a particular emphasis on aeration within the activated sludge process. Solids processing, including thickening, stabilization and dewatering, although significant in terms of energy, is not covered. In addition, management of utility rate structures, although a critical part of any discussion on energy use and optimization, is not discussed. One typical example of managing the utility rate structure involves shifting some processes to off-peak hours to take advantage of lower energy rates. In reality, this often requires ability to store effluent or biosolids, and in many instances, that is not an option.

Finally, study of energy in effluent treatment is multifaceted and covers an incredible amount of equipment, plant configurations, operating strategies, and regulatory issues. This diversity is equaled only by the amount of information and support now available. The EPA and U.S. Department of Energy (DOE) are useful resources to launch a more focused investigation into the subject.

Energy Utilization in Effluent Treatment

Electrical energy is used to power many different types of processes and equipment at a typical effluent treatment facility. Major energy consumers include pumps, blowers, mechanical aerators, and solids handling systems. In most cases, blowers and pumps claim the most electrical energy. Pumps are used to move effluent and often sludge from one point to another, when gravity flow is not feasible or possible. Blowers are used to move air and provide one of the ways effluent is aerated. Air can also be used in various physical separation processes like dissolved air flotation (DAF); however, its predominate use is in aeration. Figure 29.1 shows approximate breakouts of electrical energy costs at a typical municipal activated sludge effluent treatment plant.

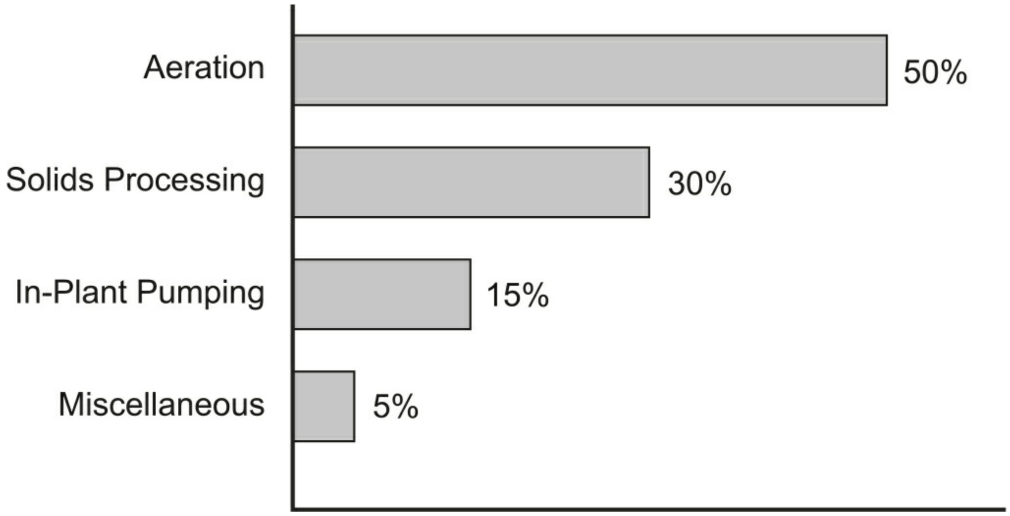


FIGURE 29.1 Electric energy breakout at municipal activated sludge facility.

Realize that activated sludge processes treat roughly 90% of municipal effluent in the United States and represent the predominant treatment approach in many industrial applications including hydrocarbon, chemical, paper, and food processing. The predominance of activated sludge systems is due to an optimum balance between throughput, effluent quality, sludge generation, and overall cost of treatment. Other common treatment platforms include fixed-film systems like trickling filters, rotating biological contactors (RBC), and ponds.

Each of these configurations has its own unique energy signature.

Figures 29.2 to 29.4 show the indexed percentage of electrical energy consumed by various processes and operations at typical 10, 20, and 100 mgd (26, 53, and 263 m^3/min, respectively) municipal activated sludge facilities. The disproportionate percentage attributed to aeration, diffused aeration in this case, underscores the importance and reliance on aerobic treatment in effluent. Figures 29.5 to 29.7 show the indexed percentage of electrical energy consumed in similarly sized plants featuring a trickling filter process, which is a common treatment approach in municipal effluent treatment. Note that in this configuration, pumps consume the largest percentage of energy, as effluent must be continually circulated over static media.

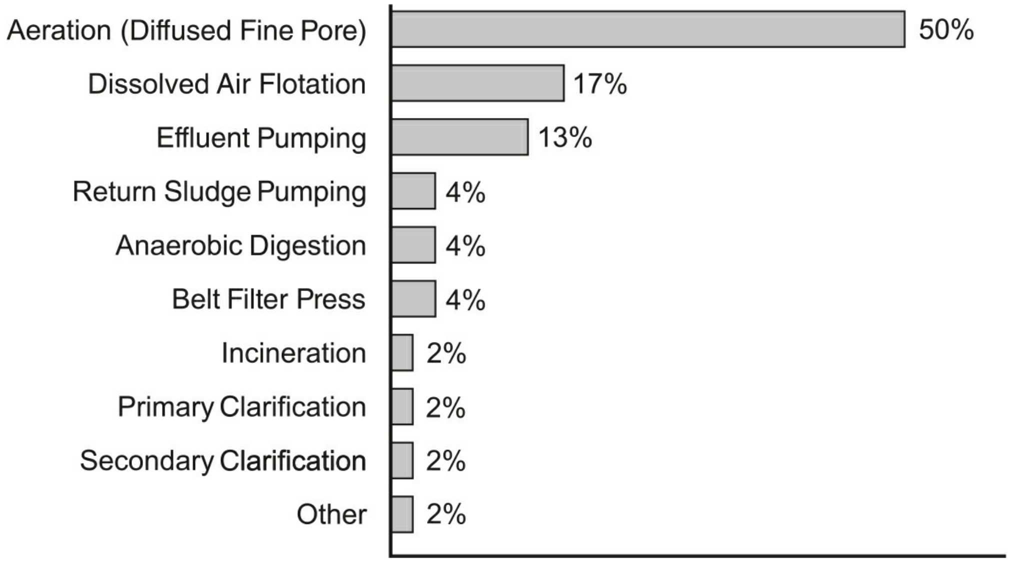


FIGURE 29.2 Electrical energy usage distribution in 10 mgd (26 m^3/min) municipal activated sludge facility with 437 kW power requirement.

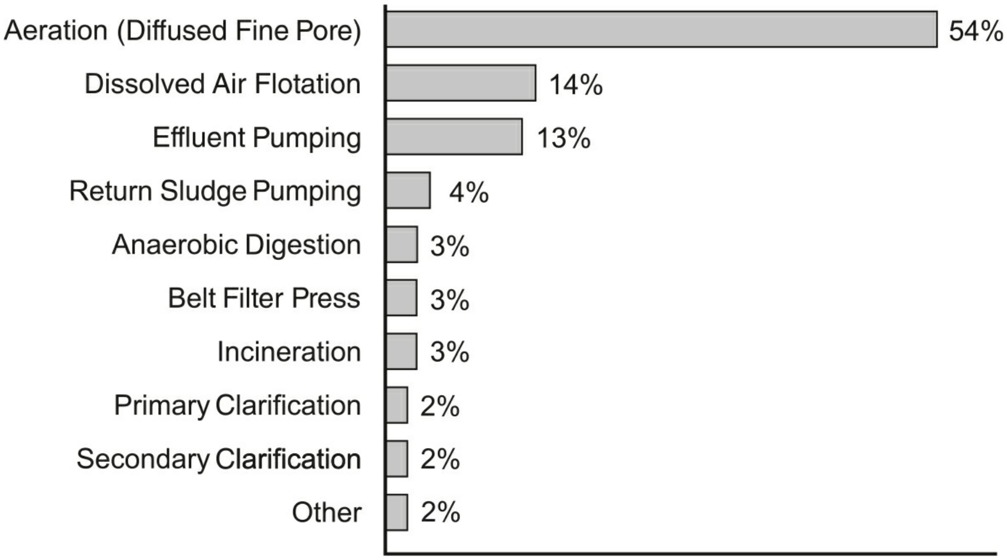


FIGURE 29.3 Electrical energy usage distribution in 20 mgd (53 m^3/min) municipal activated sludge facility with 811 kW power requirement.

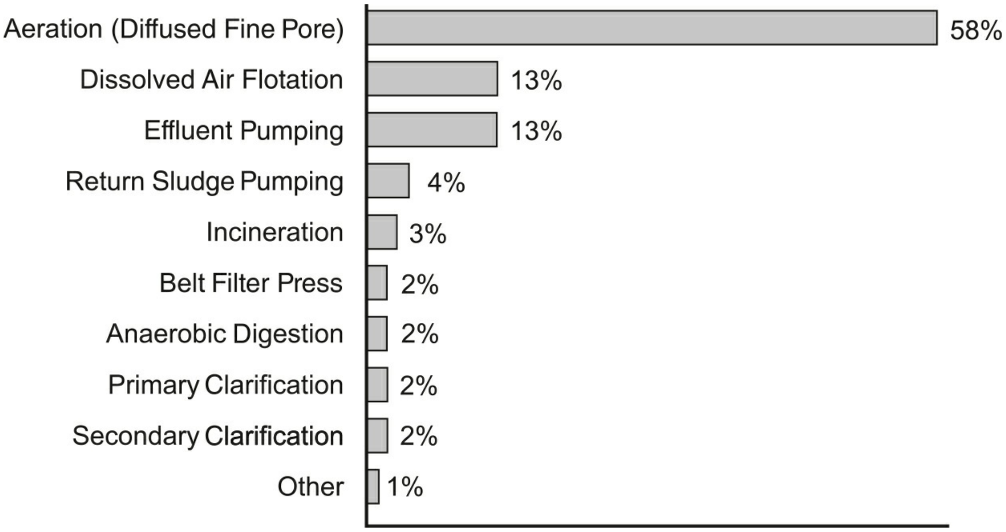


FIGURE 29.4 Electrical energy usage distribution in 100 mgd (263 m^3/min) municipal activated sludge facility with 3.8 MW power requirement.

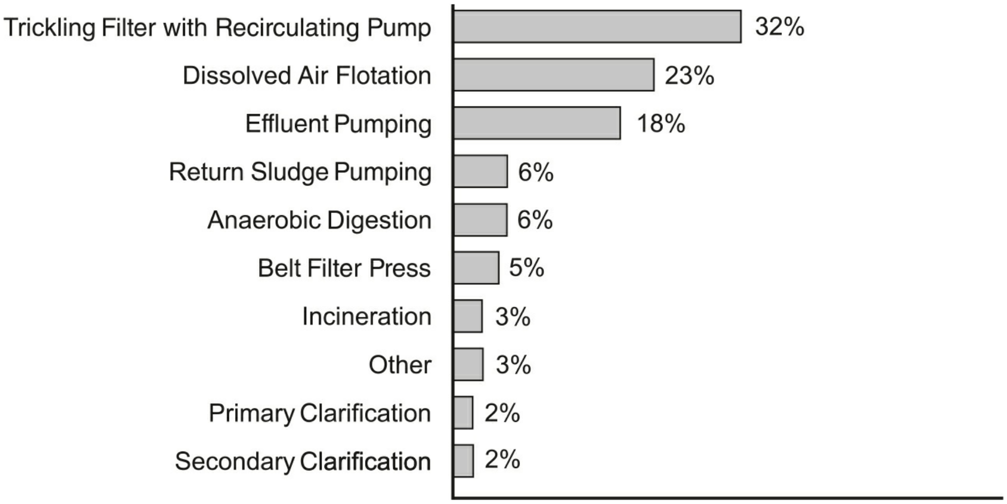


FIGURE 29.5 Electrical energy usage distribution in 10 mgd (26 m^3/min) municipal trickling filter facility with 321 kW power requirement.

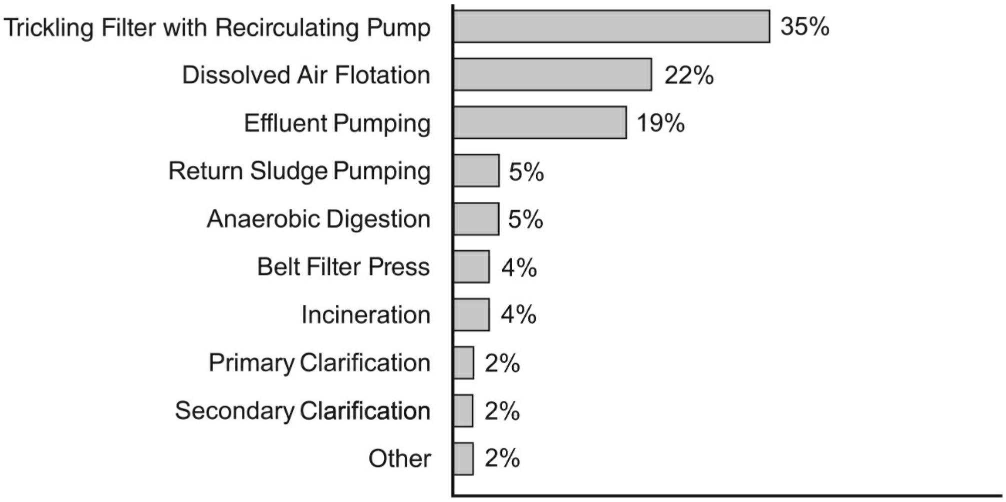


FIGURE 29.6 Electrical energy usage distribution in 20 mgd (53 m^3/min) municipal trickling filter facility with 563 kW power requirement.

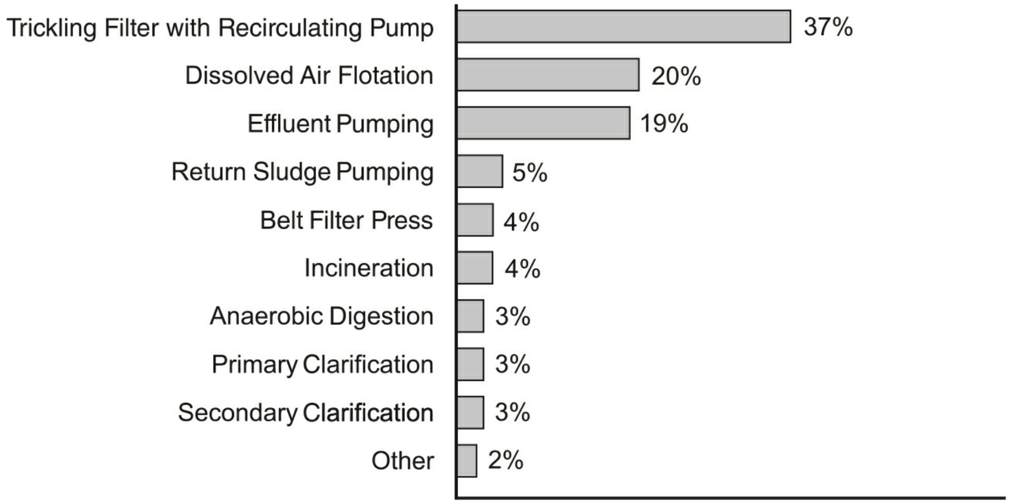


FIGURE 29.7 Electrical energy usage distribution in 100 mgd (263 m^3/min) municipal trickling filter facility with 2.5 MW power requirement.

Energy savings opportunities exist to some degree, at most effluent treatment facilities. There is increasing focus from many diverse constituencies concerning energy conservation in effluent treatment. Familiar programs like EPA Energy Star have identified effluent treatment as a focus sector among other significant users of electrical energy. A key element of the program is an online tool that allows operators (currently limited to municipal facilities) to enter equipment and operating dimensions relative to their particular plant, and get a ranking of energy usage based on a comparison to similar plants. However, variables like strength of effluent, treatment process, level of treatment, operational and maintenance choices, regulations, and current state of energy conservation initiatives make broad generalizations about energy use in effluent treatment challenging. This fact is even more pronounced in industrial effluents, including those found in food processing, paper, and refining, where all of these variables are more diverse.

An energy audit is certainly a good first step in understanding energy usage, and can be valuable even when done at a modest level. For example, questions like those below could be used to begin an evaluation of key pieces of equipment and processes. The answers to these questions help determine what processes can be modified or what equipment can be operated more efficiently, or replaced to save energy.

- Does the process or equipment need to run at all?
- Is it possible to run the process or equipment for fewer hours?

- Is it possible to shift this activity to off-peak hours (for some auxiliary functions)?
- Are energy efficiency process modifications or equipment upgrades practical and possible while maintaining equipment efficiency?
- What equipment is most energy efficient for this process?

Is it possible to run more efficient pumps for normal base loads, or to use lower efficiency larger units for only peak flows?

Motors

Motors provide the means to rotate impellers found in pumps and blowers. Recall that pumps move liquids and sludge in effluent treatment, while blowers move air. Taken together, pumps and blowers can account for more than 80% of the total electrical energy consumed in an effluent treatment plant. Because of their high efficiency and low maintenance requirements, three-phase squirrel cage induction motors are most prevalent.

Motors are rated in units of power (horsepower or watts) based on the maximum amount of work they are capable of performing. Actual power consumed at any given time by an operating motor is in direct proportion to the work being performed. The primary goal in choosing a motor is to be sure the motor selected has adequate power to drive the intended load throughout the entire anticipated load range. In general, motors are usually specified 10 to 20% larger than actually required. A secondary goal is that the motor be energy efficient and economical.

The Energy Policy Act of 1992 set out to establish standards for energy efficient motors. Energy efficient motors consume less energy and can lead to a significant decrease in operational costs as compared to standard motors. This is possible because of design improvements and more accurate manufacturing tolerances. They are more durable, have an overall longer lifetime, lower heat output, less noise and vibration, and improved tolerance to over-voltage. Energy efficient motors typically cost 10 to 30% more than standard motors, but can be up to 8% more efficient.

In 2001, the National Association of Electric Manufacturers (NEMA) implemented a new NEMA Premium® Efficiency Motor Standard. Under this voluntary program, a motor may be marketed as a NEMA Premium motor if it meets or exceeds a set of NEMA minimum full-load efficiency levels. Note that these levels are higher than the minimum full-load efficiency standards for energy efficient motors under the Energy Policy Act of 1992.

Energy efficient motors should be considered for all new purchases and replacements; however, selecting the proper motor size can be complicated and compounded by factors that are not immediately obvious and beyond the scope of this book.

Variable Control Devices

Variable control devices are typically located between the driver or motor and driven element, like an impeller, and are often referred to simply as drives. Categories of drives include mechanical, electromechanical, and electronic devices. Direct current (DC) motors can be controlled with variable resistance drives like rheostats, which decrease current to the motor resulting in decreased power to the motor. Alternating current (AC) motors can be equipped with drives that provide variable voltages or variable frequencies. Current industry preference is for variable frequency drives (VFD) because of their high efficiency, good reliability, and reasonable economics.

The key benefit of a VFD is that it allows motor speed to be matched to demands of the work being performed, which can often result in energy savings. For example, a VFD allows more precise control of processes such as aeration and sludge pumping. Relative to single speed motors, a VFD permits gradual ramp up to operating speed. This lessens mechanical and electrical stresses on the motor system, and can reduce maintenance and repair cost, extending motor life. A VFD can reduce energy use of a pump by as much as 50%, but this benefit is highly dependent on system variables like pump size, static head, friction, and flow variability. Consequently, it is important to examine each application before specifying a VFD. For example, a large effluent treatment plant may be better served by having constant speed pumps for the base load, and perhaps one pump with variable control to respond to changing flow conditions.

Aeration

Overall, aeration and related operations are the single most significant consumer of electrical energy in most secondary and advanced effluent treatment facilities. Estimates put the cost for electrical energy for aeration in the 40 to 60% range or greater, of the total electrical energy consumed. Aeration is necessary to support aerobic respiration, and to keep contents of the aeration basin sufficiently mixed. In most instances, meeting the aeration requirement satisfies the mixing requirement. Note that aeration is used in aerobic sludge digestion, and in some physical separation processes like DAF that are unrelated to aerobic respiration. In general, these uses are small by comparison.

The amount of oxygen required is factored from carbonaceous demand, endogenous demand, nitrogenous demand, initial dissolved oxygen (DO) deficit, and degree of stabilization required. Determining initial oxygen requirements for a new activated sludge system is usually based on conservative analysis, featuring a large safety factor to ensure adequate oxygen supply is always available for peak load conditions.

Aeration power requirements can be calculated once loading, flow rates, and equipment oxygen transfer performance are known. To illustrate this concept, consider that the aeration power requirement is expressed by Eq. (29.1).

$$E = QdL/q \tag{29.1}$$

where E = aeration power requirement, hp (kW)
Q = flow, mgd (m^3/h)
d = density of liquid, lb/gal (kg/L)
L = loading, mg/L
q = standard aeration efficiency (SAE), lb O_2/[hp·h] (kg O_2/kWh)

For example, oxidation of 300 mg/L biochemical oxygen demand (BOD) in a 10 mgd (1577 m^3/h) municipal effluent treatment plant using aeration equipment with SAE of 2.5 lb O_2/[hp · h] (1.52 kg O_2/kWh) would suggest the following power requirement.

U.S. Units

$$\begin{aligned} E = {} & (10\ \text{mgd})(8.33\ \text{lb/gal})(300\ \text{mg/L})/ \\ & (2.5\ \text{lb}\ O_2/[\text{hp}\cdot\text{h}])(24\ \text{h/d}) = 417\ \text{hp} \end{aligned}$$

Metric Units

$$E = (1577\ \text{m}^3/\text{h})(1\ \text{kg/L})(300\ \text{mg/L})(1000\ \text{L/m}^3)/(1.52\ \text{kg/kWh})(10^6\ \text{mg/kg}) = 311\ \text{kW}$$

Note that design safety factors increase the calculated power requirement further.

Operators typically use mixed liquor dissolved oxygen (MLDO), commonly referred to as just DO, in managing the aerobic process. Conveniently, there is rarely a need to operate an activated sludge process at a DO concentration above 2 mg/L. It is possible to operate successfully at DO concentrations closer to 1 mg/L with 1 to 1.5 mg/L being a good operational range to target. Caution should be exercised when the DO level approaches 0.5 mg/L, and as a rule, DO should never be allowed to drift below 0.5 mg/L. At the other extreme, excess aeration, aside from being costly, can interfere with flocculation, causing poor settling in the secondary clarifier. Although establishment of a DO target is a reasonable approach, various factors can affect efficiency of oxygen transfer and use and more importantly, efficiency of energy use. For example, the number of aeration tanks in service, air rate per diffuser, presence of nitrification when not required, food-to-microorganism ratio (F:M), aerator submergence, and air cleanliness can all affect overall efficiency.

Finally, there are special situations, often found in processes downstream of secondary treatment that endeavors to establish different respiratory pathways. For example, in biological denitrification, an anoxic environment is created to establish nitrate (NO_3^-) as opposed to molecular oxygen (O_2) as the ultimate electron acceptor.

Aeration Equipment

Transfer of oxygen from air to waste or effluent is relatively inefficient and energy intensive. The fraction of oxygen in air bubbles supplied by aeration equipment that dissolves in clean water is called the standard oxygen transfer efficiency (SOTE). SOTE divided by energy used per unit weight of oxygen delivered is the SAE. SAE expresses the weight of oxygen dissolved per unit of energy used by aeration equipment. Actual or field oxygen transfer efficiency (FOTE) differs from SOTE because real conditions differ from test conditions. The ratio of normalized FOTE to SOTE, literally the ratio of the oxygen transfer rate in effluent to that in clean water, is referred to as the alpha factor. The alpha factor can be influenced by many variables. For example, surfactants typically depress FOTE and reduce alpha to below one. Strict rules for performance testing of aeration equipment have been established by independent groups such as the American Society of Civil Engineers (ASCE). Most equipment manufacturers follow these rules when evaluating and representing their products.

Diffused Aeration

Diffused aeration delivers compressed air through submerged porous or perforated diffusers that create bubbles, ultimately transferring oxygen as they rise. Deeper tanks enhance oxygen transfer efficiency (OTE) by lengthening bubble rise and increasing hydrostatic pressure on the bubbles, both of which hasten oxygen transfer. However, increasing hydrostatic pressure requires more blower capacity and energy along with greater capital expenditure.

There are two general categories of diffusers: course bubble and fine bubble. The number of bubbles produced per unit volume of air and bubble diameter differentiates the two systems. EPA defines fine bubble diffuser equipment as its ability to produce bubbles with an average diameter of 2 mm. Course bubble diffusers (Fig. 29.8) generally represent older technology, and they are typically less costly to construct and maintain. SAE for course bubble diffusers is about 2 to 3 lb O_2/[hp · h] (1.2–1.8 kg O_2/kWh).

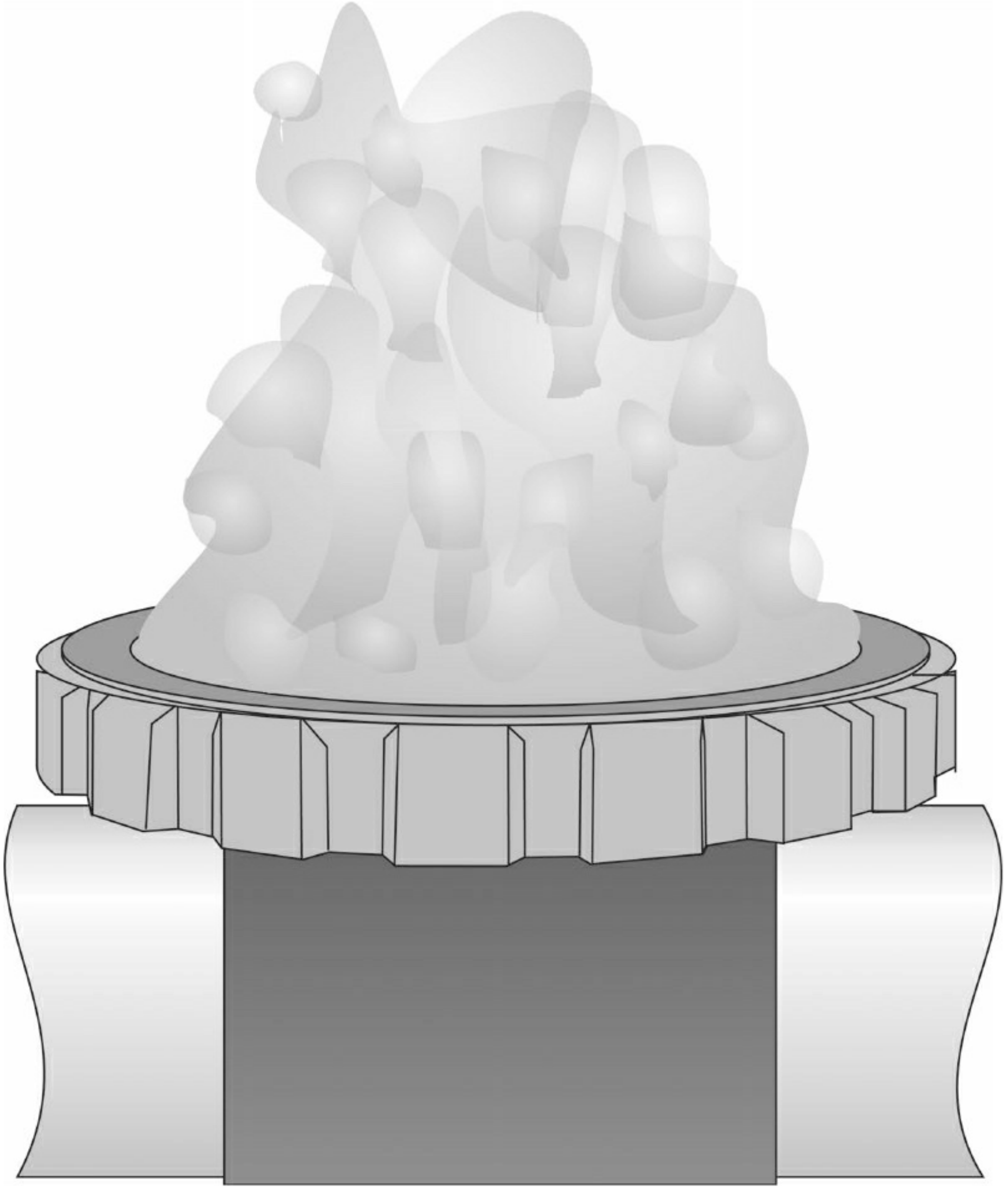


FIGURE 29.8 Typical coarse bubble diffuser.

Fine bubble diffusers (Fig. 29.9) have grown in popularity because of rising energy costs. Smaller diameter bubbles produced by fine pore diffusers provide more surface area per volume, thereby facilitating higher OTE values. Furthermore, small bubbles tend to rise more slowly, and additional contact time increases OTE. However, fine bubble diffusers cost more initially, require cleaner air, and usually require more maintenance than course bubble diffusers. They are typically constructed in the shape of plates, discs, domes, or tubes made of plastic or ceramic. In some installations, flexible sheath tubes are used. Fine pore diffusers have SAE of 4 to 7 lb O_2/[hp · h] (2.4–4.3 kg

O_2/kWh), with some advanced membrane systems reaching even higher efficiencies. Fine pore systems, when operating at peak efficiency, can use as a minimum 25% less energy than course bubble or mechanical counterparts. Simple payback economics of fine bubble retrofits are quite favorable in the 2 to 5-year range. As expected, payback is shortest in situations where electrical energy costs are highest. The biggest potential negative factor in considering a fine bubble system involves increased maintenance costs due to fouling.

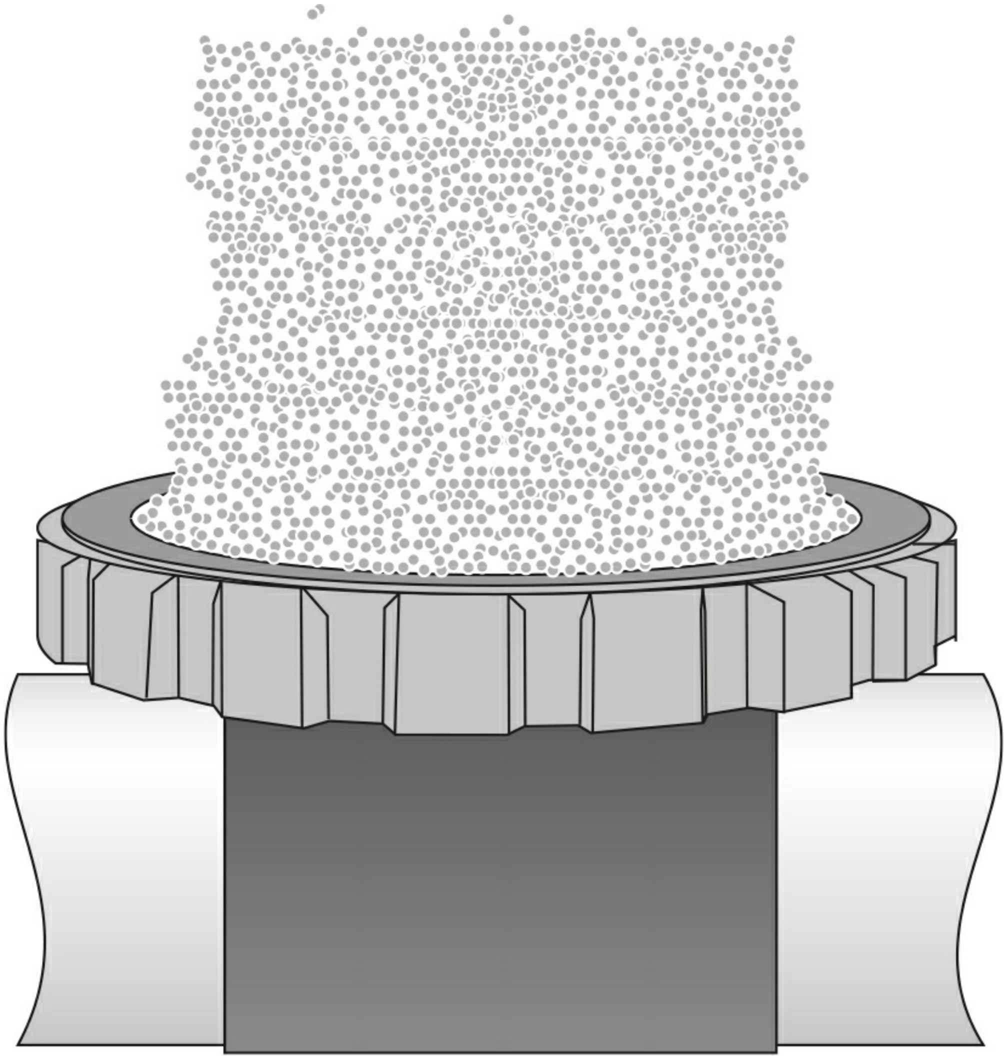


FIGURE 29.9 Typical fine bubble diffuser.

All diffusers are subject to fouling from the waterside, airside, or both. Significant fouling wastes energy and reduces ability of the system to deliver sufficient oxygen to the basin. Course bubble diffusers have relatively large orifices and consequently are less prone to fouling with air or waterside impurities. Natural fouling that tends to occur in course bubble diffusers can be reversed to a large degree by periodically blowing out diffusers with excess air. Fine bubble diffusers are more problematic because their smaller diameter pores are more easily fouled. Air-side fouling is often the result of poor air filtration and other material originating after filtration. Foulants can include dust, dirt, rust, and scale from air pipe corrosion, construction debris due to poor cleanup, and mixed liquor solids entering through leaks and breaks. Water-side fouling can occur from precipitated solids, biological growth, organic and inorganic material entering the media at low or zero pressure, oils and grease, etc.

Detection and rate of diffuser fouling is of obvious importance. Historically, a rise in backpressure signaled fouling. While overall system pressure monitoring serves as an indicator of extreme fouling, it lacks sensitivity, particularly relative to increased diffuser head loss. Buildup of head loss and flux rate, defined as airflow rate per diffuser(s) divided by the effective diffuser area, may have a significant effect on aeration system capacity or OTE. Further, fouling of only a portion of the diffuser area may lead to substantial redistribution in airflow, but little increase in overall system pressure. Today, better methods exist to measure performance of operating aeration systems, allowing for more effective preventive and maintenance programs. For example, dynamic wet pressure (DWP) can allow measurement of head loss across the air distribution control orifice and across the diffuser. Head loss across the orifice is used to determine the rate of flow through the diffuser, while head loss across the diffuser media indicates the degree to which the diffuser has been fouled. Note that heavily fouled fine bubble diffusers have OTE comparable to course bubble diffusers.

Methods of cleaning fine pore diffusers can be in situ or ex situ. In situ means diffusers are cleaned in the basin, either drained or full, while ex situ means diffusers are removed from the basin. Ex situ methods include refiring of ceramic diffusers, high-pressure water jetting, and washing with silicate–phosphorous, alkali, acid, or detergent. Ex situ methods are expensive and reserved for situations that do not respond to less invasive approaches. In situ methods include physical, chemical, and biological procedures. Diffusers may be physically washed with water, air, or steam. Chemical options include treatment with gaseous compounds like hydrogen chloride, chlorine, or gaseous biocides applied to the air side and liquid acid or detergent for cleaning of diffuser surfaces. Choice of cleaning method is often by trial and error.

Where fine bubble systems have replaced mechanical aerators, aeration basin geometry and the need to install blowers and air piping are important considerations. Where fine bubble systems have replaced course bubble diffusers, air systems are usually more than adequate, since fine bubble diffusers provide a higher OTE. Sometimes, an activated sludge plant capacity can be increased by a fine bubble retrofit, particularly if the plant is aeration limited.

Mechanical Aeration

Mechanical aerators are commonly divided into various categories, but essentially, they all use motors to rotate propellers, blades, or brushes that reside close to the surface of the effluent, or slightly submerged, to vigorously move the water, thereby increasing diffusion of oxygen into water (Figs. 29.10 and 29.11). These devices are typically driven by an electric motor either directly or through some type of transmission or gearbox that can be horizontal or vertical relative to the rotating element. Mechanical aerators can be expected to have SAE of 2 to 4 lb O_2/[hp · h] (1.2–2.4 kg O_2/kWh), which is similar to course bubble diffusers; however, mechanical systems are observed to have slightly higher efficiencies. Options for adjusting air delivery to oxygen demand include submergence adjustment, speed adjustment, and powering up and down.

FIGURE 29.10 Details of construction of a fixed-position surface aerator, shaped to produce high-volume pumping and air entrainment. (*Courtesy of Infilco Degremont Inc.*)

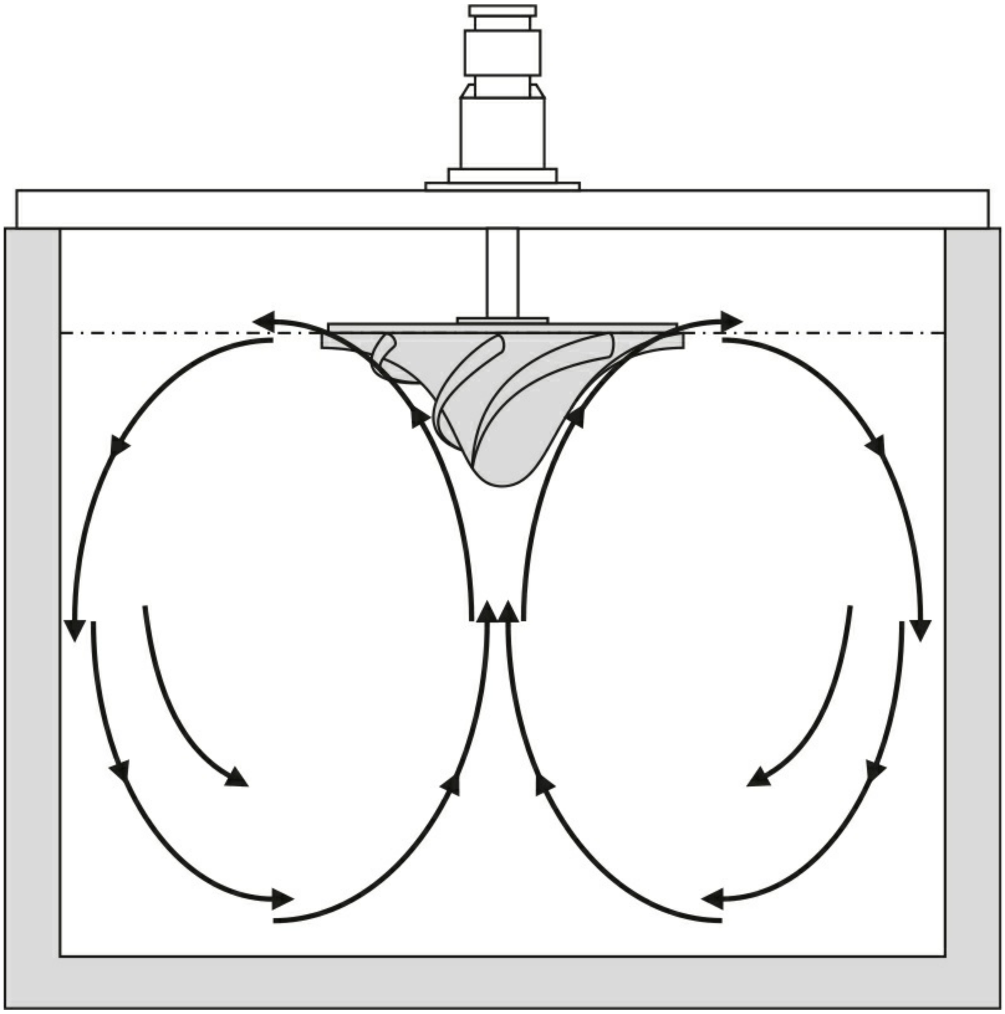


FIGURE 29.11 Typical flow pattern of a surface aerator. Sufficient mixing in the basin is very important for good aeration.

Aeration Control and Monitoring

The most common cause of aeration system inefficiency is excessive DO in mixed liquor. Due to oversized equipment, inefficient operation, or lack of controls, the amount of air delivered to the aeration basin is often much more than required for supporting aerobic respiration or mixing. Excess air represents wasted energy, and highly aerated effluent can lead to settling problems and solids carryover.

Use of DO probes in aeration tanks with blower feedback control systems and variable speed drives can result in substantial energy cost savings with relatively modest payback periods. Ideally, air delivery is controlled to match instantaneous oxygen demand relative to a set point. Automated controls can match air delivery to oxygen demand, more accurately and efficiently than manual controls. It is not uncommon to achieve a 20% energy savings after retrofit with monitoring and automatic controls. Payback can be expected to fall in the 1 to 4-year timeframe, with larger facilities achieving payback sooner. However, DO probes require careful selection, placement within the basin, calibration, process monitoring, and maintenance, and as a result, some operators have resisted their deployment and use.

Aeration system controls can be applied to either mechanical or diffused aerators, but are more likely to be installed on diffusers. Capital cost of a control system for course bubble aerators is higher than that for fine bubble systems, because the former likely has larger motors and variable speed drives.

Preliminary and Primary Effluent Treatment

Primary effluent treatment including treatment ahead of the primary treatment process, sometimes called preliminary treatment, is mainly responsible for removing settable solids and floating material from effluent. Primary treatment typically removes 50 to 60% of total suspended solids (TSS) and 30 to 40% of BOD in the influent.

The typical primary settling tank, often referred to as primary clarifier, employs relatively small motors for various mechanisms and pumps. This equipment may include primary sludge pumps, collectors, skimmers, and sprays. Because primary treatment relies on gravity separation, energy requirements are usually relatively small.

Primary sludge pumping is typically the largest energy consuming operation in primary treatment. One energy conserving measure (ECM) available in primary treatment is to ensure that primary sludge pumping rates are adjusted to match primary sludge accumulation, generally a function of flow in the primary clarifier.

One of the most ignored but potentially beneficial ECM’s available to effluent treatment facilities is to address poor removal, including both BOD and TSS, in primary treatment. Poor removal can lead to greater use of energy in secondary treatment and other downstream processes. For example, dye tests conducted at one facility revealed that improving the flow split to multiple clarifiers, and installing baffles to reduce clarifier short-circuiting improved BOD removal significantly. This, in turn, reduced BOD loading and corresponding oxygen demand in secondary treatment, leading to more cost-effective operation.

One notable exception with regard to modest energy use in primary treatment can be found in instances where air is used to assist in the separation process. Examples include aerated grit chambers found in municipal effluent treatment, and DAF units found in effluents typical of the hydrocarbon and food processing industries. These operations can use considerable amounts of energy, and reducing blower output could result in reduced in energy use. However, matching blower output with the optimum air requirement is largely a trial and error process.

Recycle flows should be inventoried, as they can undermine the relatively energy efficient primary treatment process. For example, anaerobic digester decant is often sent to primary treatment, where it can initiate biological activity, and undermine performance of the primary treatment process. Other potential flows include sludge dewatering supernatant, and sludge drying bed drainage. Off peak treatment of these flows, if possible should be evaluated. Finally, intermittent use of air and water sprays for foam and scum control should be considered as opposed to their continual use.

Chemicals can be used to enhance primary treatment, and should be selected on a cost performance basis. In general, primary treatment offers a more energy efficient way to remove contaminants, and operators should seek to maximize removal potential of primary treatment. That said complete accounting of energy necessary to process primary treatment solids should be included.

Secondary Effluent Treatment

Following preliminary and primary treatment, effluent contaminants consist primarily of colloidal matter that is highly organic, along with small amounts of dissolved organic matter, nutrients, and dissolved inorganic solids. As defined by the Clean Water Act (CWA), secondary treatment should produce effluent with not more than 30 mg/L BOD and 30 mg/L TSS.

The primary operational objective of secondary effluent treatment is to create and maintain an aerobic environment. Secondary treatment processes can remove up to 90% of BOD in effluent by utilizing biological processes. Since the two have significantly different oxygen requirements and therefore energy requirements, BOD can be further divided into carbonaceous BOD, and nitrogenous BOD. Historically, BOD is determined experimentally by measuring oxygen uptake over a 5-day period and noted as BOD_5. During this time, biodegradable organic carbon is biologically oxidized, while oxygen is reduced proportionally. Note that for practical purposes, this test, in terms of time, is often shortened and results extrapolated.

Chemical oxygen demand (COD) is another measure for evaluating effluent. Unlike BOD, COD represents all oxidizable material in water. COD is always greater than BOD, and more importantly, some percentage of COD cannot be removed biologically.

High electronegativity (measure of the attraction for electrons) of oxygen creates a large potential energy drop for cellular respiration, allowing organisms using aerobic respiration to produce much more adenosine triphosphate (ATP) than anaerobic organisms, thereby making aerobic respiration more favored. Aerobic respiration makes possible stabilization of large quantities of contaminants found in effluent. These contaminants can be quickly and efficiently oxidized, or destroyed, with carbon dioxide, water, and new cell mass as the only tangible respiration by-products.

Bacteria in an effluent treatment plant comprises both heterotrophic and autotrophic microorganisms. Heterotrophic or carbonaceous bacteria are the predominant group of organisms. They are characterized by feeding mainly on organic carbon molecules rather than inorganic ones. By contrast, autotrophic microorganisms take in inorganic chemicals and use them in synthesis of organic compounds. Nitrifying bacteria, known by their ability to remove ammonia and ammonia compounds from effluent, are the most important of this group. There are fewer known species of autotrophic microorganisms, and since they have relatively slower growth rates, they tend to be out-competed by faster growing heterotrophic microorganisms. Often, effluent facilities use bioaugmentation, the purposed addition of bacterial cultures, when nitrification has been reduced or is not ongoing.

Without artificial introduction of air into effluent, by some method, the DO level would fall, and aerobic respiration would cease to be the predominant respiratory pathway. As discussed earlier, the process of dissolving oxygen in effluent is complex, relatively inefficient, energy intensive, and complicated by many factors including diffuser device type, basin geometry, diffuser depth, turbulence, ambient air pressure, temperature, spacing and placement of aeration devices, variations in flow, and loading.

Finally, most secondary treatment systems employ a secondary clarifier for capture and recirculation of solids generated in the aeration basin. Secondary clarifiers are not large consumers of energy and have energy requirements close to that of primary clarifiers. However, excess pumping of return activated sludge (RAS) is one area that should be investigated for potential energy savings.

There are numerous processes available for secondary effluent treatment, but most can be categorized as suspended growth or fixed film.

Suspended Growth Processes

Activated sludge, oxidation ditches, sequential batch reactors (SBR), and membrane bioreactors (MBR) are all examples of suspended growth systems. The most recognized and predominant suspended growth example can be found in the activated sludge configuration, although it is interesting to note that MBR are the fastest growing segment, albeit from a much smaller base. As mentioned previously, activated sludge systems treat roughly 90% of municipal effluent volume in the United States, and represent the predominant treatment approach in many industrial applications. In suspended growth processes, microbial growth is predominantly planktonic. Suspended growth processes sustain a viable population of target microorganisms by carefully controlling various parameters such as DO level, substrate concentration (food), mixed liquor volatile suspended solids (MLVSS), RAS pumping rate, waste activated sludge (WAS) pumping rate, temperature, toxicity, and nutrients.

One key variable strongly associated with energy usage in suspended growth processes like activated sludge is mean cell residence time (MCRT), or sludge age as it is also known. Simply put, MCRT is a measure of how long a microorganism has been in the secondary treatment process. To understand this concept, consider that viable microorganisms that comprise MLSS of an activated sludge process are in either the active stages of BOD removal and cell proliferation, or what is known as the endogenous phase of their life cycle. In both cases, oxygen is consumed, but only in the former is significant BOD removal underway. Shortening the MCRT has the effect of limiting microorganisms that are in the endogenous growth phase, thereby making the process with respect to BOD removal more aeration energy efficient. However, this concept has several drawbacks, including the fact that more solids are generated due to increased sludge wasting. Settling may be negatively affected, and there may be insufficient time for nitrification. For example, poor settling may require additional chemicals, while increased solids have a negative effect on solids handling operations, particularly where disposal costs are high. In essence, a trade-off is created between aeration and solids generation and treatment.

Fixed Film

Trickling filters and RBC are the primary forms of fixed-film systems. These systems use pumping energy in the case of trickling filters and mechanical energy in the case of RBC to introduce oxygen into effluent. In the case of a trickling filter, effluent is allowed to flow over static media like rocks or plastic. To be effective, effluent is often pretreated and pumped multiple times over the media, sometimes equaling three times the daily influent flow. In the case of RBC, media rotate with a portion exposed to effluent and the alternating portion exposed to air. Often, effluent is circulated by pump within the basin. Fixed-film processes use less energy than suspended growth processes, as seen previously in Figs. 29.2 through 29.7, but do not achieve as high a treatment level. As an example, a 100 mgd (263 m^3/min) tricking filter facility would likely have a total electrical energy cost in the neighborhood of 20% less than its activated sludge counterpart. However, fixed-film systems are prone to odors and often require additional equipment to address these odors. Once odor control systems are installed, the relative energy efficiencies, or at least overall operating costs, of fixed-film processes begin to approach those of suspended growth processes.

Tertiary Effluent Treatment Processes

There are various processes within effluent treatment that aim to achieve even higher effluent quality or address an aspect of treatment that may be difficult to achieve within the secondary effluent treatment process. Some ways in which these objectives can be satisfied include filtration, carbon adsorption, and chemical treatment. In general, these operations lead to a relatively insignificant contribution to total energy usage. That said, biological nutrient removal (BNR) could significantly add to the energy burden of an effluent treatment facility.

BNR can be managed as part of tertiary treatment and continues to be an area of focus and increasing regulation. Achieving targets for nutrient removal can put additional energy load on a facility, depending on the removal strategy. Both phosphorous and nitrogen can be removed biologically, although it is probably more practiced with nitrogen removal. Historically, phosphorous has been removed from effluent by chemical precipitation with metal salts. Biological processes can be used, whereby anaerobic selectors stress microorganisms before their return to the aeration basin. Stressed microbes then take up more phosphorous than they would under more normal conditions.

Nitrogen is often removed by biological nitrification and denitrification. Oxygen requirements for nitrification are more demanding than for BOD removal. For instance, 1.5 lb (kg) of oxygen are required to treat 1 lb (kg) of BOD; however, 4.6 lb (kg) of oxygen are required to oxidize 1 lb (kg) of ammonia (NH_3) to nitrate (NO_3^-). Nitrification is accomplished by a set of highly specific microbes referred to as nitrifiers. Biological nitrification is an energy intensive process that can be rather delicate to establish and maintain, because of the nature of nitrifying bacteria. As compared to a facility that does not have to nitrify, electrical energy requirements can be increased by 40 to 50% when nitrification is ongoing.

Be aware that in some cases nitrification is not necessary, yet can be an active process when among other things, solids retention time (SRT) exceeds 3 to 6 days, and oxygen and temperature are adequate. If a facility that is not required to nitrify has some nitrification underway, there can be rather significant yet unnecessary use of energy being consumed for aeration.

Although conversion of ammonia to nitrate is often sufficient from a regulatory point of view, there are instances where nitrogen must be completely removed. This process, called denitrification, can be done both chemically and biologically, and results in nitrogen gas being liberated under the biological approach. In biological denitrification, nitrate (not oxygen) is reduced in a process commonly known as anoxic respiration. Although anoxic respiration does not require the aeration energy necessary to maintain an aerobic environment, it does require high recirculation rates along with an added carbon source, which is often methanol.

One ECM for reducing energy involves creating an anoxic zone, about 15% of total tank volume, at the front of the aeration basin. In this case, BOD is removed anoxically, using nitrate, not aerobically. For facilities with diffused aeration systems, the anoxic zone is facilitated by locally reducing airflow, providing just enough flow for mixing.

CHAPTER 30

Energy in Cooling Systems

As ambient air temperature increases, many heat-producing processes become cooling limited, making it useful to know the answer to the question "What is the value of one degree colder water?" This value can be difficult to calculate, due to the complexity of some industrial processes. However, the question "What is the cost of one degree warmer water?" may be easier to answer. For instance, a rough answer can sometimes be obtained in the plant's control room. In the middle of a very hot and humid stretch of weather, this statement might be heard: "The cooling water temperature has gone up two degrees; cut production back 10%." The two-degree rise in cooling water temperature can equate to a revenue and profitability loss represented by a 10% process throughput reduction. Therefore, a neglected cooling tower, where thermal performance has decreased, can have adverse consequences on the ability of any plant to achieve revenue and profitability goals.

Financial Impact of Inefficient Heat Rejection

When cooling tower cold water temperature approaches the point where 100% process throughput can no longer be sustained, resourceful process operators try anything to avoid reducing process throughput. Typical strategies include:

- Increase blowdown to introduce more cold makeup water into the system.
- Introduce cold makeup water immediately ahead of a critical heat exchanger.
- Rent portable, temporary cooling towers.

Increased cooling tower blowdown can reduce cooling water supply temperature, if enough makeup water is added to the tower basin water. However, this action reduces the concentration ratio (CR), and may require increased chemical inhibitor feed rate. Adding cooler makeup water before a critical exchanger or adding additional cooling capacity also reduces water temperature of an under-performing cooling system. All of these actions increase the costs of water, discharge, and chemical treatment, ultimately reducing profitability of any facility. Inefficient cooling tower operation can have significant financial consequences on any process operation through increased costs and loss of revenue (Fig. 30.1). Loss of revenue from reduced process throughput is the largest cost resulting from an under-performing cooling tower.

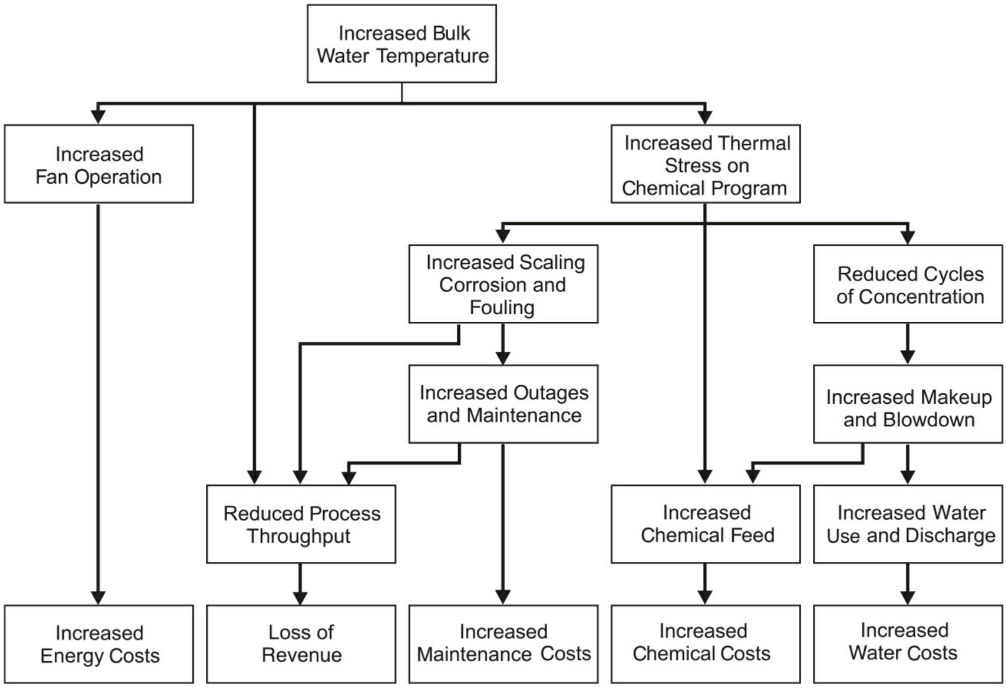


FIGURE 30.1 Consequences of inefficient cooling tower operation. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

Energy consumption in cooling towers is only due to pumps and fans. Of these, pumps consume the most energy, usually at a constant, year-round rate, except in unusual service conditions. Fans are powered by single-speed motors, two-speed motors, or variable-speed drives and can be operated at reduced speed or shutdown in cooler weather. Under-performing cooling towers require higher fan speed, resulting in increased energy costs. However, these energy cost increases will be small compared with the loss of production efficiency due to decreased tower performance.

Warmer cooling tower supply and return water, increases thermal stress on the chemical inhibitor program in two areas:

1. Increased fouling, scaling, and microbial growth potential in cooling tower fill (particularly film fill)
2. Increased scaling and corrosion potential in heat exchange equipment

The effect of temperature on deposition and corrosion is covered in Chap. 15 and Chap. 16, respectively.

Each of these problems has serious consequences for both thermal performance and reliability. Normal chemical inhibitors can become less effective in higher temperature situations. If water temperature cannot be reduced, addition of high cost contingency chemical supplements may be required. If scaling and corrosion are not prevented, online cleaning or system shutdown with offline chemical cleaning may be needed. Cooling tower and heat exchanger maintenance costs and the cost of reduced production can be high. Lost production can reach millions of dollars, especially if there is an unplanned outage.

Cooling Tower Thermal Performance or Thermal Capability

The range or delta T (ΔT) of a cooling tower is the temperature drop of the water passing through the tower. The range is the hot return water temperature (T_1), minus cold supply water temperature (T_2), as shown in Eq. (30.1). This ΔT is controlled by the process heat load and is independent of the cooling tower.

$$\Delta T = T_1 - T_2 \tag{30.1}$$

Approach temperature is dictated solely by the cooling tower. The approach temperature (T_A) is the cold water temperature (T_2), minus the ambient wet bulb temperature (T_{WB}), as shown in Eq. (30.2). The approach temperature and cold water temperature are higher than design values in an under-performing cooling tower. However, the approach temperature can often be higher than the design value during normal operation, especially if other system parameters are not at the design values. This is particularly true in colder climates during winter, when the wet-bulb temperature is very low. The range and approach temperature of a tower are represented in Fig. 30.2.

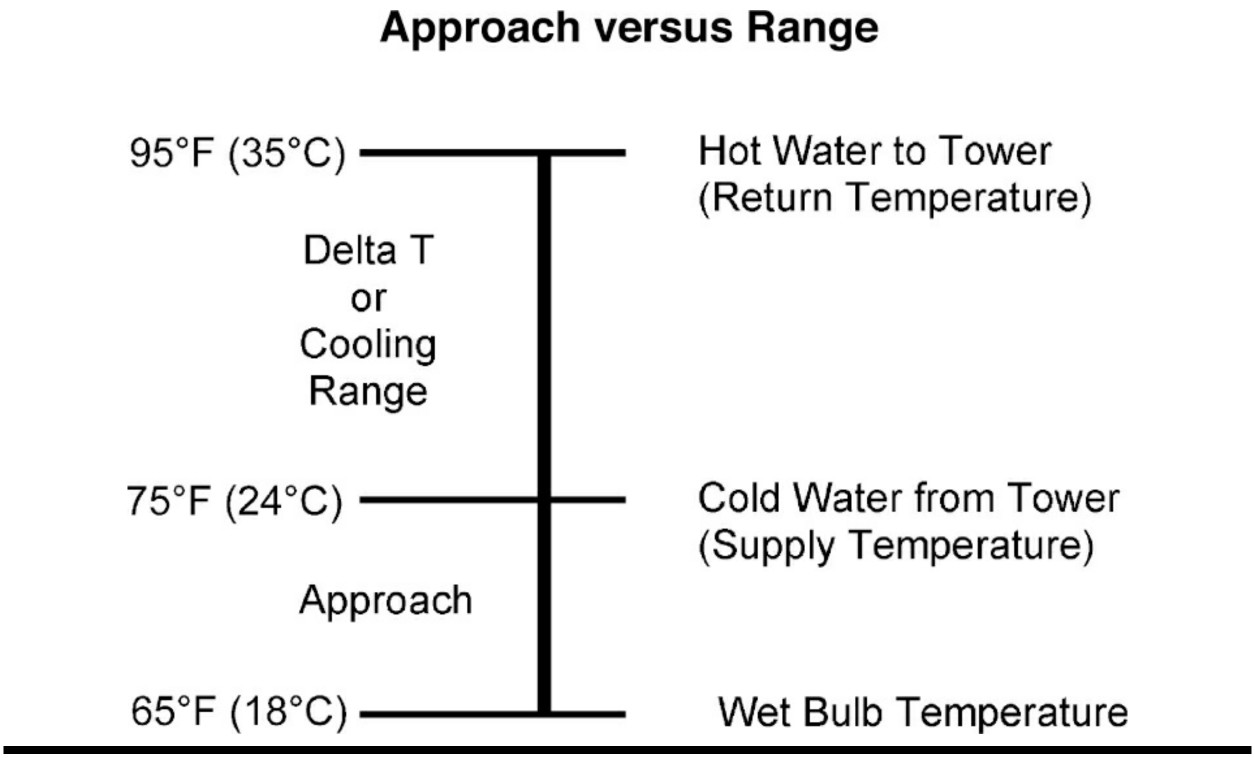


FIGURE 30.2 Illustration of cooling tower range (ΔT) and approach temperature.

$$T_A = T_2 - T_{WB} \tag{30.2}$$

When cold-water temperature increases to the point that the process is affected, then process throughput must be reduced. Decreased throughput reduces heat load on the cooling tower and therefore reduces ΔT. Thermal performance of the cooling tower may influence the decision to reduce process throughput, and therefore heat load, but the cooling tower always accepts whatever heat load is directed to it. Cooling tower thermal performance is the calculated ability of the cooling tower to achieve the design approach temperature, and is expressed as a percentage of the design thermal performance. This cooling tower thermal capability is often referred to as cooling tower efficiency.

Thermal performance of a cooling tower is specified by the cooling tower supplier, at a design operating point defined by hot water temperature, cold water temperature, wet bulb temperature (WBT), water flow rate, and fan power or Liquid/Gas (*L/G*) ratio. Usually, the tower supplier provides the tower owner with a set of performance curves (cold water temperature versus WBT), for a selection of water flow rates and heat loads that bracket the design operating point.

The *L/G* ratio equals the mass of water circulating over the cooling tower divided by the mass of air passing through the cooling tower as shown in Equation 30.3.

$$L/G = R/F_{\text{air}} \tag{30.3}$$

where R = recirculation rate of tower water, lb/min (kg/min)
F_{air} = airflow through tower, lb/min (kg/min)

An example can illustrate the effect of the *L/G* ratio. A system with three fans and three recirculating water pumps has only two fans and two recirculating pumps operating. To obtain colder temperature water from the cooling tower is it better to turn on one more pump or turn on one more fan?

This can be answered easily by looking at the impact of each change using an example of a tower performance curve (Fig. 30.3). If water flow is increased, L increases, and the *L/G* ratio increases. From Fig. 30.3, if *L/G* increases at constant WBT, cold water temperature increases, and performance of the system decreases (Arrow 1 in Fig. 30.3). The change shown in Fig. 30.3 would increase cold water temperature about 4°F (2.2°C). However, if airflow is increased, the *L/G* ratio decreases, and cold water temperature decreases at constant WBT (Arrow 2 in Fig. 30.3). This decreases approach to the WBT, and improves tower performance. Arrow 2 shows cold water temperature would decrease about 4°F (2.2°C). Therefore, the correct action is to turn on an additional fan.

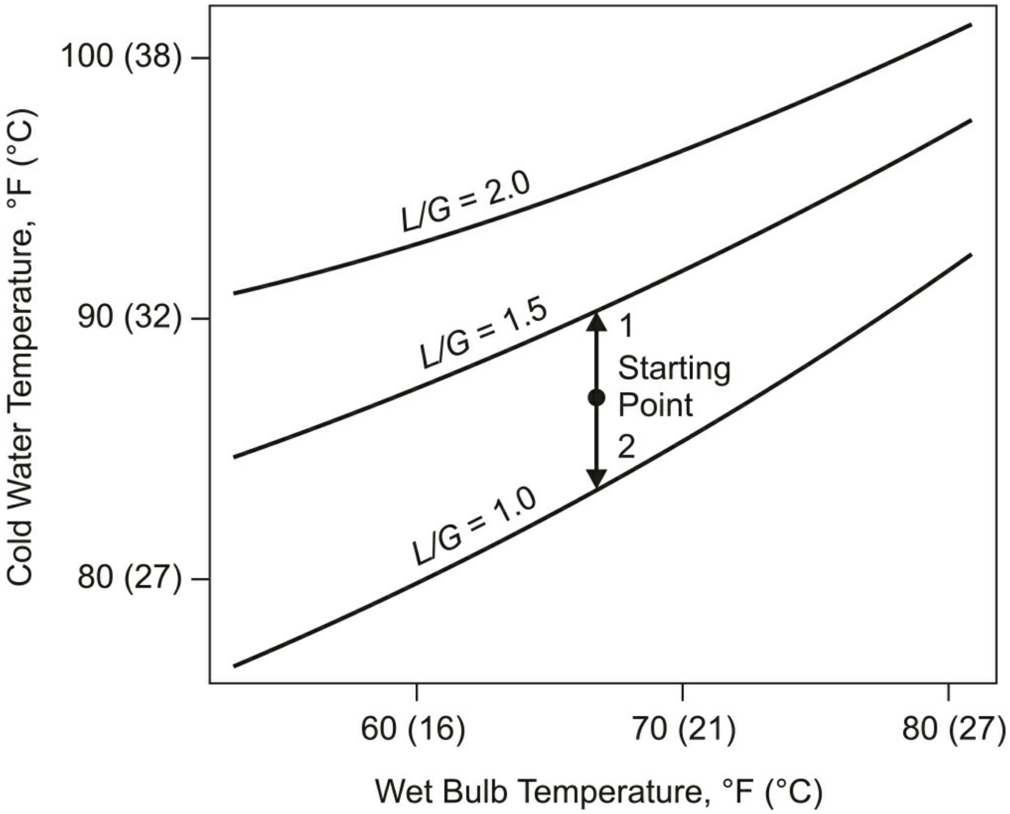


FIGURE 30.3 Arrows show effect on cold water temperature of increasing (Arrow 1) or decreasing (Arrow 2) *L*/*G* ratio from a given starting point in a cooling tower.

Increasing water flow over a cooling tower (increasing *L*/*G* ratio) decreases cooling tower ΔT and increases cold-water temperature. Increasing airflow through a cooling tower (decreasing *L*/*G* ratio) does not affect ΔT but decreases cold-water temperature.

In multi-cell cooling towers, the *L*/*G* ratio for individual tower cells should not vary widely from cell to cell, otherwise thermal performance is degraded. Ideally, each cell of a four-cell cooling tower would use 25% of the total fan power, deliver 25% of the total airflow, and reject 25% of the total heat, while using 25% of the total water flow.

However, multi-cell towers are not usually perfectly balanced in the real world. A thorough mechanical survey of a multi-cell cooling tower can identify under-performing cells and determine the nature of the problem. A performance grade can be assigned for each cell for the purpose of prioritizing and scheduling planned maintenance activities.

Figure 30.4 shows an airflow problem in Cell 1, because the percent power is significantly greater than the percent airflow. Plugged or fouled fill or drift eliminators, excessive air leakage at the fan blade tips or fan hub, or fan stall (described later) could cause reduced airflow. An exit air velocity profile can be used to identify the precise cause.

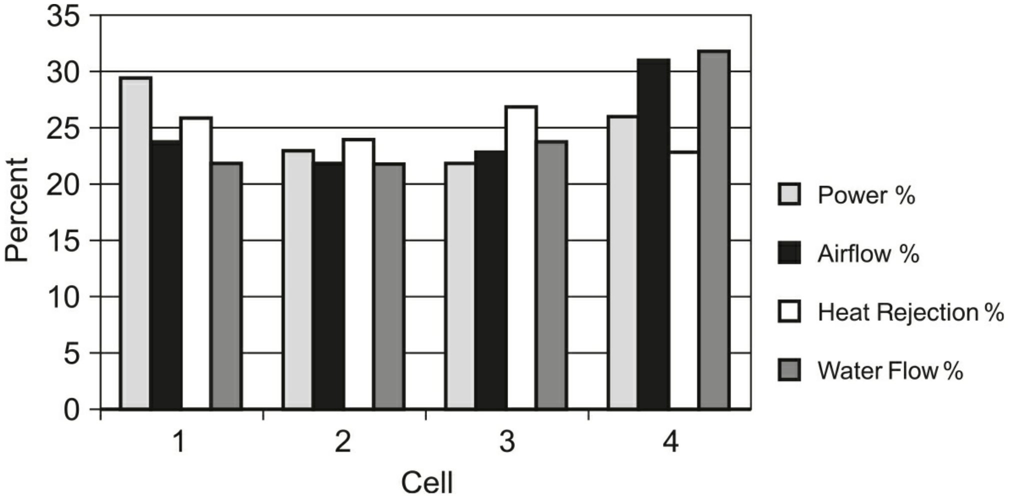
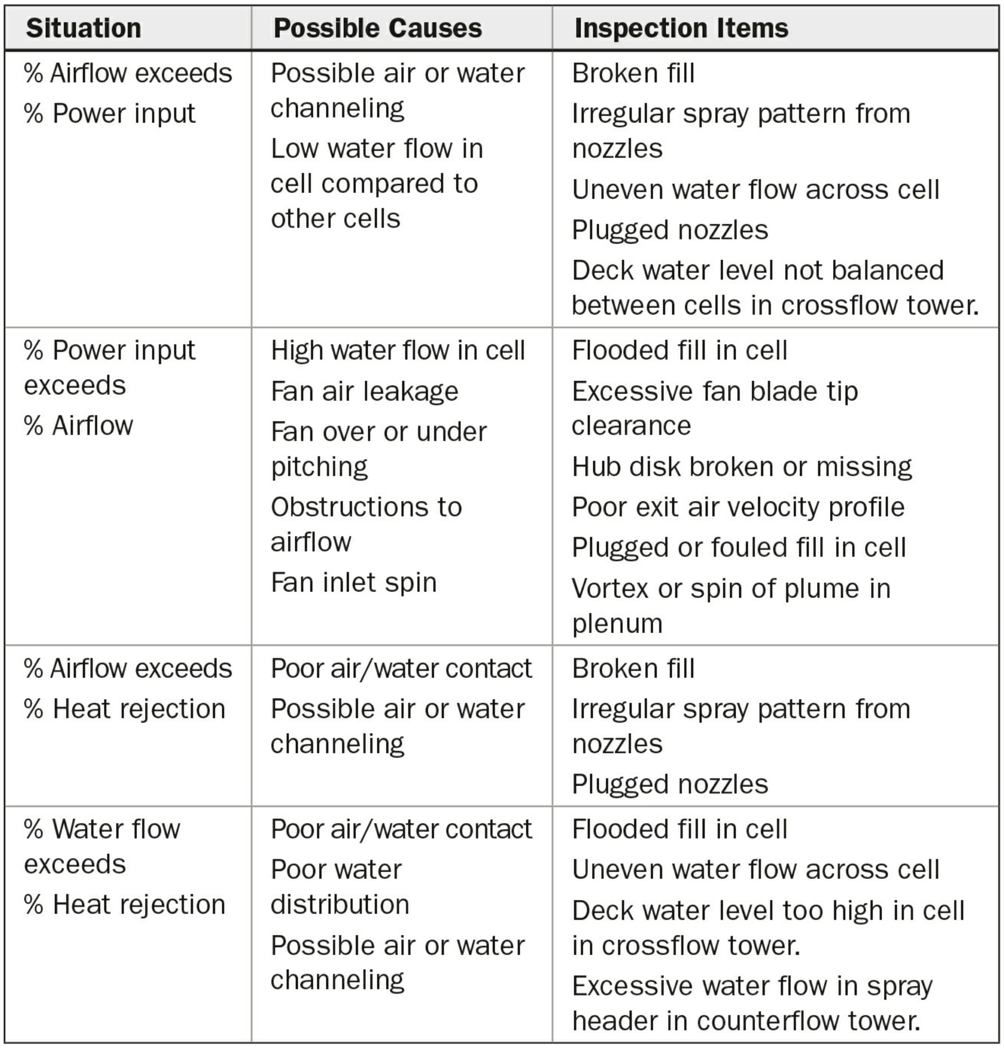


FIGURE 30.4 Typical cooling tower cell performance distribution illustrating uneven loading and heat rejection. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

Figure 30.4 also shows a thermal problem in Cell 4, as percent heat rejection is significantly lower than either percent airflow or percent water flow. Poor air/water contact from distribution or channeling problems can cause this, and nozzle spray patterns and fill condition should be checked. Cells 2 and 3 are giving satisfactory thermal performance and need no attention.

By identifying problem cells and the nature of the problems, maintenance can be prioritized and scheduled to maximize thermal performance. Downtime and maintenance costs can be minimized by delaying repairs with lower thermal performance benefit, and by avoiding unnecessary maintenance on cells that provide satisfactory thermal performance. This technique is particularly useful when planning for plant shutdown, where budgets and available repair time are tightly controlled.

As indicated in Fig. 30.4, some situations can be positive. Higher percent heat rejection than percent airflow in Cell 1 can indicate good contact between water and air in that cell. Similarly, percent heat rejection that is greater than percent water flow can indicate good air/water distribution and good contact. Table 30.1 shows some of the problems, causes, and possible points to inspect in a tower for the situations shown in Fig. 30.4. Several of the inspection items fit several situations.



Situation	Possible Causes	Inspection Items
% Airflow exceeds % Power input	Possible air or water channeling Low water flow in cell compared to other cells	Broken fill Irregular spray pattern from nozzles Uneven water flow across cell Plugged nozzles Deck water level not balanced between cells in crossflow tower.
% Power input exceeds % Airflow	High water flow in cell Fan air leakage Fan over or under pitching Obstructions to airflow Fan inlet spin	Flooded fill in cell Excessive fan blade tip clearance Hub disk broken or missing Poor exit air velocity profile Plugged or fouled fill in cell Vortex or spin of plume in plenum
% Airflow exceeds % Heat rejection	Poor air/water contact Possible air or water channeling	Broken fill Irregular spray pattern from nozzles Plugged nozzles
% Water flow exceeds % Heat rejection	Poor air/water contact Poor water distribution Possible air or water channeling	Flooded fill in cell Uneven water flow across cell Deck water level too high in cell in crossflow tower. Excessive water flow in spray header in counterflow tower.

TABLE 30.1 Example Causes of Imbalances in Power Use, Heat Rejection, Water Flow, and Airflow between Cells in a Cooling Tower

Cooling Tower Performance Problems

An under-performing cooling tower confronts the tower operator with a variety of choices to fix the system. The most common repairs performed on cooling towers are fill and nozzle replacement. However, these repairs may not solve the basic performance problem, if a thorough mechanical survey with performance testing of the system has not been undertaken. The basics of a complete Mechanical-Operational-Chemical (MOC) audit were described in Chap. 14. Repairs that do not address the root causes of the performance problem waste the maintenance budget and possibly result in further deterioration in thermal performance of the cooling tower.

Excluding safety, health, and environmental issues, common cooling tower performance related problems can be categorized in four ways:

1. Air-side thermal performance issues
2. Water-side thermal performance issues
3. Energy
4. Reliability

Air-Side Thermal Performance Issues

Airflow problems are usually more difficult to identify than water flow problems. Water flow is easier to measure than airflow, and flow variation or water channeling in tower fill can be visually observed. One method of analyzing airflow requires plotting results of multiple radial air velocity measurements of the fan cylinder exhaust plane (Fig. 30.5) to generate a profile of exit air velocity along the radius of the fan stack.

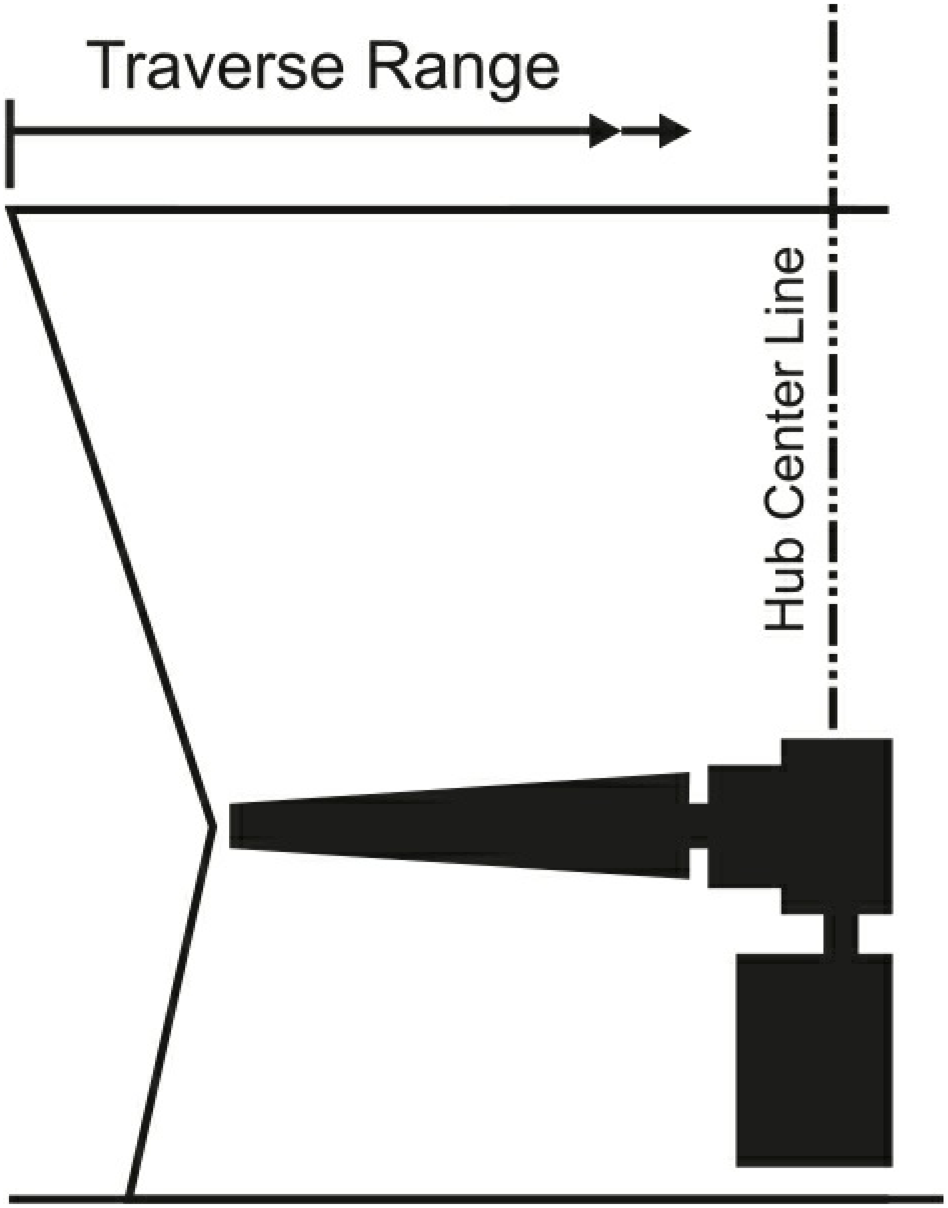


FIGURE 30.5 Exhaust plane velocity traverse. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

An in-service field test on a tapered-blade fan, installed in a properly operating cooling tower, would produce a radial exit air velocity profile similar to Fig. 30.6. Maximum air velocity occurs at mid-blade. Deviations from the ideal profile can reveal a variety of problems such as excessive blade tip clearance, hub seal disc leakage, blade deposits or pitting, airflow obstructions, fan blade aerodynamic stall, or under pitching. This enables the tower operator to target the most urgent problems with minimum delay and expense. Figure 30.7 indicates average airflow improvement opportunities for various problems of fan operation, which are described in more detail below.

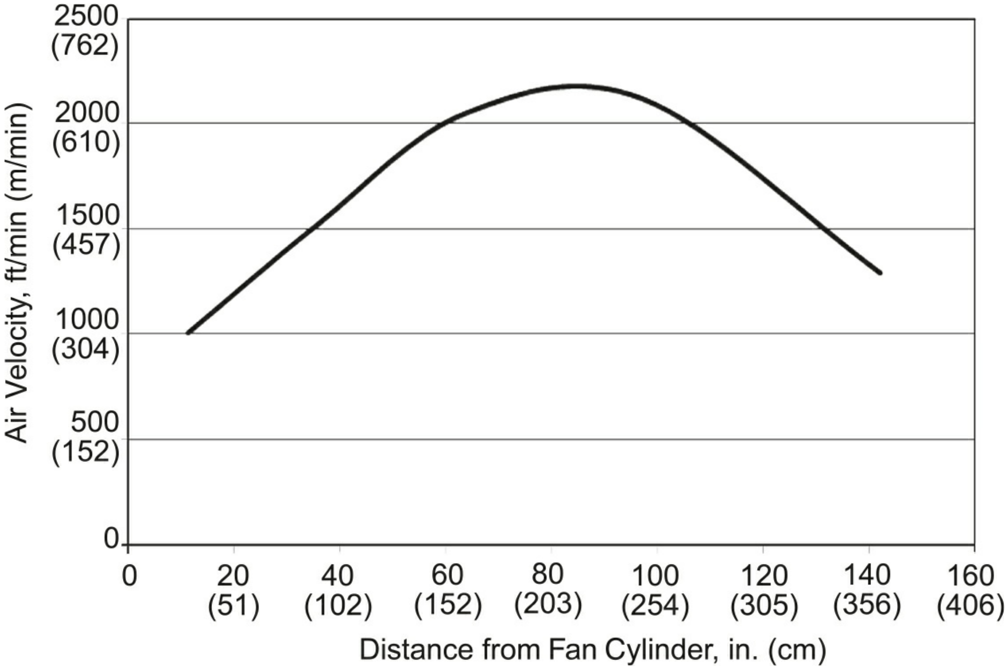


FIGURE 30.6 Normal exit air velocity profile along radius of fan stack. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

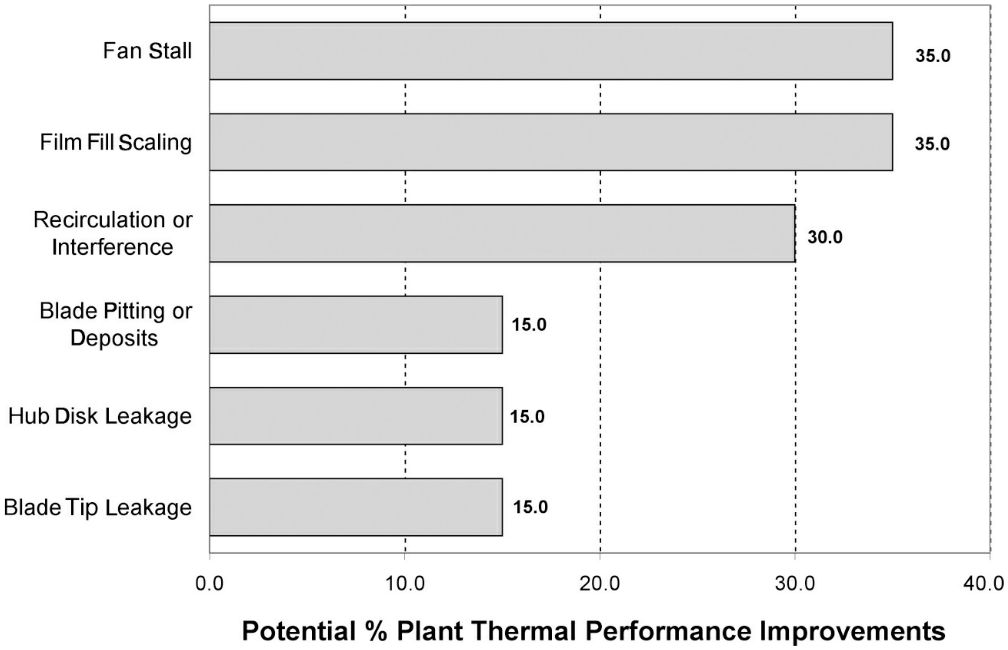


FIGURE 30.7 Air-side improvement opportunities.

Blade Pitch

The pitch or angle of attack of a variable-pitch fan blade can affect airflow through the tower. Loss of lift on airplane wings, which causes the plane to stall, is a similar effect. When the angle of an airplane wing relative to the incoming wind (angle of attack) is too steep, airflow separates from the top of the wing, increasing drag and turbulence, causing a loss of lift. An angle of attack that is too small also reduces lift. An angle of attack that is too low in a tower fan blade is often called under pitching and an angle of attack that is too high is called over pitching (Fig. 30.8).

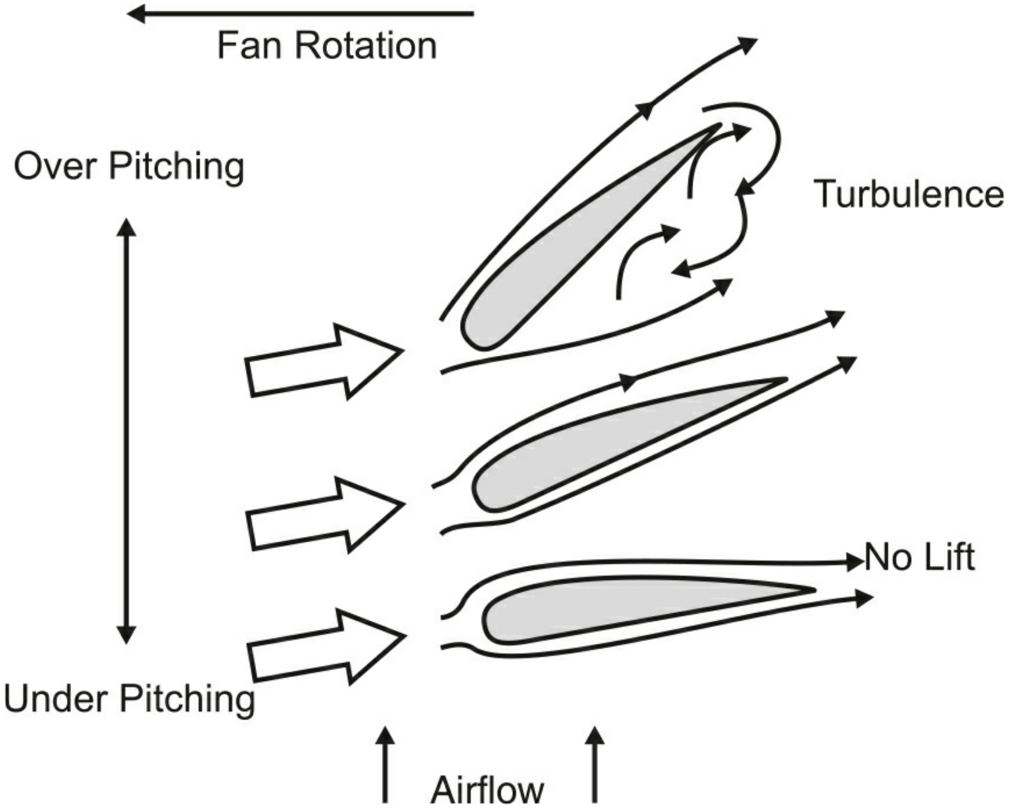


FIGURE 30.8 Illustration of fan stall from excessive angle of attack.

Under pitching cooling tower fan blades reduces airflow created by the fan. Over pitching fan blades increases blade turbulence and drag, also reducing airflow. Like an airplane wing, over pitching is known as fan stall and cannot be detected from fan motor power measurements. Once the stall point is exceeded, increasing blade pitch reduces airflow, while increasing fan motor power due to increased drag. Fan stall can also be caused by throttled airflow and high altitude. Fan stall has a significant adverse effect on cooling tower thermal performance. Reduced airflow through cooling tower fill from either condition increases the *L*/*G* ratio and the approach temperature, reducing tower thermal performance.

Fan Leakage

Air leakage around or into the fan suction side can reduce airflow and tower performance (Fig. 30.9). Fan leakage occurs from two main causes:

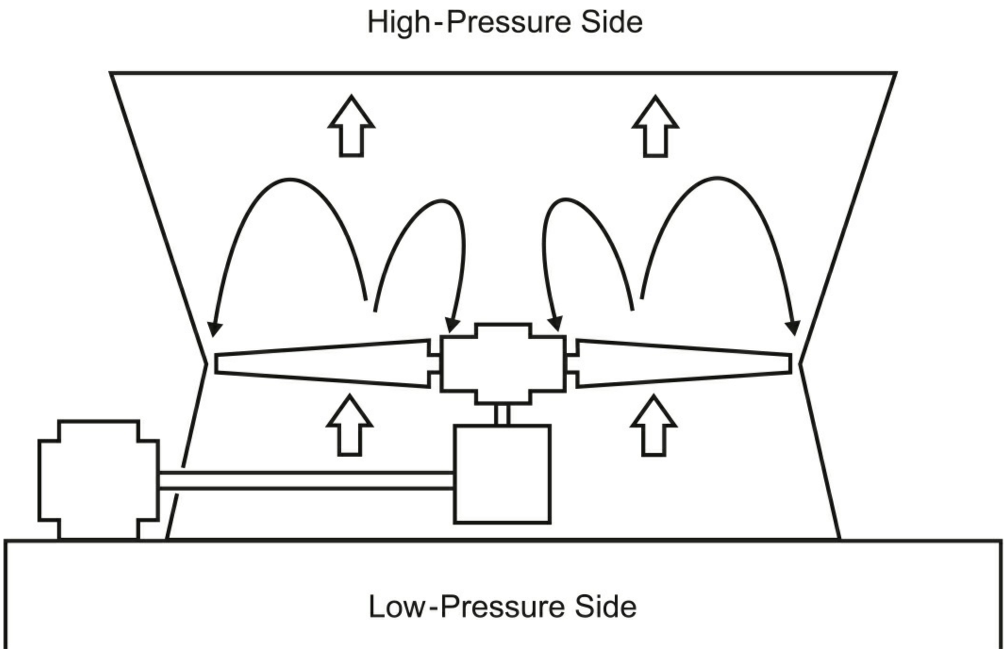


FIGURE 30.9 Potential locations of air leakage around cooling tower fan.

1. Air leaking from the high-pressure side of the fan to the low-pressure side, either at the blade tip or at the hub
2. Air leaking into the fan cylinder at holes or gaps in the fan stack, such as where the motor shaft goes through the fan cylinder (Fig. 30.10)

FIGURE 30.10 Air leakage can occur through holes and gaps in the fan stack.

Excessive blade tip clearance results in air leakage between the blade tip and fan cylinder. Poorly designed, broken, or missing hub discs result in air leakage through the hub. Hub discs are installed to control air passing through the hub area of the fan. Some hub designs, for example, spoke designs, are more prone to leakage. Figure 30.11 shows a fan with a hub disk installed.

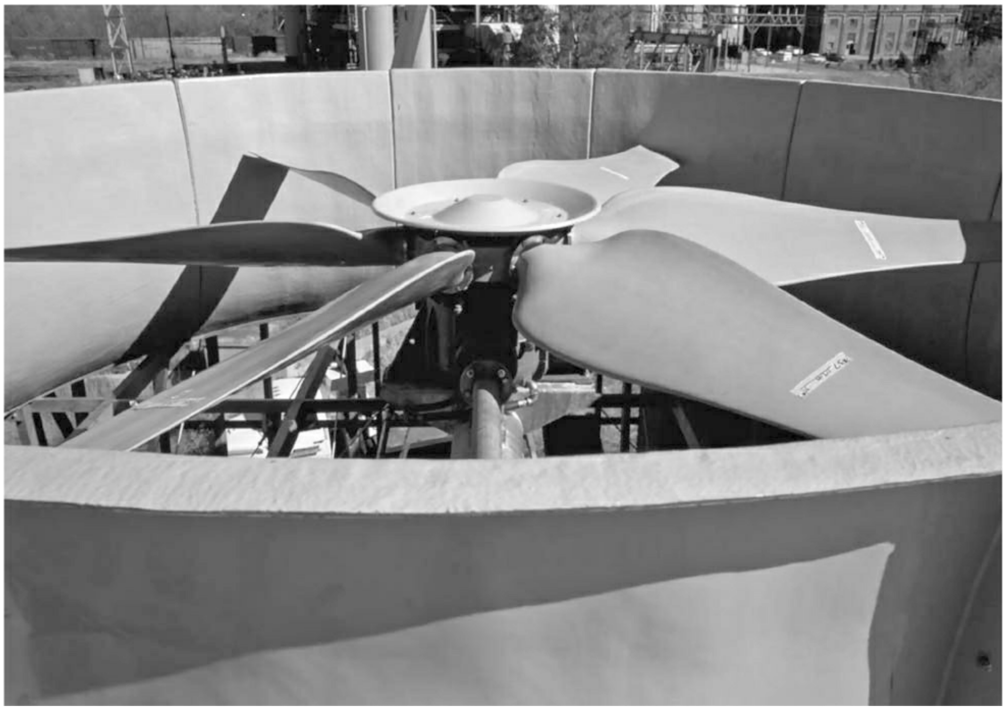


FIGURE 30.11 Fan with a hub disk installed to prevent air leakage from the high-pressure to the low-pressure side of the fan. (*Courtesy of SPX Cooling Technologies, Inc.*)

Blade Condition

Blade wear typically occurs in the form of pitting from droplets of water entrained in the airflow (called drift). This pitting initially occurs at the highest air velocity point on the blade. Blade wear or deposits create turbulence, disrupt airflow over the blade airfoil, and increase drag, resulting in reduced airflow and increased fan power requirement.

Plenum Spin/Fan Inlet Spin

When fans are tested in a laboratory wind tunnel, airflow straighteners are often installed directly upstream of the fan being tested to achieve maximum performance. Absence of airflow straighteners in normal cooling towers may cause air in the fan inlet to spin as it approaches the fan. This is known as fan inlet spin or fan inlet swirl (Fig. 30.12). Rotation of air can occur in the plenum too. This produces the same effect as an aircraft losing lift if it was to try to take off going with the wind. For example, a fan could be designed to rotate at 100 rpm. If air in the fan inlet spins at 10 rpm as it approaches the fan, the effective speed of the fan is reduced to 90 rpm. Actual airflow will be 10% less than design, because fan airflow is directly proportional to fan speed.

Increasing fan blade pitch to compensate can offset this reduced airflow, but may create a fan stall condition, which is much worse.

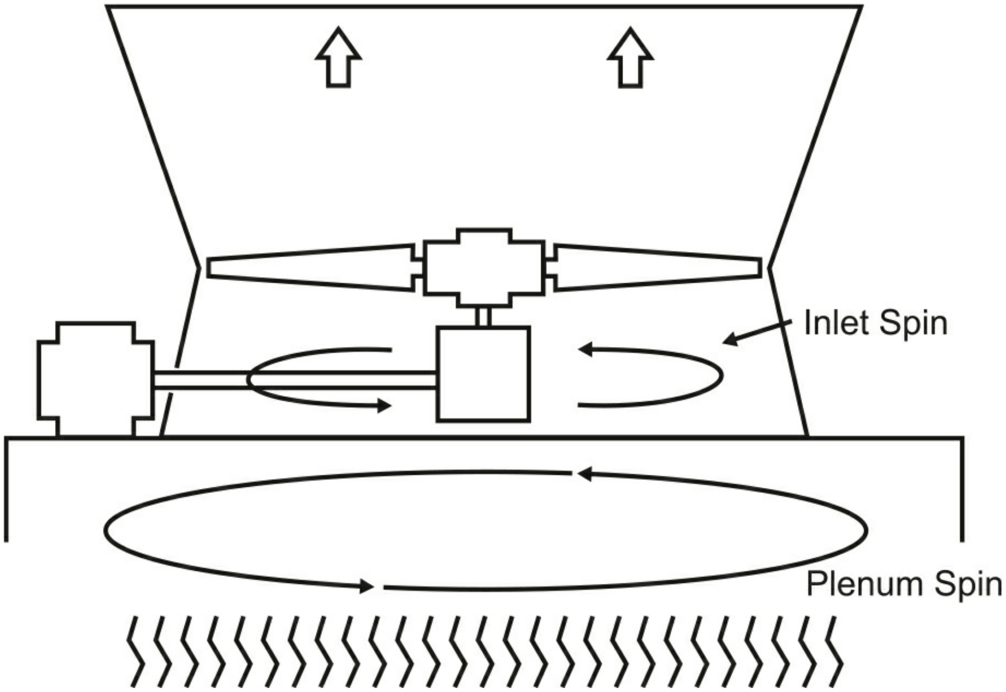


FIGURE 30.12 Illustration of inlet and plenum spin induced in air entering fan stack.

Air Channeling

Flowing air always takes the path of least resistance, for example, where tower fill is broken or missing or where lowest water flow exists. Air that bypasses contact with water compounds the adverse effect of water channeling on thermal performance of the tower.

Air Velocity

High air velocity, whether resulting from poor design, air channeling, or obstructions can cause various problems in different parts of the tower. For instance, excessive airflow velocity in film fill can result in cooling water evaporating to dryness in the fill pack, causing scaling that can progress at an alarming rate.

Cell Balancing

For optimum thermal performance, airflow needs to be equally distributed among cells to maintain design *L/G* ratio. This was illustrated earlier in Fig.

30.4.

Recirculation and Interference

Recirculation occurs when cooling tower inlet air is adulterated by exit air from the same cooling tower. Interference is when cooling tower inlet air is adulterated by exit air from an adjacent cooling tower or warm or moist air from another source (Fig. 30.13). While some cooling tower designs are more prone to recirculation and interference, other factors such as location, orientation, and wind direction have significant impact.

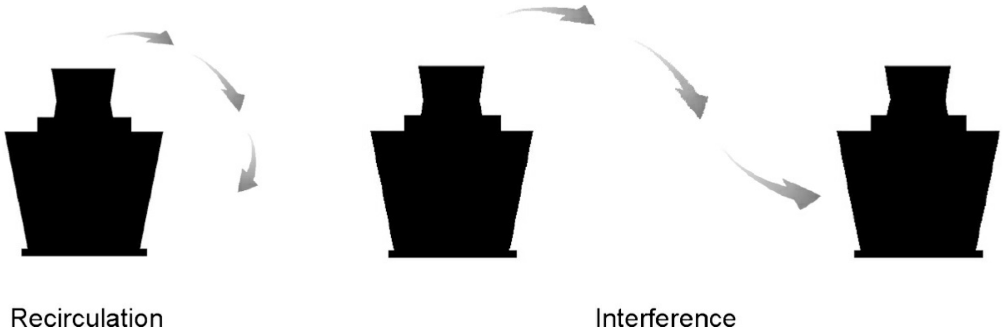


FIGURE 30.13 Recirculation and interference. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

Water-Side Thermal Performance Issues

Water flow and airflow must be uniform throughout the tower to achieve optimum cooling tower thermal performance. On crossflow cooling towers, water flow on the tower deck should be balanced between each cell or each side of a cell. As airflow takes the path of least resistance, air is preferentially drawn through the side of the cell with the least water flow, reducing thermal performance efficiency. This can be caused by different water levels in the water distribution deck of different cells, or different sides of the same cell, as shown in Fig. 30.14. The lower water level on the right side of the deck reduces water flow and increases airflow through that side of the cell.

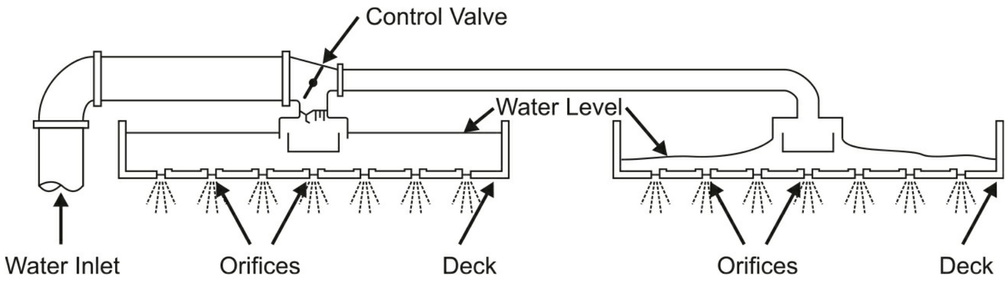


FIGURE 30.14 Water level on the deck of a crossflow cooling tower can affect water flow and airflow through each part of the tower. The section of fill under the deck on the right may have insufficient water flow.

Measurements of water flow in a crossflow cooling tower (Fig. 30.15) illustrate this point by showing how airflow can be different between cells, or between different sides of the same tower cell. Although Cells 3 and 4 have the same total water flow, one side of each cell has double the flow of the other side. Performance loss from this water-side channeling is compounded by airflow channeling that also occurs in these cells. Water flows over each side of Cells 1 and 2 are balanced, but Cell 1 has double the flow of Cell 2. Higher *L/G* ratio in Cell 1 can reduce thermal performance. Analysis of individual cell flows and deck water levels are useful in comparing fill water loadings with design values.

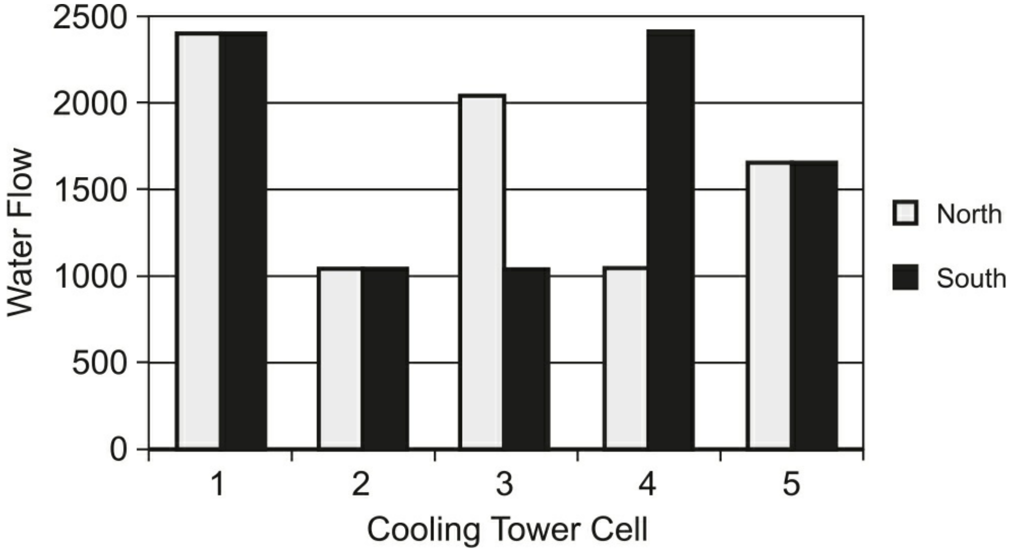


FIGURE 30.15 Water flow on a multi-cell crossflow cooling tower. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

Fill Water Loading

Both high and low fill water loadings can cause performance and reliability problems. For optimum thermal performance, water flow needs to be equally distributed among cells to maintain the designed *L/G* ratio. Channeling or nonuniform water flow through fill causes preferential air channeling through fill areas where there is the least water. This reduced contact between water and air, reduces evaporation and tower performance. Excessive water loading of film fill can hold back airflow, until the air finally percolates through the increased amount of water. Insufficient water loading on any part of a film fill pack results in evaporation to dryness and progressive scaling of the fill.

Film Fill Scaling

In addition to low water loading that causes dryness in the fill, scaling in tower fill can occur from a number of causes. Other causes can include high temperature stress, low inhibitor dosage, or even rapid carbon dioxide stripping from water in the tower fill. As scale thickness increases in film fill, the fill pack becomes progressively heavier due to the combined weight of scale and additional water. This may continue to the point where the support system fails, and fill falls into the basin.

Water Bypassing Fill

There are a variety of causes of water channeling in crossflow and counterflow cooling towers. Some spray from perimeter nozzles is often directed down cell partitions, bypassing fill and avoiding contact with air. This can be kept to a minimum by installing deflectors to redirect water back onto the fill. Broken or plugged spray nozzles can affect water flow in either type of tower (Fig. 30.16). A broken nozzle, or one with a broken splash or spray bar, may not spread water properly over fill. The fill under a plugged nozzle has little or no water flow. In a counterflow tower, low system water pressure in the distribution header for spray nozzles can reduce water flow for an entire cell.

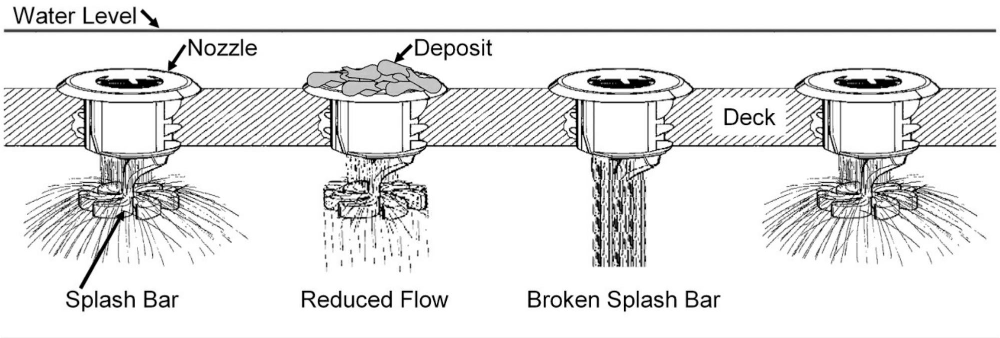


FIGURE 30.16 Examples of spray nozzle problems in a crossflow tower that can cause water channeling.

Cooling Tower Energy Balance

The ever-increasing cost of energy is driving the need for efficient process operations. A mechanical audit of the cooling tower, including testing to evaluate tower performance, can provide vital information enabling the tower operator to compare operating costs to design values.

Typically, cooling tower operating energy is 2 to 6% of total energy (heat rejection plus operating energy equals total energy). These estimates vary with climate, tower design, plant layout, and cooling duty. Pump energy consumption is approximately 85% of total operating energy, depending on tower design and plant layout. Figure 30.17 shows the typical breakdown of energy usage by cooling tower equipment. Performance of pumps and fans should be maintained at peak levels to maintain efficiency. However, thermal energy rejected by the cooling tower should be the focus of efforts to maintain performance of the entire system.

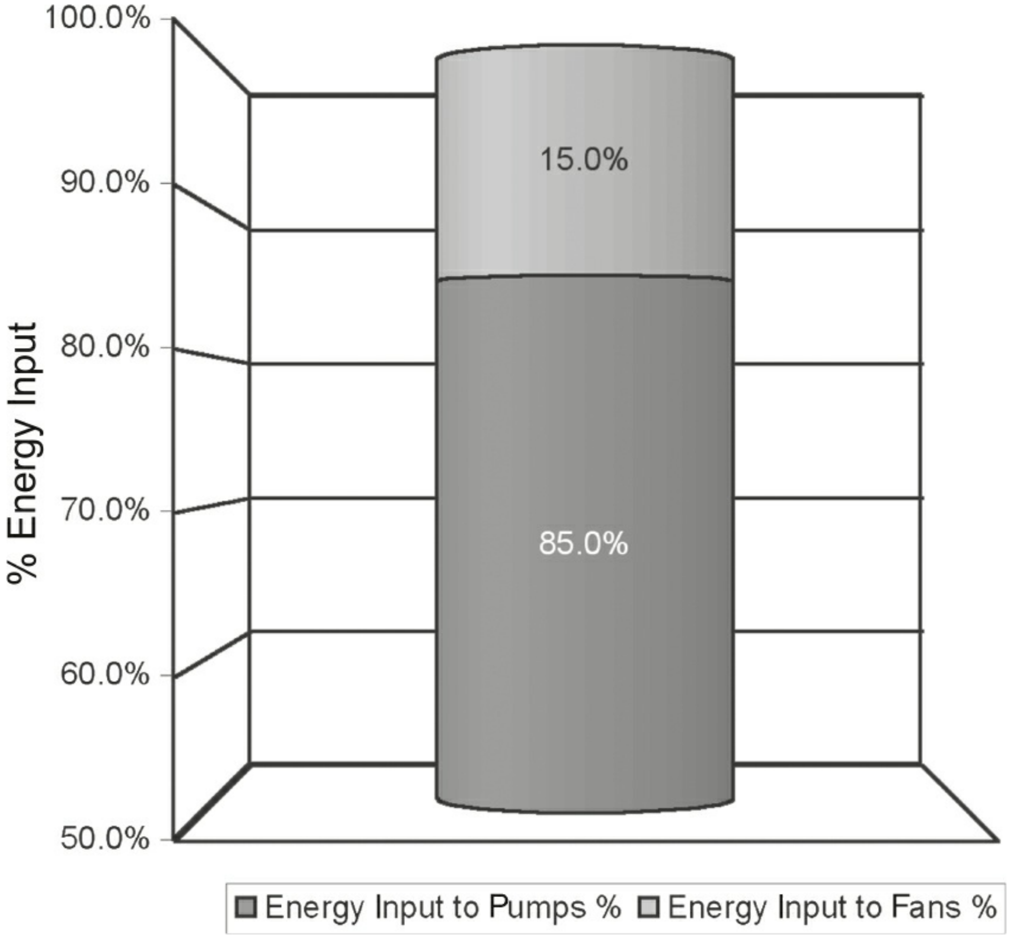
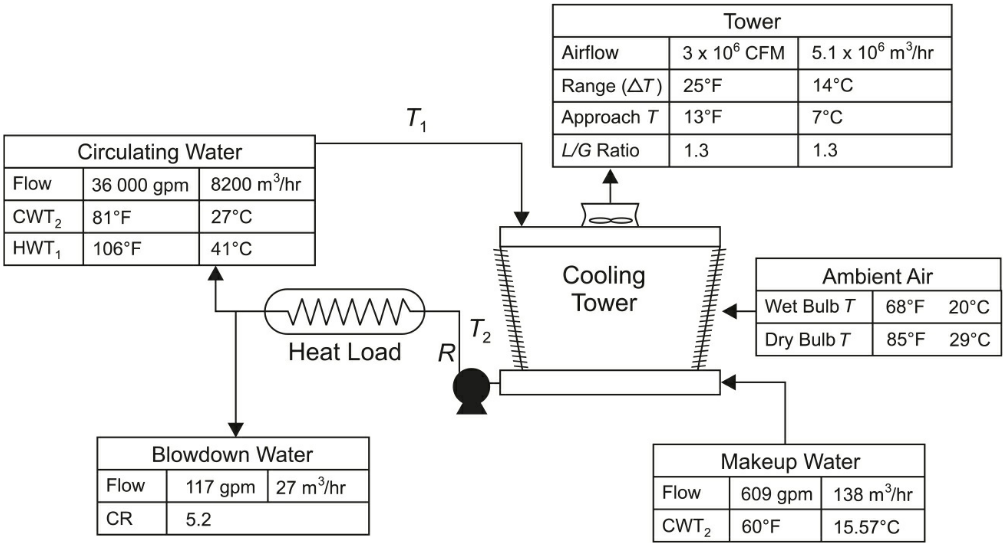


FIGURE 30.17 Energy consumption in a cooling tower system.

A mechanical audit of the tower to evaluate performance should collect a wide variety of inputs, including flow and temperature data. Typical data for water and airflow are shown in Fig. 30.18. Other data, like the fan exit air velocity profile and inspection points described in this chapter, should be part of a complete mechanical survey of a cooling tower. The data in Fig. 30.18 can be used to calculate the *L/G* ratio and heat balance. A variety of other tower characteristics like CR of the water can be determined using equations in Chap. 14.



Tower		
Airflow	3 x 10^6 CFM	5.1 x 10^6 m^3/hr
Range (ΔT)	25°F	14°C
Approach T	13°F	7°C
L/G Ratio	1.3	1.3

Circulating Water		
Flow	36 000 gpm	8200 m^3/hr
CWT_2	81°F	27°C
HWT_1	106°F	41°C

Ambient Air		
Wet Bulb T	68°F	20°C
Dry Bulb T	85°F	29°C

Blowdown Water		
Flow	117 gpm	27 m^3/hr
CR	5.2	

Makeup Water		
Flow	609 gpm	138 m^3/hr
CWT_2	60°F	15.57°C

FIGURE 30.18 Inputs and outputs from a cooling tower that can be used to calculate performance and energy balance.

The *L/G* ratio and approach temperature are two of the more important data points that can be determined from this input data. If either water or airflow changes, then the *L/G* ratio changes. As described earlier in this chapter, a decrease in *L/G* ratio reduces approach temperature and cold water temperature of the tower. The opposite happens if water flow increases, causing an increase of *L/G* ratio. While airflow is more difficult to measure, water and air temperatures can be measured easily. Changes of approach temperature and range (ΔT) of the cooling tower can signal that something else has changed. Many things can affect these two parameters. A detailed analysis of a complete mechanical audit of the tower performance would be needed to determine the root cause of a change in approach temperature or ΔT.

For example, if ΔT of the tower decreases, two of the possible causes are, a drop in heat load from the process or an increase in water flow, which increases the *L/G* ratio. Change in airflow does not affect ΔT. If approach temperature increases, possible causes include, an increase in heat load or water flow increase (*L/G* ratio increases). Approach temperature would also increase if ambient air humidity increases. Thus, it is necessary to have a complete set of information in order to assess tower performance.

Reliability Issues

In a cooling tower, reliability issues can involve everything from structure to mechanical equipment to water treatment. Structural issues are outside the scope of this chapter, and water treatment issues are covered elsewhere in this book. The most critical mechanical equipment is fans, pumps, and their respective motors. Premature or unexpected failure can result in reduced cooling capability, at best causing reduced process throughput or at worst an unplanned outage.

Fan and Pump Motor Reliability

Power supply quality and current draw are indicators of the health of a pump or fan motor. For instance, an extreme case of phase voltage unbalance can reduce expected life of a fan motor from 20 years to 9 months.

Fan Vibration

Fan vibration is an indicator of an unbalanced fan or drive shaft. Vibration that continues or worsens may result in fatigue failure of a coupling, drive shaft, gearbox, or fan blade, ultimately destroying the fan.

Pump Cavitation

Cavitation is the implosion of vapor voids or bubbles in water due to rapid localized changes in pressure (Fig. 30.19). This can be caused by low pump suction pressure. Cavitation erosion of pump internals can be very severe, and pump flow declines as impeller erosion progresses.

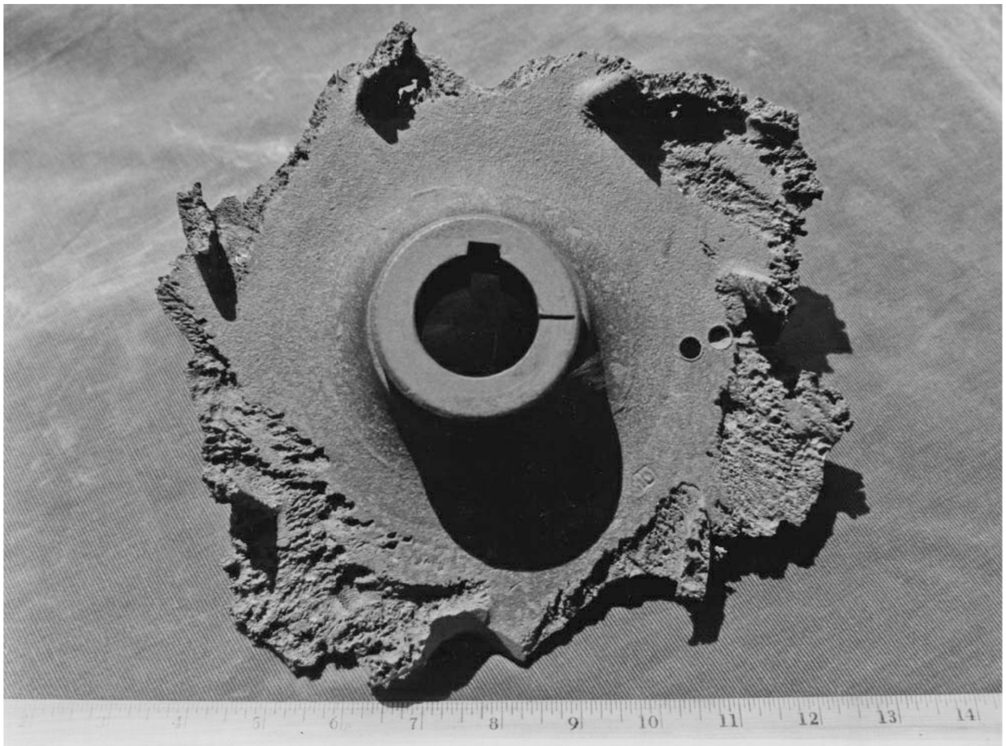
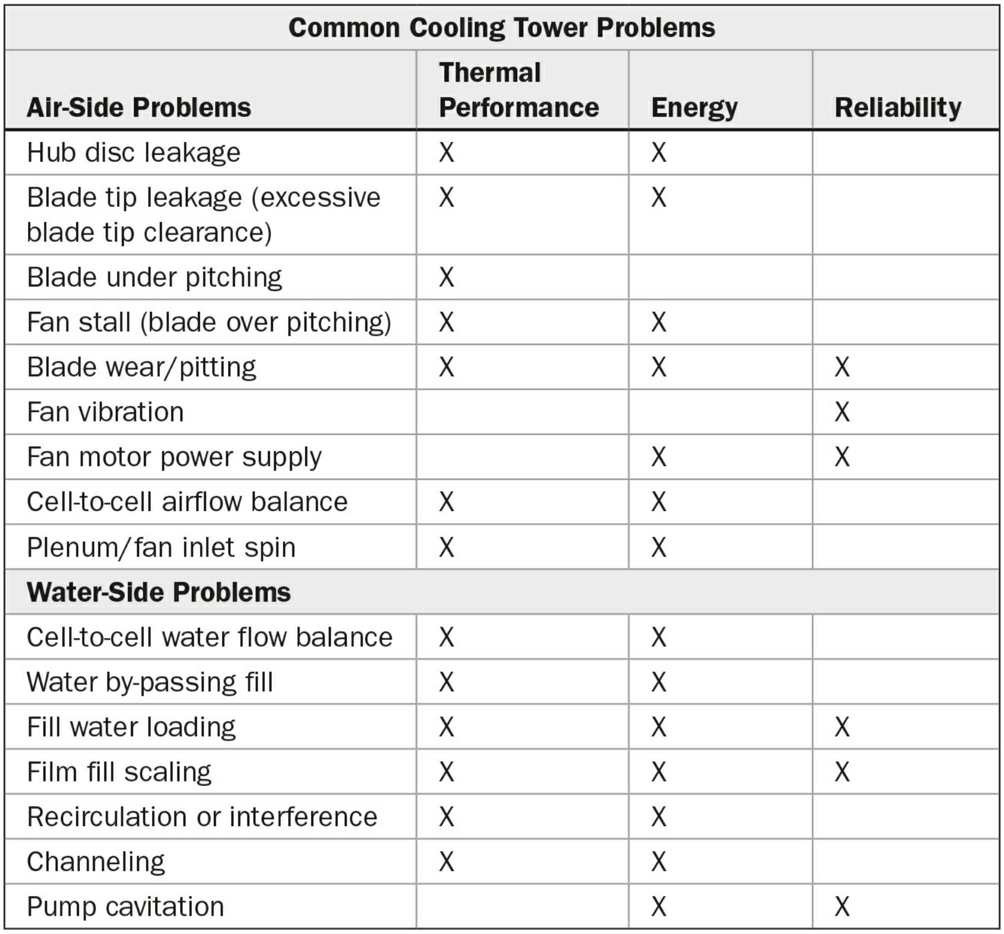


FIGURE 30.19 Cavitation damage on pump impeller.

Inefficiency in Older Cooling Towers

Continuing improvements in design of cooling towers and their component parts has resulted in reduced cooling tower size and increased reliability. Components that are particularly noteworthy are nozzles, fill, and drift eliminators. Counterflow cooling tower nozzles now produce much more even spray patterns and are more reliable than older versions. Film fill is now available for a range of water qualities and for applications from comfort cooling to industrial production. Due to additives in the plastic, film fill life expectancy is significantly longer. Cellular drift eliminators can now limit drift to 0.0005% of the recirculating rate, while maintaining satisfactory static pressure drop. As a result, older cooling towers not equipped with these newer design components can suffer greater thermal loss from under performance.

The causes of thermal performance, energy wastage, and reliability problems that have been presented in this chapter are summarized in Table 30.2. Many of these problems can only be found by inspection or by specialized test measurements of a system. These should be undertaken during a complete mechanical audit of the cooling system that measures performance of key cooling tower parameters.



Common Cooling Tower Problems

Air-Side Problems	Thermal Performance	Energy	Reliability
Hub disc leakage	X	X	
Blade tip leakage (excessive blade tip clearance)	X	X	
Blade under pitching	X		
Fan stall (blade over pitching)	X	X	
Blade wear/pitting	X	X	X
Fan vibration			X
Fan motor power supply		X	X
Cell-to-cell airflow balance	X	X	
Plenum/fan inlet spin	X	X	
Water-Side Problems			
Cell-to-cell water flow balance	X	X	
Water by-passing fill	X	X	
Fill water loading	X	X	X
Film fill scaling	X	X	X
Recirculation or interference	X	X	
Channeling	X	X	
Pump cavitation		X	X

Courtesy of Diagnostic Cooling Solutions, Inc.

TABLE 30.2 Summary of Common Cooling Tower Problems and Impact on Performance

Cooling Tower Performance Testing

The dilemma of deciding what repairs to undertake with a limited repair budget has resulted in wider use of cooling tower testing to verify contractual thermal performance, and to diagnose root causes of problems.

Early cooling tower performance curves were published in 1943. The Cooling Technology Institute (CTI) (formerly Cooling Tower Institute) published the most comprehensive book of cooling tower characteristic charts in 1967. These charts were used to size a cooling tower for a specific process heat load, and to enable cooling tower thermal performance to be checked against design specifications. These performance calculations and comparisons are now totally computerized. The CTI also publishes the Cooling Tower Acceptance Test Code, for contractual thermal performance verification of new and refurbished cooling towers. CTI reports annually on results of cooling towers that have been tested in accordance with the code.

Cooling Tower Acceptance Testing

The CTI test code provides acceptance test procedures for various tower types. There are two basic test methods: the performance curve method and characteristic curve method. Both methods require specialized testing equipment for data collection. Because measured values of hot water temperature, cold water temperature, WBT, water flow rate, fan power, and *L/G* ratio are not likely to match design values, calculations of performance and corrections can be complex. Therefore, an experienced individual is recommended to carry out testing and analysis.

The main purpose of the CTI Acceptance Test Code is to verify contractual performance guarantees of a new or refurbished cooling tower. The test can be used to compare current cooling tower thermal performance to the original, repaired, or contractual performance guarantee. During the test, cooling tower operating conditions such as recirculation and interference can degrade cooling tower thermal performance. Because these factors are outside of the control of the cooling tower supplier or repair contractor, the CTI Acceptance Test Code is designed to exclude effects of recirculation and interference from the performance test. As a result, cooling tower thermal performance as determined by the CTI Acceptance Test can exceed actual performance experienced with a cooling tower, if recirculation or interference is occurring.

Where thermal performance is in question, the CTI Acceptance Test Code has often been used as one method to check the status of older cooling towers. However, because the CTI Acceptance Test does not have specific diagnostic capabilities, it usually can only verify that the cooling tower is under performing, as was previously suspected, without determining why.

Cooling Tower Performance Audit

Diagnostic performance testing of a cooling tower as part of a complete MOC system survey can help find the root cause of tower performance problems. The mechanical portion of the survey should collect current and design operating parameters for the cooling tower system. Basic calculations that define dynamics of a cooling tower are described in Chap. 14. Test methods to evaluate performance of fans, pumps, water flow, airflow, etc. require specialized equipment, procedures, and knowledge. An individual who is trained for this type of testing should perform the audit. Typical goals of diagnostic testing include:

- To troubleshoot and restore cooling tower thermal performance
- To predict cooling tower thermal performance at alternative operating conditions, such as various water flows or heat loads
- To upgrade cooling tower thermal performance to accommodate process changes or plant expansion
- To identify, target, and prioritize needed repairs within each cell
- To identify and prioritize repairs before a planned plant shutdown, so that sufficient maintenance time and budget can be allocated
- To monitor cooling tower film fill thermal performance

Diagnostic testing has the advantage of being carried out on an operating cooling tower, whereas an inspection requires a planned outage. Thermal performance impact of identified problems can be determined when the cooling tower is in operation, and can help prioritize necessary repairs. For instance, in the case of a planned cell-by-cell refurbish of a multi-cell cooling tower, a diagnostic test can define the order in which cells should be restored for optimum thermal performance.

The capability to identify obscure problems can be important on large multi-cell cooling towers, where blanket or random repairs would involve excessive downtime and expense with no guarantee of success. Examples of information that would be beneficial to obtain during a performance audit include:

- Cell water flow balance
- Fan motor diagnostics
- Fan stall
- Fan inlet/plenum spin

- Cell fan power, airflow, and heat rejection balance
- Cell fan and pump operating energy balance
- Cell operating energy efficiency

The ability of diagnostic testing procedures to detect and isolate performance problems, particularly obscure problems, can be beneficial in maximizing the value contribution of a cooling tower to the entire production process.

CHAPTER 31

Energy in Steam Systems

Energy is the largest part of a facility's costs associated with the generation of steam, that is, fuel, water, chemicals, labor, and maintenance. Typically, 60 to 70% or more of the cost of steam comes directly from the fuel consumed. By comparison, 5% can be attributed to the cost of water, and typically, less than 3% is from water treatment costs. Since fuel is the largest cost, it is obvious that any improvement that directly saves energy, and thus fuel, is of great interest.

Recent studies of industrial boiler/steam generation plants show significant opportunities exist to reduce energy wastage and fuel consumption. Beginning in fiscal year 2006, the U.S. Department of Energy (DOE) started an industrial assessment campaign, which involved the largest energy-consuming manufacturing plants in the United States. Trained assessment teams identified and evaluated promising opportunities in a site's steam system for the ability to cut energy use and reduce carbon emissions. Results of the top 10 steam saving opportunities for the first 114 steam assessments are shown in Fig. 31.1. This useful checklist provides key energy saving project areas or opportunities for many plants.

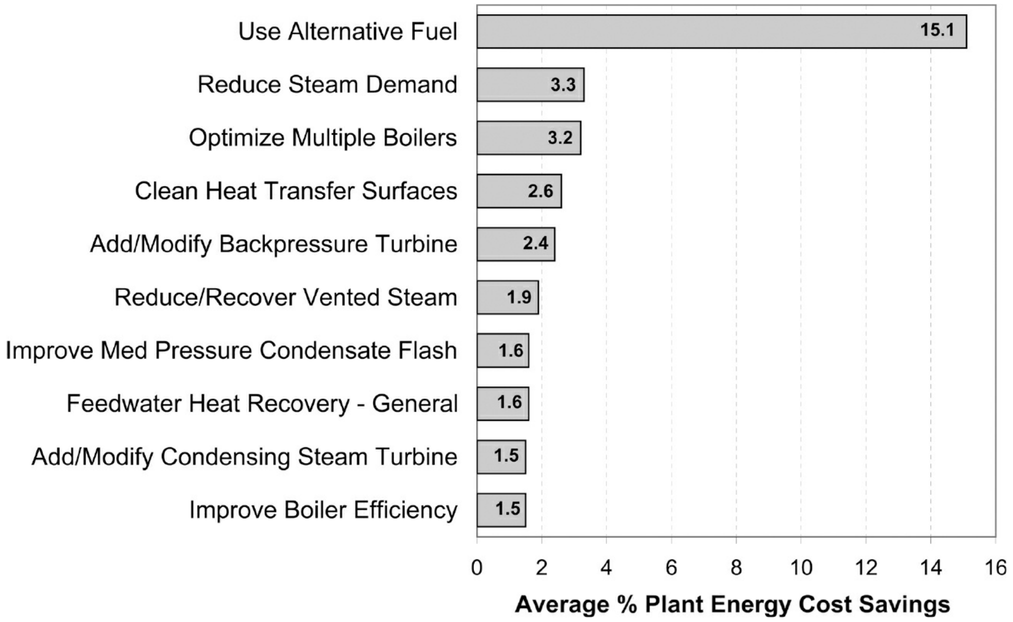


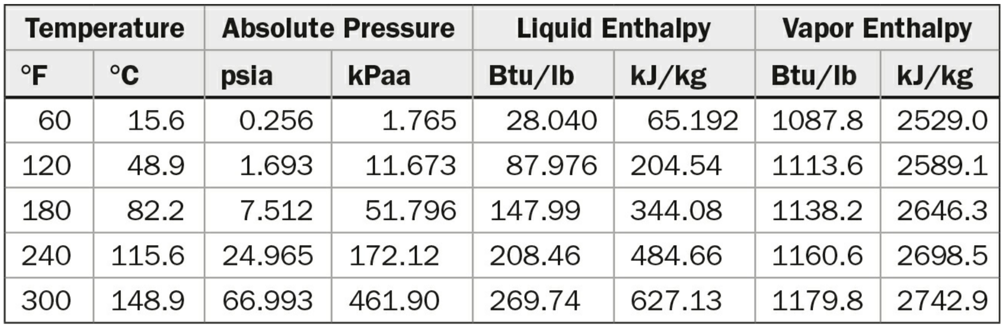
FIGURE 31.1 Top 10 steam savings opportunities. (*Source: Data compiled from ORNL/TM-2007/138.*)

Energy Basics for Steam Systems

As heat is supplied to water, the temperature increases until boiling occurs at 212°F (100°C) under atmospheric pressure. At the boiling point, the temperature remains constant until all the water is converted to vapor. The specific heat of water is 1 Btu/[lb · °F] (4.184 kJ/[kg · °C]), and 152 Btu/lb (353 kJ/kg) is needed to raise the temperature of water from 60°F (15.6°C) to 212°F (100°C). In contrast, the heat of vaporization for water at 212°F (100°C) is 970 Btu/lb (2256 kJ/kg) to change water to steam. Therefore, about six times more energy is needed to evaporate water at the atmospheric boiling point than to heat the water from 60°F (15.6°C) to 212°F (100°C).

If the pressure of the water is increased, as it is in a boiler, the boiling point also increases, requiring the application of still more heat to raise the temperature and vaporize the water. Steam at higher pressure, then, has a higher temperature and contains more energy than steam at atmospheric pressure. Another important change is the reduction in volume as the pressure increases.

Steam tables have been developed to relate these properties of steam and water at various temperatures and pressures. Table 31.1 illustrates some of the information found in steam tables. A complete discussion of steam tables is beyond the scope of this book, but some basic orientation is necessary for understanding power generation processes.



Temperature		Absolute Pressure		Liquid Enthalpy		Vapor Enthalpy	
°F	°C	psia	kPaa	Btu/lb	kJ/kg	Btu/lb	kJ/kg
60	15.6	0.256	1.765	28.040	65.192	1087.8	2529.0
120	48.9	1.693	11.673	87.976	204.54	1113.6	2589.1
180	82.2	7.512	51.796	147.99	344.08	1138.2	2646.3
240	115.6	24.965	172.12	208.46	484.66	1160.6	2698.5
300	148.9	66.993	461.90	269.74	627.13	1179.8	2742.9

TABLE 31.1 Saturated Steam Table Example

Enthalpy

The term enthalpy denotes the heat content of a substance, expressed in Btu/lb (kJ/kg). It is most typically represented by the symbols H or h. Since water changes from liquid to solid below 32°F (0°C) at atmospheric pressure, this discussion is limited to higher temperatures.

In discussing energy, the heat content of water and steam, as well as the amount of energy added, must be calculated. The change in energy needs based on potential energy saving projects, and how this translates into energy costs or savings must also be calculated.

Here is a simple example. How much energy is required to raise the temperature of water in a heat exchanger from 60 to 120°F (15.6–48.9°C) when the water flow is 100 gpm (22.7 m^3/h)?

Steam tables can be used to determine the enthalpy of water at 60°F (15.6°C) and 120°F (48.9°C). From Table 31.1, the values are 28 and 88 Btu/lb (65 and 205 kJ/kg), respectively. The difference in enthalpy is 60 Btu/lb (140 kJ/kg). To find the rate of energy addition to heat the water in this example, the calculation is:

$$(60\ \text{Btu/lb})(100\ \text{gpm})(8.33\ \text{lb/gal}) = 49\,980\ \text{Btu/min}$$

$$(140\ \text{kJ/kg})(22.7\ \text{m}^3/\text{h})(1000\ \text{kg/m}^3)(1\ \text{h}/60\ \text{min}) = 52\,970\ \text{kJ/min}$$

Steam Quality

The terms saturated, dry, and moist are often used in describing steam. What the steam tables call saturated steam could also be called dry and saturated. In other words, it is vapor in equilibrium with water at the boiling temperature, containing no liquid. Steam that contains water droplets is called wet steam. Steam issuing from the spout of the teakettle on the stove is colorless or invisible, just as it leaves the spout; this is dry saturated steam. A short distance from the spout it turns white. This “cloudy steam” contains less heat per pound (kilogram) and is wet steam, because some of the vapor has given up its heat and condensed into tiny droplets of water.

Wet steam always has less heat per pound (kilogram) than dry steam; consequently, it does less work. The term quality is often used to denote the dryness of steam: 100% quality means dry and 90% quality means the steam contains 10% moisture by weight.

After vaporization, additional heat may be added to the steam, increasing its temperature and energy; this is called superheated steam. Superheating not only increases the energy content, but also permits transporting the steam through pipelines with less condensation. Condensation decreases the efficiency of heat engines (turbines) and causes heat loss and water hammer in steam lines.

Boiler Efficiency

In most plants, the operation of a boiler system consumes more energy than any other area of the plant, and for this reason, it is very important that the boilers operate efficiently. Typically, the economic impact of any boiler-related changes is quantified in terms of changes in boiler efficiency. However, before discussing boiler efficiency, it is necessary to first discuss the relationships between capacity and efficiency.

Like many other types of mechanical equipment, boilers are expected to operate over a wide range of capacities or steaming rates. Because the efficiency of a boiler varies with the boiler steaming (firing) rate, a single arbitrary rating is not only meaningless but also apt to be misleading. For the proper analysis of the operational characteristics of a boiler installation, it is necessary to have performance curves. Figure 31.2 shows typical performance curves for packaged watertube boilers.

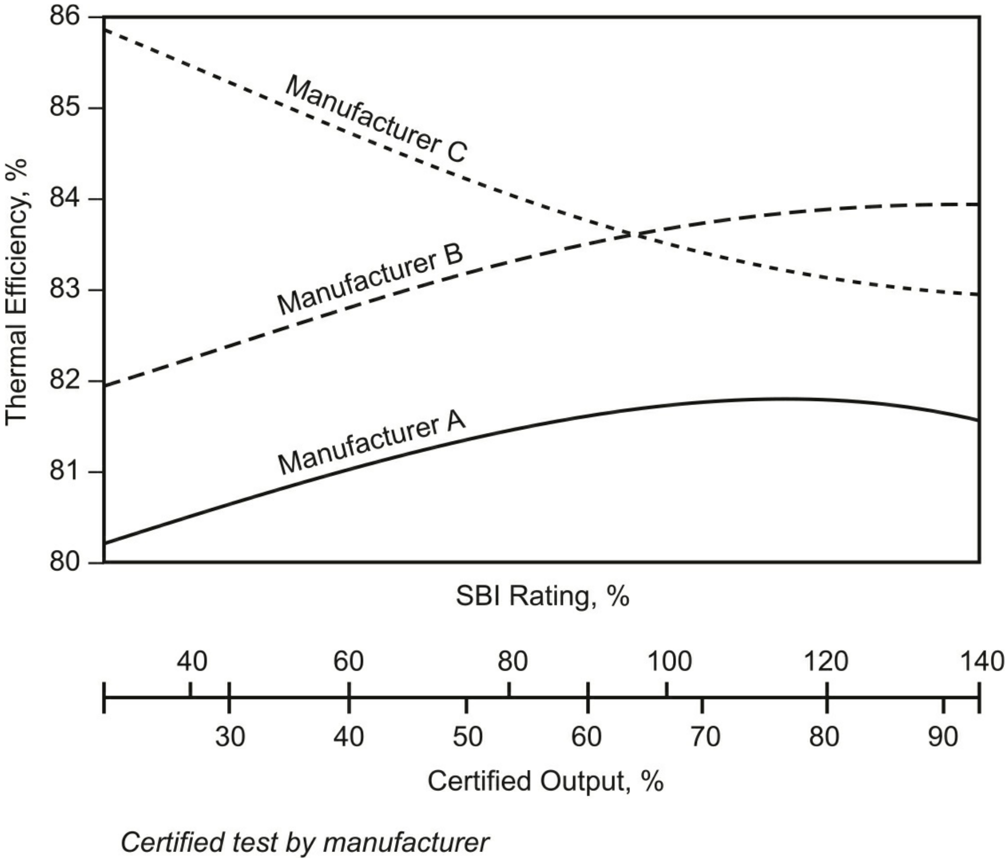


FIGURE 31.2 Typical packaged watertube boiler performance curves.

The measure of the ability of a boiler to transfer heat from the furnace to the water and steam is its boiler efficiency. This typically takes into account the furnace, superheater, reheater, economizer, and air preheater. In measuring efficiency, it is not usually practical to separate burner (or grate), furnace, and boiler efficiencies. The efficiency of a boiler is considered the combined efficiency of all its elements and is generally expressed as a percentage figure.

The determination of the efficiency of a boiler is in reality a performance test. On large installations, such tests are conducted during actual operation; smaller boilers are tested either in the laboratory or in the field under semi-controlled conditions. There are many ways to track boiler efficiency; some methods are quite complex, requiring special tools to measure the efficiency.

The average efficiency of a boiler and burner installation will vary based on operating conditions. The determination of the maximum attainable efficiency depends on the following:

- Boiler design, including heating surface arrangement and effectiveness of direct and indirect surface placement; furnace volume and shape; combustion product flow through the boiler passes; and water and steam circulation within the boiler

- Built-in losses, such as heat transfer through boiler walls and setting, and irrecoverable flue gas and ash heat losses
- Built-in heat recovery equipment, such as air preheaters, economizers, and blowdown heat recovery systems
- Type of fuel burned and its inherent characteristics
- Rate of firing in relation to furnace volume and heating surface
- Controllability of the variable conditions

In any given installation, boiler efficiency will vary from hour to hour, day to day, and season to season, depending on the following variable conditions:

- Condition of the fuel when fired
- Draft as affected by barometric pressure
- Burner adjustment
- Percentage of excess air
- Cleanliness of heat absorbing surfaces
- Rate of firing
- Temperature and humidity of combustion air
- Incompleteness of combustion or unburned carbon
- Type of operation, whether continuous or intermittent, on–off, high–low, or modulating

Therefore, boiler efficiency is not a static value for a given boiler installation but rather is constantly changing with operating conditions. This is important to remember for two reasons:

1. It is not necessary to spend great time and money to obtain an exact value for boiler efficiency. Simple calculations and rules-of-thumb are probably adequate to evaluate and justify energy saving projects.

2. The change in boiler efficiency due to energy saving projects is the important concept to capture in cost saving calculations, not the absolute boiler efficiency itself.

Boiler efficiency is important, because this value is used in economic calculations for energy saving projects and evaluations. When calculating the potential cost savings for steam system projects [blowdown heat recovery equipment, increased cycles of concentration (COC), increased steam condensate recovery, etc.], the boiler efficiency is used to translate the potential heat or energy savings to fuel savings, which can then be expressed in monetary terms.

Anyone planning to conduct boiler efficiency measurements is encouraged to read the U.S. DOE Steam System Survey Guide (ORNL/TM-2001/263). The rigorous methods to conduct boiler efficiency tests and calculations are described in the American Society of Mechanical Engineers (ASME) Power Test Code (PTC) 4.1, Steam Generating Units.

Definitions

Before calculating boiler efficiency, a number of terms and measurements need to be understood. The following are the important ones to obtain a valid result for boiler efficiency.

Combustion Efficiency

Combustion efficiency is similar to boiler efficiency, with shell, blowdown, and miscellaneous losses omitted. It is expressed as a percentage of total fuel input energy.

Combustion efficiency is an indication of the burner's ability to burn fuel. The amount of unburned fuel and excess air in the exhaust are used to assess a burner's combustion efficiency. Burners resulting in low levels of unburned fuel, while operating at low excess air levels, are considered efficient. Well-designed burners firing gaseous and liquid fuels operate at excess air levels of 15% and result in negligible unburned fuel. By operating at only 15% excess air, less heat from the combustion process is used to heat the combustion air, which increases the heat available to generate steam.

Combustion efficiency is not the same for all fuels. Gaseous and liquid fuels burn more completely than solid fuels, but some fuels, such as natural gas, lose a portion of the fuel energy up the stack with the water vapor formed during combustion. Table 31.2 shows typical combustion efficiency by fuel type.

Fuel Type	Fuel	Efficiency (%)
Solid	Coal	89
	Wood	74
Liquid	No. 2 Oil	88
	No. 6 Oil	88
Gas	Natural Gas	85

TABLE 31.2 Typical Combustion Efficiency by Fuel Type

Boiler Efficiency

The term boiler efficiency is often used interchangeably with the terms thermal efficiency or fuel-to-steam efficiency. Where the term boiler efficiency is used, it is important to know which type of efficiency is being represented, because thermal efficiency, which does not account for radiation and convection losses, is not an indication of the true boiler efficiency. Fuel-to-steam efficiency, which does account for radiation and convection losses, is a true indication of overall boiler efficiency. The term boiler efficiency should be defined and understood before it is used in any economic evaluation.

Fuel-to-Steam Efficiency

This is a measure of the overall boiler efficiency, including radiation and convection losses, ambient air temperature, burner efficiency, and fuel type. This should take into account the effects of an economizer and air preheater. It is an indication of the true boiler efficiency and should be the efficiency number used in economic evaluations. The fuel-to-steam efficiency may also be called boiler efficiency or total thermal efficiency.

As prescribed by the ASME PTC 4.1, Steam Generating Units, and the actual fuel-to-steam efficiency can be determined in two ways:

1. Input–output or direct method
2. Heat loss or indirect method

Input–Output or Direct Method

Commonly called the direct method; this value is calculated by dividing the boiler steam output, by the boiler fuel input, and multiplying by 100. This measurement provides a snapshot boiler efficiency, given accurate input and output rates. The actual input and output of the boiler are determined through direct measurements, and the data are used to calculate the fuel-to-steam efficiency. Accurate results for the average operational efficiency of the boiler can be calculated using steam and fuel totalizer data.

Heat Loss or Indirect Method

Known as the indirect method, this procedure is often used when fuel usage or steam output is not available. It is calculated by subtracting the stack, blowdown, shell, and miscellaneous losses, in percent, from 100. Since miscellaneous losses are usually very small, they can often be ignored. This measurement characterizes total boiler efficiency under specific conditions and accurately reflects snapshot boiler performance only.

Stack Losses

The stack temperature is the temperature of the combustion gases (including water vapor) leaving the boiler and reflects the energy that did not transfer from the fuel to the steam or water. It is a good indicator of boiler efficiency. The lower the stack temperature, the more effective the boiler design, and the higher the fuel-to-steam efficiency. A rule-of-thumb sometimes used is that a 1% gain in boiler efficiency can be achieved with each 40°F (22°C) reduction in stack temperature. Economizers, air preheaters, soot-blowing devices, and combustion aid chemicals can help reduce the stack temperature.

Another contributor to stack losses is the use of excess air beyond that needed for combustion. Excess air above the theoretical requirement is always used, because the driving force of the excess oxygen ensures that all of the fuel is burned rapidly and efficiently before it leaves the furnace. However, excess air takes energy from the fuel, because it has to be heated to the temperature of the other furnace gases. The heat acquired by the excess air becomes another loss (increasing unavailable energy) in the exit stack gas. Excess air requirements vary with the fuel and burner or stoker used.

Blowdown Losses

All boilers (except once-through boilers) use boiler water blowdown to control the boiler water chemistry within specified limits and minimize scale and corrosion on the waterside. Boiler blowdown is the intentional removal of boiler water, continuously, intermittently, or both.

While boiler water has not evaporated to steam, it still contains a great amount of heat energy that it obtained from the burning fuel. Depending on the boiler operating conditions, the heat loss from boiler blowdown can be significant. Decreases in boiler blowdown can be accomplished by improved pretreatment of feedwater, by operating the boiler at a higher concentration of dissolved solids, or by returning more condensate. Blowdown heat recovery equipment can be used to capture most of the blowdown heat, increasing the overall boiler efficiency.

Radiation and Convection or Shell Losses

All boilers have radiation and convection losses. The losses represent heat radiating from the boiler shell. Radiation and convection losses are essentially constant throughout the firing range of a particular boiler, but vary between different boiler types, sizes, and operating pressures.

Higher Heating Value

The higher heating value (HHV) is the energy produced by the complete combustion of one unit of fuel. By definition, this is the amount of heat released by a specified quantity of fuel [initially at 77°F (25°C)] once it has combusted and the products have returned to a temperature of 77°F (25°C). This value is typically used in the United States when calculating boiler efficiency (Table 31.3).

Fuel	Energy Content (HHV)		Fuel Density	
	Btu/lb	kJ/kg		
Natural gas	23 300	54 159	42.92 lb/1000 ft^3	0.6875 kg/m^3
No. 2 fuel oil	19 400	45 094	7.21 lb/gal	863.9 kg/m^3
No. 6 fuel oil	18 800	43 699	7.95 lb/gal	952.6 kg/m^3
Eastern coal	13 710	31 868		
Western coal	10 090	23 454		
Green wood	5250	12 203		

TABLE 31.3 Typical Fuel Energy Content and Density

Lower Heating Value

The lower heating value (LHV) is the HHV of fuel minus the latent heat of vaporization of the water formed by burning the hydrogen in the fuel. This value is typically used in Europe when calculating boiler efficiency.

Input–Output or Direct Method

In this method of calculating boiler efficiency, the energy obtained from the boiler in the form of steam is divided by the energy supplied to the boiler in the form of fuel. This number is multiplied by 100 to convert the result to a percentage. Equation (31.1) shows the calculation.

$$E = (100)(m_s)(h_s - h_{\text{fw}}) / (m_f)(\text{HV}) \tag{31.1}$$

where E = boiler efficiency, %
m_s = steam mass flow, lb/h (kg/h)
h_s = steam enthalpy, Btu/lb (kJ/kg)
h_{fw} = feedwater enthalpy, Btu/lb (kJ/kg)
m_f = fuel mass flow, lb/h (kg/h)
HV = heating value of fuel, Btu/lb (kJ/kg)

Using Eq. (31.1) requires making several measurements during boiler operation. These measurements should be made during periods of steady boiler operation, in which the boiler has been producing steam at a constant rate for at least one hour. During the data-gathering period, the steam drum water level should be constant.

The feedwater enthalpy (h_{fw}) should be obtained before an economizer, because an economizer is an integral part of the boiler and recovers heat from the flue gas.

As previously stated, the absolute boiler efficiency value is not that important, because the actual efficiency is constantly changing with operating conditions. Rather, it is more important to focus on the relative change in boiler efficiency and the corresponding effect on purchased fuel consumption. While the adjustments below can be incorporated, unless they truly affect the comparison between a base case and an improvement, they can usually be ignored.

- Typically, the enthalpy in the feedwater (h_{fw}) after the deaerator but before the economizer is subtracted from the enthalpy of the steam (h_s), because the boiler does not have to add this amount of energy in the production of steam. If, however, boiler efficiency is used to calculate potential fuel savings for a proposed energy project, the makeup enthalpy value can be used in place of the feedwater enthalpy value to reflect the heat already added to the feedwater. Whichever value is used, it must be used consistently.
- Use superheated steam enthalpy when the boiler contains a superheater. Generally, the effect of attemperation water is ignored but can be included if desired and known.
- Complex utility boiler systems often include reheaters in addition to superheaters. If desired and known, the energy transferred to the reheat steam can be added to the numerator.
- Gaseous fuels are often measured and reported in volume units rather than mass units. Simply adjust Eq. (31.1) as needed to obtain the energy input as Btu/h or kJ/h in the denominator.
- HHV is generally used in the United States, while LHV is commonly used in Europe, for the heating value (HV) of the fuel. It is best to use the actual HV of the fuel being burned, and suppliers can often provide this value. If the actual value is unavailable, use the typical values in Table 31.3.

Heat Loss or Indirect Method

In this method, heat losses are estimated and reported as a percentage of total fuel input energy. The losses are then subtracted from 100% to show the resulting boiler efficiency. Equation (31.2) shows the calculation.

$$E = 100 - \text{Losses} \qquad (31.2)$$

where E = boiler efficiency, %
Losses = total estimated heat losses, %

In theory, the calculated boiler efficiency should be the same regardless of which method is used. In practice, however, measurement errors, unsteady boiler operation, and the omission of some boiler heat losses cause the values to differ slightly. As previously stated, the absolute boiler efficiency value is not as important as the effect of a change in boiler efficiency on fuel consumption.

The heat losses usually included in this method are:

- Stack losses
- Blowdown losses
- Shell losses (radiation and convection)
- Miscellaneous losses

Stack Losses

By far, stack losses are the largest heat losses in a boiler. Many factors affect stack losses, but the largest contributors are boiler design (economizer, air preheater, watertube, or firetube), boiler load, waterside or fireside fouling, failed flue gas path component, and excess combustion air. Stack losses can represent 5 to 30% of the fuel energy. A rule-of-thumb sometimes used is that a 1% gain in boiler efficiency can be achieved with each 40°F (22°C) reduction in stack temperature. Another rule-of-thumb states that each 1% increase in excess oxygen results in a 0.5 to 1% loss of boiler efficiency.

Stack losses are generally estimated by measuring the flue gas exit temperature, ambient air temperature, and flue gas oxygen content. Carbon monoxide and carbon dioxide meters may also be present. Many new boilers are equipped with on-line instruments to measure these parameters continuously, and some boilers even adjust firing conditions automatically to optimize the fuel-to-air ratio. If on-line instruments are not available, portable instruments can be used for spot measurements.

The boiler manufacturer might provide tables or charts showing stack loss versus excess oxygen or air and net flue gas temperature. These tables are also available elsewhere, for example, the ASME PTC 4.1.

Blowdown Losses

Boiler water removed from the boiler to maintain the boiler water chemistry within specified guidelines contains a significant amount of heat. In the absence of blowdown heat recovery, blowdown losses typically represent the second largest energy loss from a boiler. Blowdown losses are usually less than 2% of the total fuel input and can be calculated using Eq. (31.3).

$$L_{\text{bd}} = 100(m_{\text{bd}})(h_{\text{bd}} - h_{\text{mu}})/(m_f)(\text{HV}) \tag{31.3}$$

where L_{bd} = blowdown losses, %
m_{bd} = boiler blowdown mass flow, lb/h (kg/h)
h_{bd} = boiler blowdown enthalpy, Btu/lb (kJ/kg)
h_{mu} = boiler makeup water enthalpy, Btu/lb (kJ/kg)
m_f = fuel mass flow, lb/h (kg/h)
HV = heating value of fuel, Btu/lb (kJ/kg)

The heating value (HV) of the fuel can be either the HHV or the LHV, depending on historical site preference. It is best to use the actual HV of the fuel being burned, and suppliers can often provide this value. If the actual value is unavailable, use the typical values from Table 31.3.

The two mass flow rates can be measured or calculated, and the enthalpy values obtained from saturated steam tables after measuring the temperature of the streams.

Shell Losses

Shell losses represent the radiation and convection losses from the boiler's external surfaces. Expected shell losses are typically less than 1% of the total fuel input for watertube boilers, and less than 0.5% of the total fuel input for firetube boilers, both operating at or close to full load. Expected losses assume there are no problems with the boiler refractory or cladding. Larger boilers lose a smaller fraction of their heat through radiation (Table 31.4).

Boiler Size lb/h (kg/h)	Radiation Heat Loss (%)
200 000 (90 718)	0.5
100 000 (45 359)	0.7
50 000 (22 680)	0.9
20 000 (9072)	1.0

Source: Council of Industrial Boiler Owners, Energy Efficiency Handbook, latest edition.

TABLE 31.4 Radiation Heat Loss at Full Load versus Watertube Boiler Size

Firetube boilers have lower shell losses than watertube boilers, because the shell on a firetube boiler contacts boiler water rather than combustion gas. Since boiler water has a lower temperature than combustion gas, the expected radiation and convection losses are lower.

For a given boiler, the gross magnitude of shell losses does not change significantly with boiler steam load. Therefore, if the loss is considered as a percentage of total fuel input energy, the loss percentage increases with decreasing boiler steam load.

Actual shell losses should be obtained from equipment manufacturers or estimated based on the protocol provided by ASME PTC 4.1. In situations where an exact value is not required, use Table 31.4 for watertube boilers and 0.5% for firetube boilers.

Miscellaneous Losses

Miscellaneous losses include:

- Unburned fuel in the boiler ash
- Effect of attemperation water

Generally, these losses represent less than 0.5% of the fuel input energy and are ignored.

Comparison of Methods

The following parameters may be difficult to measure:

- Fuel mass flow rate
- Fuel HV
- Flue gas temperature
- Flue gas oxygen content
- Steam flow rate

Water flow rates, pressures, and temperatures can usually be measured without significant difficulty. Steam flow rates can often be accurately estimated based on mass balance calculations involving measured feedwater flow and feedwater and blowdown tracer components. Determining which method to use usually depends on which parameters are easiest to obtain.

The average boiler efficiency for modern boilers is 80%. Individual values vary considerably depending on boiler type, size, operating conditions (load, excess oxygen, etc.), and fuel used. Table 31.5 shows boiler efficiency relative to boiler size and fuel type. Table 31.6 shows boiler efficiency relative to excess air. If the calculated value is significantly lower, the boiler might be operating inefficiently, and further investigation is warranted to determine the cause of the inefficient operation. Potential areas to investigate include:

	Boiler Efficiency, %			
Fuel	**10 000–16 000 lb/h (4536–7257 kg/h)**	**16 000–100 000 lb/h (7257–45 359 kg/h)**	**100 000–250 000 lb/h (45 359–113 398 kg/h)**	**250 000–500 000 lb/h (113 398–226 796 kg/h)**
Gas	80	80	81	81
Oil	84	84	85	85
Coal-stoker	81	81	82	83
Coal-pulverized	83	83	86	86

Source: Department of Energy DOE/CS/40325-T1-Vol.2, Taback, H.T.; Macko, J.F; Thompson, R.E., Energy Efficiency of Industrial Steam Boilers. Final Report, July 01, 1982.

TABLE 31.5 “As Found” Operating Efficiency for Boilers

Excess Air, %	Natural Gas, %	No. 2 Oil, %	No. 6 Oil, %	Bituminous Coal, %
2.0	83.08	–	–	–
2.5	82.37	85.35	88.91	–
3.0	81.68	84.63	86.11	87.58
3.5	80.71	83.61	85.22	86.74
4.0	79.72	82.57	84.22	85.79
4.5	78.60	81.40	83.08	84.72
5.0	77.31	80.05	81.78	83.48
5.5	75.32	78.51	80.27	82.07
6.0	74.03	76.68	78.51	80.40
6.5	72.01	74.52	78.43	78.42

Data are representative of boilers equipped with economizers and air preheaters.
Source: Council of Industrial Boiler Owners, Energy Efficiency Handbook, latest edition.

TABLE 31.6 Typical Boiler Efficiencies for Common Fuels versus Excess Air

- Optimize burners to minimize excess air
- Install blowdown heat recovery equipment
- Improve feedwater quality to increase boiler cycles
- Install economizer
- Install combustion air preheater
- Check boiler shell for hot spots
- Operate most efficient boilers at most efficient loading; lay-up other boilers
- Maintain clean surfaces on both waterside and fireside
- Check fireside for gas leaks or gas by-pass

For more information on boiler efficiency, including calculations and measurement methods, refer to the ASME PTC 4.1 Steam Generating Units and the U.S. DOE website.

Heat Transfer Surfaces

Boiler scale typically occurs when calcium, magnesium, iron, and silica, common to most water supplies, react with other contaminants present and exceed their solubility under boiler conditions. The scale forms a continuous layer of material on the waterside of the boiler tubes, causing poor heat transfer.

Scale creates a problem because the thermal conductivity of scale is an order of magnitude less than the corresponding value for mild steel. Even a very thin layer of scale can effectively retard heat transfer. In low-pressure boilers with low heat transfer rates, the scale impedes heat transfer, and boiler efficiency is lost. Deposits may build up to a point where they completely block the boiler tube. At the higher heat transfer rates normally found in higher-pressure boilers, the scale causes the carbon steel tube temperature to increase dramatically, and the metal begins to deteriorate as temperatures exceed 900°F (482°C). Tube failure is typically noted rather than significant efficiency loss in these boilers.

Fuel waste due to boiler scale may be up to 2% for watertube boilers and up to 5% in firetube boilers. Energy losses as a function of scale thickness and composition are shown in Table 31.7.

Scale Thickness, inches (mm)	Fuel Loss, % of Total		
	Scale Type		
	Normal	High Iron	Iron Plus Silica
1/64 (0.4)	1.0	1.6	3.5
1/32 (0.8)	2.0	3.1	7.0
3/64 (1.2)	3.0	4.7	--
1/16 (1.6)	3.9	6.2	--

"Normal" scale is usually encountered in low-pressure applications. The high iron and iron plus silica composition results from high-pressure service conditions.
Source: DOE Steam Tip Sheet #10, Revised June 2001.

TABLE 31.7 Boiler Energy Loss Due to Scale Deposits

Multiple Boilers

A boiler generally produces its maximum efficiency at about 80 to 85% of rating or design steam capacity. Therefore, a powerhouse with a number of boilers in operation gains by judicious loading of each unit. However, a boiler with full heat recovery may have such an advantage in efficiency over one with no heat recovery that it would be better in the overall picture to run the more efficient boiler even at lower ratings than to run the less efficient at its optimum rating. During a period of increased steam demand, the most efficient generators should be loaded first. Optimizing performance requires experience and study.

Alternate Fuels

Many boilers have the ability to burn multiple fuels, such as natural gas and oil or coal and wood. Since the quality of fuel (HV, moisture, sulfur, and ash content) can greatly affect boiler efficiency, the fuel or fuel ratio used should be chosen carefully. Compliance with government regulations must also be considered. Perhaps the easiest way to establish a cost-effective fuel strategy is to compare all fuels based on operating cost per million pounds (kilograms) of steam generated. This requires that the fuel price per million Btu (kJ) be established. Special handling, storage, maintenance, transportation, and other costs (soot blowing, ash removal, and emissions control) for the use of individual fuels should be added to the fuel price if known. Lastly, since different fuels have different combustion efficiencies, the expected boiler efficiency relative to a specific fuel must be considered as well. Table 31.8 shows a hypothetical comparison of the operating cost for various fuels.

Fuel	Price/Sales Unit	Cost*/ 10^6 Btu (Cost/GJ)	Total Cost†/ 10^6 Btu (Total Cost/ GJ)	Boiler Efficiency (%)‡	Steam Cost§ ($/hour)
Natural gas	\$8.00/1000 ft^3 (\$0.28/m^3)	\$8.00 (\$7.59)	\$8.00 (\$7.59)	81	1000
No. 2 oil	\$2.00/gal (\$0.53/L)	\$14.30 (\$13.56)	\$14.75 (\$13.99)	85	1750
No. 6 oil	\$1.50/gal (\$0.40/L)	\$10.04 (\$9.52)	\$11.30 (\$10.72)	85	1340
Coal¶ (stoker)	\$40/ton (\$44.09/tonne)	\$1.46 (\$1.38)	\$2.10 (\$1.99)	82	260

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[*] Using values from Table 31.3.

[†] The total cost estimate includes costs to use fuel, which depend on equipment, equipment age, fuel impurities, soot blowing, local ash disposal, and maintenance. The projected increase based on these items may not be representative of individual circumstances. In addition, the biggest obstacle in burning No. 6 oil or coal is often the initial capital cost of equipment.

[‡] Using values from Table 31.5.

[§] 100 000 lb/h (45 360 kg/h) saturated steam at 600 psig (4.1 MPag) with 1203.4 Btu/lb (2798 kJ/kg) enthalpy and 5 psig (34.5 kPag) deaerator with liquid enthalpy of 195.45 Btu/lb (454.42 kJ/kg). The deaerator liquid enthalpy is subtracted from the steam enthalpy. Steam cost shown excludes cost of water, chemicals, sewer, pretreatment, labor, etc.

[¶] Eastern coal from Table 31.3.

TABLE 31.8 Hypothetical Comparison of Cost to Burn Alternate Fuels

Reduce Steam Demand

A reduction in steam demand can usually be accomplished by maintaining the steam distribution system in good physical condition and by optimizing the operation of steam using process equipment.

Steam pipe leaks should usually be repaired as quickly as possible. Not only do steam pipe leaks present a physical hazard, but they also result in considerable energy waste. Tables 31.9 and 31.10 estimate steam loss per hour at various pressures using Napier's formula. Steam traps that fail open are a form of steam leak and probably account for a large portion of steam loss, relative to pipe leaks, within a facility. They are also more difficult to find. It is common to find 15 to 20% of a trap population not working properly, although not all of these will be failed open. A maintenance program focused on finding and repairing steam leaks is essential to the efficiency of a steam system.

Gauge Pressure (psig)	Nozzle Diameter (inches)							
	1/8	1/4	3/8	7/16	1/2	3/4	7/8	1.0
	Flowrate (lb/h)							
5	12	50	112	153	200	449	611	798
10	16	63	141	192	251	564	768	1003
15	18	74	166	226	295	663	903	1179
20	22	88	199	270	353	795	1082	1413
26	26	103	232	315	412	927	1261	1647
51	41	165	372	506	661	1487	2023	2643
100	72	289	651	886	1158	2605	3545	4631
150	104	416	935	1273	1662	3740	5091	6649
200	135	542	1219	1659	2167	4876	6636	8668
250	167	668	1503	2045	2672	6011	8182	10 686
300	199	794	1787	2432	3176	7146	9727	12 705
350	230	920	2070	2818	3681	8282	11 273	14 723

TABLE 31.9 Steam Loss versus Nozzle Size and Pressure (U.S. Units)

Gauge Pressure (kPag)	Nozzle Diameter (mm)							
	3.2	6.4	9.5	11.1	12.7	19.1	22.2	25.4
	Flowrate (kg/h)							
35	6	22	51	69	90	202	276	360
70	7	28	64	87	113	255	347	453
100	8	33	75	102	133	300	408	533
140	10	40	90	122	160	360	489	639
180	12	47	105	143	186	419	571	746
350	19	75	168	229	299	674	917	1198
689	33	131	295	402	525	1181	1607	2100
1034	47	188	424	577	754	1696	2309	3016
1378	61	246	553	753	983	2212	3011	3932
1723	76	303	682	928	1212	2727	3712	4849
2067	90	360	811	1103	1441	3243	4414	5765
2412	104	418	940	1279	1670	3758	5115	6681

TABLE 31.10 Steam Loss versus Nozzle Size and Pressure (Metric Units)

Insulation is another aspect to monitor closely. Insulation can typically reduce energy losses by 90%. Insulation assures that steam quality and pressure are maintained from the boilers to the point of use. Damaged, inadequate, or missing insulation allows steam to condense early, giving up a portion of its heat as radiation and convection losses. This loss can be significant. For example, at 100 psig (689 kPag) steam contains 1190 Btu/lb (2766 kJ/kg), whereas condensate contains only 309 Btu/lb (719 kJ/kg). Insulation should be quickly repaired or replaced following any maintenance work. Valves and flanges are often left uninsulated and can result in significant energy loss.

Unused steam lines and traps should be turned off, since they can result in significant steam consumption without providing any value. Steam present in unused lines condenses; it might be recovered, or it might be discarded. The steam does not provide useful work and may even result in corrosive damage to the system. Unless isolated, the pipe remains at pressure with a continuous supply of steam to condense.

Proper steam system design improves operational efficiency. Poorly designed systems are most likely to function improperly and fail early. Steam systems should be designed with adequate metering to be able to track steam consumption and routinely monitor usage on a facility-wide basis. Ideally, high-pressure steam should not be reduced through pressure control valves. Venting of steam at any pressure should be minimized, unless it is necessary for the proper operation of specific equipment, such as a deaerator.

Reduce Boiler Blowdown

Boiler blowdown contains a tremendous amount of heat, and efforts to reduce the quantity of blowdown can save both energy and money, if blowdown heat recovery is not utilized. The blowdown rate from a boiler should be established based on several parameters:

- Boiler pressure
- Feedwater silica, conductivity, and alkalinity
- Steam purity required
- Potential for contamination of the feedwater or condensate

The simplest approach to reduce boiler blowdown is to increase the cycles of concentration (COC). However, this must be accomplished carefully and thoughtfully to avoid creating operating problems, such as boiler water carryover into the steam and boiler deposits. The "Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers" (CRTD, Volume 34, latest revision) published by ASME is a good guide to determine the maximum COC for a boiler. If exceeding the ASME guidelines is desired, boiler testing, such as steam purity studies to determine carryover and transport studies to determine deposition, should be conducted. Typically, adhering to the ASME guidelines provides reliable results.

In systems using only manual control of boiler blowdown, installation of automatic blowdown control can often be justified. Because automatic blowdown controls can limit the boiler water conductivity to within 5% of the set point, the average facility might reduce boiler blowdown by about 10 to 20%, when changing from manual control.

The internal treatment program can affect maximum COC. Inorganic additives, such as sulfite and phosphate, contribute to boiler water conductivity, which is one of the ASME limits. In some cases, changing to organic treatment products can reduce boiler water conductivity and allow higher COC. This approach should be evaluated on a case-by-case basis.

If further increase in COC is desired, improved makeup water pretreatment can be considered. For example, replacing conventional ion exchange softeners with demineralizers or reverse osmosis (RO) membranes, allows higher COC by reducing the mineral content of the makeup water. This is akin to higher condensate recovery discussed below. However, the upgraded makeup water pretreatment is more expensive, in both capital and operating costs. For each application, the increased makeup water pretreatment costs must be compared with the decreased boiler operating costs, to determine if this project is justified.

Savings that can be achieved by higher COC are significantly lower, if blowdown heat recovery exists.

Recover Blowdown Heat

During the boiler blowdown process, water is discharged from the boiler to mitigate scale formation, corrosion, and boiler water carryover. However, boiler blowdown wastes energy, since the lost liquid is at about the same temperature as the steam. Much of this heat can be recovered by routing the boiler blowdown through a flash tank to recover low-pressure steam and to a heat exchanger that preheats the boiler makeup water.

Typical blowdown flows range from 0.5 to 20% of feedwater flow. Any boiler with continuous surface blowdown exceeding 1% of the feedwater flow rate is a good candidate for blowdown heat recovery. The heat exchanger should be located downstream from the makeup water pretreatment process to minimize fouling of the heat exchanger.

The heat recovery potential depends on boiler size, system pressure, annual hours of operation, boiler load, and the boiler COC. Heat recovery potential can be calculated using Eq. (31.4):

$$\mathrm{HR} = (m_{\mathrm{bd}})(h_{\mathrm{bd}} - h_{\mathrm{mu}})E \qquad (31.4)$$

where HR = heat recoverable, Btu/h (kJ/h)
m_{bd} = blowdown mass flow, lb/h (kg/h)
h_{bd} = blowdown enthalpy, Btu/lb (kJ/kg)
h_{mu} = makeup enthalpy, Btu/lb (kJ/kg)
E = heat recovery equipment efficiency, decimal

An important advantage of continuous blowdown is that it permits heat recovery from the blowdown water. The use of a blowdown flash tank and heat exchanger minimizes the heat losses and maximizes energy reuse. Flash tanks permit the recovery of low-pressure steam that may be used in the deaerator or air preheat coils; the use of a heat exchanger allows for the recovery of additional heat from the hot flash tank water. In a low-pressure system, a heat exchanger can be used by itself.

Flash tanks are of benefit only when additional low-pressure steam can be used (e.g., in a deaerator, air preheat coils, and process heater). Blowdown heat exchangers are most often used to preheat boiler makeup water before the deaerator, but can be economically used to heat process streams. Figure 31.3 shows a typical heat recovery system.

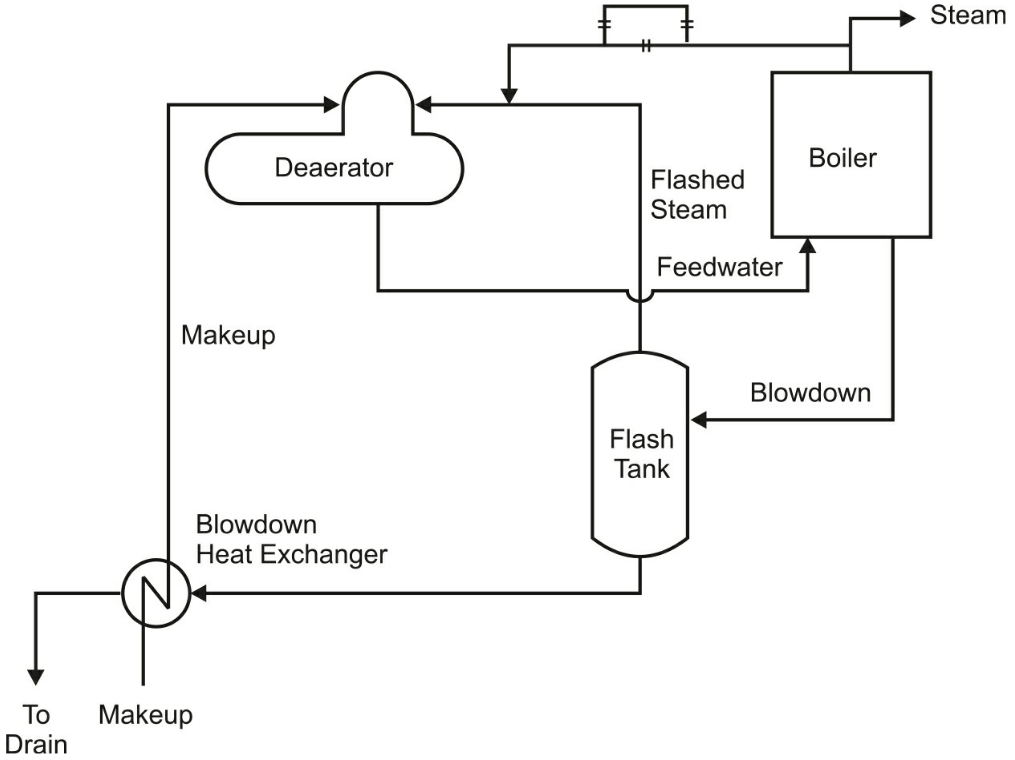


FIGURE 31.3 Typical boiler blowdown heat recovery system.

The blowdown heat exchanger must be installed in a location where inspection, maintenance, and cleaning can occur, at least during boiler outages. Installing the exchanger in a remote, nonaccessible location only means loss of heat transfer efficiency over time and energy (money) lost. Installation of simple dial temperature gauges on the inlet and outlet of the makeup water and blowdown is highly recommended. Although mass flows are not exact, a reasonable energy balance can be done with this simple, inexpensive equipment (making sure they are visible to workers). By using simple temperature monitoring, the decision on whether to schedule cleaning or maintenance of the blowdown heat exchanger can be made.

Flash Tank

Flash tanks are commonly used to generate flash steam, supplementing steam generated in fired boilers. Flash steam is often used in the deaerator. The flash steam is generated by directing continuous boiler blowdown, condensate, or other hot water stream to a flash tank that operates at a lower pressure. The lower pressure environment allows some of the water to flash, creating the flash steam, while most of the water remains liquid at lower pressure and temperature. The most common use of a flash tank is to recover heat from boiler blowdown.

In some lower-pressure systems, a flash tank is used only to reduce the pressure and temperature of water before discharge. In these systems, the flash tank is not used to recover heat and generally operates at atmospheric pressure.

Figures 31.4 and 31.5 shows the amount of flash steam available at various inlet and flash tank pressures. The amount of flash steam from a flash tank can be calculated using Eq. (31.5):

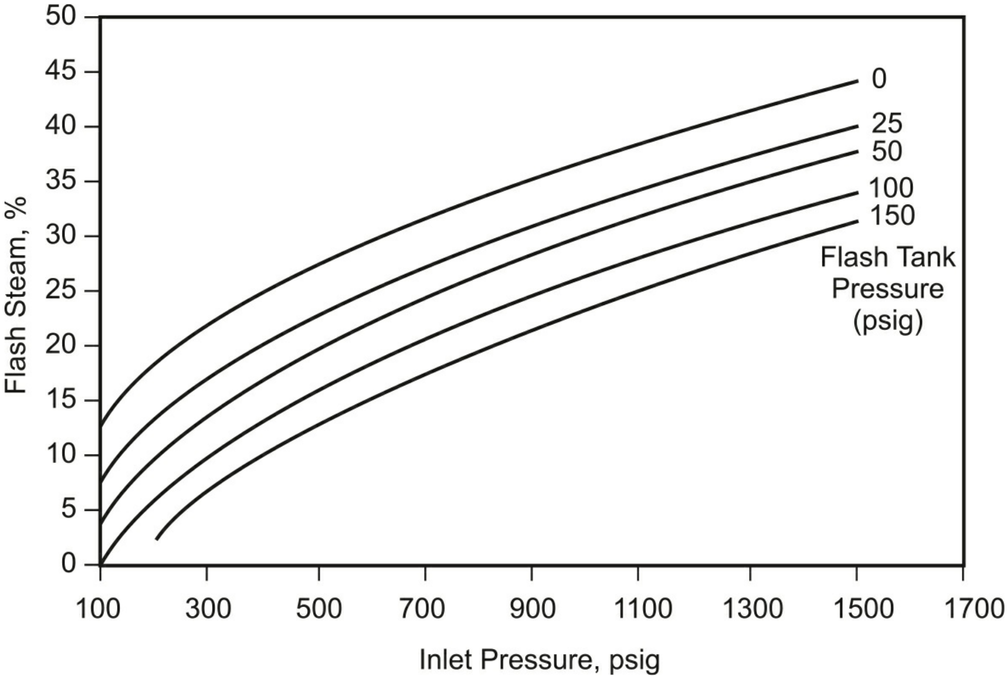


FIGURE 31.4 Percent flashed steam from flash tank.

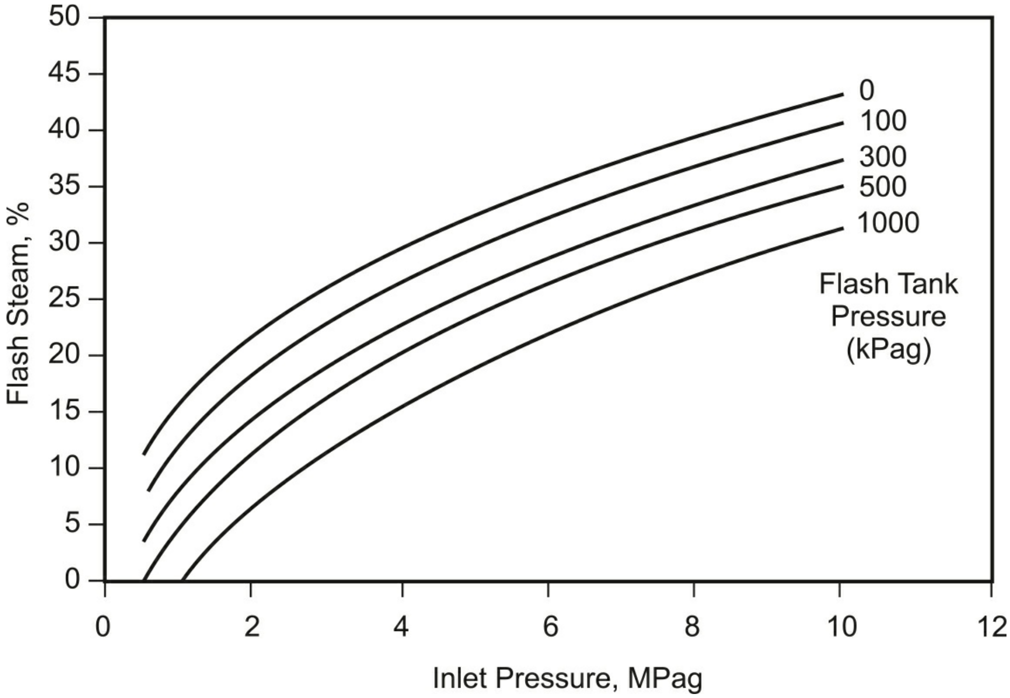


FIGURE 31.5 Percent flashed steam from flash tank (metric units).

$$m_{\text{fs}} = (m_i)(h_i - h_{\text{fl}})/(h_{\text{fs}} - h_{\text{fl}}) \tag{31.5}$$

where m_{fs} = flash steam mass flow, lb/h (kg/h)
m_i = inlet mass flow, lb/h (kg/h)
h_i = inlet liquid enthalpy, Btu/lb (kJ/kg)
h_{fl} = flash tank liquid enthalpy, Btu/lb (kJ/kg)
h_{fs} = flash tank steam enthalpy, Btu/lb (kJ/kg)

The flash tank recovers energy in the form of steam that otherwise would be lost, and reduces the required boiler steaming rate. The recovery of heat using flash steam from boiler blowdown typically recovers 30 to 80% of the heat that is otherwise lost.

Optimize Condensate Recovery

Returned condensate, being condensed steam, is of high purity and has a relatively high heat content, making it ideal, both economically and technically, for boiler feedwater. Economically, the more condensate returned, the less makeup water required, thereby saving on both water and feedwater pretreatment costs. The high purity of condensate allows the boiler to operate at higher COC while maintaining conductivity standards, thereby reducing costly water and energy losses to boiler blowdown. The higher heat content of condensate [158 Btu/lb at 190°F (367 kJ/kg at 88°C)] as compared to makeup water [28 Btu/lb at 60°F (65 kJ/kg at 15.6°C)] directly reduces the fuel requirements of the boiler to convert feedwater into steam. All condensate collection tanks and return lines should be insulated to assure that condensate is returned at the highest temperature possible.

Technically, the high purity of condensate reduces the overall scale-forming tendency of boiler feedwater, regardless of the sophistication of the makeup water pretreatment system. This results in cleaner heat transfer surfaces and optimal heat transfer rates. Higher quality feedwater reduces the possibility of boiler tube failure due to excessive scaling.

To realize the benefits of a condensate return system, a program of corrosion control must be implemented. Left untreated or treated improperly, condensate can become very corrosive to plant piping and equipment. The resulting products of corrosion can enter the feedwater and form harmful, tenacious deposits on boiler heat transfer surfaces. The lack of condensate corrosion control can ultimately result in the loss of heat transfer efficiency and ruptured boiler tubes, a leading cause of unscheduled plant shutdowns.

Reduce System Pressure

Oversized boiler plants with steam distribution systems using saturated steam are potential candidates for reducing the steam system operating pressure. Steam pressure reduction is accomplished by lowering the boiler pressure. This action typically affects only the highest-pressure part of the steam system. Pressure reducing valves provide the correct pressure in the lower pressure portions of the system—at least in theory.

Savings are primarily in the high-pressure section of the system. They result from reduced energy losses in multiple areas such as steam leaks, boiler radiation and convection loss, piping heat loss, steam trap leakage, combustion loss, and blowdown heat loss. In addition, since the boiler is operating at a lower pressure, less fuel is required to boil a pound (kilogram) of water.

While energy savings can certainly result from reducing steam pressure, there are a significant number of problems that can occur and that may reduce the operational effectiveness of the system. Pressure reducing valves, safety valves, flow devices, and high-pressure steam traps may not work properly and may need to be replaced. Boiler carryover may readily occurs causing wet steam, steam system erosion, and water hammer. Circulation problems may occur in watertube boilers, leading to tube blockage and overheating. Lower steam pressure increases steam velocity within a pipe, and this may lead to excessive noise and pressure drop.

Pressure reduction is not to be taken lightly. A full assessment of the boiler plant and steam system should be made before any attempt at pressure reduction. This assessment should include analysis of the average and peak steam loads in relation to plant capacity. Data on piping, insulation, pressure reducing valves, safety valves, and steam trap condition should be collected. Lastly, steam pressure reduction should be tested to establish the minimum workable pressure for a steam load that is above average but below peak. This test will improve reliability of savings estimates.

Anyone considering steam system pressure reduction for energy savings is encouraged to read the U.S. DOE Steam Technical Brief, “Steam Pressure Reduction: Opportunities and Issues,” DOE/GO-102005-2193.

Optimize Turbine Operation

Power plants that operate condensing turbines can justify careful attention to maintaining a clean condenser. Good heat transfer here means better vacuum and more heat energy available to the turbine. As a rule-of-thumb, unit efficiency decreases by 1 to 2% per inch Hg decrease in backpressure (0.3–0.6% per kPa). Power plants with condensing turbines are not very efficient, as they tend to use only 30 to 43% of the available steam thermal energy, with the remainder lost to the environment when steam is condensed in the condenser.

Most industrial turbines are backpressure or extraction turbines. A condensing turbine may also be present at the facility but is typically used only to balance the steam and electrical demands. A system with both types of turbines is most efficient, when operated at maximum extraction and minimum condensing. An industrial plant burning oil, finds it cheaper in most cases, to buy power than to try to produce it by operating a turbine, where the steam must go to a condenser. However, power generated with extraction or in noncondensing turbines usually costs less than purchased power. This is the essence of the trend toward cogeneration, or “topping” a process need for steam with a turbine exhausting to the process steam line.

Figure 31.6 shows the operating constraints on an extraction turbine generating electric power and exhausting the used steam to a process. The process requirements have a direct bearing on how much power can be generated. Generally, process requirements are rated in Btu/h (kJ/h) and easily converted to pounds per hour (kilograms per hour) based on the enthalpy of the steam.

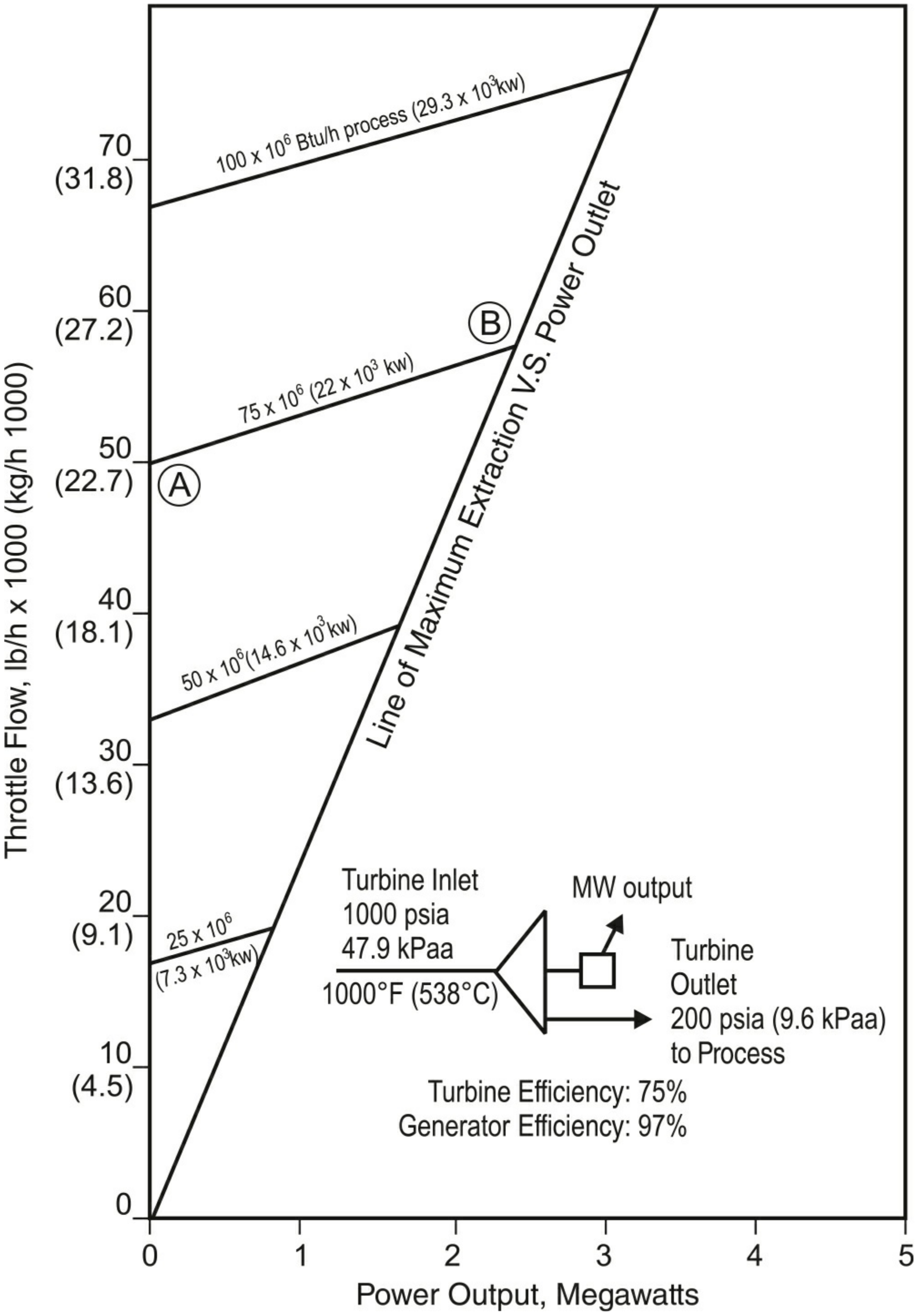


FIGURE 31.6 Throttle flow versus power output at various process steam requirements for fictional noncondensing turbine. Point A represents no electric load; point B represents maximum load.

If the process requires 75 million Btu/h (79 million kJ/h), which is 50 000 lb/h (22 680 kg/h), the power plant could theoretically generate zero power (Fig. 31.6 point A) or progressively up to approximately 2.4 MW (Fig. 31.6

point B), while at the same time supplying the required energy to process. However, in going from zero to 2.4 MW, the turbine throttle flow increases from 50 000 to 57 000 lb/h (22 680–25 850 kg/h). Even though the steam flow increased, the Btu (kJ) per hour to the process remains constant, because the enthalpy in the exhaust steam decreases a proportionate amount.

Some industrial systems are operated to supply a constant electrical demand. As steam demand fluctuates, excess steam not needed by the process may be vented. These systems should consider using a portion of the vented steam to increase feedwater or process water temperatures. Each 10°F (5.6°C) increase in feedwater temperature usually results in a 1% savings in total fuel input, for a typical industrial steam plant that has excess exhaust steam. There is a maximum feedwater temperature, however, which is determined by equipment design. A feedwater temperature that is too high can cause economizer and boiler circulation problems.

SECTION 5

Industries

CHAPTER 44

The Municipal Sector

CHAPTER 32

The Paper Industry

We interact with paper-related products countless times during our daily activities and these interactions can be very different. On one hand, we might bring a new appliance into our house in a cardboard box, where linerboard grade paper laid over corrugated medium provides protection for the product. On the other end of the spectrum, tissue and towel grades of paper touch us in more delicate ways than the corrugated medium. It would be accurate to say there is no single paper industry; rather, it is a collection of industries that produce different grades of paper to serve us in many different ways.

As a major user of water, the paper industry is challenged to balance its water use to meet economic, social, safety, and environmental objectives. Water is one of the major lifelines in the paper making process. It is used as a medium to transport pulp, conduct and retain heat, form a finished product and remove contaminants. Without it, different grades of paper cannot be made. On average, 7800 gallons of water are required to produce one ton of paper product (FisherSolve database). According to the National Council for Air and Stream Improvement (NCASI), water is typically recirculated within the paper making process up to 10 times in the mill before discharge and 88% of the influent water is returned back to waterways. The remaining water is lost through evaporation, within the final product or included in sludge waste. Figure 32.1 shows the typical water footprint of an integrated mill.

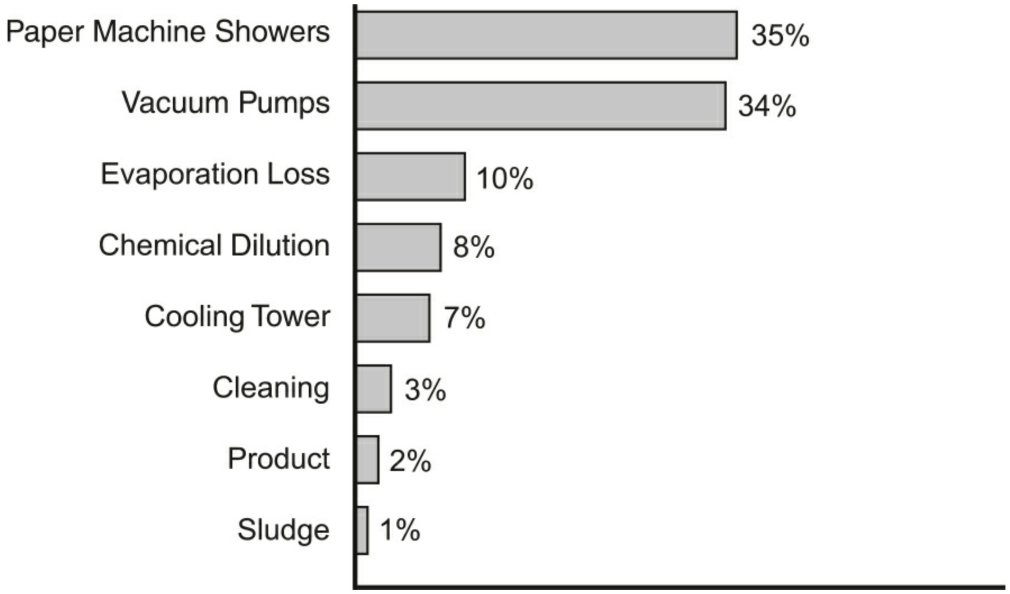


FIGURE 32.1 The typical water footprint of a nonintegrated mill. (*Source: Data compiled from Nalco Water sources.*)

When leaving the headbox of a paper machine, the stock solution is typically 99% water and 1% fiber, as shown in Fig. 32.2. In tissue manufacturing, the consistency might be as low as 0.2% fiber, with 99.8% of the mass being water. When the production process is completed and the sheet is taken up on a reel, the final product may be about 5% water and 95% fiber. Therefore, the paper machine, the essential production component in the papermaking process can be seen as doing two primary tasks. First, it organizes the fibers and additives intended to give the final sheet its desired properties, in accordance with the specifications of that grade of paper. Secondly, it extracts water from the sheet as economically as possible. That is papermaking in its most simple terms, and managing water quality and demand is an integral component of the task.

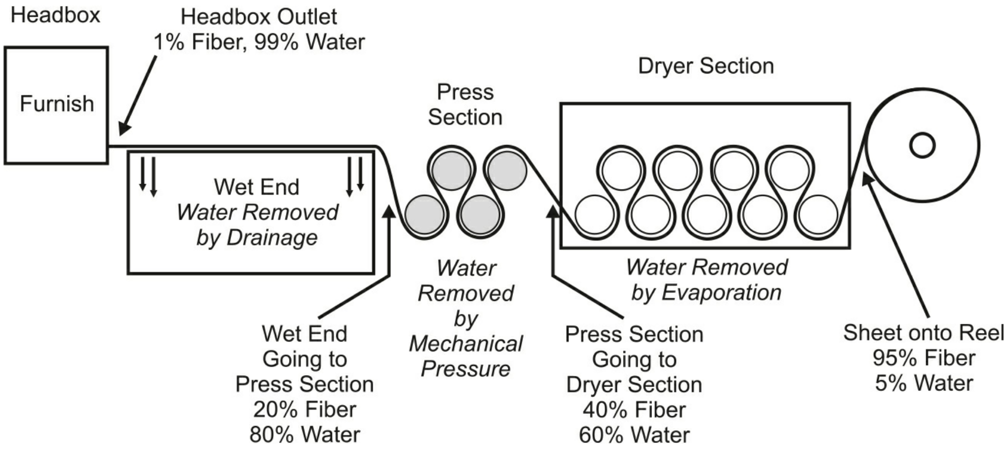


FIGURE 32.2 Water and fiber mass fractions along a paper machine.

With growing concerns of water scarcity, the paper industry is striving to reduce overall water demand to achieve a more sustainable approach to pulp and paper manufacturing. For example, in Fig. 32.3, the U.S. pulp and paper industry significantly reduced its water usage over the last 30 years. The rate of decline of water use has slowed in recent years mainly due to economic barriers to reuse and recycle water while maintaining productivity and meeting product quality specification. As a mill becomes more water closed, the water environment evolves into a new state that most likely introduces and accumulates contaminants such as suspended solids, total dissolved solids, and organic species within the system. In addition, the changing environment can have an impact on physical and chemical characteristics such as increased soluble charge, conductivity, temperature, and lower dissolved oxygen concentration. Evolving conditions can result in deposits, scale, corrosion, increased microbial activity and reduced performance of chemical programs. As these challenges unveil, high capital investments along with associated energy demands, maintenance and real estate footprint would need to be considered as part of the solution. These investments along with the low cost of water often become the main hurdle to execute water closure projects.

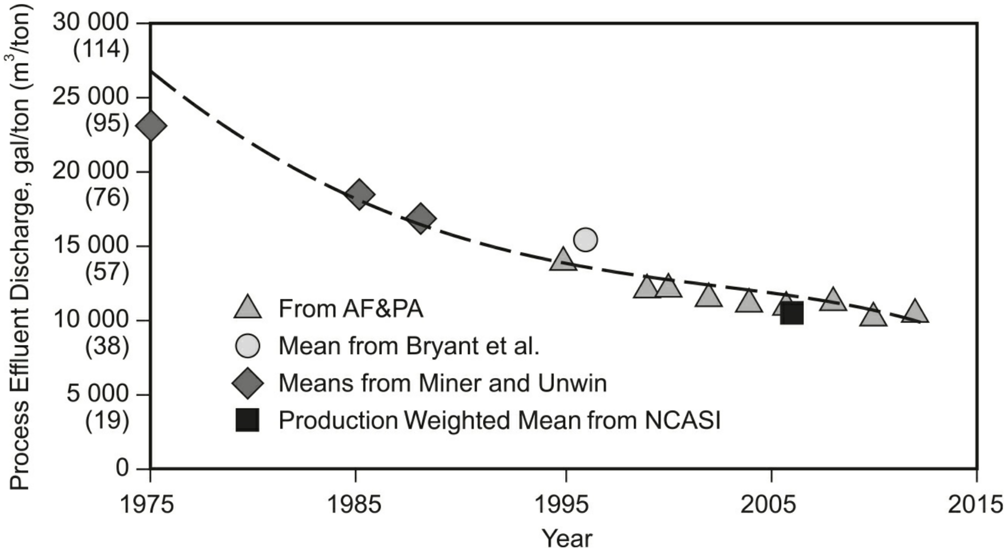


FIGURE 32.3 Trend of effluent volume in the U.S. pulp and paper industry. Note, AF&PA stands for American Forest and Paper Association. (*Source: Reuse of Process Effluents: Research Roadmap; Agenda 2020 Technology Alliance, March 2016.*)

The importance of economical paper production cannot be overstated. Paper producers are not only competing with each other for market space, but they must also compete with other products or media that can provide the same functions as those made of paper. In the grocery store checkout line, we might be asked "paper or plastic?" This is a case where a paper-derived product is directly competing with one made from petroleum. In other examples the competition might not be seen as so direct. For example, the Internet supersedes the daily newspaper as the primary source for current information about the world around us.

This competition demands that paper producers be incredibly focused and agile on providing the precise performance characteristics when marketing their products. Whether it is strength in packaging materials, softness in tissue grades, or printability in graphic and specialty grades, producers try to make paper in a cost-efficient manner with minimum downtime of fixed-cost assets and use of natural resources. Industry operating teams know whether their paper machine is operating on a world-class basis, making them a so-called reference machine that all others strive to match, or if they fall into the dreaded fourth quartile, where any change in product demand or cost structure may target that mill or machine for closure. The one sure thing about the paper industry is the constancy of change. These changes include an influx of new competition from other sources that take market space from paper, such as cost of raw materials and energy required for production, regulatory concerns and general changes in the global market where supply and demand move constantly.

There are other products that are sometimes associated with paper production that are important in their own ways, but secondary in terms of volume and value. Wood is still a valued construction material, and there are still saw mills that cut trees into lumber. In addition, lumber is not always the form that a wood-derived construction material will be made. Plywood, chipboard, and Oriented Strand Board (OSB) are widely used in building construction. In addition, organic chemicals found in wood in widely differing amounts can be extracted for any number of industrial purposes. Turpentine is derived from what we might call the sap of pine trees, and it is still used in paint and coating applications. Tall oil can be similarly extracted from wood during the production process, and it is used in a number of industrial chemicals. Novel uses for waste materials from the papermaking process are put into practice continuously. Recycled fibers that are not acceptable for paper production, are mixed with grass seed in such a way that the fiber holds moisture to improve seed germination as it is applied to poor soils or areas subject to erosion before the grass roots can take hold. Waste wood or fiber that cannot be otherwise used for paper production has a considerable value as an energy source. In most cases, the paper mill uses the fuel value of these wastes to generate the steam and electricity needed to produce the paper. In some cases, there are stand-alone power stations that burn wood waste and supply electricity to the distribution grid.

Industry Profile

Table 32.1 shows paper production rates on a global basis in 2016. The global perspective is particularly important to consider, because both supply needs and demand capabilities are changing rapidly.

Major Grade	% of Global Production Asia Pacific (excludes Greater China)	Europe	Greater China	Latin America	North America
Market Pulp	11%	14%	7%	50%	18%
Newsprint	9%	7%	2%	1%	5%
Packaging	46%	43%	66%	31%	48%
Printing and Writing	25%	23%	14%	8%	16%
Specialties	4%	6%	4%	1%	4%
Tissue and Towel	6%	8%	8%	9%	9%

Source: Compiled using data from FisherSolve.

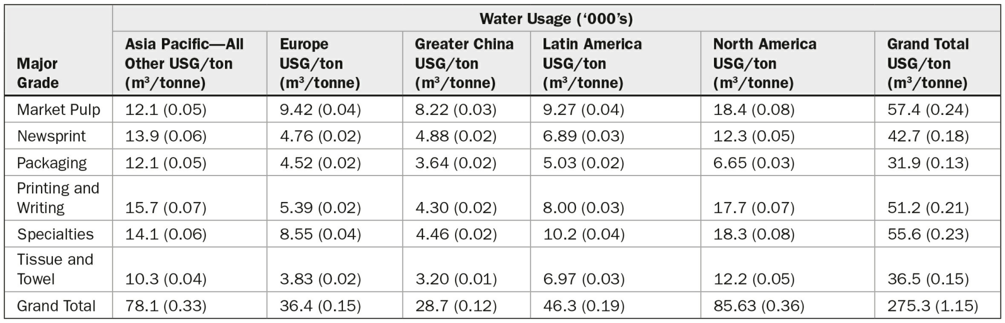
TABLE 32.1 Global Paper Production Statistics, by Grade

The North American and Western European Paper consumer markets are considered mature with minimal or no growth in the volume of paper-related products sold. However, consumer markets in Eastern Europe, Greater China, and Asia Pacific are growing. These areas are increasing their production capabilities, and they may not be export targets for producers in the more mature geographic areas. Latin America exhibits growth in paper product consumption, but it is a rapidly growing producer of market pulp, in addition to finished paper products.

Along with segmentation by paper grade produced, the paper industry is segmented by fiber source used in the process and might be called feedstock. In most cases, the highest value paper products are associated with those mills using virgin fiber, in other words, trees as the starting point for their production processes. Converting a tree into a finished sheet of paper or bale of pulp requires a considerable number of unit operations, and therefore is considerably capital intensive. The availability of water is equally important. Most mills in the world are in areas with both extensive forests and access to large volumes of water. The southeastern United States, Scandinavian region, Brazil in Latin America, and Indonesia in Asia meet these requirements, and are recognized areas where virgin fiber pulp and paper mills are located.

However, there are disparities in these regions as to the intensity of tree farming, which is becoming a primary source of fiber supply to the mill. In an area such as northern Canada, the growing season for a tree is quite short, and mills require trees to have a longer grow period, perhaps 25 to 35 years. Therefore, trees are sent to the mill from further distances. A contrast to this would be Brazil, where selective breeding of Eucalyptus tree has resulted in tree farms that can be harvested in amazingly short time periods. Trees 7 to 10 years old are commercially usable in this region, and further improvements in the growing processes are still being pursued.

As previously stated, paper production often requires large volumes of water for various unit operations. Table 32.2 shows typical water use per ton (tonne) of production by paper grade produced, and its relativity to world areas where production occurs.



	Water Usage ('000's)					
Major Grade	Asia Pacific—All Other USG/ton (m^3/tonne)	Europe USG/ton (m^3/tonne)	Greater China USG/ton (m^3/tonne)	Latin America USG/ton (m^3/tonne)	North America USG/ton (m^3/tonne)	Grand Total USG/ton (m^3/tonne)
Market Pulp	12.1 (0.05)	9.42 (0.04)	8.22 (0.03)	9.27 (0.04)	18.4 (0.08)	57.4 (0.24)
Newsprint	13.9 (0.06)	4.76 (0.02)	4.88 (0.02)	6.89 (0.03)	12.3 (0.05)	42.7 (0.18)
Packaging	12.1 (0.05)	4.52 (0.02)	3.64 (0.02)	5.03 (0.02)	6.65 (0.03)	31.9 (0.13)
Printing and Writing	15.7 (0.07)	5.39 (0.02)	4.30 (0.02)	8.00 (0.03)	17.7 (0.07)	51.2 (0.21)
Specialties	14.1 (0.06)	8.55 (0.04)	4.46 (0.02)	10.2 (0.04)	18.3 (0.08)	55.6 (0.23)
Tissue and Towel	10.3 (0.04)	3.83 (0.02)	3.20 (0.01)	6.97 (0.03)	12.2 (0.05)	36.5 (0.15)
Grand Total	78.1 (0.33)	36.4 (0.15)	28.7 (0.12)	46.3 (0.19)	85.63 (0.36)	275.3 (1.15)

Source: Compiled using data from FisherSolve.

TABLE 32.2 Water Usage per Ton (Tonne) of Paper Production, by Grade and Region

These values follow trends that might be expected based on a cursory understanding of the processes used. Tissue production typically uses market pulp supplemented with recycled fiber as a feedstock, and the pulping processes to convert a tree into usable fiber are not often present. Therefore, water usage associated with these pulping, and especially bleaching operations, is not present. Behind packaging, tissue production requires the second least water per ton (tonne) of production. Newsprint is increasingly made from recycled fiber sources, which requires less water than other production methods.

Market pulp, specialties and printing grades require the most water. These grades are being made to higher brightness or whiteness standards, and contaminant removal to achieve these specifications demands more production process steps as well as water usage. The packaging grade of paper shows the widest range of water utilization. In cases where virgin fiber is used, water use can be high. Some packaging grade mills using recycled fiber as feedstock operate with a zero-liquid discharge (ZLD) where no wastewater is discharged. In these mills, water discharges to the atmosphere through process evaporation and drying of the sheet in the dryer section; in addition, through sludge waste and in the final paper product. Not surprisingly, water reuse and recycle procedures in these mills are most advanced, and the volume of influent is low.

Virgin Fiber Production

Despite ever-increasing efforts to maximize recycling of existing paper products; there still is a considerable need to harvest trees for paper production. With well-managed tree farms now the norm, wood is seen more as a crop than an irreplaceable resource. While requiring more processing steps than recycled fiber supplies, virgin fiber is preferred for the production of several important paper grades.

Wood Yard Operations

A tree destined to become paper, enters the mill through the wood yard. Some mills receive whole trees (called "longwood") on trucks or rail cars. Logs can also come into the wood yard precut to a specified length. Wood in this form is called bolts. Trucks or rail cars are also used to deliver trees in this form. Some mills receive wood already chipped to the specification of their process, and other than chip storage, have minimal wood yard operations. Very few mills still have logs floating into the mill on the local surface water source anymore. This scenario is more from the industry's past than future.

Mills receiving either longwood or bolts must debark the wood before chipping. Debarking involves a rotating drum, where the bolts rub against each other and the surface of the drum. The intent is to remove only the bark and a minimal amount of useful fiber. Water is used in relatively small volumes in the debarking process. To some degree, water serves as a sort of lubricant in assisting bark removal, but more importantly, water added in the debarking process aids in minimizing dust and fiber fines generation. Wastewater from the process is laden with suspended solids and organics from the wood, and goes directly to the waste treatment primary clarifier. Water from this part of the mill is not a good candidate for reuse or recycling. Figure 32.4 is a picture of a debarking process in operation at a mill site.

FIGURE 32.4 Bark removal from cut wood in a rotating debarking drum.

Chipping

The preparation of wood chips is a seemingly simple operation, but one that has considerable importance in the process. Mechanical paper grades are made directly from wood processed through a large machine called a refiner. This is advantageous because each unit of wood mass entering this process yields about 0.9 lb (0.4 kg) of resulting pulp, the highest fractional recovery of any preparation process. (Refining is a term also used in stock preparation operations. This term has multiple uses, which can be confusing.) However, the strongest paper grades are made from a process whereby the fiber is separated from the other constituents of the wood, following a process of digestion. Preparing chips to consistent dimensions is critically important to the digestion process, since the chemicals and heat used must penetrate the chips to liberate the fiber, without degrading the fiber. Having uniforms chips is an important parameter in modern papermaking.

Following the chipping process, the wood is moved via conveyor to a chip storage area. In an attempt to collect stray metal that may be present, most mills today have magnets hung over various locations along the chip conveyor system. Metal would damage or otherwise interfere with downstream processing steps. Chip storage is an often-overlooked operation. A large pile of chips will quickly begin to decompose, or compost, with a resulting loss of fiber mass and quality. Some mills cannot receive wood throughout the year due to local weather conditions, and these mills typically have larger chip inventories. These mills will have bulldozers working the chip pile to prevent the composting reaction.

Very little if any water is involved in the chipping process. In a few cases, control of fugitive dust emissions from the chipping process necessitate that something be sprayed onto the chip pile. Since water would accelerate the composting reactions that decompose the wood, foam generated from water, a surfactant chemical, and air, is used so that less water mass is applied to the chips. Ideally, the foam dries into a crust on the top layer of chips, which limits the ability of prevailing winds to blow fiber fines and dust around the surrounding environment.

Groundwood Pulping

Many pieces of print advertising material need to be produced as cheaply as possible, and there is no intention that this information will need to be saved or archived. Therefore, the most economical process that can be used to make a reasonably good sheet of paper with acceptable printing characteristics is used. The pulp that becomes this sort of paper is made by simply grinding the debarked wood into individual fiber strands by pressing the wood against a rotating wheel. There is a slight loss of organic material from the wood, but nearly 90% of the wood mass entering the grinding process leaves as finished pulp when it is prepared in this way (Fig. 32.5).

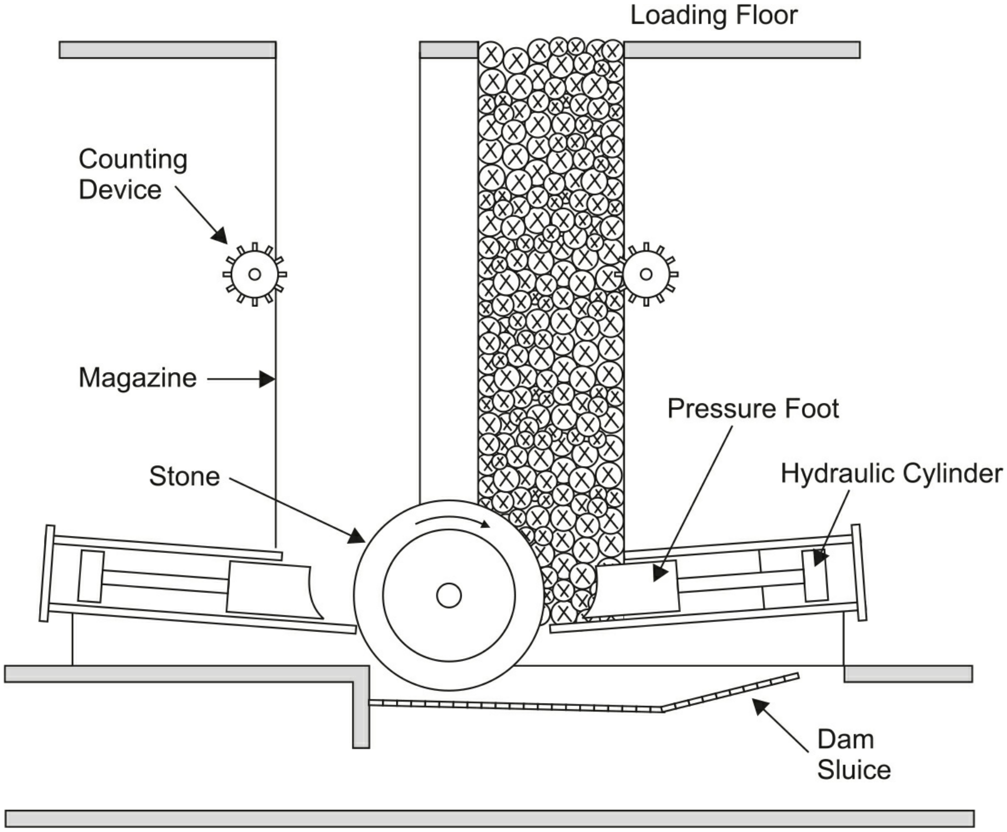


FIGURE 32.5 Logs are forced against a grinding stone to produce groundwood pulp. (*Adapted from Pulp and Paper Science and Technology, Volume 1: Pulp, McGraw-Hill, 1962.*)

Mechanical pulp is quite weak. To achieve the resulting sheet quality required, it is sometimes blended with pulp made in other ways. The primary utility used in the production of mechanical pulp is the electricity needed to rotate the grinding wheel. Producers of this pulp grade pay extraordinary attention to minute-by-minute changes in electrical costs, and can choose to stop production if the cost is too high. Water is only used to sluice the fibers from the grinding process toward final sheet production, and although a large volume of water is used in this process, its quality is not so important. Water reuse is not widely used, because of the tendency of the water to extract organics from the pulp. Too high an organic content can make production of acceptable sheet brightness difficult to achieve.

Thermomechanical Pulping

An advancement over groundwood pulping for the production of primarily newsprint grade paper that has come into widespread use in the industry is thermomechanical pulping, often simply called TMP. The application of steam to the wood chips in a confined chamber allows for pulp of better quality, resulting in better sheet strength. TMP rivals chemical pulp in quality, but uses considerably less water, chemicals, and energy. While the fiber yield is not as high as is achieved with mechanical pulping, it is considerably higher than what can be accomplished with a chemical pulping process. In the highly cost competitive world of newsprint paper production, the TMP process, or some derivation, has assumed the leadership position.

The TMP process begins with wood chips first washed with water. The water quality is not important at this stage, and a recycled stream is often used. Chemicals may be applied at this early stage, to have a maximum effect at partially dissolving the bonds holding the fibers together. This step is called impregnation. In some cases, this system is called CTMP, reflecting the addition of chemical to the classic TMP process. The material then passes into a heating chamber, where the direct application of steam heats and softens the fibers. Finally, mechanical grinding results in the pulp quality required for production, with multiple adjustments being possible to yield optimal fiber length and strength.

Another version of the process is called BCTMP, where bleaching additives result in a whiter pulp for higher value paper production. Hydrosulfite and hydrogen peroxide addition accomplish the brightening of the pulp.

Chemical Pulping—Kraft Process

The last part of the 20th century saw the Kraft process become the dominant method for chemical pulp preparation in papermaking. Because of intensive recycling of chemicals, the generation of steam as a by-product, and dramatically reduced environmental impacts, the favorable performance characteristics of Kraft pulping are seen worldwide. Figure 32.6 shows the Kraft pulping process in a schematic form, and the following discussion will describe the various unit operations and the role water and steam have in many of them.

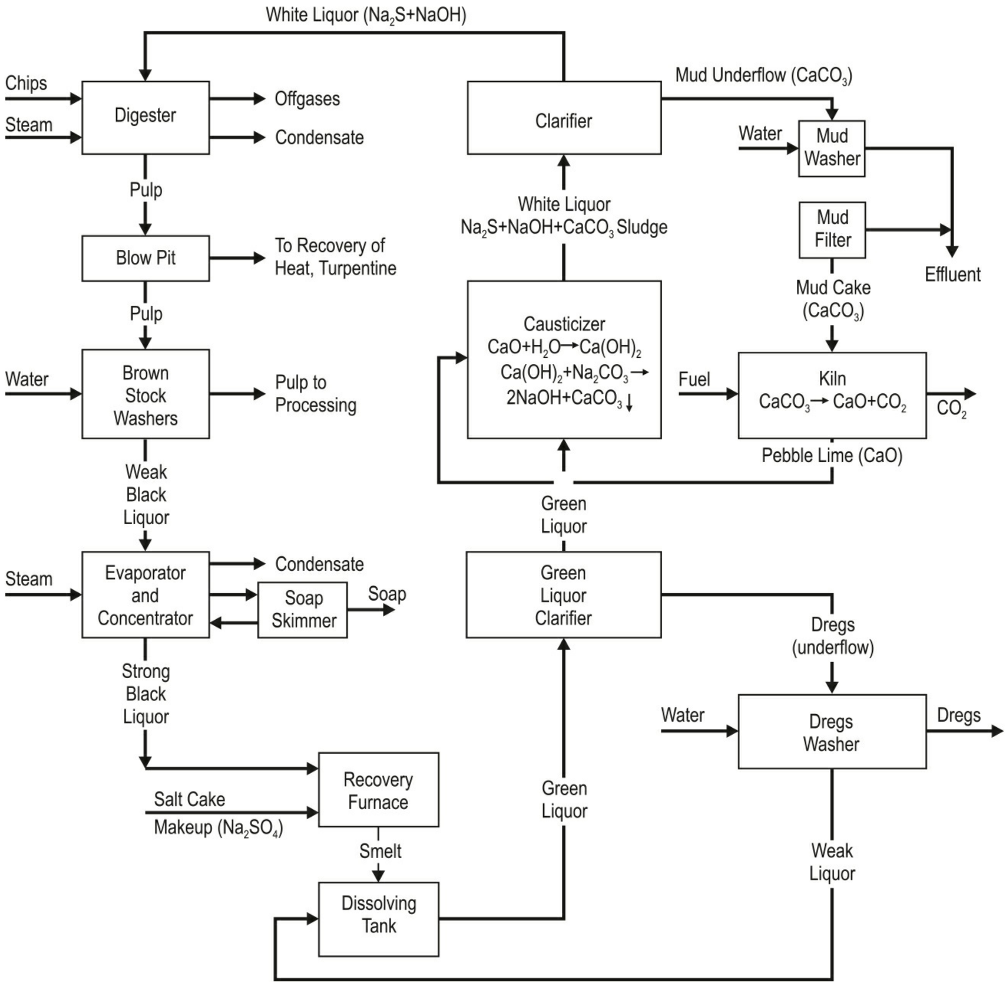


FIGURE 32.6 Kraft pulping process flow diagram.

Digestion

As with any cyclic process, it is sometimes difficult to find a point of entry. This discussion will start at the point where the wood chips enter. The chemicals used to dissolve the internal bonds holding the wood chip together are sodium sulfide and sodium hydroxide. These chemicals called white liquor when combined together, contact the chips in a pressurized vessel called the digester. In earlier times, batch digesters were the norm, and a mill would have a series of these vessels in a line to provide a nearly continuous supply of pulp. Continuous digesters are now the norm, and the Kamyr brand (Fig. 32.7) is nearly ubiquitous. After a contact period of about an hour at a temperature near 250°F (121°C), depending on the species of wood, complete chip heating and dissolution of the bonding elements is achieved.

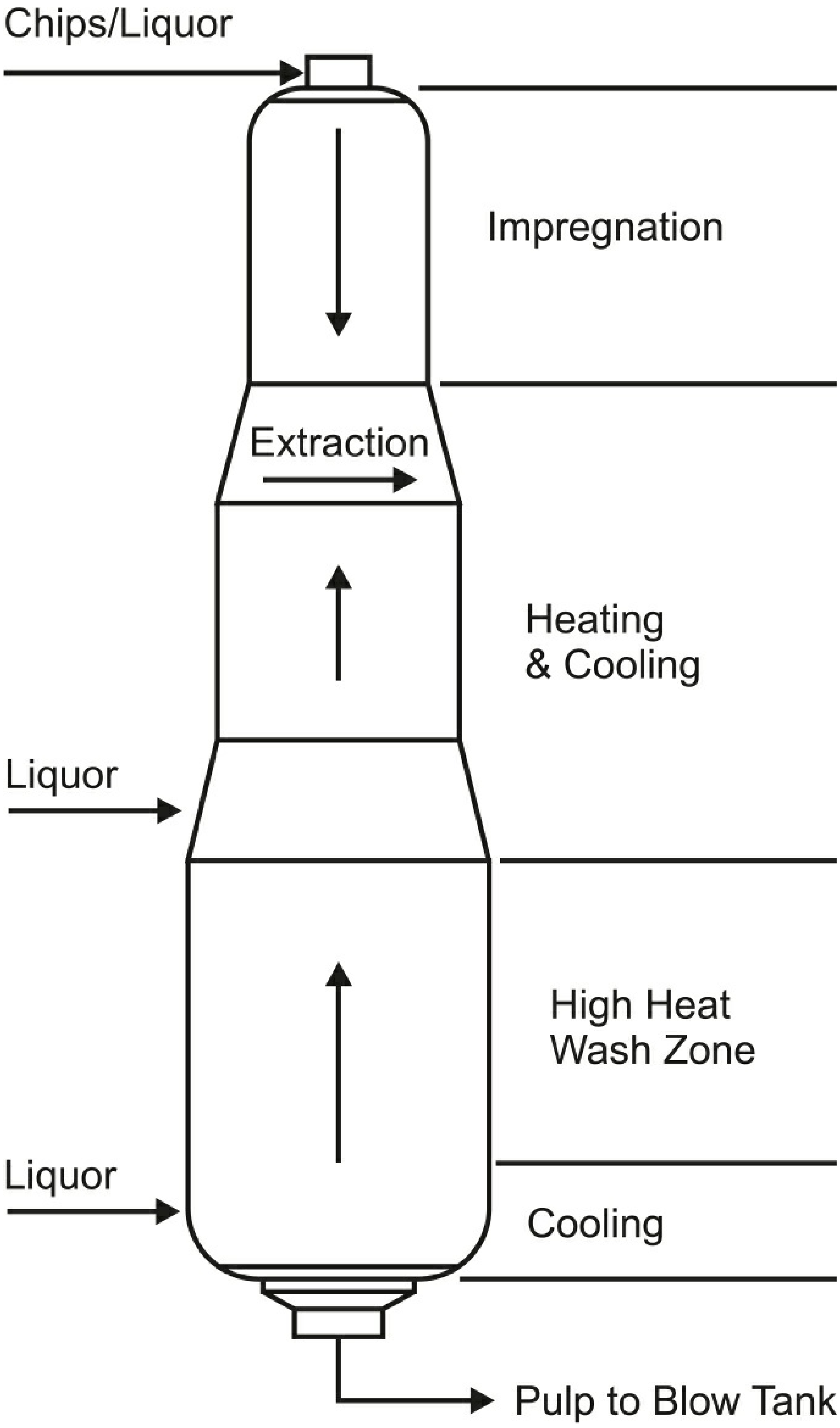

Chips/Liquor
Impregnation
Extraction
Heating
& Cooling
Liquor
High Heat
Wash Zone
Liquor
Cooling
Pulp to Blow Tank

FIGURE 32.7 Compartments of continuous digester.

A major difference between how batch and continuous digesters function is seen in how steam is used to heat the solution. In a batch digester, steam is directly applied to the chips and chemicals. This results in no condensate being returned to the powerhouse for reuse as boiler feedwater. The continuous digester has indirect heaters, which adds the heat to the chemical solution across a heat exchanger. This allows the steam condensate to be returned to the powerhouse, resulting in water and energy savings. However, the possibility of chemical contamination should a heat exchanger leak, requires additional monitoring of the condensate quality, and best practice is to have diversion capability should a leak occur.

Blow Tank

The pulp leaves the digester and enters the blow tank. In the blow tank, the pressure established in the digester is released. The drop in pressure causes moisture that has penetrated the chip interior to flash, which blows the chip apart, releasing the fibers for processing as pulp. Steam vapor is condensed and collected, with process water being heated on the other side of the heat exchanger. Free water drained from the pulp and the condensate stream is routed to an evaporator system, so that the spent chemicals from the process can be collected, regenerated, and reused. Failure to collect the cooking chemicals and the waste gases associated with the process would make Kraft pulping economically unattractive and an environmental nightmare.

Brown Stock Washing

The next step in the process is called brown stock washing. Here, the pulp and water collected from the evaporator set downstream are contacted across a series of vacuum rotary drums (Figs. 32.8 and 32.9). The chemical residuals remaining in the pulp are diluted in this part of the process. Each stage of washing can achieve about 80% dilution of the chemicals, and three or four stages of washing are used to get to 99% ionic removal efficiency.

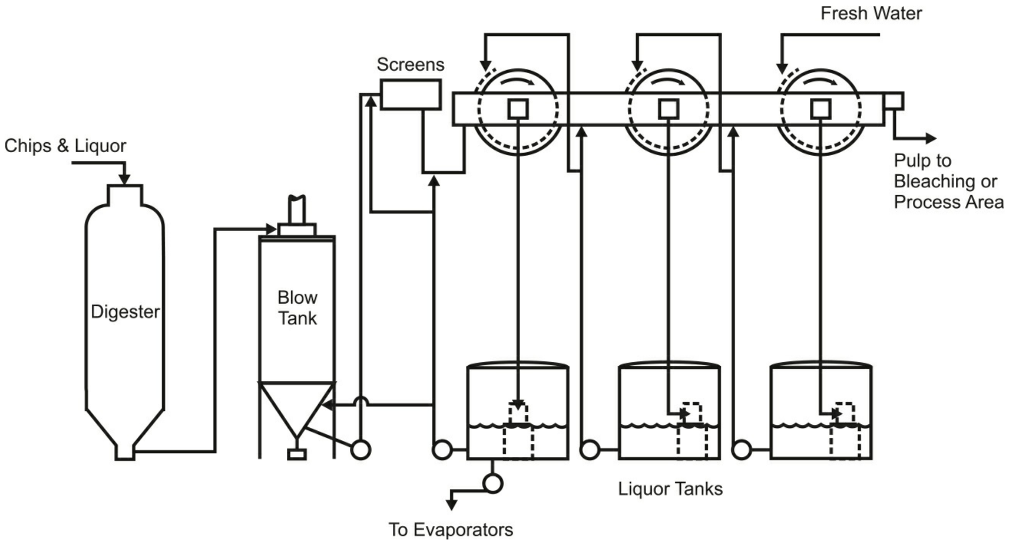


FIGURE 32.8 Diagram of a brown stock washing system.

FIGURE 32.9 Photograph of a brown stock washing system.

There are several mechanical, operational, and chemical factors that impact brown stock washer efficiency. The entrainment of air with the pulp can generate considerable foam, and the application of chemical defoamers to the process is quite common. Oil-based defoamers dominated this application for many years, but the global cost of hydrocarbon added to environmental concerns over volatile organic carbon (VOC) emissions from industrial sources has led to wide acceptance of silicone as the carrier solution for modern defoamer products. The replacement of oil-based by silicone-based defoamer products has resulted in improved cost-effectiveness and better paper machine runnability.

The pulp streams leaving the brown stock washers go on to either bleaching or directly to paper production, and a liquid waste stream called weak black liquor. Except for the cellulose fiber, the white liquor used as the cooking solution in the digester now contains all of the organics present in the original wood supply, so it is considerably darker in appearance. Since it has no further purpose in the paper production process, the weak black liquor can be thought of as a waste stream. Instead of disposing of the weak black liquor, paper mills embark on a process of chemical recovery, so that the chemical can be reconstituted for another pass through the digestion process. This process begins in a multiple effect evaporator set.

Evaporator Operation

The solids concentration of weak black liquor is increased by the evaporation of the accompanying water phase by heating the solution until the water flashes. This is done is a series of vertically oriented shell-and-tube heat exchangers, that have steam as the heat source on the shell side, and the concentrating black liquor on the tube side. Historically, the black liquor flow has been in an upward direction on the tube side of the exchanger, which is called rising-film operation. More recently, improved process efficiency has been realized with falling-film units, where the liquor flow is downward. As previously mentioned, black liquor concentration is conducted in a series of evaporation exchangers called effects, but steam from the powerhouse is only used in one, where the liquor reaches its highest concentration, usually around 55 to 60% solids (Fig. 32.10).

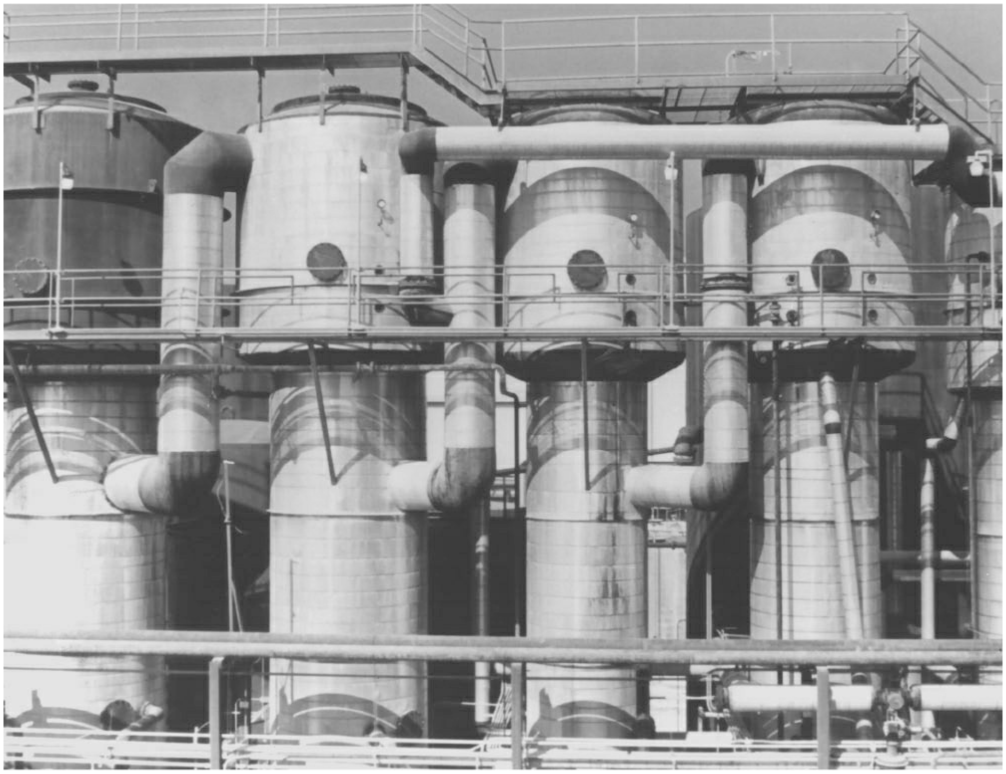


FIGURE 32.10 Kraft process multiple-effect evaporator set. (*Courtesy of HPD Corporation*.)

The evaporation is performed in a series of exchangers, so that they can be operated at different pressures, using the decreasing pressure as the chance to flash vapor from the remaining energy present in the condensate phases. The first effects (or the last effects, depending on the mill's numbering system for the effects) operate at greater than atmospheric pressure. However, the other end of the evaporator set is under vacuum conditions, so that even more water can be evaporated as the heating medium cools. This is an important energy savings aspect of the design, and allows for more pounds (kilograms) of water to be driven from the liquor than pounds (kilograms) of powerhouse steam are used. In fact, systems are operated to routinely achieve 4 to 5 lb (kg) of water evaporated from the liquor per pound (kilogram) of steam applied, and the most modern system will design for 6 to 7 lb (kg) of evaporation per pound (kilogram) of steam used. This concept of steam economy is very important to the cost-effective operation of the Kraft pulp process.

As the water is driven from the liquor, liquid condensate is formed in each evaporator body. This form of condensate has several names: foul condensate, dirty condensate, or contaminated condensate. It is not pure enough to be returned to the powerhouse for use as boiler feedwater, but it has an important role in the process as the wash water used in the brown stock washers to dilute the concentration of cooking chemicals remaining with the pulp.

Depending on mill nomenclature, the first or last effect uses the fresh steam from the powerhouse. This condensate can be returned to the powerhouse for reuse as boiler feedwater, but only if certain precautions are taken to assure that the black liquor has not leaked into the low-ionic content condensate. The best practice is for systems to have in-line conductivity sensors on the condensate flow that trigger a diversion valve if a higher conductivity value is detected. An important design consideration is for the lag time between the conductivity sensor and the diversion valve to be less than the time it takes for the liquor to flow between the points in the systems. Most mills have their own individual horror stories about what happens to their systems, when a liquor leak occurs and the diversion system fails to operate. Therefore, it is becoming standard practice to have redundant capabilities, one located and maintained in the pulp mill area, and a second at the powerhouse as additional protection for boiler feedwater.

At the other end of the evaporator set is a condenser to extract the last heat content from the flashed vapor. Water conservation in this cooling application is accomplished by having a cooling tower service this condenser, but the frequency of process intrusions into the cooling water makes the operation of this tower very demanding. Since it is the purpose of the cooking chemical to help dissolve the wood chips in the digester, when contact is made with a cooling tower made from wood, a similar digestion process can occur. In addition, the organics that come along with the cooking chemicals offer a food source for microbial populations, which can be troublesome to both the tower and the performance of the condenser. It is necessary to monitor the structural integrity of cooling towers that service evaporator systems to be sure they are safe.

Cascade Evaporation

The solids content of liquor leaving the evaporator set is usually around 55 to 60%, but this is still below the desired threshold for burning in the recovery boiler. Therefore, an additional concentrating step is taken. In older recovery operations, this was done by contacting the black liquor with the flue gas from the recovery boiler in a device called a cascade evaporator. Cascades are in disfavor for modern mill operation, because they represent a fire hazard and because of the environmental challenge they cause in controlling odors emanating from the recovery process. A cascade evaporator can increase the solids content in the now concentrated black liquor, up to 65 to 70%, which is readily combustible in the recovery boiler.

Concentrator Operation

An alternate to the use of the cascade evaporator for extracting the final amount of water from the black liquor is called a concentrator. This unit looks very much like an additional effect in the evaporator set, and functions in the same way (Fig. 32.11). Concentrators can be designed to provide liquor solids up to 80%, which makes the combustion more efficient, since there is less energy required to evaporate the water present in the liquor. At this solids concentration, black liquor is quite viscous and hard to pump, but these are challenges that operating teams handle in exchange for the benefits they derive. Again, steam from mill headers is used as the heating medium in the concentrator, and precautions against contaminated condensate being returned to the powerhouse must be taken. As the liquor leaves the concentrator or the cascade evaporator, it is ready to be burned in the recovery boiler, a combustion unit unique to the Kraft process and the economic heart of this mill design.

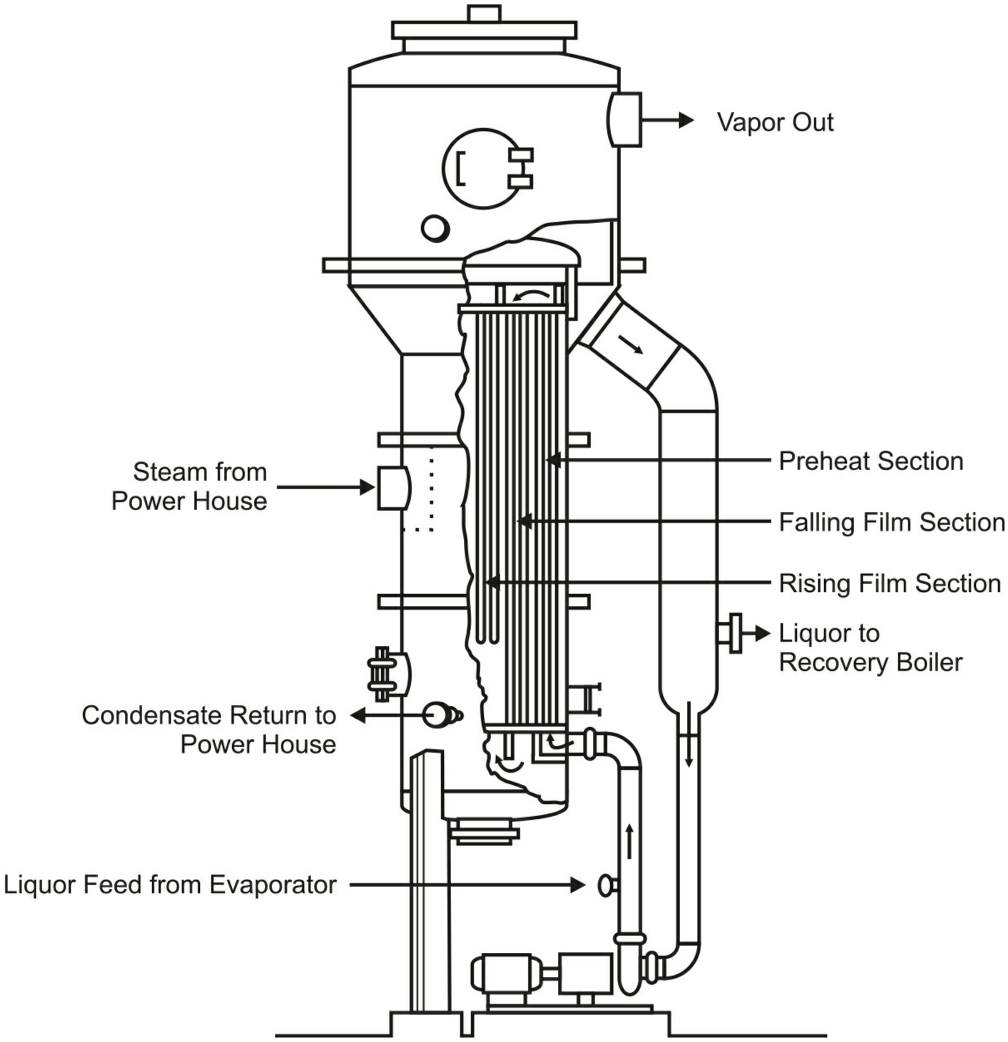


FIGURE 32.11 Black liquor concentrator.

Kraft Process Recovery Boiler

It is hard to imagine that any other piece of industrial equipment that does not touch the product being produced, in this case the sheet of paper or pulp, is more critical to the financial success or failure of the mill than the Kraft process recovery boiler. This unit performs two indispensable feats in an incredibly economical way. However, for these benefits, there are also unique challenges that must be faced and overcome in operating these units.

On the fireside, the Kraft process recovery boiler is unique in that its fuel is the concentrated black liquor that contains the spent chemicals from the digestion process. By managing the air input to this boiler, it is possible to begin the process of reconstituting the cooking chemicals, instead of treating them as a waste and discharging them to the environment. The organics present along with the cooking chemicals serve as the boiler fuel. Once the combustion process is in sustained operation, the recovery boiler can be generating 40 to 50% of the entire mill's steam requirement at zero purchased fuel cost. While this process was developed at a time when environmental impacts and energy costs were of less importance to the survival of the paper mill, the process has been optimized and improved over the years to become essential.

The concentrated black liquor is simply sprayed into the fireside of the boiler. Some drying occurs immediately, with the moisture going upward with the flue gas flow, and the inorganic cooking chemicals and the organic fraction of the wood falling to the bottom of the furnace. The lowest part of the furnace is maintained in an oxygen-deprived condition, so that the organics can keep burning. The process obtains oxygen from the sulfate ion present, reducing it to the sulfide ion form used in the digester. What develops at the bottom of the recovery boiler furnace is a liquid pool called smelt, molten sodium hydroxide and sodium sulfide. This liquid moves out of the furnace through several channels called smelt spouts, where it is combined with a large volume of water in the smelt dissolving tank.

One unique aspect of the recovery boiler fireside is how the air is managed. In normally fired boilers, the air required to provide oxygen for the combustion process is usually mixed in with the fuel to achieve the cleanest and most efficient burning. The recovery boiler segments the injection of air into three or possibly more separate systems. The primary air zone at the bottom of the furnace is closely monitored to limit oxygen in the smelt bed, so that the reduction of the sulfate fraction of the liquor is complete. A secondary air zone, higher in the furnace, provides sufficient air for final combustion of the organics, and the third or tertiary air injection system is used to assure environmental compliance is maintained. Old recovery boilers have a single forced-draft fan to provide the three air streams that are regulated by louvers or dampeners in the air flow path. Modern units have individual fans on the different air systems for more efficient control.

From a waterside perspective, the operation of the Kraft process recovery boiler is a lot like many other industrial boilers. These are often quite large units, and because of the fouling nature of the inorganic materials on the fireside, the unit heat input factors are quite low, minimizing driving forces that contribute to the accumulation of waterside deposits. The water volume of the boiler is large compared to the steaming rate, so chemical excursions of water chemistry occur more slowly, deflect the water chemistry to a lesser extent, and rebound from the excursion over a longer period. The modern design for a recovery boiler usually incorporates a very large economizer, so that maximum heat can be collected from the flue gas stream. The operation of these recovery boiler economizers is often a major problem for the mill. According to the Black Liquor Recovery Boiler Advisory Committee (BLRBAC), up to 40% of forced outages to these units are caused by economizer failures.

What makes the operation of the Kraft process recovery boiler so demanding is what can happen in the event of a waterside tube failure. With most other boiler designs, a tube failure requiring the boiler to be shut down can cause a loss of production and some increased cost for maintenance. However, water entering the smelt bed could cause a smelt/water explosion capable of causing severe damage to the unit. It is this concern regarding the potential for smelt/water explosions that causes this boiler design to be one of the most closely monitored in any industry. The reason the BLRBAC organization exists is that years ago explosions of this type were disturbingly common. Explosions cause a huge financial hardship for the mill as well as serious safety hazards that includes deaths. In many cases, paper corporations will not rebuild failed boiler systems, causing permanent mill shutdown. As shown in Fig. 32.12, the incidence of these events is now rare.

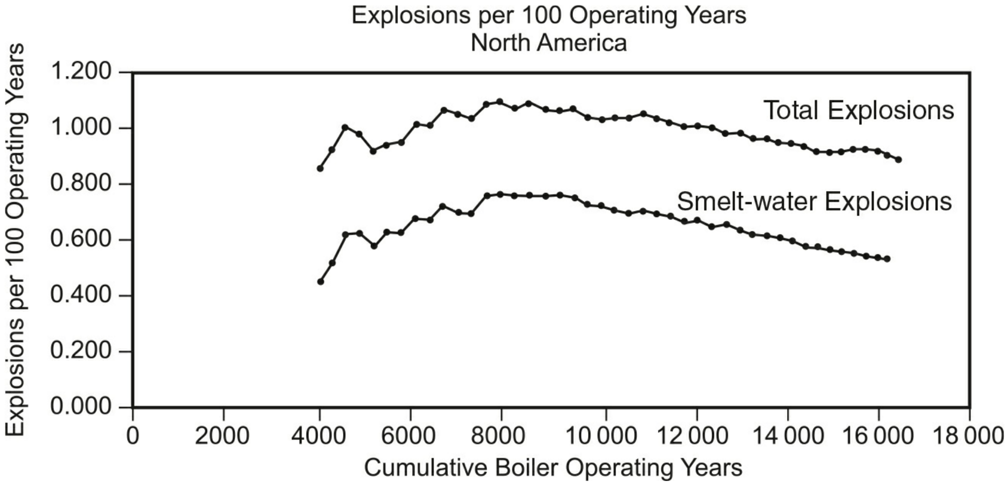


FIGURE 32.12 BLRBAC data documenting recovery boiler operating incident rates. (*Courtesy of BLRBAC.*)

Because of this possibility of an explosion resulting from what would otherwise be a routine part of boiler operation, water treatment for recovery boilers receives special attention. In some mills, higher-quality water is segregated for use in the recovery boiler. Chemical treatment selection gets special attention, and boiler waterside inspections are conducted with increased intensity. It is common for tube specimens to be cut from areas in the lower recovery boiler furnace, where the heat input is the highest and where deposits are most likely to develop. Some paper corporations have strict guidelines requiring that they chemically clean their recovery boilers after five years of operation, despite the absence of any indication that deposits are accumulating at a rate that would cause overheat failures. It would be very rare for any company operating a recovery boiler to attempt to clean the boiler while in service, since deposits coming off the surfaces could either preferentially accumulate in the hottest areas, or could bridge across a tube opening and cause a short-term overheating failure. Because of the intense scrutiny that these units receive, which is appropriate for their importance to the mill, water system failures are quite rare. This is a compliment to the science of water treatment that has been fully utilized in this critical aspect of mill operation, and the dedication of the crews that work on these units on a daily basis.

Smelt Spouts

There are several troughs at the bottom of the recovery boiler that allow the smelt to be conducted into the smelt-dissolving tank, where it can be more fully prepared as the cooking chemical for the Kraft process another time. The most common spout design has an internal cooling water path than maintains the metal temperature in a protective range. One issue that can arise is that the metal can get too cool, causing the smelt to congeal, a process called "jellyrolling." This is avoided by having both minimum and maximum temperature controls on the smelt spout cooling water system. It is an operating practice that these spouts are simply discarded after one year of service. There is a small but growing number of so-called dry spouts on the market that use advanced refractory materials, and thus do not require the same cooling water system. A common operating problem with recovery boilers arises when one or more spouts become plugged by frozen smelt. An uncontrolled "rush" of smelt that occurs when a plugged spout is reopened has caused more explosions since 2002 in the smelt-dissolving tank, than the classic smelt-water reactions inside the recovery furnace area.

Smelt-Dissolving Tank

As the smelt leaves the smelt spout, it is contacted by a large flow of water, which quenches the molten smelt and dissolves the chemicals as ionic salts. This solution falls into the smelt-dissolving tank. Some rumbling is a normal occurrence, although tanks have been bounced off their foundations by larger events. At this point of the process, the dissolved smelt has a greenish tint due to contact with steel materials of construction, and it is called green liquor. Once formed as green liquor, this chemical solution leaves the recovery boiler area, and enters the recausticizing process.

Recausticizing Process

The recausticizing process is a three-step procedure, with several recycle loops associated with each step. The process description provided here will not get the depth of attention as the other parts of the Kraft process. However, this area has a significant impact on mill performance.

Green Liquor Clarification The green liquor clarifier (Fig. 32.13) receives the green liquor from the recovery boiler, and serves to collect undissolved solids called dregs that would cause operational problems downstream in the recausticizing process. A suspended solids concentration in the green liquor coming to the clarifier of about 1000 mg/L (or 0.1% of total flow) is typical. An anionic flocculant is often used to enhance settling of the dregs, resulting in a final concentration of 70 to 80 mg/L in the clarified liquor. This represents 92 to 93% removal efficiency. The dregs from the bottom of the green liquor clarifier are washed by a liquid stream, resulting in some weak liquor that is added to the smelt-dissolving tank.

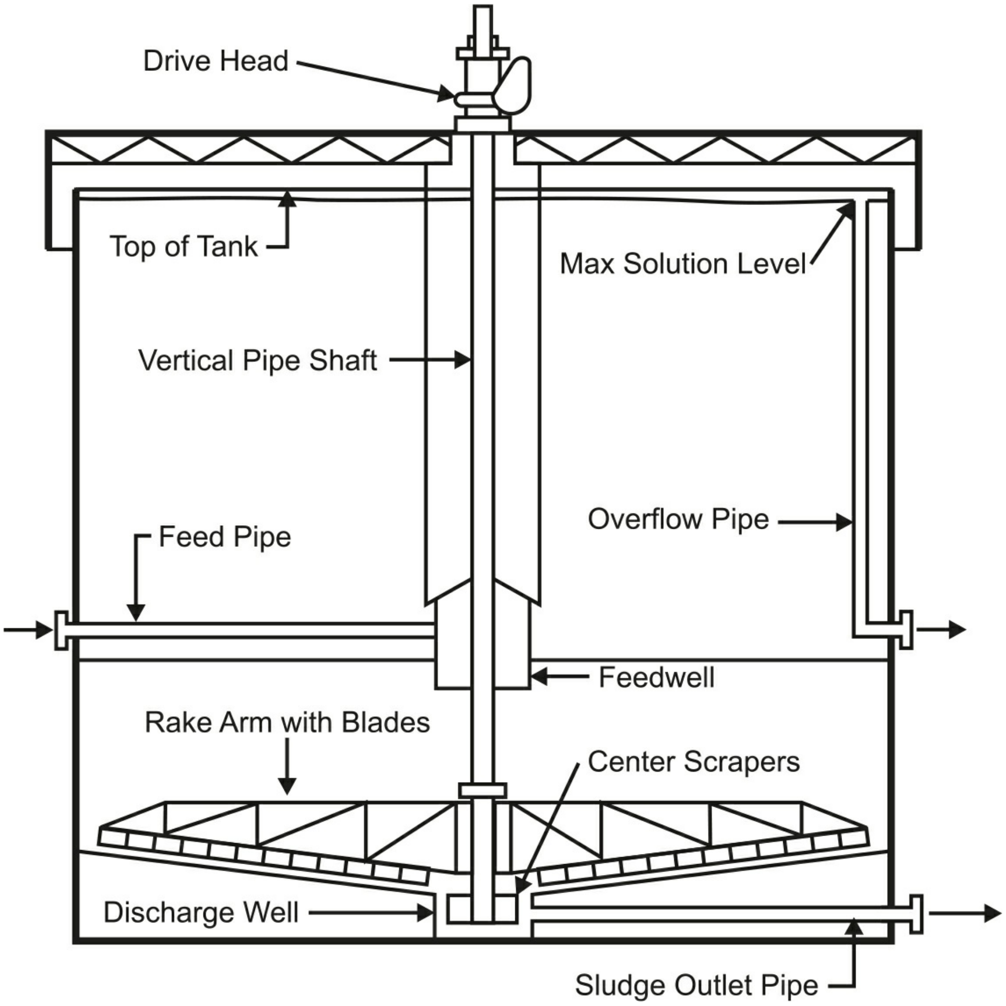


FIGURE 32.13 Green liquor clarifier.

Causticizer The formal conversion of green liquor to the white liquor used for chip digestion occurs in the causticizer system. Green liquor and pebble lime coming from the lime kiln feed the causticizer, where aggressive agitation results in the hydration of the calcium oxide (CaO) chemical form of pebble lime to slaked lime [$Ca(OH)_2$]. Slaked lime is needed to undergo a chemical reaction with sodium carbonate present in the green liquor, which is ineffective in the digestion process. The resulting reaction forms insoluble calcium carbonate, which is separated from the white liquor in the white liquor clarifier, and then goes to the limekiln to be converted back to pebble lime. The water solution in the causticizer is hot, and gets hotter because of the exothermic reactions that occur. This improves calcium carbonate removal, since this molecule, unlike many others, is less soluble in higher temperature solutions than cooler ones. Causticizers are essentially mixing vessels, and a series arrangement is used to promote the chemical conversions. A slight excess of lime (about 1–2%) promotes causticizing efficiency, but too much can hamper solids removal in the white liquor clarifier.

Lime Kiln Many mill engineers have sought refuge from cold weather conditions under the lime kiln. A limekiln is a slightly inclined rotating cylinder, nearly horizontal to ground. Inside the cylinder, the calcium carbonate slurry from the causticizer is exposed to a heated combustion gas stream. Most lime kilns use natural gas as the heating source, but a few are now using petroleum coke and other by-product fuels to operate at lower cost. As the slurry heats and dries, the chemical composition changes, according to this reaction:

$$\mathrm{CaCO_3\ slurry} \xrightarrow{\text{heat}} \mathrm{CaO}\downarrow + \mathrm{CO_2}\uparrow + \mathrm{H_2O}\uparrow \qquad (32.1)$$

The conversion efficiency of the lime kiln is in the range of 90 to 94%. Higher conversion efficiency and a smaller particle size of lime are produced using chains inside the kiln, mostly toward the dry end. The chains do nothing more than flop around as the kiln rotates, literally bashing the particles into a granular form. One operational problem that occurs in lime kilns is the formation of rings, which blocks the flow of the lime particles down the kiln. Some kilns have wet scrubbers on the outlet flue gas stream, to collect the smallest lime particles that are entrained along with the gases. The presence of calcium salts from the kiln makes chemical treatment of this system demanding, even when the water supply is high quality.

White Liquor Clarifier The calcium carbonate precipitates formed in the causticizers are separated from the ionic sulfide and hydroxide salts in the white liquor clarifier. Clear white liquor is needed for the digestion process to avoid contaminating the pulp, which makes subsequent bleaching to produce white paper grades more difficult and costly. A clarifier similar to the green liquor clarifier is used, operating at rise rates of 1.6 to 1.8 ft/h (0.49–0.55 m/h). Some mills making higher-quality pulp use a polishing filter following the clarifier to ensure maximum liquor clarity. The precipitates are called lime mud, since the solids content is 35 to 40%. The lime mud is pumped through two stages of washers and filters and inventoried in a storage tank. The lime mud is the feedstock for the lime kiln, which was discussed previously.

The clear white liquor leaving the white liquor clarifier is the primary chemical additive used for the digestion of wood chips in the digestion process, discussed earlier.

Chemical Pulping—Non Kraft

Historically, several chemistries over a range of solution pH values have been used to chemically remove the cellulose fibers from the other components present in the wood chips. Currently, the Kraft process (discussed earlier) dominates the chemical pulping processes. Here, the other chemical pulping processes will be discussed to add some historical context to current operating practices.

Chemical pulping is based on a compromise; the longer the chips are cooked, the higher the resulting fiber yield, but the longer the chemicals involved in the process are exposed to the fibers, the weaker the fibers become. Therefore, close monitoring of the chemical cooking process in terms of the chemistry, temperature, and contact time is required. Before the late 1980s, most pulping operations were conducted in an acidic environment, usually based on salts of sulfur. This was efficient, but the resulting paper had a limited lifespan, since the acidic remnants left in the sheet degraded its structure over time. In addition, the acidic conditions limited the ability to use calcium carbonate filler materials because the acid and the acid-soluble carbonate filler materials are incompatible.

The use of nonfiber filler in the sheet affects the process in two beneficial ways:

1. Nonfiber filler is cheaper than wood fiber, and the cost of materials is reduced.
2. Fillers can dramatically improve the print quality of the sheet, and they are used in many graphics-related paper products.

One of the sulfite pulping processes still in some use is based on the ammonium sulfite chemistry, which is known as the Red Liquor cook. Like the Kraft process, the Red Liquor process features a recovery boiler, although the design and operating parameters are quite different from the Kraft process recovery boiler. Instead of forming a molten smelt pool in the bottom of the recovery boiler furnace, the Red Liquor recovery boiler recovers the cooking chemicals as a fume, in the gaseous state. As such, there is not the same hazard of a smelt/water explosion, but working in the area of a Red Liquor recovery boiler has its own hazards. The occasional release of gases from the boiler requires personnel working in the area to have on their person an escape respirator mask, should the surrounding air become too toxic.

Recycled Pulp Production

While it is not practical to substitute recycled fiber for all virgin fiber used in paper production, increasing the amount of recycled fiber has a number of financial and environmental benefits.

Deinking and Secondary Fiber Use

A major component of the modern environmental movement has been the push to reduce the harvesting of trees as a source of fiber for paper, relying instead on the recycling and reuse of paper as the feedstock for papermaking operations. Secondary fiber (as compared to trees, which would be the primary source) can come from several sources: industrial, commercial, or the result of municipal recycling programs. There are a number of different types of recycled paper, each having its own acronym:

- Old corrugated containers (OCC)
- Old newsprint (ONP)
- Mixed office waste (MOW)
- And many others

The challenge in using recycled fiber as a source of paper is the management of contaminants that can be reasonably expected to be present, such as printing inks, and those contaminants that are highly variable and unexpected. Traditionally, it has been assumed that all detrimental substances that must be overcome arrive with the waste paper. Inks, dirt, and stickies, which are adhesive contaminants originating from wood pitch, white pitch, fillers, etc., have all challenged the equipment and chemistries of effective deinking. However, more recently, water quality in deinking mills has become an increasingly important factor in controlling, and in certain cases, eliminating detrimental materials found to inhibit the brightening and bleaching objectives of every deinking mill.

Incoming waste paper carries with it the seed for the catalase enzyme. Catalase control and elimination has become a primary concern of any deinking mill needing hydrogen peroxide to be effective. Catalase is a detrimental enzyme that attacks and reacts with peroxide. This leaves less peroxide available to bleach the fibers in any bleaching stage (at the pulper, disperser, or at a bleaching tower). Catalase also persists throughout deinking mills in the water loops. The treatment of catalase can only be done in the water circuits, and an in-depth knowledge of dilution and consistency control is essential for treating this problem.

Flexographic ink is another contaminant problem that is most effectively handled through water clarification. Also called flexo ink, it is a water-based ink with an extremely small particle size, too small to be effectively removed through flotation operation. With the removal of almost all deinking wash operations (deckers or washers) and their subsequent replacement with flotation processes, the water clarification loops remain the most effective place in a deinking mill to remove flexo ink.

On its most fundamental level, the deinking of waste paper requires detachment followed by separation of ink, dirt, and stickies from usable fiber. Once this occurs, it is the job of the water circuits in the mill to prevent the re-attachment of any of these detrimental substances back onto the fiber. Every unit operation in a deinking mill that separates ink, dirt, and stickies presents a secondary problem in how to treat the effluent from that specific unit operation. Sewering the entire effluent stream is not feasible in all cases, as the yield of any deinking process is what benchmarks it as financially viable or not. This requires the water loops to be cleaned of detrimental substances without removing the fines and short fiber that contribute positively to the yield.

Oxidative Bleaching (P Stage)

Pulper chemistries continue to focus on ink detachment, and the best pH condition continues to be on the alkaline side. Traditional alkaline chemistries using hydrogen peroxide, sodium hydroxide, sodium silicate, and surfactant are used to swell the fiber, detach the ink, and reverse the alkali darkening process, normally created by the high pH conditions.

Reductive Bleaching (Y Stage)

Reductive bleaching has been more common as both a color stripper and a final brightness enhancer before going to the machine process. Hydrosulfite, direct borohydride injection (DBI), and formamidine sulfinic acid (FAS) are used in various deinking processes with a 1 to 3 point brightness increase being gained from their effect. If a 1 to 3 point brightness increase enables a mill to move into a more value added grade, these technologies are sometimes more cost-effective than buying brighter waste paper or installing a bleaching tower or other brightening unit operation. One drawback of some of these technologies, however, is their interaction with certain microbiological control programs.

Neutral/Near Neutral (pH = 8.0)

Limited success has been found with neutral or near-neutral pulping chemistries. The cost benefit of a near-neutral chemistry should be evaluated against the decrease in quality that occurs from the absence of a bleaching agent, and more effective ink detachment seen in an alkaline process. In many cases, a remedy should be added at the end of the process to make up for the savings realized from the near neutral technology. Much effort continues to be put toward finding more effective neutral or near-neutral pulping programs. Alternatives to both alkaline and near-neutral chemistries have started to be evaluated using enzymes and silicone-based products. Their effectiveness compared to the most recognized alkaline alternative has yet to be established.

Equipment Innovations

The two major changes in deinking mill operations are the introduction of the drum pulper and the flotation cell.

Drum Pulper Many times, a stickie particle will start in a process as a full sheet of plastic, before being twisted and disintegrated as it moves through the process. A typical batch pulper is positioned vertically, resulting in a high shear rotor and heavy fiber-to-fiber interaction. This high shear action creates a detrimental condition in terms of plastic disintegration into stickies. The smaller a stickie is, the harder it becomes to remove from the process.

The drum pulper, in comparison, is horizontally oriented and uses gravity to allow the fiber-to-fiber interactions to take place. This is a much more passive method of detaching the ink, dirt, and stickies, and allows stickies to remain in their larger forms, which makes them easier to remove.

Flotation Flotation technology came from the mining industry. Its concept allows for detached ink, which is hydrophobic in nature, to attach itself to a rising bubble in a flotation cell. The cell is designed to allow the bubbles to collect as froth at the top of the cell and be removed. The treated pulp goes forward in the process.

Flotation technology saw a dramatic improvement in yield. Flotation increased the process yield from a low of 60% to a much better 80% yield. This had a positive impact on the economics of operating a deinking mill, as an alternative source to virgin fiber.

In the early part of the 21st century, the heavy exportation of waste paper to supply the increasing Asian demand tightened the North American waste paper market. It is expected that continued tightening would increase the contaminant loads in available waste paper, demanding new and improved chemistries and equipment throughout the world.

Pulp Bleaching

If a paper mill's final product is a white grade of paper or paperboard, bleaching of the pulp is done in the pulp mill. Unbleached brown stock from the digesters is treated with chemical agents to increase brightness and give it a whiter appearance. Bleaching is accomplished by delignification, brightening of the unbleached pulp, or both. Delignification is the chemical removal of residual lignin from the pulp. Lignin absorbs light and gives unbleached pulp its brown color. Brightening simply involves a chemical alteration of those portions of lignin that impart the color so that they no longer absorb light. To produce high-quality, optically stable pulps, bleaching methods that delignify the pulp must be used. This is normally the case with chemical pulps, such as Kraft or sulfite pulps, where high brightness levels are required. With mechanical pulps, where a maintaining high pulp yields through preservation of the lignin is critical, brightening is the preferred bleaching process.

With chemical pulps, bleaching is usually achieved through a sequence of three or more process stages, each utilizing different chemicals and conditions depending upon its specific purpose. The unit operations for each stage normally include mixing, reacting, and washing. Sequences and associated process equipment can vary considerably from mill to mill, depending on the final product requirements, capital and operating cost considerations, and environmental factors.

Each different bleaching stage has been assigned an abbreviation or shorthand notation, so that sequences can be more easily described. The common bleaching processes and abbreviations include:

- C—chlorine bleaching using chlorine gas (Cl_2)
- D—chlorine dioxide (ClO_2) bleaching
- E—caustic (NaOH) extraction bleaching
- H—chlorine bleaching using sodium hypochlorite (NaOCl)
- O—oxygen (O_2) bleaching
- P—Hydrogen peroxide (H_2O_2) bleaching
- Z—ozone (O_3) bleaching

In some cases, multiple chemicals are used in a single stage, for example, caustic, oxygen, and peroxide. In the shorthand notation, this would be written as EOP or E+O+P to show that the three chemicals have been combined in a single bleaching stage. Repeated stages used to achieve higher brightness are noted by adding subscripts, such as D_1, D_2, and so on.

Figure 32.14 is an example of a typical five-stage bleaching sequence, identified by the shorthand notation $D_{100} – E_{OP} – D – EO – P$. In this example, chlorine dioxide (D) is used in the first, and third, stages. The second stage uses caustic soda (E) for extraction of residual lignin from the pulp. This particular extraction stage also utilizes oxygen (O) and hydrogen peroxide (P) to assist in bleaching, initially in combination with caustic, and with a final hydrogen peroxide only stage.

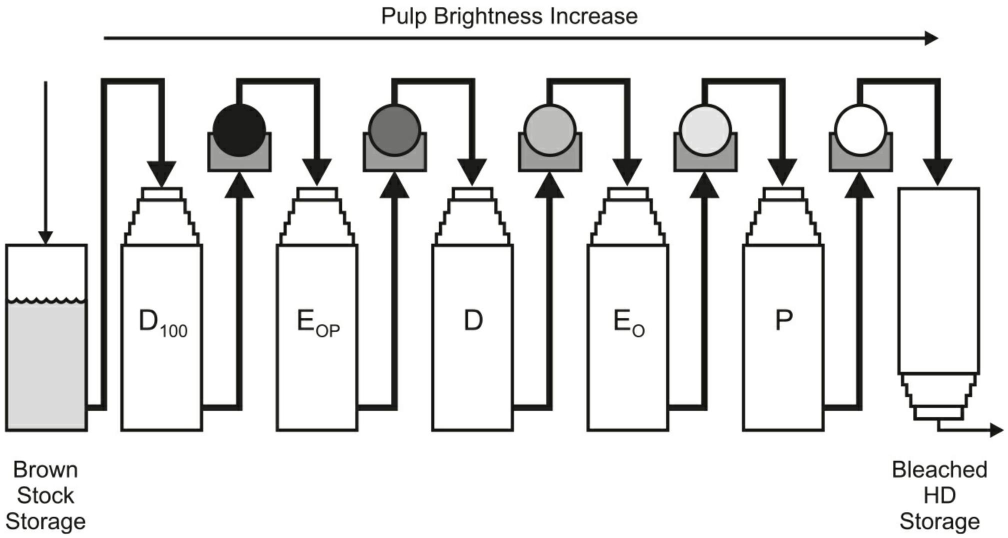


FIGURE 32.14 Typical five-stage bleaching process.

The first two stages of a bleaching sequence usually accomplish most of the delignification. Chlorine dioxide (ClO_2) is a powerful oxidizing agent, which reacts rapidly with lignin under acid conditions in the first stage, while affecting the carbohydrate fraction very little. The following extraction stage then solubilizes the lignin, rendering it susceptible to removal by the alkali and good washing. Caustic soda (NaOH) creates the strong alkaline conditions present in the extraction stage. This extraction stage also reactivates the pulp for further oxidation in the following stages. Oxygen (O_2) and hydrogen peroxide (H_2O_2) are sometimes added to the extraction stage, where they react selectively with the remaining lignin in the pulp, reducing the requirement for more expensive chlorine dioxide in the following stages.

The chlorine dioxide stages are often referred to as brightening stages, since the greatest gains in pulp brightness are achieved here, although removal of the final traces of lignin continues to take place in both stages. The specific operating conditions of time, temperature, chemical charge, and pH in the D_1 stage are established for the efficient bleaching of undesirable shives (dark fiber bundles) that may be present in the pulp.

In some cases, a second extraction (E_2) stage may be found between the final two D stages. If needed, a dechlorinating agent, such as bisulfite, may be used at the final D stage washer to control excessive chlorine dioxide residuals in the fully bleached pulp.

The process equipment depicted in Fig. 32.14 is typical of many bleach plants. However, as with sequences, specific process equipment can vary widely from mill to mill. In the example sequence, bleaching chemicals and steam (used to control the temperature of each stage) are applied to the pulp through mixers located immediately before a reaction tower. Good mixing is critical to achieve efficient bleaching. Bleach towers are normally tall cylindrical tanks, which provide the appropriate retention time for the specific bleaching reaction of each stage. Pulp discharged from a tower is then washed to remove as much of the spent chemicals and soluble reaction by-products as possible. Washing is important, since excess residual materials carried along with the pulp can interfere with the efficiency of the following stages. Hot water and machine whitewater are usually used in combination as shower water on the final bleach stage washer. Some sort of counter-current washing configuration, utilizing filtrates from each stage, is usually used throughout the remainder of the bleach plant, to achieve the greatest reduction in freshwater usage, and to minimize effluent discharge volumes. Rotary drum vacuum filters are the most common type of equipment used for washing in the bleach plant. However, other washer styles are in use across the industry, including compaction baffle pressure filters, wash presses and atmospheric diffusers to mention just a few.

The sequence shown in Fig. 32.14 is one of a variety that is referred to as elemental chlorine free (ECF) bleaching sequences. Most bleach plants now use some type of ECF sequence. Elemental chlorine in the form of chlorine gas, or in solution as hypochlorite, was used in most bleaching sequences until the 1990s. These were low-cost and effective bleaching agents, but were subsequently found to be major contributors to the formation and discharge of chlorinated organic compounds, including dioxins. Hypochlorite was also found to play a part in the generation of chloroform from bleach plants. Consequently, chlorine and hypochlorite have been eliminated almost entirely from the bleaching of pulp. They have been replaced by chlorine dioxide or other bleaching chemicals that react differently and form fewer undesirable by-products.

A few mills, primarily in North America and Scandinavia, have gone a step further to employ totally chlorine free (TCF) bleaching. The elimination of all chlorine containing chemicals for bleaching, including chlorine dioxide has led to the development of TCF bleaching sequences that use oxygen, ozone, and peroxides. Higher costs and uncertain incremental environmental benefits have limited more widespread adoption of TCF bleaching. Both TCF and ECF sequences may also supplement other novel treatments such as enzymes, chelants, and peracids.

As an environmental enhancement to the bleaching process a form of oxygen bleaching, usually referred to as oxygen delignification has become quite common across the industry. The oxygen delignification process is placed between the digesters and the bleach plant. Oxygen is used under alkaline conditions, along with elevated temperature and pressure, to reduce the lignin content of unbleached pulp by about 50% before the bleaching process. This dramatically reduces the amount of chlorine dioxide required for delignification in the bleach plant. In addition, unlike most bleach plant filtrates, the filtrate generated by oxygen delignification is very compatible with the Kraft chemical recovery system, thus reducing effluent discharge.

Another interesting pretreatment option to reduce the use of bleaching chemicals is the use of an enzyme ahead of the bleach plant. One specific enzyme treatment can reduce the amount of chlorine dioxide required for delignification by as much as 15 to 20%. The enzyme functions by solubilizing organic complexes in the pulp, allowing the lignin to diffuse more easily from the fiber in the following D stages. Being natural proteins, enzymes require a very narrow range of temperature and pH to work effectively.

As mentioned before, except from TCF sequences, bleach plant filtrates cannot be recovered like brown stock filtrates to be burned in the recovery boiler. Chlorides present in the bleach filtrates are incompatible with recovery boiler metallurgy, and would ultimately result in costly, even potentially catastrophic equipment failure. Only limited success has been achieved thus far in efforts to treat ECF filtrate streams to remove these chlorides, (or to segregate nonchloride containing portions of bleach filtrate streams) in order to accommodate chemical recovery of the bleach plant waste streams. Consequently, in the vast majority of cases, bleach plant filtrates are still sent to a wastewater treatment facility, after their use in counter-current washing on the bleach washers.

Due to the alkaline nature of most of the chemical processes involved, bleach plants are often susceptible to scale formation. This can negatively affect equipment performance, bleaching efficiency, and operational uptime. Scaling becomes even more pervasive, whenever efforts are made toward water conservation or closure of the bleach plant. The most common types of scale found in the bleach plant include calcium carbonate, calcium oxalate, and barium sulfate. If operating conditions that favor deposition of scale cannot be controlled adequately by normal process changes, chemical treatment with scale inhibiting compounds can be very effective in reducing or even eliminating scale problems.

Mechanical pulps, unlike chemical pulps discussed above, are normally bleached by brightening methods that do not remove appreciable amounts of lignin. The most common chemicals used for this purpose are sodium hydrosulfite ($Na_2S_2O_4$) and hydrogen peroxide (H_2O_2). Unfortunately, none of the bleach treatments provides a brightness gain that is completely stable on exposure to light and air. This results in the potential for a higher degree of brightness reversion (yellowing), with paper produced from bleached mechanical pulps as compared to bleached chemical pulps. This yellowing effect can be observed if a newspaper is left in the sunlight for a day, and the exposed surface is compared to any sheet in the same paper that did not experience direct sunlight.

Stock Preparation

The final steps in preparing pulp to be made into paper occur in the stock preparation processes. Refining is a very important function that has a major impact on final paper sheet performance. Pulp cleaning removes contaminants from the pulp stream, which could cause operational issues if allowed to come onto the paper machines. Stock dilution to the desired consistency occurs, in a series of tanks or silos that are most often called chests by those in the industry. In addition, the run of piping that goes from the stock preparation area to the paper machine is a location where process additives are routinely applied, and there are considerable water and energy savings to be obtained if advanced strategies are applied to this seemingly mundane part of the process.

The refining that occurs in the stock preparation section is not to be confused with the same term used in the development of mechanical pulp grades. In the stock preparation area, refining refers to the scuffing or abrading of the individual paper fibers, so that they will form properly on the paper machine. This process has also been called “beating,” and in those mills that apply this term, the refining process step is said to occur in the Beater Room. Two refiner designs are widely used: the conical design and the rotating disc. Both designs cause the fibers to rub against one another and metal surfaces in close tolerance conditions, creating individual fiber strands that can be best arranged on the paper machine.

The downside of refining is that a certain fraction of the fibers are cut or damaged in the process. This limits the number of times a given paper fiber can be recycled, since it will eventually get too short to provide adequate sheet properties. One paper manufacturer reports expecting to waste 35 to 40% of the recycle paper it buys, since the MOW paper it uses as a source of fiber, often contains a higher fraction of paper that has already been reused. The lesson here is that there can never be 100% recycling of paper, since the refining steps cause damage to the fibers as a by-product of preparing them for the final production steps.

Pulp contaminants going to a paper machine can cause any number of operational problems. Therefore, the pulp contaminants are removed to the greatest extent possible in the final stages of stock preparation in a series of screens and cleaners. Mills using recycled paper as feedstock require considerably more cleaning due to the presence of a number of foreign materials. Initial cleaning is accomplished through a series of sieves and strainers, with the openings sized to accept the target fiber size and reject larger objects. More intensive cleaning is accomplished in a series of centrifugal cleaners, where the pulp is spun in a circular manner. The heavier or denser contaminants are forced to the outside of the cylinder, while cleaned pulp is withdrawn from the center. It is difficult to size a single centrifugal cleaner to handle a large volume of pulp. Consequently, multiple centrifuge units are bundled onto a single bank, and larger facilities have a number of centrifuge pumps to handle the mass flow of pulp needed for eventual production. As is the case in the refining step, water exits to rejects or sewer. Recovery of this water ultimately occurs at the screw press where sludge is produced.

Stock storage ahead of the paper machine is a necessary step to provide the proper ratio of fiber and water going to the paper machine, and to maintain an inventory of fiber ready for conversion into the final paper sheet. When most papermaking was conducted under acidic water conditions, large tiled silos were the norm. Even if the tiles were acid resistant, the grout in between the tiles would degrade over time, requiring these chests to be rebuilt periodically. Despite having some internal mixing capability, these stock chests are never homogeneous, and problems can develop with stock spoilage from proliferating microbiological forms. Biocides are applied to prevent the microbes from reaching damaging population levels. Occasionally, studies will be done to determine the average retention time for stock in these storage chests, using nonreactive chemical additives that can be detected at very low concentrations. This determines if adequate mixing is occurring in the chest, or if some mechanical or operational changes are required.

A last piece of equipment before the paper machine is the fan pump. The purpose of the fan pump is to provide consistent slurry of water, chemicals, and fiber to be made into the paper sheet. A chemical feeding process improvement developed by Nalco in 2006, allowed the seemingly mundane task of adding polymeric retention, drainage, and formation chemicals to the stock as it flows toward the paper machine, to be a major water and energy savings opportunity. The previous practice had been to add polymeric material through a basic tee into the process line and assume that adequate mixing and dispersion was achieved. Using computational fluid dynamics modeling, Nalco scientists determined that an improved polymer mixing and distribution system could be developed. Whereas previously freshwater was used to mix and distribute the polymer, the innovative process allowed recycled process water to be used for this purpose. This development results in significant water and energy savings, since freshwater would have to be heated in the process. Improvements in polymer efficacy are also observed using this process, but the energy and water savings are the paramount benefit. One such installation resulted in reduced water usage of 200 gpm (45 m^3/h), and a reduction of boiler steaming rate of 8600 lb/h (3900 kg/h), due to recycled water being used for polymer mixing.

Paper Machine Operations

The objective of all unit operations discussed thus far in this chapter has been to create a water slurry of fiber and chemicals that can be formed into a sheet of paper desired by the marketplace. That process occurs on the paper machine, and it is a marvel of chemical and mechanical engineering. Using a newsprint grade paper machine as an example, the objective is nothing more than converting a bulk solution which contains 99.5% water, about 0.5 % fiber, and some chemicals, into a consistent sheet of paper 0.003 inches [3 mils (76 μm)] thick, at 60 mph (97 km/h), and at an economic price with minimal waste generation. Most paper machines operating in the early part of the 21st century are Fourdrinier and gap formers designs. A few older machines that make heavier, board grades of paper are called Cylinder machines.

Paper Machine Headbox

The Fourdrinier paper machine design starts at the headbox, as shown in Figs. 32.2 and 32.15. The headbox may be open to the air, in which case the furnish is gravity fed onto the paper machine, or the headbox may be pressurized. Some grades in the packaging segment, feature multiple layers or plies of paper, requiring multiple headboxes to distribute the furnish. One grade that is a particularly good example of this is the so-called White Top Liner often used in folding box board and other packaging materials. Strength and economy comes from the unbleached or brown layers, while improved printability and customer appeal are derived from a bleached paper top layer. Multiple headboxes can be present in this design. The purpose of the headbox is to convert the cylindrical flow of fiber, water and chemicals into a planar flow on the wet end of the paper machine. Sometimes, inorganic scales accumulate in the approach piping and headbox, due to calcium or barium precipitation. Unless they are excessive, these deposits are tolerated during operation, and then cleaned off during periodic maintenance shutdowns.

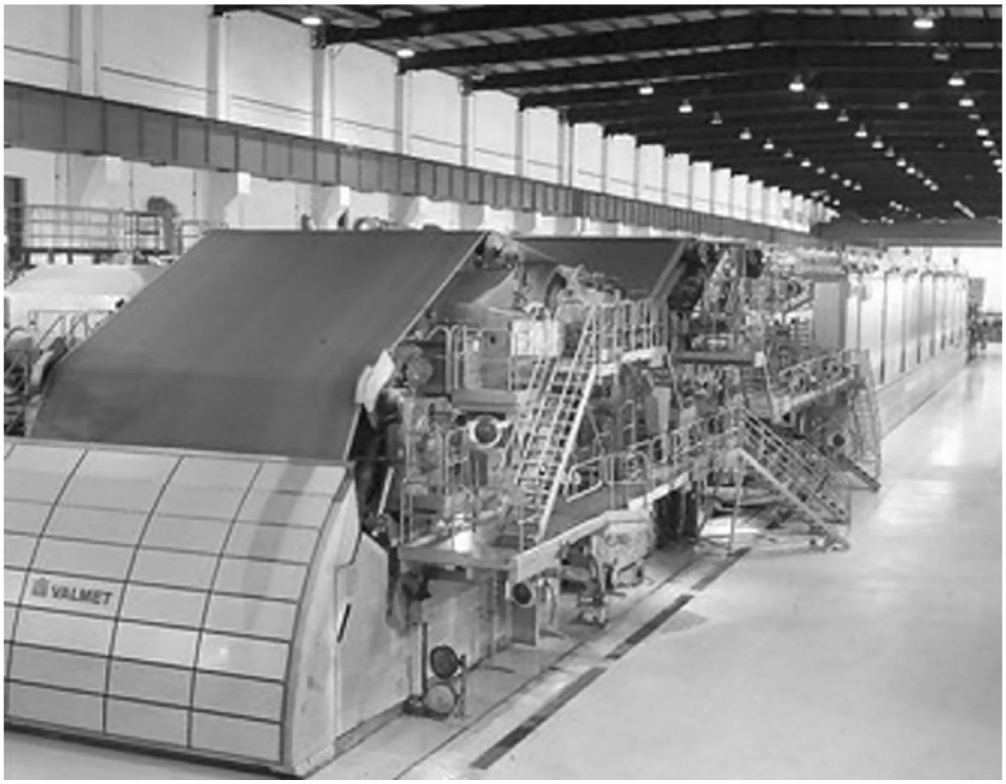


FIGURE 32.15 A modern Fourdrinier paper machine. (*Photo courtesy of VALMET.*)

Paper Machine Wet End

The 0.5 to 1.0% fiber content paper slurry is physically unstable as it emerges from the headbox, so it is spread onto a support structure called “the wire” as it begins its fast journey down the paper machine. Originally made of bronze, wires are now universally made of a plastic weave, so that water can freely drain away as the fibers get organized into a sheet. This wet end of the paper machine (Fig. 32.16) is also called the table area, and is characterized by a flat linear run. Removal of large amounts of water occurs easily at the wet end of the paper machine, enhanced by several mechanical features. After a brief span of free water drainage, more water is extracted by passing the wire over a series of foils, like inverted airplane wings that cause a vacuum gradient, to suck more water from the forming sheet.

FIGURE 32.16 Photo of a large Fourdrinier wet end.

Further down the table, the wire passes over a series of vacuum boxes, again with the purpose of sucking water easily from the sheet. The vacuum is created by a series of large, liquid-ring vacuum pumps or blowers.

Some mills pass the wire under a steam box arrangement, designed to heat the water/fiber slurry and encourage water drainage by lowering the viscosity of the water component on the sheet. The use of steam boxes is typically an expensive approach for water removal, and consideration of other benefits is a must to substantiate the investment. The Couch Roll is located at the end of the paper machine wet end where the sheet is separated from the wire for entry into the press section. At this point, many paper grades are up to 25% fiber, meaning that 95% of the water that left the headbox has been taken away from the sheet. Given that the means of water removal further down the paper machine costs more, effective water removal in the wet end is extremely important to the cost-performance of the paper machine.

A water stream is used to establish the width of the sheet as it is formed on the wet end of the paper machine. As it leaves the headbox, the water/fiber slurry tends to spill out to the side of the wire, until it achieves some dimensional stability. This results in a few inches (centimeters) of the sheet on both sides that will not meet the thickness specification of the grade being produced and that needs to be removed as early in the process as possible. This is accomplished by spraying water along the edge of the sheet as a knife, cutting the thinner paper. This water stream is sprayed through nozzles called the trim squirts. To achieve the cutting effect on the edge of the sheet, high-pressure water also known as shower water is squeezed through small tolerance openings in the nozzles, making water quality very important to the performance. Water not containing fiber or process additives, typically freshwater or recovered condensate, is usually used for this purpose. In addition, shower nozzles require periodic replacement, use of hard material or cleaning because of water high in hardness content that will form scale and wear from high velocity.

Water issues can affect the performance of the paper machine wet end in several ways. Manganese is an element found in many water supplies at a concentration of 50 µg/L or higher. The presence of manganese in the stock dilution water has been observed to form a stain-like deposit on the plastic wire that supports the water/fiber slurry. While primarily a cosmetic issue, because the manganese forms a characteristic black deposit on the white wire, the thickness of the manganese deposit can retard water removal. In addition, the water recovered from the paper in the wire pit under the wire is a classic breeding ground for microbiological organisms. The presence of organic contaminants in the incoming water has been shown to be a food source for the organisms present. By doing a better job of extracting organic contaminants from the incoming water, one mill demonstrated a 50% reduction in sheet web breaks, resulting in an annual savings of $1.1 million.

Polymeric chemical additives are fed to paper machine wet ends to enhance water removal from the sheet and retain small particulates. These are often called RDF chemical programs, speaking to improvement achieved in retention, drainage, and formation. Some mills, often in the board grade segment, operate mill water systems as zero liquid discharge (ZLD) so that no water is discharged from the process in liquid form. Ionic concentration of the circulating mill water under this operating strategy is very high, and inhibits the ability of the polymeric additives to uncoil, interfering with the polymers adsorption onto the fiber surface and performance to meet functional properties such as strength. This impact decreases the benefits that could be achieved under more normal water chemistry conditions. Special care must be taken in RDF chemical additives selection, when advanced water recycling practices are utilized.

Paper Machine Press Section

Anyone familiar with an old wringer-style clothes washer in operation will readily understand the operation of the paper machine press section. By taking the sheet, which is supported by a water absorbing fabric called a felt, between a series of rolls, water is squeezed from the sheet. This part of the process increases fiber solids in the sheet from 20% to upwards of 55%. This represents nearly 17% of the water associated with the sheet as it leaves the wet end of the paper machine.

The point at which the press rolls form a narrow passage through which the sheet must pass is called a nip, and this is where water removal by mechanical force takes place. A standard press section involves the sheet passing through three nips, as shown in Fig. 32.17. Water removal in the press section is slightly more expensive than in the wet end area, but far cheaper than evaporation, which occurs in the paper machine dryer section. Sheet consolidation and compaction occurs as a result of passing the sheet through the tight nip tolerances in the press section. In some grades, those that require greater strength, this can provide a considerable benefit.

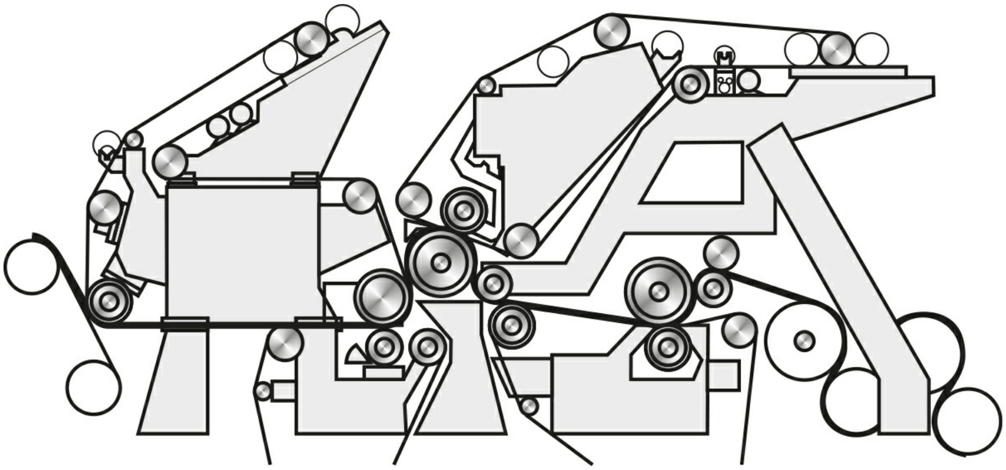


FIGURE 32.17 Standard three-nip press section.

The press section area features a vacuum section to enhance water removal. This system is comparable to what is used on the wet end of the paper machine, but instead of sucking water from the sheet through the wire the vacuum system in the press section functions by sucking water from the felts to allow more efficient water wicking from the sheet.

A major factor in effective press section performance is the cleanliness of the felts that support the sheet. Felts that become filled with fiber, organic deposits, or inorganic materials cannot pass water as efficiently. Felt cleaning is an important component of optimal press section performance. It is important for the operations team to understand the nature of their specific felt cleaning requirement, so that effective chemical additives can be applied. Deposits based on organics might require a solvent-based cleaner, whereas inorganic deposits require an acidic cleaning solution. Mills must decide if press felts require continuous cleaning, cleaning during a down, or batch cleaning while the machine stays in operation. This decision is based on individual system demands and paper grade quality requirements.

Some mills invest in packaged systems to provide high-pressure, high-temperature water systems to accelerate cleaning activities. These systems can provide a continuous flow of water/chemical combinations, at sufficient volume that provide complete coverage across the width of the machine, offering a distinct improvement over standard systems that have a single nozzle traversing the machine width.

A 2003 innovation by Nalco Water improved press section performance at several mills using a structured polymer solution sprayed onto the sheet. The result was increased water removal efficiency, which could either be seen by the mill as an opportunity to produce more tons (tonnes), or to produce constant tons (tonnes) at a reduced steam flow requirement, with increased sheet strength. Increased sheet dryness values of up to 8% leaving the press section have been observed with this program, resulting in energy savings of \$7/ton (\$7.7/tonne) of paper produced at an energy cost of \$8/million Btu (\$7.6/GJ).

Paper Machine Dryer Section

While the dryer section is only tasked with removing the remaining 4% of water that leaves the headbox, it is the most expensive section to operate. Drying occurs through water evaporation from the sheet as it passes over a series of steam heated cast iron drums (Fig. 32.18).

FIGURE 32.18 Steam heated dryers evaporating the remaining water.

Most paper grades require sheet support as it progresses through the dryer section, which is provided by dryer felts. Heavier paper grades, such as linerboard, do not require such protection.

An important consideration on the sheet side outside of the dryer cans is the movement of water vapor away from the sheet once it has evaporated. Steam is the heating medium for the air, which comes in from outside the paper machine building across a series of coils. Many machines, especially modern wide ones need to blow air into the inner areas of the dryer section, so that the moist humid air moves away and the sheet dries uniformly. Since the space in between sequential dryer can cylinders is referred to as the pocket, these are called pocket ventilation systems.

Adding steam into and extracting condensate from the spinning dryer cans is a considerable engineering challenge. This is done through a device mounted onto the dryer can called a steam joint. The steam inlet is simply that of exhausting the vapor into the can interior. Condensate removal is accomplished through a shoe-like fitting that rotates around with the dryer as it spins. Centrifugal force forces the liquid condensate to the dryer can outer wall, and a pressure drop control system allows condensate to be efficiently extracted. Some steam, called blow-through steam, is allowed to exit the dryer can with the liquid condensate as a way of maximizing condensate removal. The condensate/blow-through steam combination is routed into a steam separator tank, with the flow from several dryer cans being combined. The steam is collected from the top of the separator and used as feed for either that same group of dryer cans, or dryer cans located toward the wet end of the machine.

The condensate dryer drainage system design has a major impact on the possibility of corrosion occurring. Older machines, those built prior to 1970, almost always had a cascade design as shown in Fig. 32.19 where the steam collected in a separator tank is routed toward the wet end, since wet end dryers operate at a lower steam pressure so as not to apply too much heat to the sheet too quickly. With this design, it was common to see an increased corrosion rate in the eventual condensate stream, since the flashing of carbon dioxide (CO_2) along with the steam served to depress the local condensate pH, to the point where it would be acidic and dissolve the steel materials of construction. Amine treatment selection for cascading systems relied heavily on cyclohexylamine, which being the most volatile of the amines routinely used as condensate treatments, could best follow the CO_2 and neutralize any acid being created.

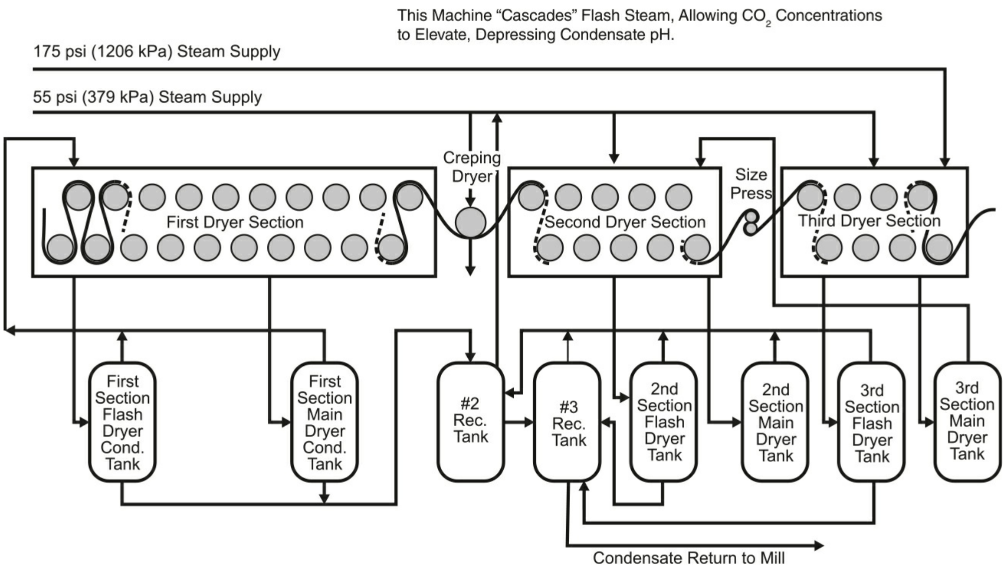


FIGURE 32.19 Cascade design paper machine condensate drainage system.

There is a condenser present at the wet end of the paper machine, where there are no lower-pressure sections to flash the steam. It condenses the steam phase into liquid condensate that can be added to the other condensate streams and pumped back to the powerhouse for reuse as boiler feedwater. These condensers typically use mill water on the shell side, and in the case of a tube leak, allow mill water to get into the purer condensate flow. A good monitoring program includes testing for hardness components and dissolved oxygen, both of which are present in mill water but not condensate. If a tube leak is found, a decision must be made to either discard the condensate, losing its thermal and water savings value, or accept the presence of the contaminants until the condenser can be repaired.

Modern paper machines feature a design that returns the steam collected in the outlet separator tanks back into the same dryer section, after having boosted its pressure via the use of a thermocompressor. The thermocompressor uses higher-pressure steam to educt the lower-pressure flash steam up to the steam pressure required for that dryer section. Because of this recycling of steam, the thermocompressor design can accumulate noncondensable gasses, and needs to be vented periodically to perform optimally. Modern paper machines tend to use the thermocompressor design as shown in Fig. 32.20, because of the ability to achieve better temperature control of the individual dryer sections. Amine treatment for a thermocompressor system is quite different than for the cascading design, since there is no mechanism to concentrate CO_2.

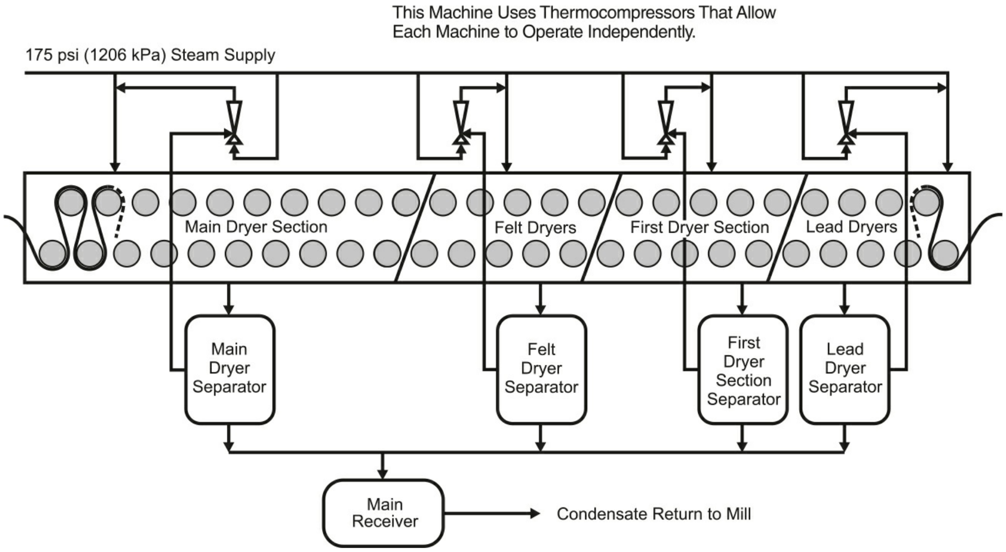


FIGURE 32.20 Thermocompressor design paper machine condensate drainage system.

Sophisticated computer controls using online sensors, control the speed at which the paper passes along the paper machine. When the targeted moisture content is achieved, the paper is taken on long rollers called reels. Samples are collected for quality control analysis, and the paper is ready to be converted into commercially sized rolls for delivery to the customer. Some paper machines apply a coating to the paper directly on the machine, usually as a liquid slurry or solution. This requires another dryer section in order to dry the sheet to its desired moisture content. Alternatively, the produced rolls of paper can be taken elsewhere for the application of a coating. There are no water treatment related applications or concerns in the converting process. Scrap paper, from either the direct production process or product not meeting targeted specification, is called broke, which is repulped and reused, much in the same way of recycled paper. This minimizes waste generated from the process.

Because their properties are so different, tissue and towel paper grades are produced on a different design of paper machine. The core of the tissue production process is a device called the Yankee dryer, which like the normal paper machine uses steam as the drying medium. Instead of using a series of dryer cans, the thinner sheet of tissue can be dried on a single dryer drum. This prevents excessive compaction of the tissue, which would reduce its tactile properties that consumers appreciate. The internals of the Yankee dryer are considerably different from the standard paper machine and can present a treatment challenge. Instead of a single pick-up shoe or siphon, the Yankee dryer internal design features a series of channels into which the condensed steam flows (Figs. 32.21 and 32.22). The term “soda straw” is often used to describe the small diameter tube inside each channel. Condensate flows through the many soda straws into a condensate collection system, and leaves the Yankee dryer, going into a tank called the First Separator. As in the standard paper machine, blow-through steam comes along with the condensate to minimize pressure drop. The flash steam leaves the First Separator and goes through a thermocompressor to be pressurized to the requirement of the Yankee dryer steam supply. This tight recycling arrangement can cause high concentrations of CO_2 to be present, making amine treatment of tissue mill systems expensive if there is no alkalinity removal in the boiler makeup water pretreatment system. In some designs, the soda straws inside the Yankee dryer are formed of copper alloys that, unlike steel, undergo corrosion under both alkaline and acidic pH conditions. This makes Yankee dryer condensate pH control an important aspect of the treatment, since corrosion products generated can plug the small openings in the soda straws and limit production.

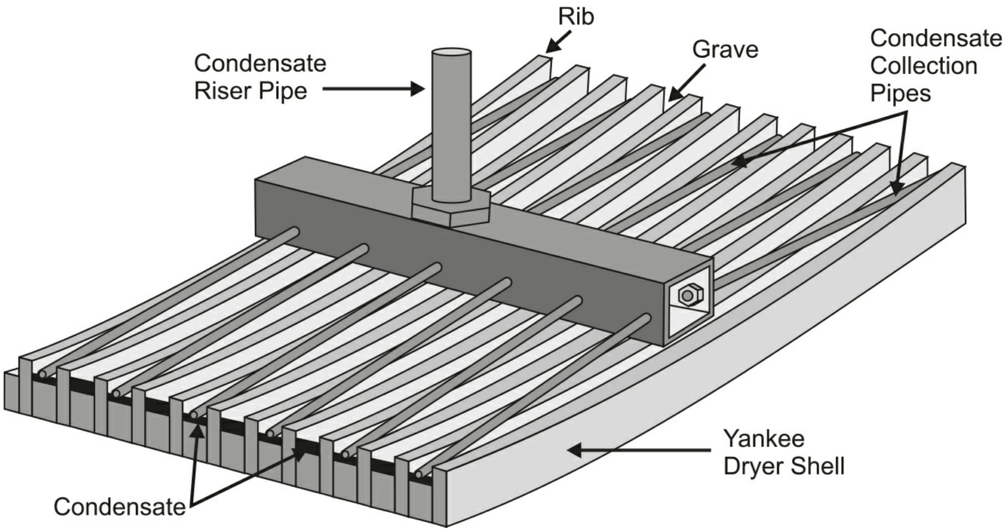


FIGURE 32.21 Yankee dryer condensate removal design.

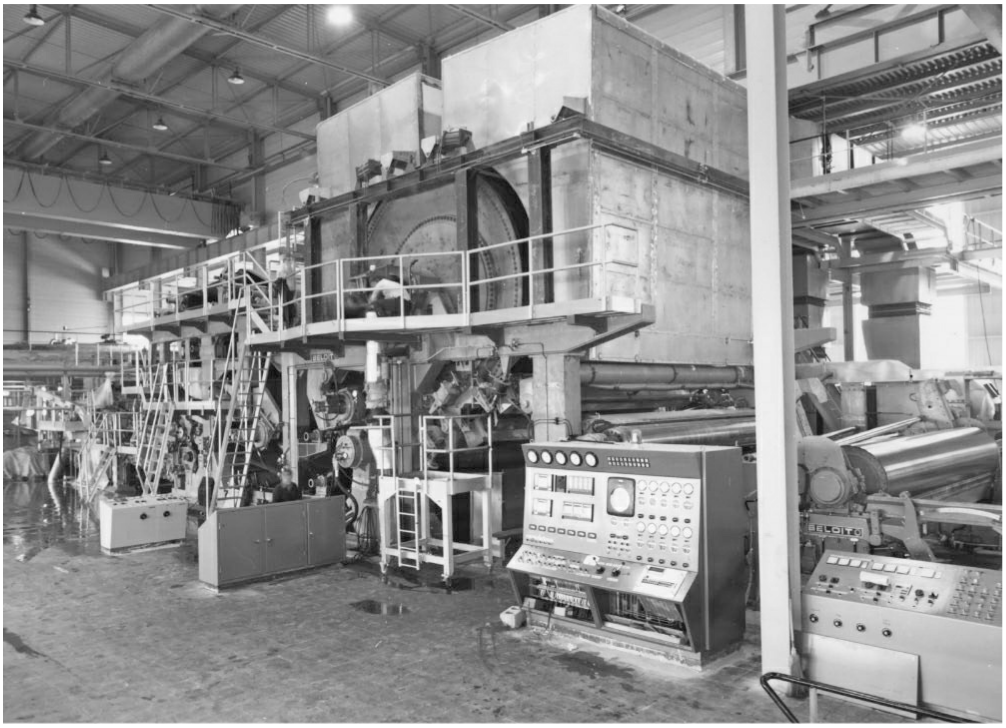


FIGURE 32.22 Yankee dryer. (*Courtesy of AER Corporation*.)

The sheet finishing, paper storage and warehousing, and loading dock areas of the paper mill have minimal water usage or water treatment needs. The exception is those mills in colder climates that require building heating. Heating systems often generate condensate that is collected and returned to the boilers for reuse as feedwater. Because these systems go off and on seasonally, and sometimes the same day, it is very likely that metal oxides will contaminate the condensate. Even though this would be a small fraction of the total condensate flow going to the powerhouse, the elevated potential for high concentrations of metal oxide contaminants warrants selection of either an advanced treatment program, mechanical filtration of the condensate, or an operational strategy to discard the condensate flow when it is most contaminated.

CHAPTER 33

The Power Industry

Steam-electric power generating plants are the largest industrial users of water in the world. As an example, the United States Geological Survey (USGS) found that in 2000, the electric utility industry withdrew 195 billion gallons of water per day (738 million m^3/d), accounting for 48% of total water withdrawals for all uses in the United States. Approximately, one-third of the total was saline, and two-thirds was freshwater.

The laws of thermodynamics limit the amount of the energy in fuel that can be converted to work by a steam turbine. More than 50% of the initially available heat remains in the exhaust steam leaving the turbine, and most of this is rejected to cooling water and then lost to the surrounding environment. Cooling water required for condensing the turbine exhaust steam in a 1000 MW plant is about 576 mgd (1500 m^3/min).

By comparison, other water requirements for steam-electric plants are small. These include replacement of losses from the steam cycle, ash transport (in coal fired plants), flue gas cleaning, equipment cleaning, and domestic uses. Once-through cooling water is used in many power plants and is returned directly to its source. Because the condenser outlet water is typically 5 to 25°F (3–14°C) warmer than the inlet, heat is a principal concern in the discharge of once-through cooling water. In many countries, the elimination of this thermal discharge, which can affect aquatic species downstream, is an environmental goal.

The difference between total water withdrawal and final discharge is primarily lost to evaporation, which occurs principally from ponds and cooling towers used in recirculating cooling water systems. There is also some water loss from the surfaces of ash settling ponds. Minor water losses can occur by seepage into the ground from unlined ponds and in wet ash or water treatment sludge hauled from the plant.

This chapter is primarily concerned with high-pressure (HP) boilers operating above 1000 psig (6.9 MPag). These boilers typically use high-purity feedwater and have high heat flux, both of which demand specialized internal boiler water treatment and careful control. Some low-pressure (LP) boilers also use high-purity feedwater and require the types of treatment programs discussed in this chapter. Chapter 11 on Boiler Feedwater Treatment discusses common internal treatment programs for lower-pressure boilers. Most often, operators of high pressure electric utility boilers take guidance from the Electric Power Research Institute (EPRI), VGB Powertech or other organizations such as the International Association for the Properties of Water and Steam (IAPWS), when selecting a treatment program and chemistry limits for the water-steam cycle.

Energy Conversion

In steam-electric power production, the chemical energy of fossil fuels or the nuclear energy of fissionable materials is converted to heat for the generation of steam, which is then converted to mechanical energy in a turbine coupled to an electric generator. Exhaust steam is condensed and returned to the boiler.

The theoretical efficiency at which heat in the steam can be converted in a turbine to work within the fluid (water-steam) cycle of a steam-electric plant is shown by Eq. (33.1):

$$\text{Percent theoretical efficiency} = 100(T_1 - T_2)/T_1 \tag{33.1}$$

where T_1 = absolute temperature of the turbine inlet steam, R (K)
T_2 = absolute temperature of the turbine exhaust steam, R (K)

Thus, the greatest efficiency is achieved by providing the highest inlet steam temperature T_1 and lowest exhaust temperature T_2 practical for a given turbine-condenser system.

In practice, upper temperatures are limited by the strength of metals available for boiler and superheater construction. Strength falls off rapidly as temperature exceeds 900°F (482°C, 1360 R, 755 K). Upper temperatures are generally limited to a maximum of about 1100°F (593°C, 1560 R, 866 K). A significant temperature difference is required to cause heat to flow from the exhaust steam to the cooling medium circulated through the condenser. The practical effect is that lower steam temperatures on condensing turbines typically range from 80 to 120°F (27–49°C, 540–580 R, 300–322 K), even with cooling water at 40°F (4.4°C) in the winter. Within these upper and lower temperatures, then, the best theoretical efficiency would be:

$$\text{U.S. Units: Theoretical Efficiency} = 100(1560 - 540)/1560 = 65.4\%$$

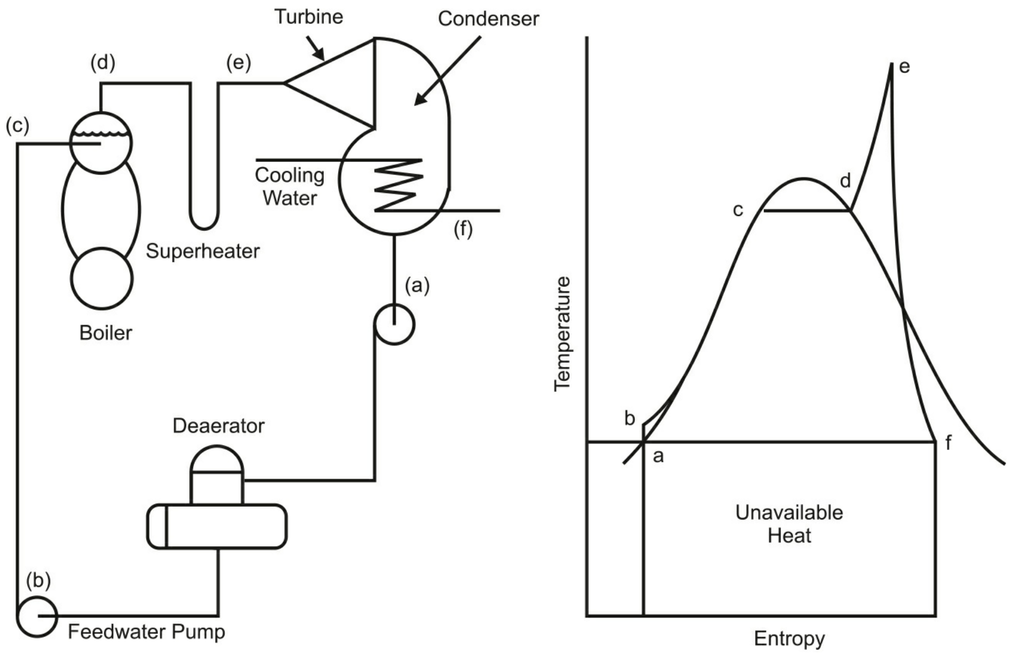
$$\text{Metric Units: Theoretical Efficiency} = 100(866 - 300)/866 = 65.4\%$$

Achievable efficiencies are considerably lower than theoretical, both for the fluid cycle and for the generating plant as a whole. Significant energy is lost in overcoming fluid and mechanical friction. Sizable amounts of energy are consumed in the operation of the plant's feedwater pumps, boiler draft fans, and other auxiliaries. A power plant's pollution control equipment, required to meet air emission and water discharge standards, can consume as much as 10% of the electrical output. Actual steam-electric plant overall efficiencies range from 35 to 45% for conventional units and 55 to 60% for modern combined cycle systems.

The Power Cycle

The energy flow through the water-steam phase changes in a steam-electric plant is called the Rankine cycle. The Rankine cycle has four basic stages: boiler, turbine, condenser, and feedwater pump.

The Rankine cycle may be illustrated by several kinds of diagrams. Figure 33.1 shows that cycle relating the change in temperature of the fluid to its entropy at each stage in the cycle. Entropy is a measure of that portion of the heat received by a cycle that cannot be converted into work, because of the random motion of gas (steam) molecules. Entropy is expressed mathematically as the ratio of heat content to temperature.



a to b: Liquid Heating and Compression (feedwater pump).
b to e: Reversible Heat Addition in Feedwater Heaters (b to c), Boiler (c to d), and Superheater (d to e).
e to f: Steam Expansion and Conversion of Heat Energy to Work.
f to a: Reversible Rejection of Unavailable Heat to Cooling Water.

FIGURE 33.1 Steps in the Rankine cycle from the introduction of water as a liquid into the system, through its phase change to steam that produces work in a turbine, to the condensing of the exhaust vapor to water again for return to the boiler.

To achieve the highest possible thermodynamic efficiency, modern fossil-fuel power cycles use steam superheaters and reheaters to raise the average temperatures (T_1) of steam flowing through the turbine. Condensers operating under vacuum permit expansion of steam to the lowest possible exhaust temperature (T_2). To further recover as much heat as possible, partially expanded steam is extracted from the turbine at various points for heating feedwater (called “regenerative heating”). Figure 33.2 illustrates a cycle having these components, and Fig. 33.3 illustrates their effect on a temperature-entropy diagram of the cycle.

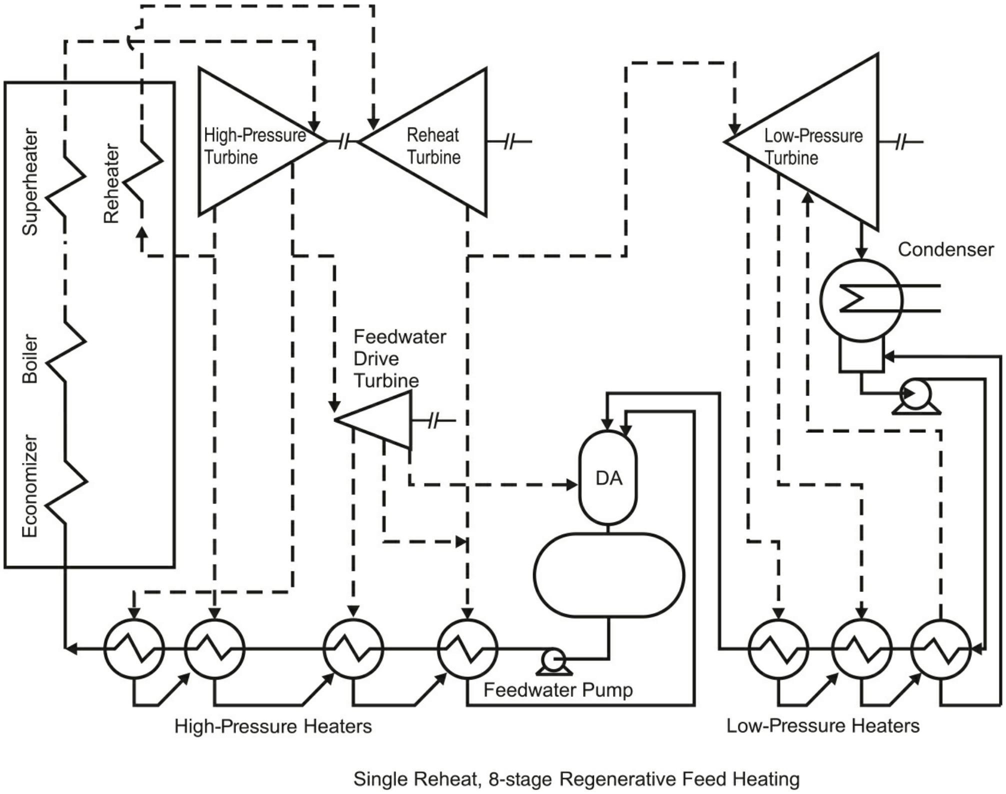


FIGURE 33.2 Addition of steam reheat and regenerative feedwater heating to increase cycle efficiency. Single reheat, 8-stage regenerative feedwater heating, 3515 psia/1000°F/1000°F steam (24.2 MPaa/538°C/538°C steam).

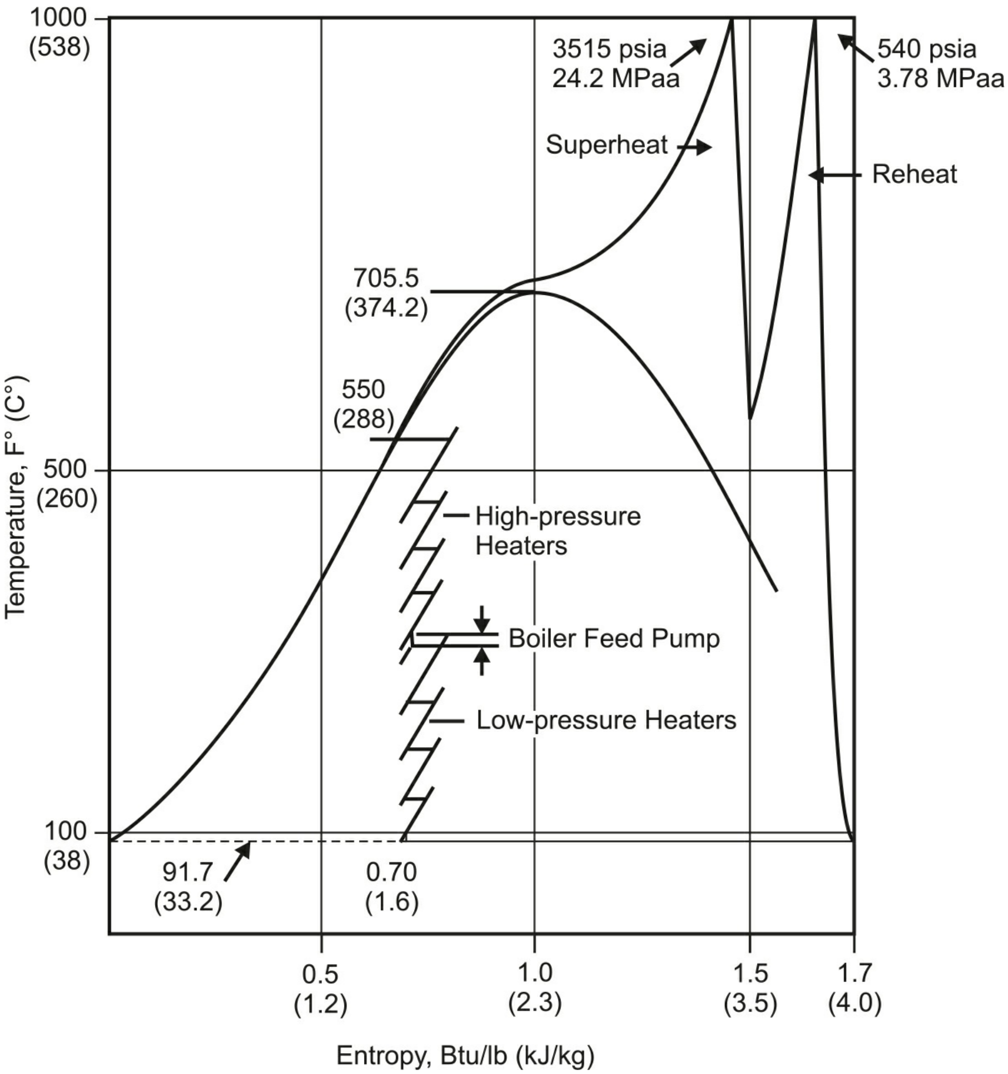


FIGURE 33.3 Modified Rankine cycle showing the effect of reheating steam and adding feedwater heaters to the cycle. (*Adapted from Steam—Its Generation and Use, Babcock and Wilcox Company, 1972.*)

Nuclear steam-electric plants of the light water reactor types typical in commercial service, cannot deliver steam at the temperatures achieved in fossil-fuel units. Nuclear pressurized water reactors (PWRs) (Fig. 33.4) employing once-through steam generators achieve a relatively small degree of steam superheat [30–60°F (17–33°C)]. In PWR cycles, employing recirculating U-tube steam generators and in boiling water reactor (BWR) cycles (Fig. 33.5), there is no superheat. For this reason, nuclear power cycles are limited to efficiencies of about 32% compared to 36 to 39% for fossil-fuel cycles, since less heat is supplied to the turbine (T_1).

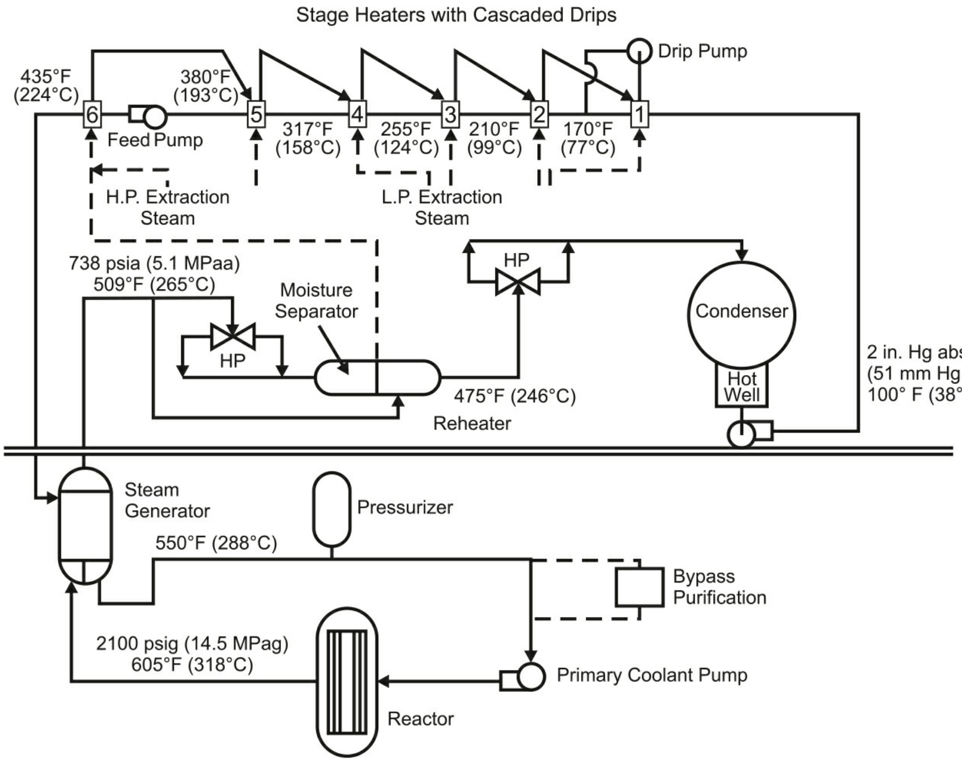


FIGURE 33.4 PWR nuclear power cycle showing major components and typical pressures and temperatures. (*Adapted from The Effects of Water Quality on the Performance of Modern Power Plants, Klein and Goldstein, NACE 1968 Conference*.)

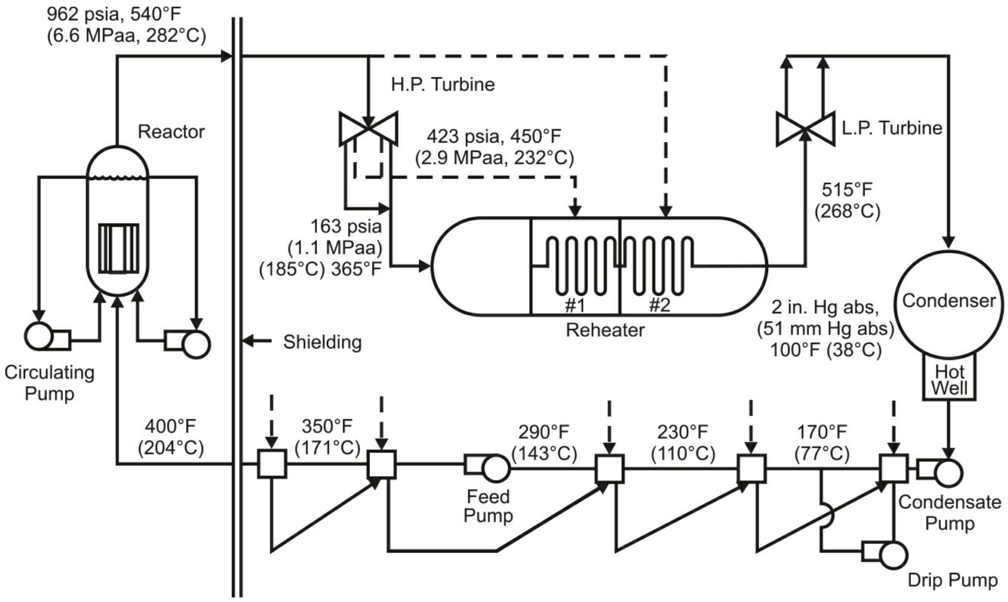


FIGURE 33.5 BWR nuclear power cycle showing major components and typical pressures and temperatures. (*Adapted from The Effects of Water Quality on the Performance of Modern Power Plants, Klein and Goldstein, NACE 1968 Conference*.)

In fossil-fuel units, further improvements in thermodynamic efficiency are achieved by economizers and air preheaters installed in the flue gas path between the boiler and stack. Economizers transfer heat from the flue gases to the feedwater. Air preheaters transfer some of the remaining flue gas heat to the boiler's combustion air supply.

For still higher efficiencies, where suitable fuels are available, combined cycle steam-electric plants combine the operation of a combustion turbine with that of a steam turbine. In combined cycle generating plants (Fig. 33.6), the hot combustion turbine exhaust gasses are used in a heat recovery steam generator (HRSG) to produce steam to drive a steam turbine.

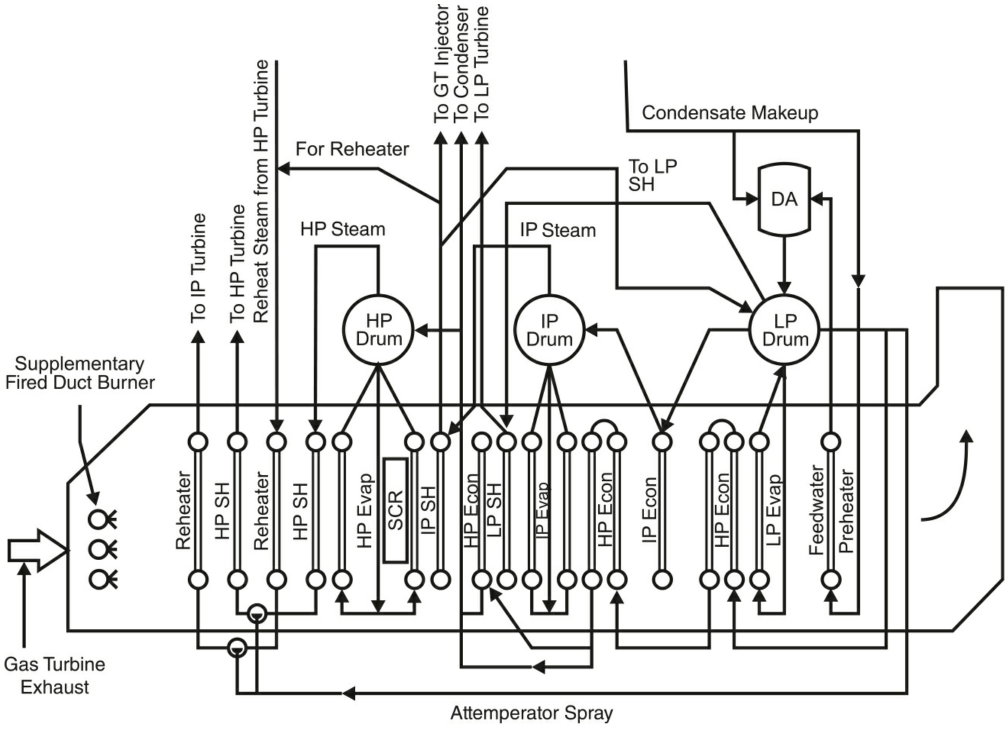


FIGURE 33.6 Combined cycle unit triple drum HRSG.

Water: The Working Fluid

In steam-electric power cycles, water is subjected to wide variations in temperature and pressure in the cyclic sequences of compression, heating, expansion, and heat rejection. Temperatures may range from 70 to 1200°F (21–650°C) with pressures from 0.5 to 5000 psia (3.4 kPaa to 34 MPaa).

As shown by the diagram in Fig. 33.7, steam density approaches that of water as pressure increases, until the critical pressure is reached at 3200 psia

(22 MPaa). A supercritical fluid exists above this pressure, which cannot be considered either steam or water. Boilers operating over 3200 psia (22 MPaa) are called supercritical units.

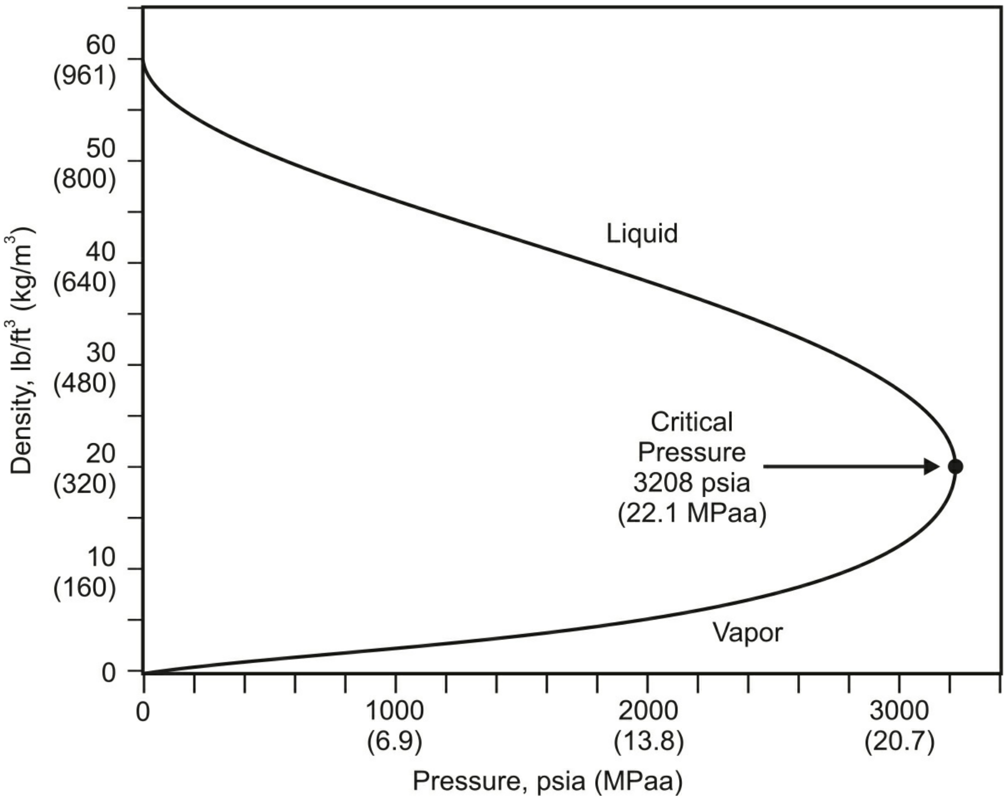


FIGURE 33.7 As boiler pressure increases, steam density and water density, which are greatly different at atmospheric pressure, approach each other, becoming equal at 3200 psia (22 MPaa), the critical pressure.

In cycles operating at pressures below critical pressure, where steam density is less than that of water, phase changes occur from water to steam, and then from steam back to water. While there are advantages favoring drum-type boilers (Fig. 33.8) for most subcritical pressure cycles, once-through boilers are sometimes used because of lower initial costs.

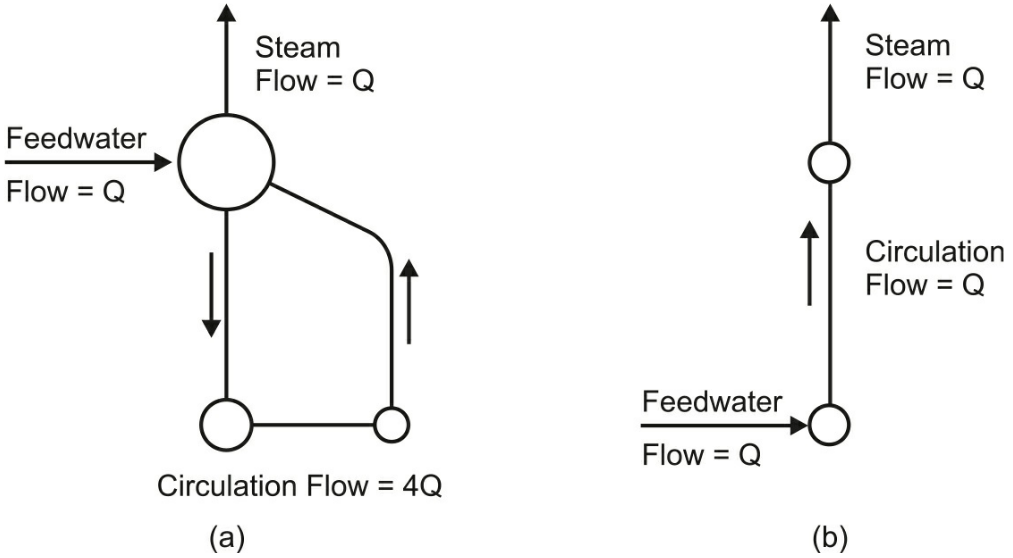


FIGURE 33.8 The basic differences between (a) drum-type and (b) once-through boilers.

Drum-type boilers have advantages in subcritical steam generation. They can produce high-purity steam with less stringent feedwater purity requirements, especially when the operating pressure is less than 2500 psig (17.2 MPag). Mechanical separation of steam from the recirculating boiler water leaves most of the undesirable solids behind in the boiler. Because boiler internal recirculation rates are about four times the rate of steam flow from the boiler, the fluid rising to the steam drum from the generating tubes will be about 75% water. This means that superheated steam, in which some boiler water impurities would become soluble, cannot exist in the boiler drum. Additionally, drum-type boilers are "simpler" to operate than once-through boilers.

In subcritical once-through boilers, a complete phase change occurs, with water entering at one end and superheated steam leaving at the other. There is no recirculation within the unit, nor is there a drum for mechanical steam-water separation. Boiler blowdown is impossible, so to prevent deposition of solids in the system beyond the point of water-steam phase change, requires stringent feedwater purity requirements, considerably higher than for drum-type boilers. In addition, that point of phase change must be located in a very low heat flux area of the boiler.

For cycles operating above critical pressure, no phase change occurs, so no steam-water separation is possible. Thus, at supercritical pressures, all steam generators are once-through.

In higher subcritical pressure cycles [2750–2850 psia (19.0–19.7 MPaa)], the margin of difference between the feedwater purity requirements of drum and once-through boilers is reduced. At such pressures, the effective mechanical steam-water separation is an advantage provided by drum-type boilers, but the advantage is limited by the increased difficulty in separating water from steam, as the densities of steam and water approach each other (Fig. 33.7). Also, mechanical separation devices in a boiler drum cannot remove the solids dissolved in the steam (vaporous carry over). For HP utility boilers, therefore, the concentration of solids in the steam is determined to an important extent, by their steam-water solubility ratios at the operating pressure. Silica is a well-known example of a compound that has increasing steam solubility with increasing pressure (Fig. 33.9).

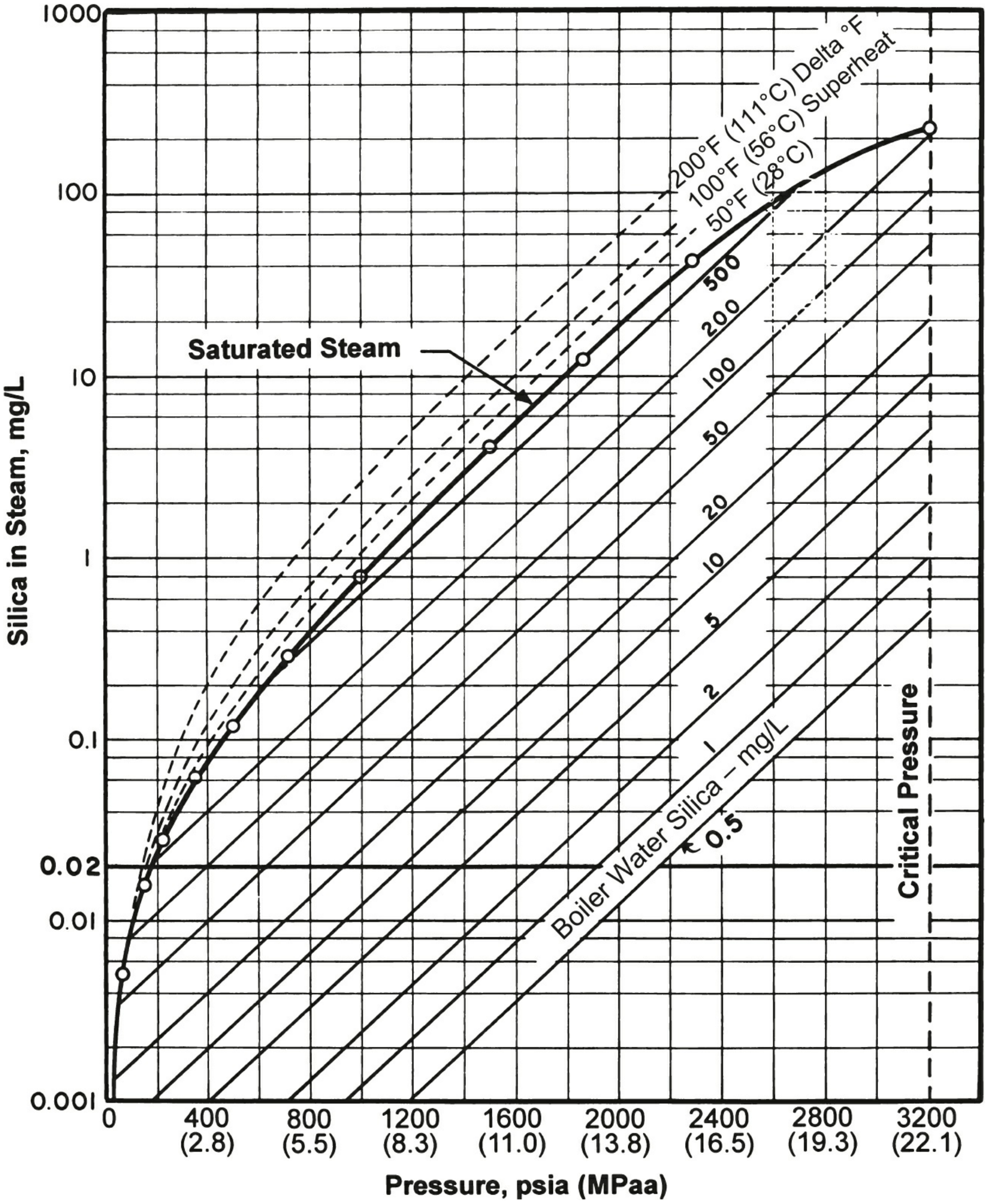


FIGURE 33.9 Distribution of silica between boiler water and steam.

If solids concentrations in the steam were to average 30 μg/L, for example, a 200 MW turbine would receive more than 200 lb/y (91 kg/y) of potential depositing solids. The portion that would deposit in the turbine and the portion that would remain in the steam to recycle with the condensate to the boiler cannot be accurately predicted. However, to avoid excessive turbine fouling, experience has shown the necessity of keeping total salt concentrations in the steam below 20 μg/L with silica not to exceed 10 μg/L. Further, to minimize any potential for stress corrosion cracking of turbine members, the steam solids should be free of sodium hydroxide and sodium chloride. While silica is potential foulant in the steam turbine, sodium hydroxide, sodium chloride, and sodium sulfate are potential corrodents (see Table 33.1).

Location	Parameter	Unit	Treatment Program			
			OT	AVT	PT	CT
Makeup	Specific Conductivity	µS/cm	≤0.1	<0.1	<0.1	<0.1
Makeup	Na, Cl, SO_4	µg/L	≤2	<2	<2	<2
Makeup	Silica (SiO_2)	µg/L	≤10	<10	<10	<10
Makeup	TOC	µg/L	≤100	<100	<100	<100
Feedwater	Cation Conductivity	µS/cm	≤0.15	0.2	0.2	0.2
Steam		µS/cm	≤0.15	0.2	0.2	0.2
Steam	Na, Cl, SO_4	µg/L	≤2	2	2	2

AVT, all-volatile treatment (oxidizing or reducing); CT, caustic treatment; Na, Cl, SO_4, sodium, chloride, and sulfate; OT, oxygenated treatment; PT, phosphate treatment; TOC, total organic carbon.

Source: EPRI Comprehensive Cycle Chemistry Guidelines for Fossil Plants, 2011.

TABLE 33.1 Feedwater and Steam Purity Specifications

Water purity is important for a different reason in nuclear power cycles. Although water becomes only slightly radioactive under neutron flux, producing only short-lived isotopes, the response of materials in the water under flux is of concern. Naturally occurring cobalt, for example, would be an extremely undesirable constituent of primary coolant water passing through the reactor core in either BWR or PWR cycles. The product would be highly radioactive, emitting high-energy gamma rays during subsequent decay. Therefore, cobalt must be avoided in such systems. Since most other metals also produce radioactive isotopes under neutron flux, the tolerance for feedwater and steam cycle corrosion products is limited in nuclear cycles for operating and maintenance safety.

Although the required degree of purity varies for different cycles, relatively high-purity water is required for all modern power cycles. Many water constituents must be measured and controlled at parts per billion (ppb or µg/L) concentration levels, compared to their measurement and control at parts per million (ppm or mg/L) concentrations in lower-pressure cycles or nonutility boilers.

Makeup water of the purity required for utility steam cycles can be produced reliably and at reasonable cost, by combinations of pretreatment equipment including reverse osmosis (RO), ion exchange, electro deionization (EDI), evaporation, and other pretreatment methods. Because makeup water volumes are usually 1% or less of total feedwater in typical power cycles, the major problem has become keeping the water pure after it has entered the cycle.

The two main sources for contamination of high-purity water are corrosion and inleakage. Corrosion represents not only metal damage, but also contamination of the system water with corrosion products that may then deposit in the boiler or turbine. Low-purity cooling water may enter the steam cycle at points of high vacuum (the surface condenser), and this inleakage is a second major sourcezof contamination. Careful design and selection of materials of construction minimize the occurrence of these problems.

Factors Affecting Chemical Treatment

HP boiler systems operate at pressures of 1000 psig (6.9 MPag) or greater. Several factors, including higher boiler water temperatures and longer boiler water holding times will dictate the choice of chemical treatment program.

Several factors must be taken into consideration when treating water in HP boilers. The most significant factors are discussed here.

Higher boiler water temperature, which increases as operating pressure increases, has significant impact on water treatment programs. At 500 psia (3.4 MPaa), for example, the saturation temperature of boiler water and boiler water-steam mixtures is 467°F (242°C). At 1800 psia (12.4 MPaa), saturation temperature is 621°F (327°C). Fireside-waterside temperature differentials are thus reduced, and as a result, boiler tube metal temperatures are higher. Tolerance for waterside deposits, which further elevate tube metal temperatures, is therefore significantly reduced. At the same time, HP boiler water temperatures often exceed permissible maximum temperatures for organic polymer chemicals that might otherwise be useful for deposit control.

Longer boiler water holding time, especially when coupled with higher boiler water temperatures, further restricts the use of thermally degradable organic treatment chemicals. With expensive high-purity feedwater, HP boilers often operate at 50 to 100 cycles of concentration (COC) (2–1% blowdown). Some utilities operate up to 200 cycles or 0.5% blowdown. This means very long residence times for each molecule of water and chemical in the boiler. Even where boiler water temperatures do not actually exceed upper limits for some treatment chemicals, holding times may need to be reduced by increasing boiler blowdown to 2% or more to achieve good results. Blowdown capability may be limited by the amount of makeup water available.

Smaller density differences between water and steam, at elevated pressures, reduce the natural tendencies of steam and water to separate from each other in a boiler steam drum. In a boiler operating at 500 psia (3.4 MPaa), for example, water is 47 times heavier than steam, but in an 1800 psia (12.4 MPaa) boiler, water is only 8.8 times heavier. Feedwater purity and proper control of boiler water concentrations, as well as the mechanical efficiency of steam separator and dryer equipment in the boiler drum, become extremely important as a result.

High saturated steam temperatures in the boiler drum significantly affect the solubility and selective carryover of certain boiler water constituents in the steam. This is particularly true of silica above 600 psia (4.1 MPaa) and to a lesser extent, sodium above 2400 psia (16.5 MPaa). As drum steam pressure and temperature increase, concentrations of silica and sodium in the steam increase with respect to the silica and sodium remaining in the boiler water.

Terminology

A familiarity with the following terms helps promote an understanding of HP boiler systems.

High-pressure boiler systems—From the standpoint of water treatment requirements, boilers in which steam is produced at or above 1000 psia (6.9 MPaa).

Units of measure—Boiler pressure is most commonly expressed in terms of pounds per square inch (psi) in U.S. units and kilopascals (kPa) or megapascals (MPa) in SI units. Readings provided by standard pressure gauges on boilers and control panels, which are only of pressures above atmospheric, are correctly expressed as psig in U.S. units and kPag or MPag in SI units. For a given gauge pressure reading, the total pressure, including atmospheric is expressed as pounds per square inch absolute (psia) in U.S. units or kPaa or MPaa in SI units. The properties of water and steam shown in engineering steam tables always express pressure in psia in U.S. units and kPaa or MPaa in SI units. Gauge readings may be converted to absolute pressure simply by adding atmospheric pressure (approximately 14.7 psi or 101 kPa at sea level) to the gauge readings.

$$1 \text{ psi} = 6.89 \text{ kPa or } 0.00689 \text{ MPa}$$

Utilities commonly use the term “cycle pressure” to describe a unit’s turbine throttle pressure, for example, 1800 psi (12.4 MPa) or 2400 psi (16.5 MPa). Steam drum pressure is normally 150 to 250 psi (1–1.7 MPa) higher than the throttle pressure. This loss is caused by pressure drop across the superheaters and connective piping.

Subcritical-pressure boilers—Those boilers that operate below the critical pressure of 3200.2 psia (22.1 MPaa), at which steam and water densities become equal.

Supercritical-pressure steam generators—Frequently encountered in some large electric utility stations, they produce steam at or above the critical pressure. Since there is no density difference by which steam and water can be separated in a boiler drum, supercritical steam generators are necessarily once-through types. Such units may be compared to a continuous length of heated pipe. The feedwater enters at one end and supercritical-pressure steam leaves the other for subsequent superheating in a conventional superheater arrangement.

Most supercritical electric utility units operate at a nominal 3800 psig (26.2 MPag) and have a turbine throttle inlet pressure of 3500 psig (24.1 MPag). Currently, the highest design pressure for a unit is about 5000 psig (34.5 MPag), and this unit actually operates at about 4500 psig (31 MPag).

Water Chemistry in Fossil-Fuel Plants—Liquid Phase

Apart from steam purity considerations, a major goal of cycle water chemistry and treatment control is the prevention of tube metal failures in HP steam generators.

Because makeup water is demineralized and essentially free of measurable hardness and other solids, tube failure due to waterside scale and deposits is far less likely to occur in utility plants, than in lower-pressure industrial boilers. Instead, in power plant drum-type boilers, tube metal failures are more commonly due to highly localized “crater” or “ductile gouging” forms of waterside corrosion, waterside hydrogen penetration and embrittlement of carbon steel, and corrosion fatigue.

The ductile gouging form of corrosion is a chemical attack characterized by irregular craters in the tube wall. The tube fails when wall thickness at the point of wastage is insufficient to withstand the internal pressure. The most common chemical agents in this form of attack are sodium hydroxide and phosphate. Even with a bulk boiler water within acceptable levels of contaminants as determined by usual methods of testing, a porous deposit on the tube wall provides a mechanism for concentrating chemical in contact with the tube surface, to several thousand milligrams per liter. Sodium hydroxide and phosphate concentrate in this manner and react first with the magnetite tube surface, and then with the elemental iron of the tube to form soluble iron complexes. For example, in the case of sodium hydroxide:

$$4\mathrm{NaOH} + \mathrm{Fe_3O_4} \rightarrow 2\mathrm{NaFeO_2} + \mathrm{Na_2FeO_2} + 2\mathrm{H_2O} \tag{33.2}$$

$$\mathrm{Fe} + \mathrm{NaOH} + \mathrm{H_2O} \rightarrow \mathrm{NaFeO_2} + 3\mathrm{H} \tag{33.3}$$

The parent tube metal is thus exposed to react with water to reform protective magnetite.

$$3\mathrm{Fe} + 4\mathrm{H_2O} \rightarrow \mathrm{Fe_3O_4} + 8\mathrm{H} \tag{33.4}$$

In either case, localized wastage of tube metal occurs and hydrogen is produced as a reaction product. The atomic hydrogen thus produced is capable of intergranular penetration of steel and of reaction with carbon in the steel to form methane gas.

$$4H + C \rightarrow CH_4 \qquad (33.5$$

Not only is the steel thus weakened by decarburization along its grain boundaries, but the formation of methane develops pressure between grains in the steel microstructure, producing intergranular cracks. The result is failure of the tube wall, when such intergranular decarburization and micro fissuring have sufficiently reduced its strength. Although some waterside wastage of metal may have occurred in the corrosion reaction that produced the hydrogen, hydrogen damage normally results in thick-edged fracture before the wall thickness is reduced to the point that stress rupture occurs. In such thick-edged or “brittle” fracture failures, it is not uncommon for an entire irregularly shaped “window” to be blown out of an affected tube (Fig. 33.10).

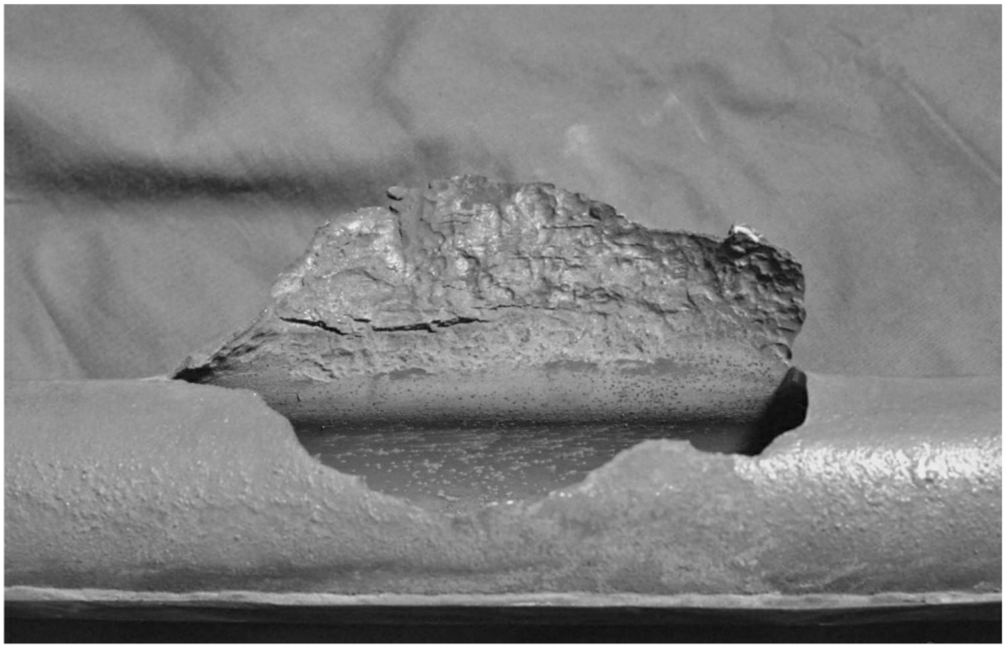


FIGURE 33.10 Example of hydrogen damage resulting in a thick-edged failure window in a boiler tube.

In summary, the major causes of ductile gouging and hydrogen damage of carbon steel tubes are (1) a chemical agent that will be corrosive if sufficiently concentrated and (2) a concentration mechanism. For more information on boiler failure types and causes, refer to The Nalco Guide to Boiler Failure Analysis, 2nd edition

There are several mechanisms capable of producing high, localized salt concentrations. Any condition of heat input, in excess of the cooling capacity of the flow of fluid circulating through a tube can result in film boiling on the metal surface, with evaporative concentration of salts occurring. Localized pressure differentials, as created by high velocity through a tube restriction such as a welding back-up ring can result in small pockets of "flashing" water, concentrating salts on the downstream side of the restriction. The most common mechanism is preboiler corrosion, with pickup of metals and the subsequent deposition on heated boiler tube surfaces, where they function as porous deposits. Evaporation beneath the deposit draws in boiler water to replace evaporation loss, but prevents solids from leaving the area. This phenomenon is commonly called "wick boiling" and is shown in Fig. 33.11.

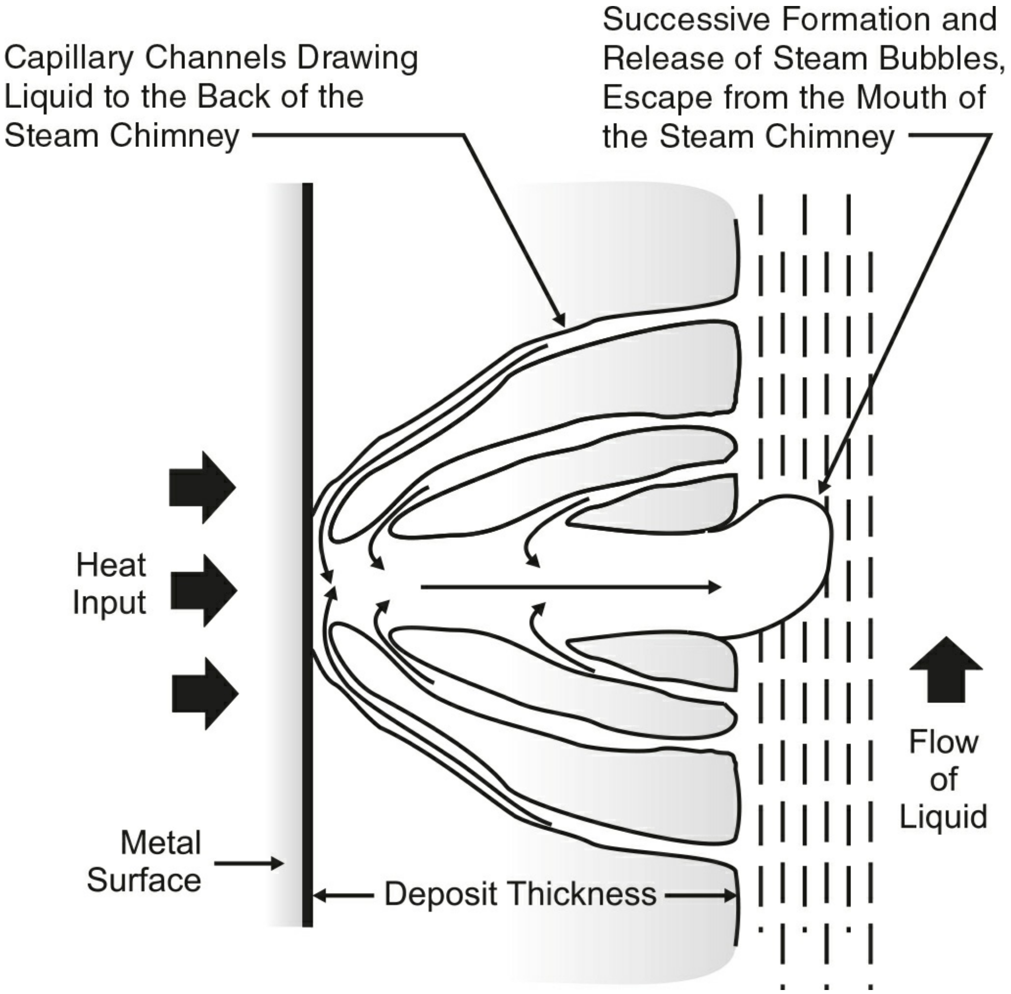


FIGURE 33.11 Wick boiling.

To prevent such corrosion and hydrogen damage, all concentration mechanisms must be eliminated, or potentially corrosive chemical agents must be excluded from the boiler water. Since porous deposits of preboiler corrosion products create the most common mechanism for chemical concentration, strict attention to protection of preboiler metal surfaces is critical, and periodic chemical cleaning to remove these deposits is required.

A significant characteristic of modern utility cycles is the high ratio of preboiler surface area to that in the boiler itself. While a ratio of about 0.3 would be typical in a 750 psia (5.2 MPaa) system, a ratio of about 1.3 would be typical at 2800 psia (19.3 MPaa). This is a reflection of the multiple stages of regenerative feedwater heating, commonly employed to increase cycle efficiency. To the water engineer, the higher ratio means that the area from which metals can be picked up is larger than the area on which they are likely to deposit.

Metals used in fabrication of condensers and feedwater heaters are commonly stainless steels and alloys of copper, such as brass, cupro-nickel, and monel. Thus, iron and copper are the principal contaminants likely to be acquired by feedwater en route to the steam generator.

Feedwater pH is an important factor in minimizing preboiler corrosion of metals. For iron and its alloys, feedwater pH values in the range of 9.2 to 9.6 are considered optimum. For copper and its alloys, feedwater pH values generally should be in the range of 9.0 to 9.3. Volatile alkalis such as ammonia and organic amines that will not contribute dissolved solids are commonly used for pH control in the condensate-feedwater portion of the steam cycle.

Feedwater oxygen also has a great bearing on preboiler corrosion and contamination. An oxygen level of 10 μg/L or less at the condensate pump discharge is usually specified. The largest potential for oxygen admission occurs in the high-vacuum portions of the cycle. Oxygen can be reduced to low levels mechanically, either in deaerating surface condensers or in separate deaerators located ahead of HP feedwater pumps. For removal of residual oxygen, reducing agents like hydrazine may be injected continuously immediately downstream of the condenser. Hydrazine is a chemical oxygen scavenger that introduces no solids to the cycle. Its concentration is controlled in the range of 10 to 20 μg/L in the feedwater, usually measured at the economizer inlet. Because of the potential risk to personnel handling hydrazine, a carcinogen, proprietary substitutes have been developed that react very much as hydrazine. The most widely used substitutes contain carbohydrazide or iso-ascorbic acid.

System metallurgy must also be considered when selecting feedwater and condensate treatment programs. The preboiler equipment in many plants contains both copper alloy and mild steel metallurgies. Current technology can optimize the passivation of each of these materials separately, but not for both materials in the same system. Copper oxide formation, for example, requires a strong reducing environment, while steel oxides become more passive under neutral or slightly oxidizing conditions. For example, dissolved oxygen (DO) levels of 2 to 4 μg/L provide the optimum environment for passivation of all-steel systems, but would cause corrosion of the copper alloys.

Many plants utilize online oxidation-reduction potential (ORP) analyzers to monitor the oxidizing environment in the condensate and feedwater. The same measurement can be used to control passivator/scavenger feed. Increasing DO increases the oxidizing potential (ORP) of the condensate and feedwater.

Based on EPRI studies conducted in 2000, maintenance of a reducing environment is essential in controlling copper corrosion in the condensate and feedwater cycles. Copper corrosion control is accomplished by converting cupric oxide (CuO) to cuprous oxide (Cu_2O), which forms a stable and more durable protective film. For copper-based systems, it is imperative that the condenser, feedwater heaters, and piping be maintained in a reducing state of at least -50 mV at all times, including standby conditions. The recommended limits for normal operation are -150 to -250 mV in the feedwater of mixed metallurgy systems. (These limits are extremely difficult to meet in cycling units and may require unit specific standby procedures to accomplish.)

Newer combined cycle HRSG and coal-fired units are constructed without the use of copper alloys in the steam cycle. In addition, many older coal-fired units replaced copper-alloy feedwater heater and condenser tubes, to remove the corrosion and deposition problems associated with copper alloys. That enables these units to focus specifically on minimizing steel corrosion. Fundamentally, oxide films formed on mild steel are more durable when formed at higher pH and with greater concentrations of oxygen. Durability increases as a result of plugging the voids and imperfections in the magnetite (Fe_3O_4) film with hematite (Fe_2O_3). This “plugging” action helps prevent impurities from reaching the base metal. Improved stability in the oxide film reduces both general corrosion and flow-accelerated corrosion (FAC), critical to reduction in corrosion product transport and chemical cleaning frequency requirements. Current guidelines recommend that the room temperature ORP in all-ferrous feedwater systems be controlled between ≥0 and +50 mV for all-steel systems. EPRI recommends that units with high-purity feedwater (<0.2 µS/cm cation conductivity) and low DO (<10 µg/L at the condensate pump discharge) eliminate the use of oxygen scavengers/passivators. Iron transport and soluble iron studies should be performed before and after eliminating the oxygen scavenger/passivator to confirm iron transport values are reduced, preferably below 5 µg/L. Feed of oxygen scavenger/passivator may provide a benefit, if the boiler feedwater purity degrades, if the unit changes to cycling duty, or if the unit is removed from service on a frequent basis. Iron transport and soluble iron studies are essential in evaluating the need for, and the impact of, oxygen scavenger/passivator feed.

Ammonia, an important variable in copper alloy corrosion, is generally present in power cycles, either due to direct addition or decomposition of chemicals such as hydrazine or amines that have been added to the system. In sufficient concentrations, ammonia reacts directly with copper to form soluble complexes, or it can contribute to stress corrosion cracking of copper alloy tubes. Even at lower concentrations, ammonia can react with protective copper oxides on condenser and heater tube surfaces, exposing parent metal to wastage by reaction with oxygen in the feedwater. To minimize copper corrosion, many operators limit the maximum cycle ammonia concentration to 0.3 to 0.5 mg/L. The ammonia limits can be met, by carefully controlling chemical additions to the cycle, and by proper regeneration of condensate polishers. If the ammonia concentration increases beyond the desired maximum, temporarily dumping the normally recycled air removal system's after-cooler drains (Fig. 33.12) will help remove the excess from the system.

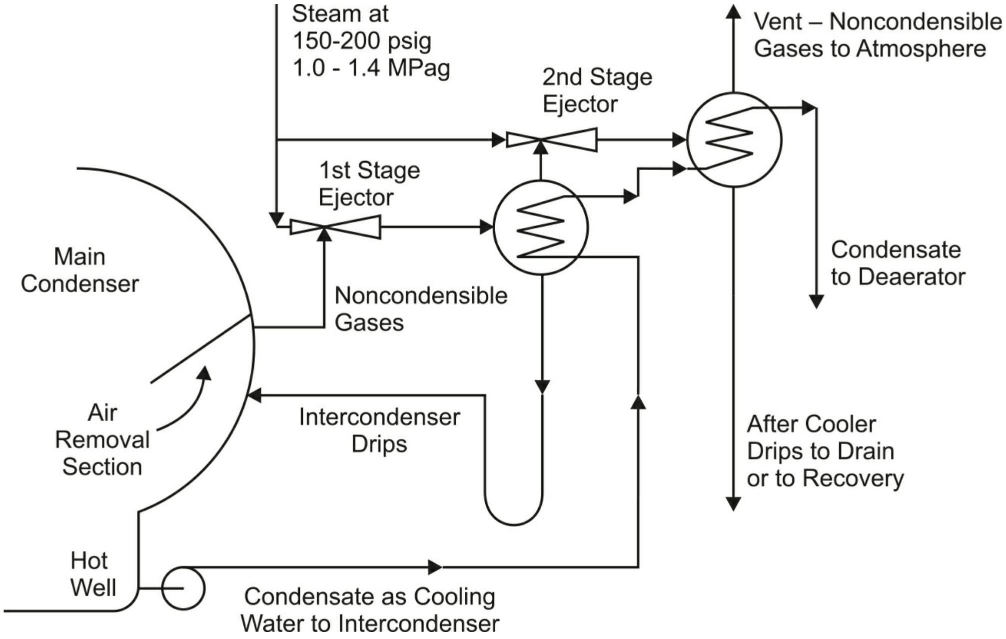


FIGURE 33.12 Noncondensable gases, including air from inleakage and ammonia from the steam cycle, are removed by ejection and inter and after-condensers. Final drips may be reclaimed or discarded, if concentrations are too high.

Good design calls for careful selection of materials of construction to withstand the environment of the preboiler system. Condenser tubes in freshwater coolant service are commonly brass, cupro-nickel, stainless steel, or titanium. LP stage heaters commonly use brass, cupro-nickel, or stainless steel alloys, except for supercritical pressure cycles, where even minute concentrations of copper can cause serious turbine fouling problems and the use of steel alloys is required. HP stage heaters are fabricated of cupro-nickel alloys, stainless steel, and carbon steel.

It is common practice to reduce metallic “crud” in utility feedwater by polishing the condensate through a filter of mixed cation and anion exchange resins. Filtration removes the insoluble crud, and ion exchange removes any dissolved contaminants that have entered the cycle by inleakage.

As shown in Fig. 33.13, polishers are generally located between the condenser and the first feedwater stage heater. This is due to the fact that a large part of the vulnerable preboiler metal surface area is in the condenser and on the steam side of stage heaters, cascading heater condensate drips back to the condenser. This placement protects high-temperature feedwater heaters, the steam generator, and the turbine from deposit-forming contaminants. Temperature limitations on ion exchange resin control the location of polishers in the cycle. Regenerable polishers can withstand only about 120°F (50°C) and must be confined to the condenser outlet. Powdered resin units may be placed in higher-temperature locations, but still in the lower-pressure stage heater train.

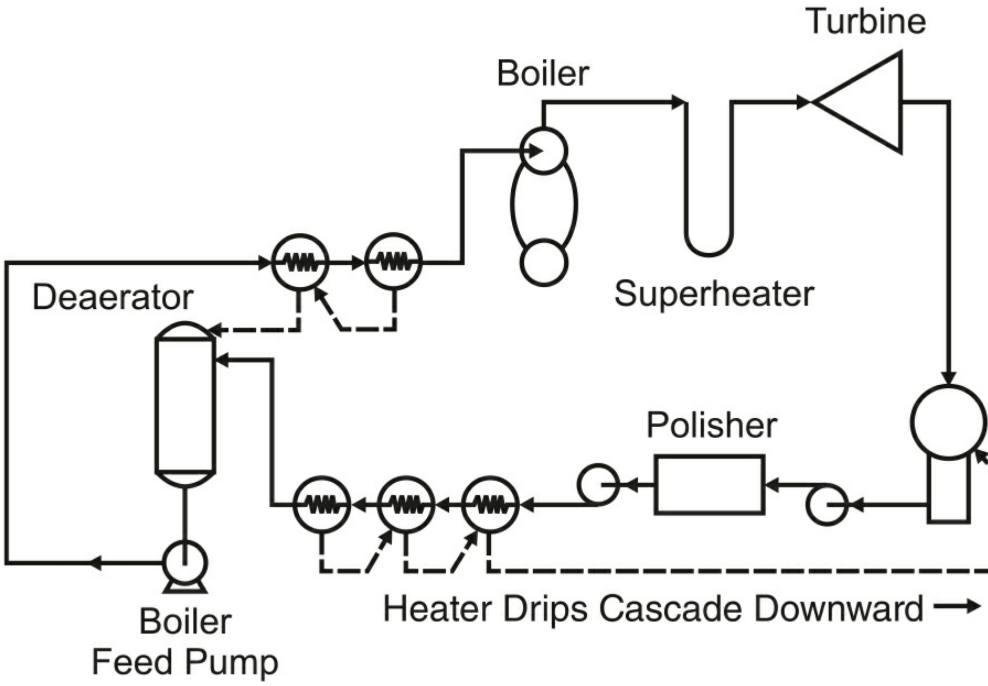


FIGURE 33.13 Power cycle with full-flow condensate polishing.

For the best cost performance, regenerable mixed bed polishers are commonly operated at service flow rates over 50 gpm/ft^2 (122 m^3/[h · m^2]), about 10 times the rate employed in raw water demineralization. In some cases, to avoid any possibility of contaminating cycle water with regenerant chemicals, resins are removed from the polisher for external regeneration and periodic cleaning.

Nonregenerable powdered resin polishers have found wide acceptance in utility systems. The finely ground resin particles provide good filtration and excellent kinetics for ion exchange. This type of condensate polisher is typically operated at service flow rates of about 4 gpm/ft^2 (10 m^3/[h · m^2). During cycle cleanup, such as during start-up, an inexpensive cellulose filter aid may be included in the powdered resin mixture. In any case, when the resins become fouled or exhausted, they are discarded.

For either regenerable or nonregenerable polishers, the cation exchange resin can be used in ammoniated form to prevent removal of ammonia from the cycle. Anion resins are in the hydroxide form.

Virtually all once-through boilers, because of their especially high-purity water requirements, employ polishing of feedwater. Many plants polish the total feedwater flow; some polish as little as 20% at full load with increasingly higher portions as load is reduced.

In drum-type boiler systems where water purity is less critical, condensate polishing may not be economically justifiable for normal day-to-day operations. However, even in these systems condensate polishing may be worthwhile, in order to protect the boiler and turbine from the high levels of crud and silica common during initial start-up and subsequent restarts. A polisher can greatly shorten the unit start-up time and often pay for itself in the cost of purchased power that would otherwise be necessary during the start-up period.

Condensate polishing eliminates most deposit-forming materials that create chemical concentration mechanisms in steam generator tubes, but such measures are never completely effective. Long-term accumulations of such deposits, principally iron and copper oxides, on boiler tube surfaces are removed by periodic cleaning. Utility boilers are generally considered “clean” with deposit weight densities less than 5 g/ft^2 (5.4 mg/cm^2) of tube area. Subcritical pressure boilers are considered dirty when accumulations exceed 12 to 40 g/ft^2 (12.9–43.1 mg/cm^2), depending on pressure. Supercritical boilers are considered dirty at accumulations over 12 g/ft^2 (12.9 mg/cm^2). Utility boilers with normal feedwater conditions may be routinely chemically cleaned every three to six years. Many boiler operators minimize cleanings by carefully monitoring deposit weight density in high heat flux areas of the furnace, through tube sampling and analysis during planned maintenance outages.

Corrosion and hydrogen damage of boiler tubes are not likely to occur, where rigorous control of preboiler chemistry, condensate polishing, and periodic cleaning keeps boiler surfaces clean. Since clean tube surfaces cannot be assured at all times, and conditions other than waterside deposits can create chemical concentration mechanisms, it is general utility practice to avoid high concentrations of potentially aggressive sodium hydroxide in the boiler water, less than 1 ppm.

Corrosion of boiler steel is a function of pH (Fig. 33.14), and pH values ideally should fall within a general range of 9.0 to 11.0. A safe value must be achieved without producing excessive residuals of sodium hydroxide. In utility practice, this is accomplished either with a selection of sodium phosphate salts, sodium hydroxide or with a “zero solids” treatment using all-volatile chemicals.

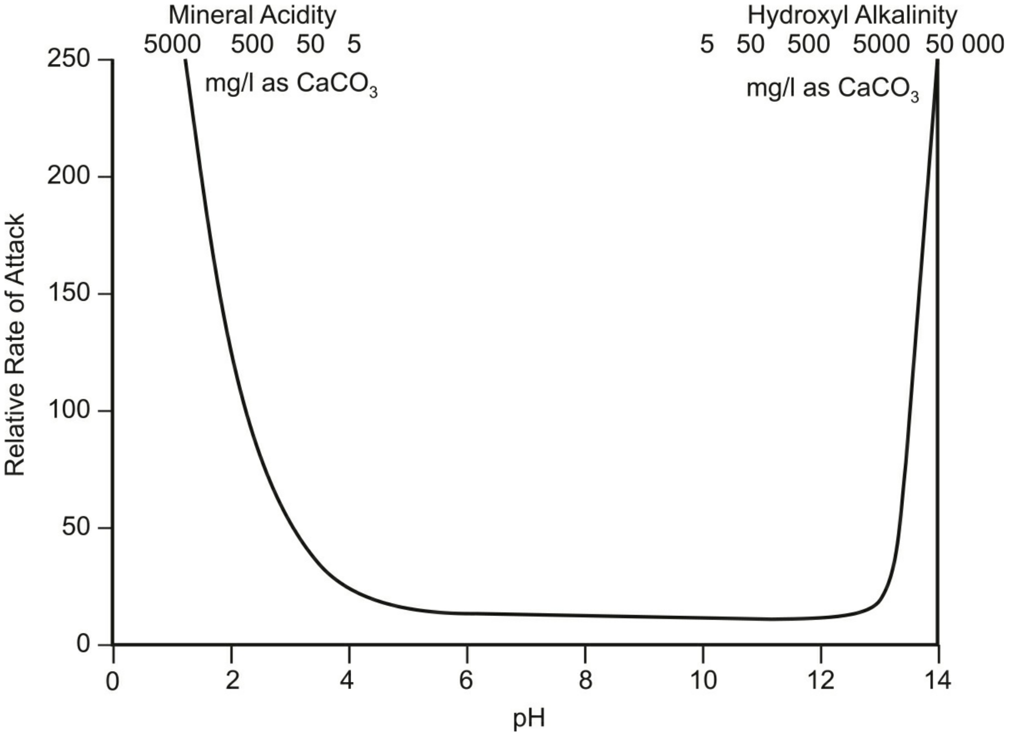


FIGURE 33.14 Relative corrosion rate of boiler steel versus pH and caustic concentration.

Phosphate treatments (PTs) have been applied to subcritical boilers for decades, and continue to be a primary treatment used in drum boilers today. Historically, there has been a multitude of phosphate compounds and mixtures blended with other treatment philosophies. Some of the traditional PTs such as congruent phosphate treatment (CPT), coordinated PT, and equilibrium phosphate treatment (EPT) have been used over the last 50 years across the fleet of fossil boilers and HRSG evaporators, sometimes successfully, sometimes resulting in tube failures and other problems. Use of CPT, where mono- and/or di-sodium phosphate are used to develop operating control ranges below sodium-to-phosphate molar ratios of 3:1, has resulted in acid phosphate corrosion in certain boilers/HRSG evaporators which have heavy deposits and have experienced phosphate hideout. Use of EPT forced many operators to use very low levels of phosphate (<0.20 mg/l), which essentially provided poor protection in the cases of acidic contaminants from condenser leaks or other sources.

Most recent guidelines from EPRI and others stipulate the use of a blend of trisodium phosphate (TSP) as small additions of sodium hydroxide (caustic) to achieve pH control in drum boilers. The use of monosodium and disodium phosphate is not allowed. This PT is defined by a pH and phosphate control range as shown in Fig. 33.15. The PT range is bounded by sodium to phosphate molar ratio of 3:1 and TSP + 1 mg/l NaOH with a pH above 9.0 and a minimum phosphate limit above 0.3 mg/l. The goal of this treatment is to ensure a solid-alkali-based pH/alkalinity in the boiler or HRSG to provide a noncorrosive pH and neutralize acid forming contaminants such as chlorides and sulfates. Figure 33.16 indicates the areas under risk from tube failure.

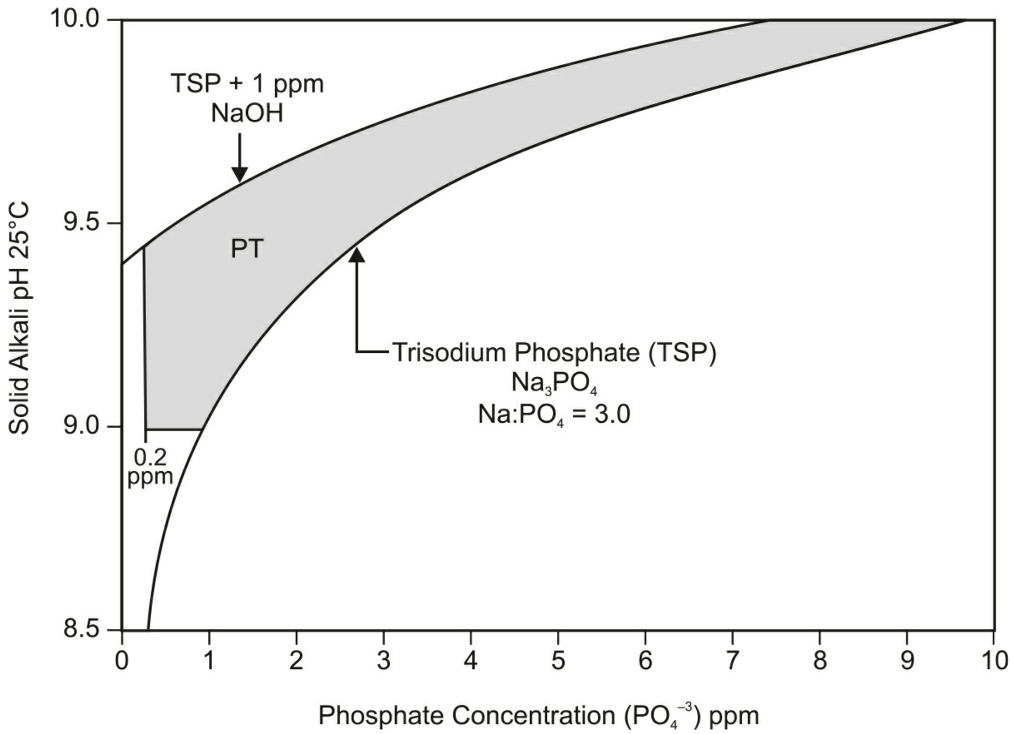


FIGURE 33.15 Operation range for PT. (*Source: EPRI Comprehensive Cycle Chemistry Guidelines for Fossil Plants 2011.*)

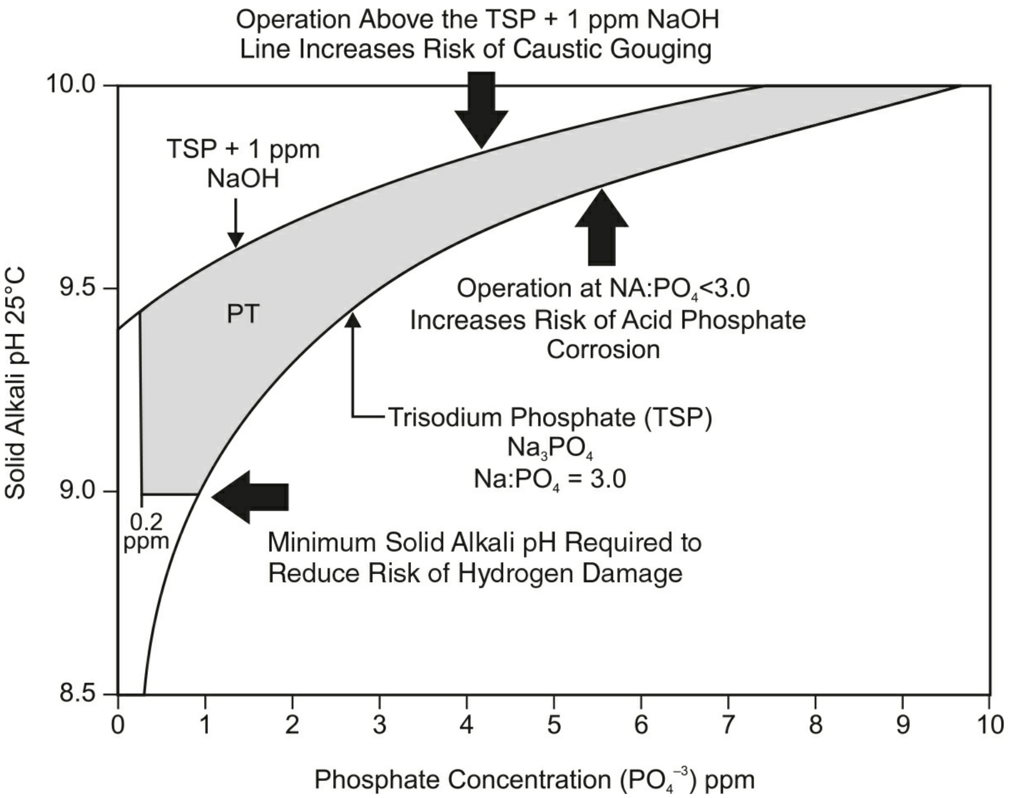


FIGURE 33.16 Operation range for PT including areas identified as risk of tube failures. (*Source: EPRI Comprehensive Cycle Chemistry Guidelines for Fossil Plants 2011.*)

Caustic Treatment (CT) is another solid alkali boiler water treatment program. Drum pH is maintained through the addition of sodium hydroxide only. Candidates for CT include boilers with severe phosphate hideout, a history of condenser tube leaks, or saline cooling water. Such systems would not be able to use all-volatile treatment or adequately control PT. Maximum allowed boiler water chloride concentration varies with unit pressure. For example, chloride must be less than 0.3 mg/L if drum pressure is 2500 psia (17.2 MPaa). Sodium hydroxide dosage is 2.5 times the chloride concentration. Sulfate concentration must be less than twice the chloride concentration.

CT programs can be difficult to control; however, and therefore, they require extra diligence to minimize both high and low pH excursions. There are three possible choices employing all-volatile chemistries:

1. All-volatile treatment with reducing agents or AVT(R)
2. All-volatile treatment without reducing agents or AVT(O)
3. Oxygenated treatment (OT)

No solids are added to the boiler or HRSG if all-volatile treatment is used. Since no phosphate or caustic is added to the drums, the feedwater treatment becomes the boiler treatment, providing boiler water pH buffering through the ammonia or amine used for control of the feedwater system pH. As the ammonia or amine pH buffer is weaker than the sodium phosphate or caustic pH buffer of the solids treatment options, the use of AVT requires consistently high-purity feedwater.

It is important to understand the difference between “feedwater” and “drum internal” treatment programs. Both AVT(O) and AVT(R) programs can be used as feedwater treatments, even if phosphate or caustic is added to the drums for internal pH control. It is good practice to differentiate between the two. For example, a plant with copper alloy feedwater heaters would normally utilize AVT(R) feedwater treatment, but could use either phosphate or caustic for boiler internal treatment (PC or CT). If no phosphate or caustic were used, then the drum internal treatment program would also be AVT(R).

Both AVT(R) and AVT(O) are excellent treatment options for drum-type boilers and HRSG, if the feedwater purity will support them. AVT is an excellent choice for systems with condensate polishers, all-steel plants with air-cooled condensers, and a requirement for once-through boilers.

All condensate and feedwater systems in utility steam cycles are treated with all-volatile treatment, as steam attemperation water is taken from the feedwater pump discharge. All-volatile treatment is also the default program for the low-pressure (LP) drum of combined cycle HRSG, when the LP drum acts as an integrated deaerator. In plants of this type, LP boiler water becomes feedwater for the intermediate-pressure (IP) and high-pressure (HP) drums and is used for steam attemperation. Where this is the case, all-volatile treatment is the only option, since no solids (phosphate or caustic) can be present in the attemperation water. AVT is also the default program during steam blows and initial boiler commissioning. AVT is easy to apply and control, providing the feedwater purity remains within specification.

The AVT(R) program must be used for systems containing copper alloy feedwater heaters, where a reducing environment is required to minimize corrosion. Primary pH control is achieved with either ammonia or amine. Passivator (generally either hydrazine or carbohydrazide) is used to control the reducing environment in the condensate-feedwater system.

The AVT(O) program is used for all-steel systems, and no passivator is typically fed. In some cases, a reduced level of passivator can be used or in some cases a small amount of DO may have to be added. The presence of small amounts of DO promotes the formation of a more adherent iron oxide passivation layer and lowers the potential for FAC. The need for passivator feed in all-steel plants can best be determined through a detailed soluble and insoluble iron transport study.

Both AVT(R) and AVT(O) treatments require very high-purity feedwater at all times. Feedwater cation conductivity must remain less than 0.2 µS/cm, and DO at the condensate pump discharge must remain less than 10 µg/L.

OT is the third treatment option for all-steel systems with condensate polishers. OT minimizes corrosion of all-steel systems by promoting the formation of mixed iron oxides to form a more tightly adherent passivation layer. It results in lower metal transport and minimizes the need for chemical cleaning. OT is the preferred treatment for most supercritical boilers. It is also a strong candidate for drum-type units with all-steel construction, and full-flow condensate polishers or air-cooled condensers.

OT requires extremely high-purity makeup, high-purity condensate, and extremely tight control. OT programs will be corrosive, if contamination of the feedwater provides the electrolyte necessary to support the corrosion reaction. Many systems otherwise meeting the criteria for OT cannot achieve the tight control required. Cation conductivity must always be less than 0.15 µS/cm, without exception. OT is extremely effective in the right situation and is the first treatment choice, if the unit meets the criteria.

As stated earlier, a disadvantage of AVT for drum-type boilers is that the boiler water is lightly buffered, and in the event of feedwater contamination, is subject to significant and rapid pH excursions. There is no tolerance for condenser cooling water inleakage, unless condensate polishing is provided.

Contaminant salts entering the cycle from other sources may produce acids or alkalis capable of being concentrated locally to corrosive levels. Typical contaminant sources are:

- Condenser leakage
- Treated makeup water contamination by evaporator carryover or demineralizer leakage
- Regenerant contamination from ion exchange units
- Incomplete removal of chemical cleaning solvents or alkalis

Of these, condenser leakage is the most significant. Boiler tube hydrogen damage that results from condenser leakage is particularly likely to occur, where the cooling water is brackish. The reactions of contaminants such as calcium chloride and magnesium chloride in boiler water, after depletion of any soluble phosphates, are:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl \tag{33.6}$$

$$CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl \tag{33.7}$$

In high-purity unbuffered boiler water, very small cooling water leaks can reduce pH to 4 or less. Where the acid is concentrated locally within a deposit at a tube surface, corrosion and hydrogen damage proceed rapidly. While protection is afforded by condensate polishers, strict surveillance of condenser leakage is prudent for drum-type boiler cycles without polishers. Generally, leaks causing 0.5 mg/L (total chloride and sulfate) feedwater concentrations can usually be accommodated in normal operation without serious difficulty. Feedwater concentrations of 2 mg/L of total chloride and sulfate may be tolerated for short periods, but immediate boiler shutdown is usual when a condenser leak produces concentrations greater than this. Immediate boiler shutdown is always indicated where acceptable boiler water pH cannot be maintained.

The necessary continuous surveillance of condenser leaks usually relies on cation conductivity monitoring, which effectively senses concentration changes as small as 2 µg/L. In this method, a condensate sample passes through a column of acid-form cation resin to convert sulfate, chloride, and nitrate salts to more electrically conductive sulfuric, hydrochloric, and nitric acid. The conductivity is then measured in the resin-treated sample.

Monitors for silica and sodium are alternative devices for detection of condenser leaks. Against background concentrations commonly encountered in turbine condensates, available monitoring equipment can reliably detect changes of 20 µg/L or less in either of these contaminants.

Steam Phase Problems

In the 1950s, it became apparent that the silica in steam that was causing deposits on the LP stages of utility turbines was not carried out of the boiler in droplets of the boiler water, but rather it was a gaseous fraction of the high-temperature vapor. (This was a contribution to water chemistry from the field of geology.) Previously, it had been long recognized that carbonates would break down to yield carbon dioxide (CO_2) in steam, but now, there was growing evidence that minerals might actually volatilize and leave the boiler in the gas phase too. With development of the once-through boiler, it was apparent that any minerals in the feedwater, volatile or not, would be passed along to the turbine and condenser. This led to the development of polishing demineralizers for the condensate stream to prevent buildup of minerals in the cycle that would lead to deposits. It also led to development of AVT, or the use of volatile chemicals such as ammonia and hydrazine, as the only chemical treatment applied to the cycle.

The purity of makeup improved greatly in the succeeding years. Demineralizers replaced evaporators not only based on economics but also on quality. Evaporators (as then designed) were unable to produce the low silica levels needed to avoid turbine deposits.

The newer systems began to experience turbine blade cracking, generally occurring on the last two wheels, and it was found that the cracking was caused by caustic. Furthermore, ammonia concentrations and pH were difficult to control, because the polishing demineralizer removed ammonia (usually causing an increase in sodium) and erratic control often led to attack of copper alloy heater tubes.

Because of these problems, it became necessary to study steam-phase conditions throughout the cycle. This required the development of sophisticated and reliable isokinetic sampling systems capable of handling both superheated and wet steam, at high pressure and under vacuum. Analyses were made of the nature and causes of system deposits, and basic research was undertaken in the physical chemistry of the elements and compounds found. In response, limits were placed on sodium, chloride and sulfate levels, because these seem to be the major cause of stress corrosion cracking and corrosion fatigue attacks on turbine blading, a problem more common to AVT systems than to drum-type boilers using PT.

There is still more to be learned about vapor-phase chemistry, but present state-of-the-art calls for extensive sampling and continuous analysis of makeup, condensate, deaerated water, feedwater at the economizer inlet, boiler water, superheated steam, and selected stage heater drains. The analyses include continuous measurement of conductivity, pH, DO or room temperature

ORP, sodium, and silica (on demineralized makeup); iron, copper, and nickel on feedwater, heater drains, and condensate; ammonia before and after condensate polishers; hydrazine or passivator on feedwater; and boiler water testing (with drum-type boilers). With this type of monitoring, conditions can be continuously scrutinized both during steady load and during shutdown and start-up, so that corrective adjustments can be made in chemical treatment, or operating problems (demineralizer regeneration, control of air inleakage, control of condenser leakage, etc.) can be corrected.

Subsequently, it was found that even if the low levels of sodium, chloride, and sulfate were maintained in the steam, that deposits may still form on the LP stages, but that it wasn't until out of service conditions exposed these deposits to an oxygenated liquid or humid environment, that the corrosion processes were initiated. Today then improved lay-up protection for turbines is recommended using nitrogen or dehumidified air to prevent LP turbine corrosion.

The steam-phase chemistry relative to geothermal plants is completely different from conventional plants, as the vapor often contains additional contaminants (e.g., boron and sulfur compounds) at parts per million (mg/L) rather than parts per billion (μg/L) levels.

Water Chemistry in Nuclear Plants

The nuclear PWR (Fig. 33.4) has two major water systems:

1. The primary loop or reactor coolant system
2. The secondary loop or steam generator-turbine cycle

Components of the primary loop are the reactor vessel, a pressurizer, steam generators (heat exchangers), and circulating pump. In the primary loop, water temperature is allowed to rise only about 50°F (28°C) passing through the reactor, so recirculation rates are quite high to absorb the amount of heat generated. Pressure of the recirculating water is kept high enough to keep the water from boiling. The pressurizer maintains this pressure and absorbs changes in volume produced by changes in temperature. For maximum corrosion resistance, wetted surfaces in the primary loop are usually stainless steel or nickel-based alloys.

High purity must be maintained in the primary loop water to minimize fouling of reactor and exchanger heat transfer surfaces, and to avoid contaminants that could form undesirable radioactive isotopes under neutron flux. Controlled additions and removals of boric acid in the primary loop water provide the correct concentration of neutron-absorbing boron needed to control neutron flux and energy transfer. Chemicals such as lithium hydroxide, forming relatively safe radioisotopes under neutron flux are used for pH control in the primary loop.

Under nuclear radiation in passage through the reactor, some of the primary loop water is decomposed into hydrogen and oxygen as follows:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{33.8}$$

To suppress oxygen generation and to scavenge oxygen entering the system, hydrogen gas is commonly added. Primary loop water purity is usually maintained by continuously passing a portion of the circulating water through a mixed bed demineralizer. These generally utilize anion resins in the borate form, to avoid removal of boron from the water. As impurities accumulate, these resins tend to become radioactive and regeneration becomes impractical. The resins are disposed of as a solid radioactive waste.

Two basic heat exchanger designs are employed as secondary loop steam generators in PWR systems. The recirculating U-tube type (Fig. 33.17) is analogous to a drum-type boiler in a fossil-fuel system. Having an internal recirculation rate of 3 to 4 times the steam flow, the unit provides mechanical water separation and continuous blowdown. However, it differs from fossil-fuel boilers in that there is no provision for superheating the steam.

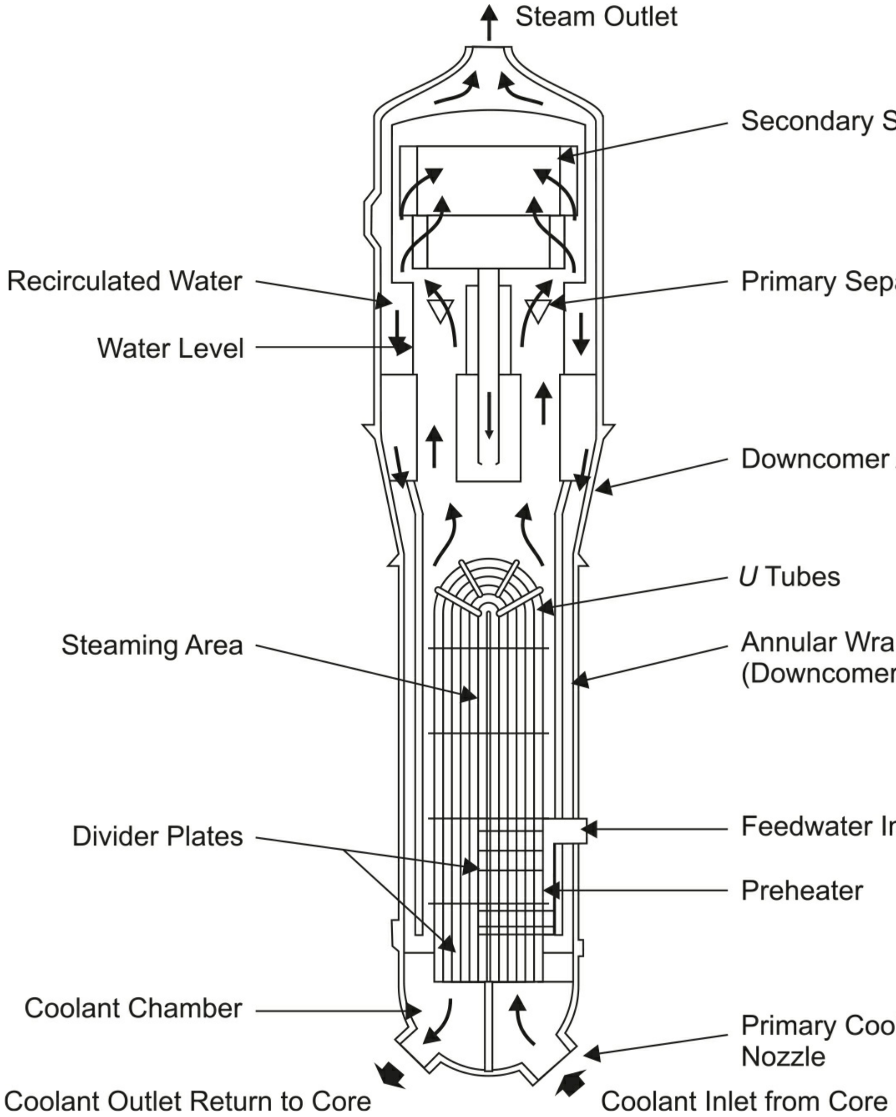


FIGURE 33.17 PWR vertical U-tube recirculating-type steam generator with integral feedwater preheater.

The other PWR heat exchanger design (Fig. 33.18) provides once-through-type steam generation. The heat exchanger is baffled so that incoming feedwater first flows down through an outer annulus in which it is heated to saturation temperature, and then it is converted totally to steam and is slightly superheated in a single upward shell-side pass through the tube bundle. Depending on load, up to about 60°F (33°C) superheat can be achieved.

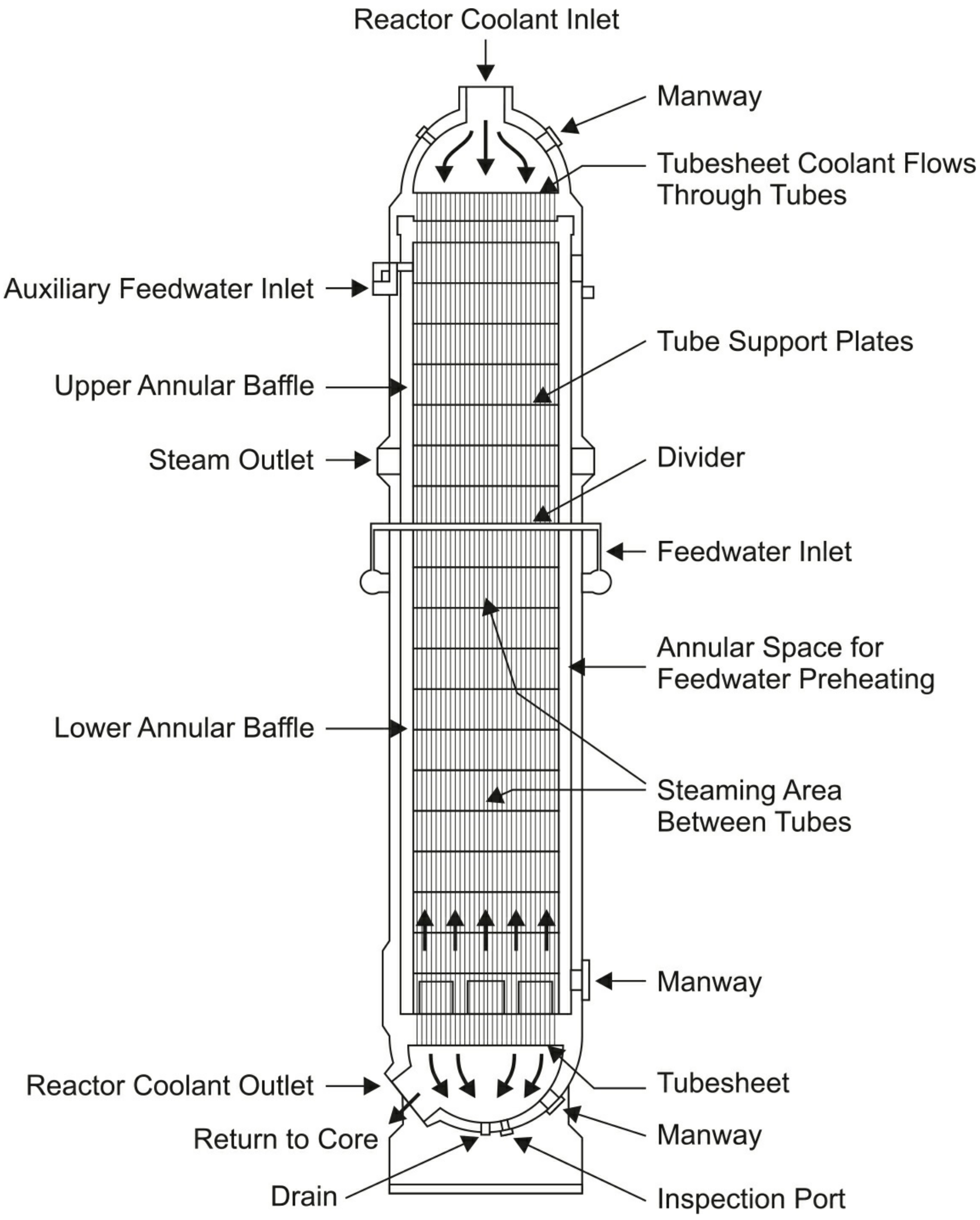


FIGURE 33.18 PWR once-through-type steam generator. (*Adapted from Steam—Its Generation and Use, Babcock and Wilcox Company, 1972.*)

Either type steam generator requires maximum corrosion resistance on the primary side, so tube materials are commonly special nickel-iron-chromium alloys (e.g., alloys 600, 690, and 800). Carbon steel shells are generally used, although those parts of the shell surface constituting the primary coolant inlet and outlet plenums are clad on the coolant waterside.

AVT treatment is commonly practiced for all types of nuclear PWRs. Ammonia, as well as low-volatility organic amines (monoethanolamine, methoxypropylamine, or morpholine) are in common use. The low-volatility amines are present in higher concentrations in the moisture separator reheater drains of the PWR, providing a higher pH and lower corrosion as a result. This application has reduced corrosion product transport to the steam generators.

In the nuclear BWR (Fig. 33.19), boiling occurs in the reactor itself. The same water serves as the cycle working fluid, the reactor coolant, and the nuclear reaction moderator. BWRs are comparable to drum-type boilers. A portion of the water passing through the core is converted to steam. The steam-water mixture is then separated, with the steam going to the turbine and boiler water returning through circulating pumps to the core inlet.

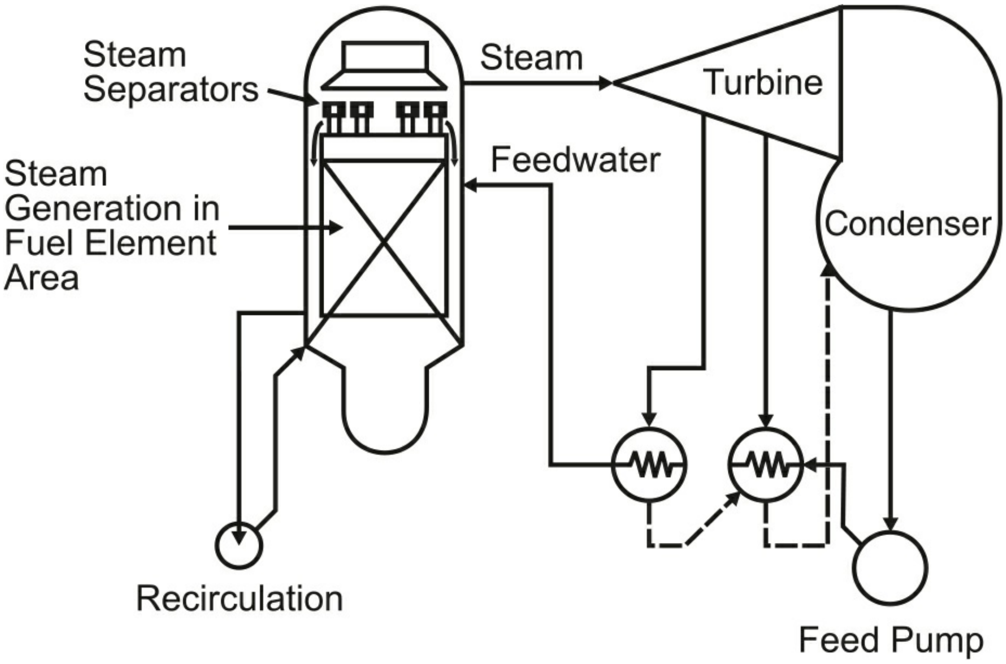


FIGURE 33.19 In a BWR, steam is generated in the same vessel that contains the fuel elements, as shown in this simplified diagram.

An important aspect of BWR operation is the effect on the working fluid of direct exposure to nuclear radiation. Some of the water is decomposed into hydrogen and oxygen. It is not possible to inject hydrogen as in the PWR, because of the need for continuous removal of all noncondensable gases at the condenser to maintain the vacuum required for turbine efficiency. Thus, steam produced by a BWR reactor contains high concentrations of oxygen, an important factor in corrosion.

Nitrogen entering the cycle by air inleakage or decomposition of nitrogenous compounds can react to form nitric acid:

$$5O_2 + 2N_2 + 2H_2O \rightarrow 4HNO_3 \qquad (33.9)$$

Additives for pH control and oxygen scavenging such as amines and hydrazine are not usable in BWR cycles, because they are subject to nuclear decomposition. Thus, corrosion control relies primarily on the corrosion resistant materials used throughout the cycle.

Metallic contaminants in the cycle water, either from condenser leakage or corrosion of system metals, are subject to stringent limitations to avoid formation of hazardous isotopes and to avoid deposition of crud on the core heat transfer surfaces. Copper is specifically limited, because of its tendency to foul the orifices of the reactor core water distributor. Makeup water is demineralized to less than 0.1 µS/cm specific conductivity and 10 µg/L silica. Full flow condensate demineralization is then employed to maintain cycle water purity at limits established by the reactor manufacturer. Typical limits are 30 µg/L total metals, 2 µg/L Cu, 2 µg/L NaCl, and 0.1 µS/cm conductivity at 25°C. Resultant feedwater is essentially neutral, with pH equal to 7.0.

Where deep bed demineralizers are used in BWR condensate polishing, resins are usually sluiced to external vessels for scrubbing and regeneration. The regenerant wastes generally contain low-level radioactivity, which requires processing in the liquid radwaste system. Where nonregenerable powdered resin units are used for polishing, the spent, sluiced resin must be processed.

Blowdown Control

The primary factors that limit COC in HP boiler waters are total dissolved solids (TDS) and silica.

TDS are limited primarily to ensure steam purity. Limits are more stringent at higher drum pressures, because of the decreasing steam-water density differences that tend to increase mechanical carryover percentages (see Fig. 33.20). Boiler water specific conductance has a reasonably constant proportional relationship to dissolved solids and is the parameter most commonly monitored and controlled.

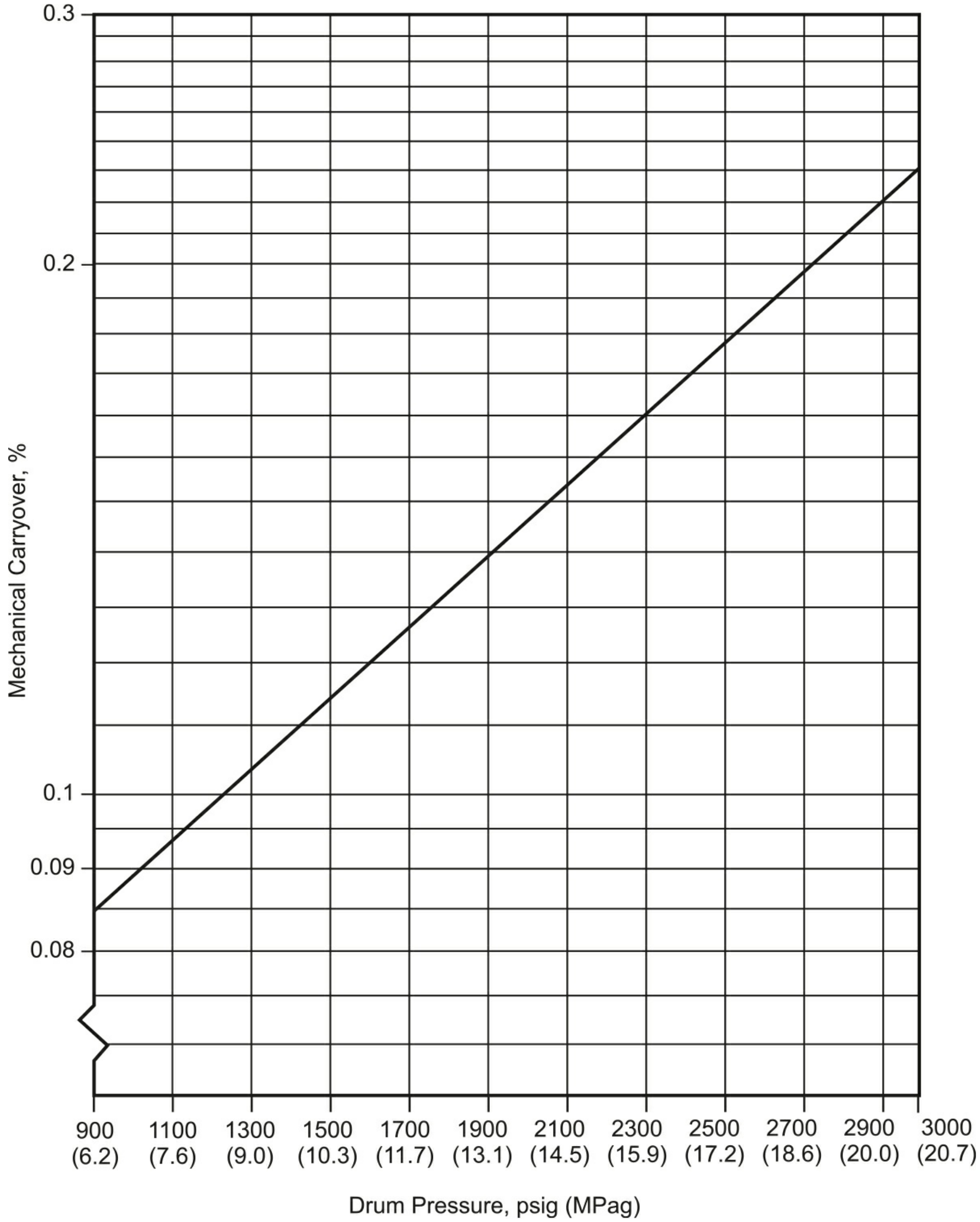


FIGURE 33.20 Mechanical carryover versus drum pressure.

To prevent silica from selectively carrying over (volatilizing), silica is kept below prescribed maximums for steam turbine operation. Silica volatility increases almost exponentially with boiler water pressure. Drum boiler water silica limits thus decrease sharply as pressure increases (see Fig. 33.21).

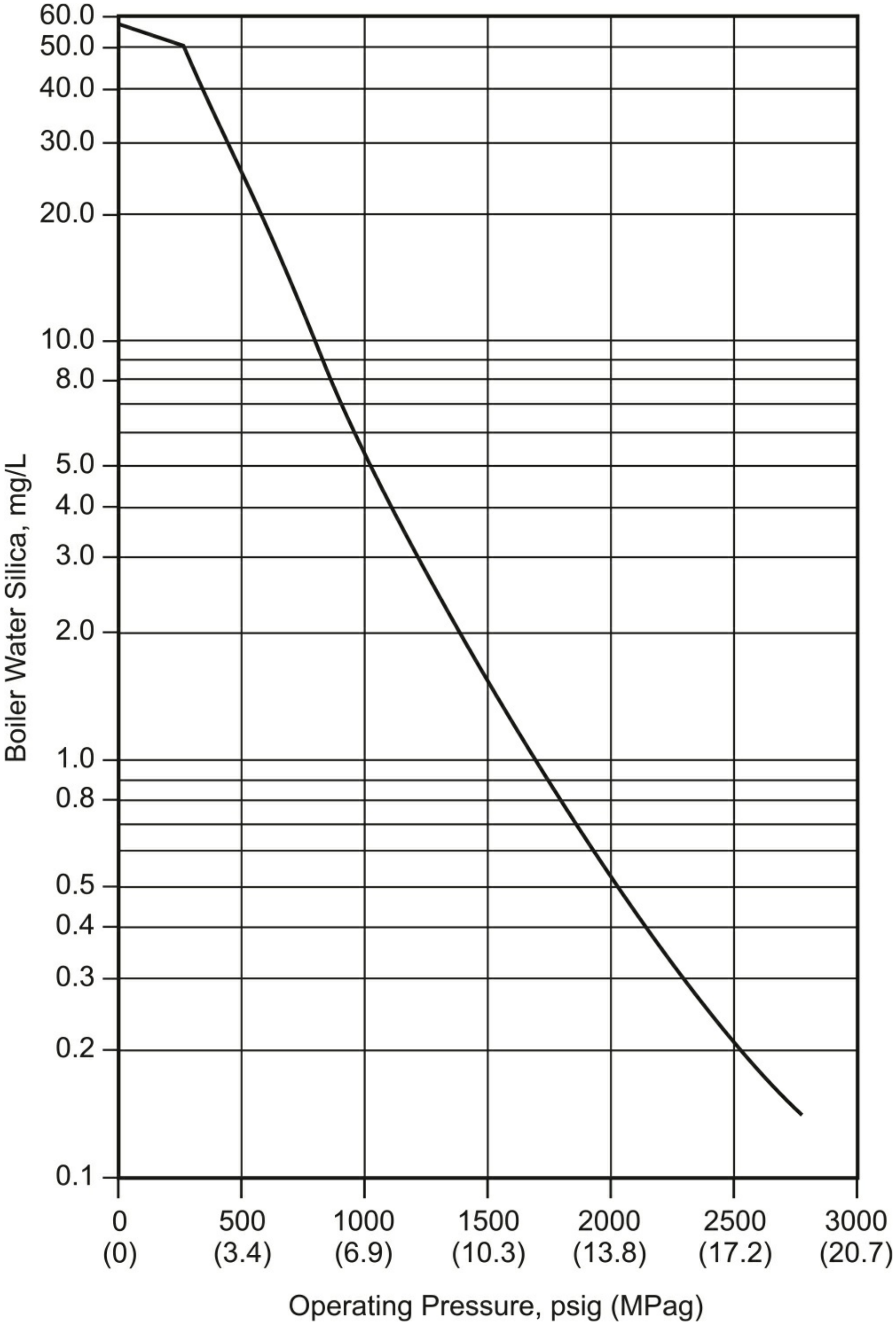


FIGURE 33.21 Recommended maximum boiler water silica concentration at pH 11.3 so as not to exceed 20 µg/L silica in steam.

Actual boiler water COC must be determined in order to calculate chemical mass balances and operating economics. However, in high-purity feedwater/boiler water systems, determining COC presents a challenge. Blowdown is rarely metered directly. In addition, feedwater and steam flow meters (where available) often lack the calibration accuracy and precision necessary to determine (by difference) the very small blowdown flows reliably. In LP systems, chemical ions in the feedwater can be used to determine boiler water COC analytically; however, the concentrations of such ions in HP boiler feedwater are typically below detectable limits, and the conductivity of the boiler water is predominately from the chemicals added to the system. If they are detectable, the concentrations are so low that even a small analytical error could cause a 50 to 100% error in calculating COC.

Blowdown flow rates can sometimes be estimated with reasonable accuracy for systems in which continuous blowdown valves with known orifice sizes are used. Valve manufacturers generally supply curves showing pounds per hour (kg/h) blowdown flow versus pressure drops for each setting of the valve. Typically, the pressure drop (ignoring piping losses) is the boiler drum pressure minus the operating pressure of the blowdown flash tank or receiver. Blowdown flow thus determined (in conjunction with either metered feedwater or steam flow rate) is then used to determine feedwater concentration ratio in the boiler.

Nonvolatile tracer ions can be used to determine boiler water COC. A known flow proportional concentration (e.g., 1 mg/L) of the tracer is metered to the feedwater until it reaches its equilibrium concentration in the boiler water. The cycles of boiler water concentration are then derived from the determination of relative concentrations of the tracer ion in the feedwater and boiler blowdown.

Another method for determining cycles of high-purity boiler water concentration is to make a slug addition of an arbitrary amount of suitable ion (soluble, nonvolatile, and accurately measurable). Because the decay of this species will be exponential, its concentration in the boiler at any time will be a function of boiler volume and blowdown rate. This relationship is shown in Eq. (33.10):

$$\ln C_t = -(\mathrm{BD}/V)t + \ln C_i \tag{33.10}$$

where C_i = initial concentration, mg/L
C_t = concentration at time t, mg/L
t = time interval between C_i and C_t, hours
V = boiler volume, lb (kg)
BD = blowdown flow rate, lb/h (kg/h)

Once the blowdown rate is determined, the feedwater rate can be calculated using Eq. (33.11):

$$\mathrm{FW} = S + \mathrm{BD} \tag{33.11}$$

where FW = feedwater flow rate, lb/h (kg/h)
S = steam flow rate, lb/h (kg/h)

The COC can then be calculated using Eq. (33.12):

$$\mathrm{COC} = \mathrm{FW}/\mathrm{BD} \tag{33.12}$$

Condenser Cooling Water

The thermal efficiency of modern fossil-fuel steam electric plants averages less than 35% for subcritical units, up to 45% for supercritical units, and 65% for combined cycle power plants. The largest part of the thermal loss, equal to about 50% of the steam energy, is rejected at the condenser as the steam is condensed to water and releases its heat of vaporization. Nuclear plants, averaging about 32% efficiency, lose even more heat at the condenser. Heat rejected at the condenser is transferred to cooling water, which subsequently releases this heat to the environment. Air-cooled plants release the heat directly to the air.

Although water circulating through the tubes of a surface condenser is called cooling water, it is important to recognize that there is no cooling of the vapor or condensate. The circulating water simply absorbs the heat of vaporization of steam leaving the turbine, converting it to liquid at the same temperature.

The primary function of a surface condenser is to maximize cycle efficiency by allowing steam to expand through the turbine to the lowest possible exhaust temperature and pressure. Just as in a boiler drum, the temperature of steam and water in a condenser is directly related to pressure. At 102°F (38.9°C), for example, the corresponding saturated steam pressure is about 1.0 psia or 2.0 in. Hg (6.9 kPaa). At this pressure, 1 lb of steam occupies 333.69 ft^3 (20.83 m^3/kg), but when condensed, it occupies only 0.016 ft^3 (0.001 m^3/kg), about 0.005% of the original steam volume. The pressure in the condenser is often referred to as the "back pressure."

Noncondensable gases (air, ammonia, etc.) in the condenser increase pressure and reduce the vacuum achievable, and such gases are continuously removed by mechanical vacuum pumps or steam jet air ejectors (see Fig. 33.12).

The ability of a surface condenser to provide the lowest possible back pressure for a given turbine load and cooling water temperature is adversely affected by such things as follows:

- Waterside scaling and fouling of condenser tube surfaces
- Partial blockage of cooling water flow through the tubes
- Inadequate removal of noncondensable gases
- Faulty distribution of exhaust steam

Waterside scaling and fouling are probably the most common causes of impaired condenser performance.

The effect of a 1.0 in. Hg (25.4 mm Hg or 3.4 kPaa) rise in back pressure in a 500 MW plant is illustrated in Table 33.2. A back pressure increase in this magnitude can decrease electrical output by 1 to 3%. A plant may avoid the loss of production by increasing the steam flow through the turbine, but this will come at the cost of higher heat rate, higher fuel consumption, and higher emissions. Effective condenser water treatment is a very important factor in preventing such losses.

500 MW Generation, Coal Fired, 1.5 in. Hg (38.1 mm Hg) Design Back Pressure*		
Actual back pressure in. Hg (abs) mm Hg (abs)	2.5 63.5	3.5 88.9
Change in heat rate Btu/kWh kJ/kWh	200 211	400 422
Additional fuel at 90% boiler efficiency million Btu/h million kJ/h	111 117	222 234
Additional fuel cost at \$1.5/million Btu at €1/million kJ	\$3996/day €2808/day	\$7992/day €5616/day
Additional carbon dioxide released to environment at 210 lb CO_2/million Btu at 90 kg CO_2/million kJ	23 310 lb/h 10 530 kg/h	46 620 lb/h 21 060 kg/h

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*Unit rating permits fixed load maintenance.

TABLE 33.2 Effect of Turbine Back Pressure Increase on Plant Efficiency

Seven basic types of condenser cooling systems are used in utility stations:

1. Once-through cooling
2. Cooling lake and cooling pond systems
3. Spray ponds
4. Wet cooling tower systems
5. Air-cooled condensers
6. Wet-dry combination cooling tower systems
7. Wet surface air coolers (WSAC)

In once-through cooling, water passes once through the condenser and returns to its source at a higher temperature. Because residence time and temperature are low, scaling is usually not a problem, although calcium scales can form with some waters. The principal fouling problems in once-through systems are usually related to microbial activity and silt deposition. Regularly scheduled biocide control usually achieves a moderate increase in condenser cleanliness for several hours. Application of a biodispersant with each application of chlorine or bromine can increase both the magnitude and duration of this improvement (Table 33.3). By increasing the effectiveness of chlorine or bromine, such biodispersants also can reduce the dosage of biocide, helping the plant meet discharge regulations.

Treatment	**Cleanliness Factor Improvement**	
	Highest Percent	**Duration***
0.05 mg/L Cl_2 residual plus 15 mg/L biodispersant	7.24%	6.5 hours
12.12 mg/L Cl_2 residual plus 5 mg/L biodispersant	2.61%	6 hours
12.4 mg/L Cl_2 residual alone (no biodispersant)	0.55%	2 hours

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*Short duration treatment applications with system blowdown closed until chlorine residual dissipated.

TABLE 33.3 Condenser Tube Cleanliness Factor Improvement Using a Biodispersant

With the advent of environmental regulations restricting thermal discharges, some once-through systems have been modified so that the condenser outlet water passes over a “helper” or thermal abatement cooling tower or through a tempering canal with floating spray modules to dissipate heat before final discharge. Since such helper additions follow the condenser, biocide and dispersant treatment of the water are the same as for conventional once-through systems.

Cooling water may be discharged to cooling lakes, which are artificial impoundments that are created by damming a stream. Condenser water is recirculated through the lake, and heat is dissipated primarily by surface evaporation. The lake receives makeup from rainfall and runoff from its drainage area. Cooling lakes make it possible to service high cooling water flow requirements from streams too small to provide such cooling capacity on a once-through basis.

By contrast, cooling ponds are defined as impoundments that do not impede the flow of a navigable stream. They are usually constructed along a stream from which makeup water may be pumped to meet evaporative losses not replaced by rainfall or runoff from surrounding drainage areas. Cooling ponds contained within earthen levees at levels above the surface water are said to be “perched.” The area required for natural evaporation is typically about 1 to

1.5 acres (4000–6000 m^2) per megawatt of capacity. A pond typically provides detention of about 5 to 15 days to produce the necessary heat dissipation.

Blowdown from cooling ponds is composed of bottom seepage and controlled overflow to the source stream. Because of the large rainfall-receiving surface areas, concentration ratios are typically quite low, up to about two times source concentration. Even such low concentration increases may be significant in terms of reduced calcium carbonate solubility, so condenser tubes are more likely to scale on pond systems than on once-through cooling systems. Scale inhibitors and dispersants are commonly applied to cooling pond systems to prevent deposition in the condenser and auxiliary cooling systems. Acid and carbon dioxide have been applied in unusual cases of high-scaling potential.

A significant aspect of cooling ponds is that they support a variety of aquatic organisms. They often have large fish populations. Specific dispersants in conjunction with periodic feed of chlorine or bromine may be needed to keep condenser tubes free of biological slimes, initiated by the microorganisms in the pond.

Spray ponds promote evaporation by mechanically dispersing water into sheets and droplets, dissipating heat more effectively so that less pond area is required. Evaporation is mechanically promoted, so it is less dependent on climatic conditions. Recirculating water treatment requirements generally correspond more closely to those of evaporative (wet) cooling towers than to cooling ponds or lakes.

Where large cooling ponds or spray ponds are impractical, cooling towers are installed to reduce thermal pollution of receiving waterways. To comply with restrictions on thermal discharge, blowdown is taken from the tower basin, having the lowest temperature of the recirculating system.

An important advantage of wet cooling towers is their ability to significantly reduce raw water withdrawal and wastewater discharge (Table 33.4).

	Once-Through Cooling System	**Wet Cooling Tower Recirculating System***
Condenser flow, gpm (m^3/h)	400 000 (90 850)	400 000 (90 850)
Evaporative concentration ratio	1	5
Makeup water flow, gpm (m^3/h)	400 000 (90 850)	10 000 (2271)
Discharge water flow, gpm (m^3/h)	400 000 (90 850)	2000 (454)

---

*Based on 20°F (11°C) temperature rise and evaporation factor of 1.

TABLE 33.4 Water Flows for 1000 MW Condenser Cooling System

Because drift (entrainment of fine mist) from a cooling tower is part of blowdown, the net discharge to the receiving stream in this example would be about 10 to 200 gpm (2.3–45 m^3/h) less than the 2000 gpm (454 m^3/h) shown.

With the increased planning for maximum water conservation, coal-fired plants may substitute cooling tower water for raw water for ash sluicing. The heat of bottom ash evaporates some sluice water, the ash retains a small amount, and the final volume of wastewater for disposal is further reduced.

Zero liquid discharge has been designed into many power plants to conserve water and reduce environmental impact. There are many strategies for implementation of zero liquid discharge from a power plant. The system may be as simple as operation at high COC in the condenser cooling system, followed by a solar evaporation pond, or as complex as a multiprocess treatment system with softening, RO, evaporation, and crystallization. In all cases, maintenance of the plant water balance is critical to the successful operation of the system.

Various processes for sidestream treatment of cooling water and for blowdown concentration, reduce final discharge volume and required evaporation pond areas. One such conceptual system is illustrated in Fig. 33.22. Although sidestream processing can control concentrations of potentially scale-forming ions, high salinity in the recirculating water is characteristic of these treatment schemes. The effects of high dissolved solids in cooling tower drift and on surrounding vegetation and structures must be considered. Cooling water TDS may be limited by air emission standards. In addition, the significantly greater impact of condenser leaks on the chemistry of the boiler water cycle must be addressed.

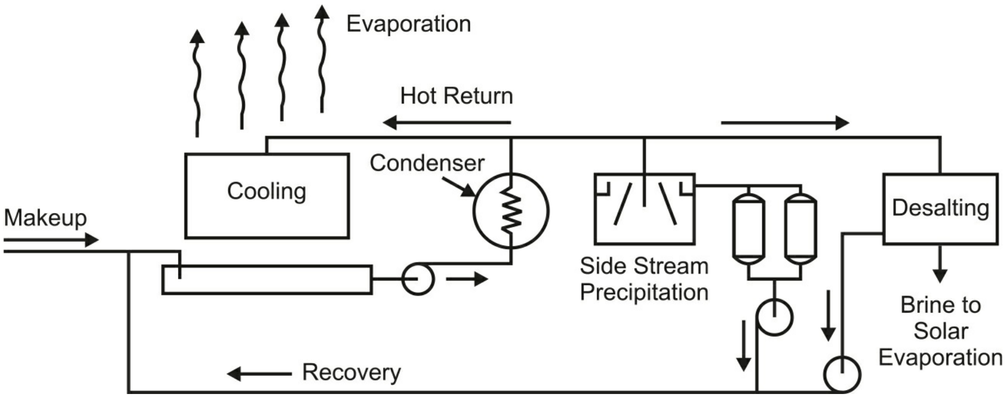

FIGURE 33.22 Simplified schematic of process to recover cooling water by sidestream treatment and desalination to yield only a concentrated brine for evaporation.

Air-cooled condensers or "dry" cooling systems are an increasingly popular option for plants sited in water-short regions, or in populated regions where cooling tower plume and drift are a concern. Moisture plumes emanate from cooling tower stacks like clouds under many weather conditions, literally dominating the atmosphere in the immediate vicinity. One means of eliminating plumes is to use nonevaporative dry cooling towers. In dry cooling towers (Fig. 33.23), heat is transferred from the recirculating water to the air by convection rather than by evaporation.

FIGURE 33.23 Typical dry cooling tower. (*Courtesy of SPX Cooling Technologies, Inc.*)

The ambient air temperature controls dry cooling tower performance, rather than wet bulb temperature as for wet cooling towers, and turbine backpressures are higher for dry tower systems than for wet towers. Therefore, the plant heat rate is higher. Combinations of wet and dry cooling towers (Fig. 33.24) may be used to advantage to alleviate plume problems with minimum loss of cycle efficiency. In addition, since dry towers handle their part of the heat load without evaporation, overall makeup and blowdown volumes are less for wet-dry cooling tower combinations. Systems may be set up with the recirculating water flowing in either series or parallel through the wet and dry towers. Designs usually provide for a means of totally or partially bypassing either air flow or recirculating water flow selectively around either the wet or dry tower, as may be required to optimize plant efficiency for varying plume abatement and water conservation requirements. Figure 33.25 illustrates an integral wet-dry cooling tower unit with provision for adjusting the balance of airflow through the wet and dry sections. Recirculating water treatment practices for wet-dry cooling tower systems are essentially the same as for straight wet cooling tower systems.

FIGURE 33.24 Large combination wet-dry tower used to cool condenser water. (*Courtesy of SPX Cooling Technologies, Inc.*)

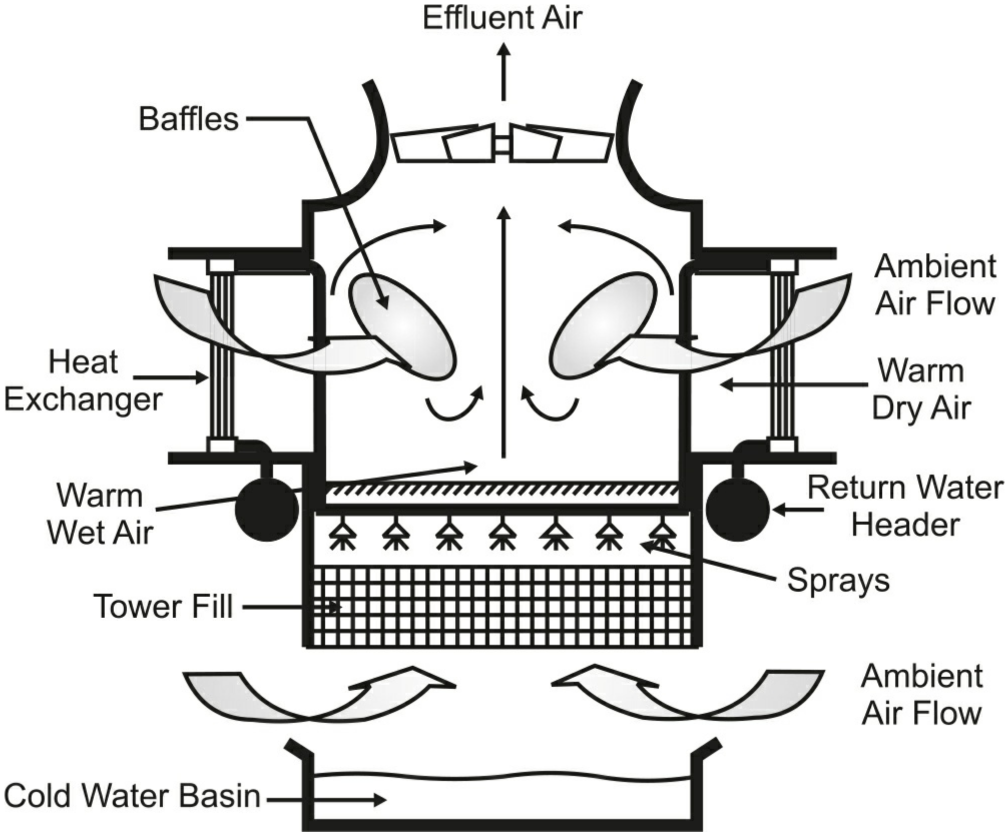

FIGURE 33.25 Integral wet-dry cooling tower with damper control. (*Courtesy of SPX Cooling Technologies, Inc.*)

WSAC may be used instead of traditional dry and open recirculating cooling water systems. For the same heat load, WSAC typically use 75% less energy than dry systems and 25% less energy than open recirculating systems. In addition, WSAC can operate at higher COC than standard cooling towers, because they are less susceptible to suspended solids fouling. Some mineral precipitation is expected. WSAC can receive blowdown from traditional cooling towers as makeup water and concentrate it further, beyond mineral solubility limits, further reducing wastewater discharge.

WSAC applications in power plants may include steam condensing, auxiliary cooling, and gas turbine air inlet cooling. Air is induced downward over the tube bundle, which is located within the actual cooling tower structure. Water flows downward along with the air. Heat from the process stream is released to the cascading water, and heat is transferred from the cascading water to the air stream via evaporation. The air stream is forced to turn 180°, providing maximum free water removal. The fans discharge air vertically at a high velocity to prevent air recirculation. The deluge effect provided by the water cascade directly over the tubes minimizes the propensity for suspended solids fouling and mineral precipitation on the tubes, thus allowing operation at higher COC.

Closed recirculating water systems handle a variety of cooling requirements in utility stations, avoiding introduction of outside contaminants that might foul heat exchanger surfaces. Systems of this type are sometimes used for cooling the hydrogen circulated for electric generator cooling. They also may be used for cooling of compressed air, jacket cooling for standby diesel engines, and for certain lube oil cooling requirements. In nuclear plants, closed recirculating cooling water systems are commonly used to handle heat loads from the reactor vessel shielding, primary coolant pump seal housings, and other heat loads within the reactor building.

Ash Handling Systems

Another major water use in coal-fired power plants, and to a lesser extent in oil-fired plants, is ash transport. The solids that fall to the bottom of the boiler furnace (bottom ash) are usually cooled and conveyed from the boiler by water. The solid products of combustion (fly ash) in the flue gas that do not deposit in the boiler convection passes or air heater are subsequently removed by electrostatic precipitators, bag filters, or wet scrubbers. Fly ash accumulations are removed from these devices either by water, or by mechanical or pneumatic means.

The quantity of water required for ash sluicing varies with design factors such as method of firing and nature of the coal. For a typical 1000 MW coal-fired plant, it amounts to about 10 mgd (1600 m^3/h).

For molten slag tap or “wet bottom boilers,” where water is used to quench molten ash, heat pick up can be in the range of 1 million Btu (1 GJ) per ton (0.9 metric ton) of bottom ash. Suspended solids in bottom ash water are of concern, if they are difficult to settle, and may be very abrasive to the ash sluice pumps. Coagulants may be needed to reduce supernatant turbidity. Dissolved solids contribution to the sluice water from the ash will vary with the nature of the ash. In some cases, the sluice water will become very alkaline and scale forming.

Fly ash is much more leachable and may contribute 50 to 800 mg/L dissolved solids to the transport water. Fly ash often contains hollow microspheres (Figs. 33.26 and 33.27), which are difficult to separate from sluice water by sedimentation. Dry transport systems are often used to handle fly ash to avoid the issue of the floating microspheres (also called centispheres).

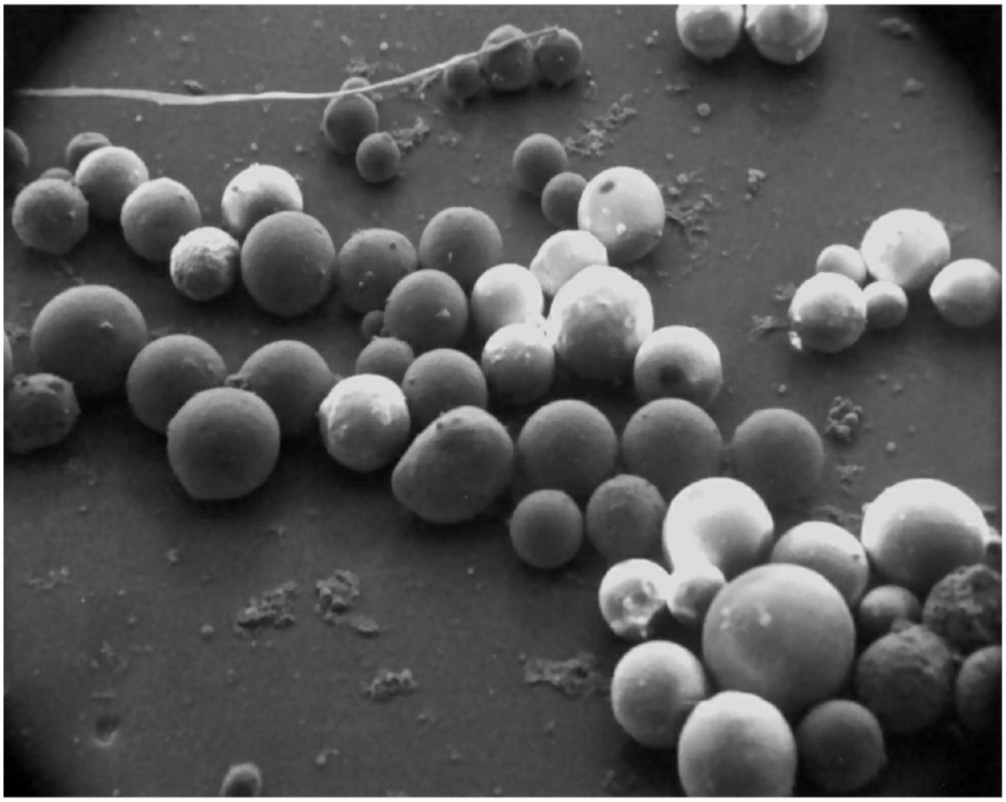

FIGURE 33.26 The suspension firing of coal produces slag in a variety of forms, including these microspheres, which float to the surface of wet ash collection ponds. Random spheres.

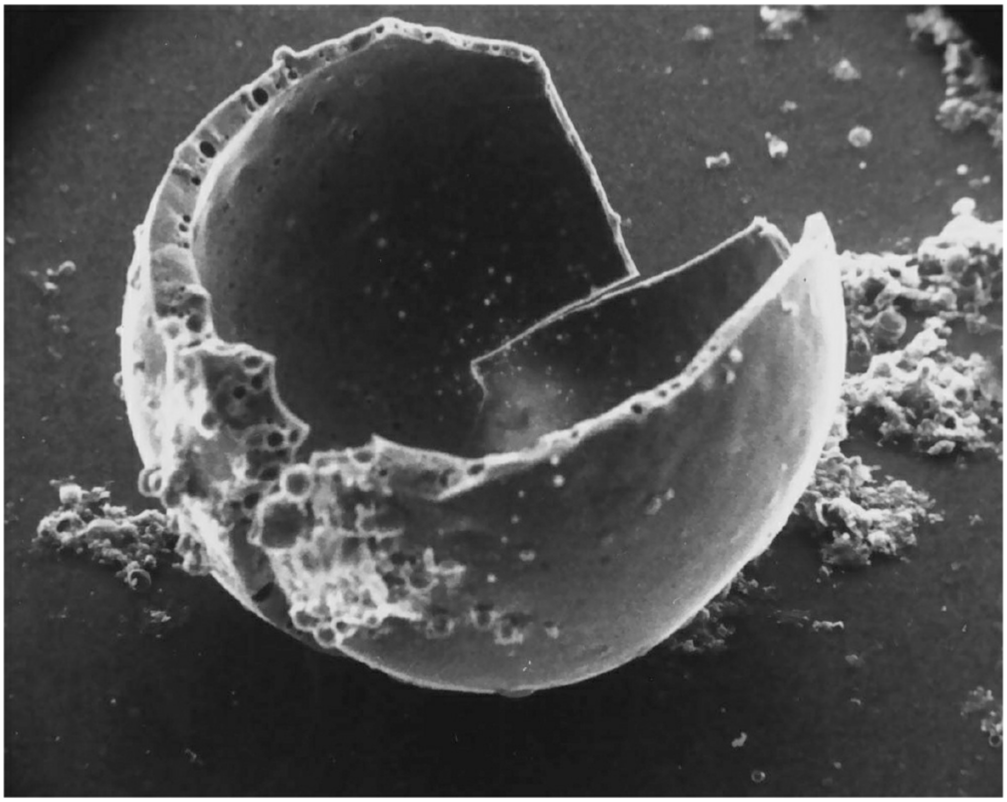

FIGURE 33.27 The suspension firing of coal produces slag in a variety of forms, including these microspheres, which float to the surface of wet ash collection ponds. Broken shells.

In oil-fired plants, ash is produced in comparatively small quantities. Bottom ash removal from the boiler by fireside washing and sluicing may be needed only occasionally. Oil ash generally does not settle in ponds as well as coal ash. While oil ash pond overflow waters have many of the same characteristics as in coal-fired plants, high concentrations of vanadium may be present, originating as an ash constituent of some fuel oils. Bottom ash in some oil-fired plants is removed by dry collection rather than by water sluicing.

Where there is a market for the bottom ash, or where insufficient land is available for settling, dewatering bins can be used and the dewatered ash trucked away. Water drainage from dewatering bins or the supernatant from ash ponds can be recycled to the sluice pumps. Makeup to such recycle systems is required for replacement of evaporative losses and moisture that leaves with the dewatered ash. Because of the poor separation of the buoyant fly ash, however, recycle systems are generally not suitable, where fly ash is sluiced to the same dewatering point as bottom ash. Chemical coagulants and flocculants are useful in the treatment of ash transport waters, to reduce suspended solids to acceptable levels for recycle or final discharge.

Flue Gas Desulfurization

Most coal-burning power plants use flue gas desulfurization (FGD) systems to control sulfur dioxide (SO_2) emissions. Water from various sources (e.g., clarified surface waters, cooling tower blowdown, and reclaim water) is used as makeup to wet FGD scrubber systems. Wet, calcium-based processes, those that use limestone ($CaCO_3$) or lime (CaO) as the alkaline reagent are the most commonly used FGD processes in utility applications. In these processes, SO_2 absorbed from the flue gas reacts with the alkaline species in the scrubbing liquor to form relatively insoluble calcium sulfite and calcium sulfate solids. These solids are concentrated in a clarifier-thickener or hydroclone separator and continuously removed from the system as a sludge requiring disposal. Throwaway disposal methods include pumping the sludge to ponds or dewatering the sludge, fixing it with fly ash and lime, and landfilling. Alternatively, byproduct gypsum may be produced for use as a raw material in the production of wallboard. To produce byproduct gypsum, a forced oxidation FGD process is used, wherein excess air is injected into the wet scrubber to oxidize sulfites to sulfate, which combines with calcium to yield gypsum [i.e., calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$)]. Figure 33.28 depicts a wet limestone forced oxidation FGD process utilized by many power plants today.

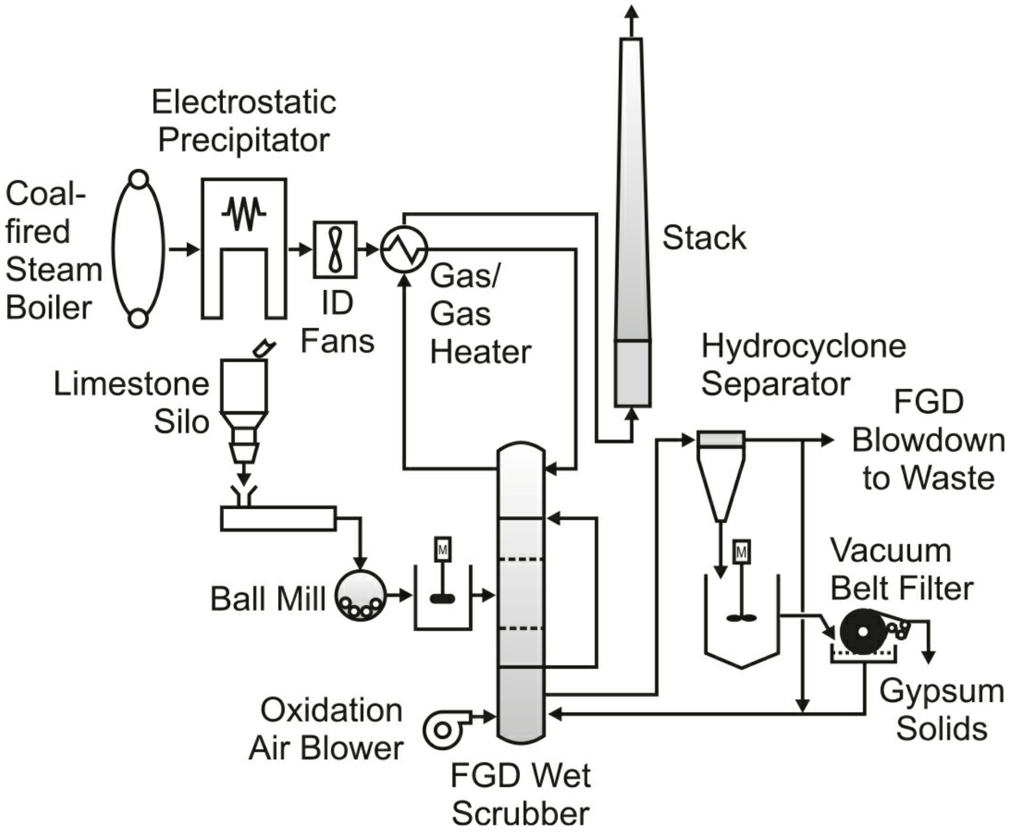

FIGURE 33.28 Simplified FGD system.

The FGD process will typically employ a blowdown or wastewater purge stream to limit the buildup of chlorides and inert fines in the scrubber system. FGD wastewaters are typically acid, highly saline solutions with variable quantities of suspended solids, metals, chlorides, fluorides, etc. FGD wastewater treatments employ a chemical/physical treatment process that includes a gypsum desaturation step using lime for pH adjustment, heavy metal removal with an organo-sulfide, coagulation with an iron salt such as ferric chloride, and flocculant addition in a secondary clarification step.

Wastewater and Discharge

Steam-electric power plants are subject to national, state/province, and local water pollution control regulations. Where these regulatory bodies differ on specific limitations for a given pollutant, the more stringent regulations generally apply. Some state/province and local regulations limit certain pollutants not limited by national guidelines.

A simplified tabulation of steam-electric plant wastewaters and their contaminant characteristics, by source categories, is shown in Table 33.5.

Source	Principal Contamination
Ash sluicing system	TSS*, TDS†, heat, oil
Low volume wastes‡	TSS, TDS, pH, oil
Metal cleaning wastes§	TSS, TDS, pH, iron, copper, other metals, oil
Boiler blowdown	TSS, iron, copper, oil
Main condensers, once-through cooling	Heat, residual chlorine
Main condensers, recirculating water blowdown	Residual chlorine, Zn, Cr, P, other cooling water additives
Area runoff¶	TSS, TDS, pH, oil
Intake water traveling screens and strainers	Solids (debris)
FGD systems and scrubbers	Solids (gypsum, sludge), TSS, TDS, pH, heavy metals

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*TSS, total suspended solids.

†TDS, total dissolved solids.

‡Low volume wastes, including wastes from ion exchange system regeneration, evaporator blowdown, flue gas wet scrubbers, floor drainage, cooling tower basin cleaning, and blowdown from recirculating service water systems.

§Metal cleaning wastes, including waterborne wastes from boiler tube cleaning, and boiler fireside cleaning, air preheater cleaning

¶Area runoff, including rainfall runoff from storage of coal, ash, and other materials.

TABLE 33.5 Major Wastewater Sources and Contaminants from Fossil-Fuel Steam-Electric Generating Plants

Principles of water recycle, reuse, and effluent treatment for steam-electric plants are generally the same as for other process industries. Figure 33.29 illustrates one reuse and effluent treatment scheme for a coal-fired plant. In this illustration, bottom ash transport water is recycled. Fly ash is separately handled in a dry system. One of the difficult problems is proper handling of coal pile runoff without interfering with coal handling procedures in the large area used for coal inventory. The runoff is often high in heavy metals, alumina, and suspended solids, and may require recycle or direct treatment (Table 33.6).

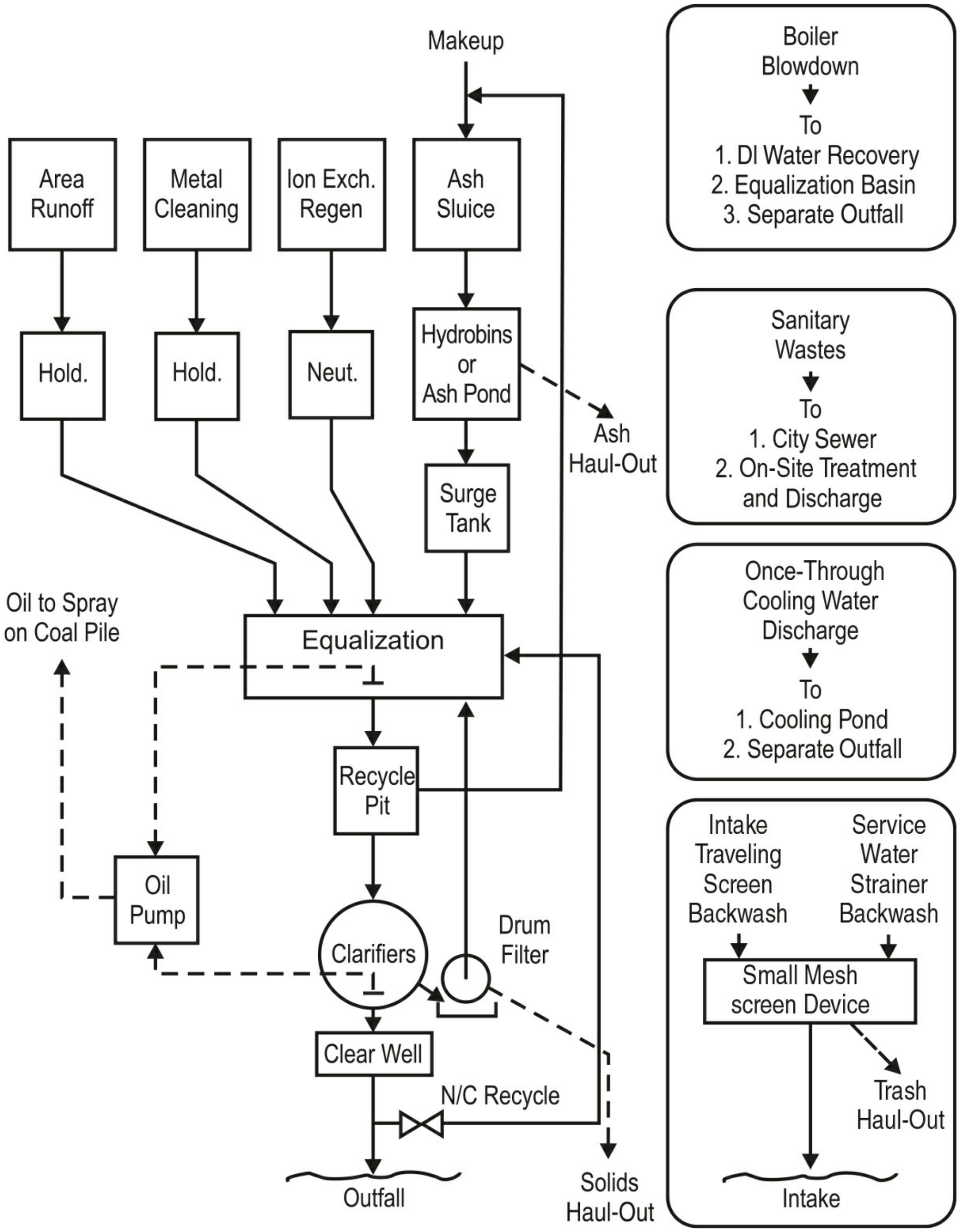


FIGURE 33.29 Water reuse and effluent treatment scheme for a coal-fired steam-electric plant.

Parameter	Concentration, mg/L
Total solids	1500–45 000
TDS	700–44 000
Total suspended solids	20–3300
Total hardness ($CaCO_3$)	130–1850
Alkalinity ($CaCO_3$)	15–80
Acidity ($CaCO_3$)	10–27 800
Manganese	90–180
Copper	1.6–3.9
Sodium	160–1260
Zinc	6.0–23.0
Aluminum	825–1200
Sulfate	130–20 000
Phosphorus	0.2–1.2
Iron	0.4–2.0
Chloride	20–480
Nitrate	0.3–2.3
Ammonia	0.4–1.8
BOD	3–10
COD	100–1000
Turbidity (JTU)	6–605
pH	2.8–7.8

Source: Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for Steam Electric Power Plants, EPA 440-1-73/029, March 1974.

TABLE 33.6 Typical Characteristics of Coal Pile Runoff

The segregation of dissimilar wastes is of special importance for nuclear power plants. High-purity (low-conductivity) wastewaters are kept separate from low-purity (higher conductivity) waters to facilitate reclamation and recycle of the high-purity waters. Chemical wastes, including ion exchange regenerants and chemical cleaning wastes, should be segregated from detergent wastes, because of their differing requirements for final treatment before discharge or reuse.

CHAPTER 34

The Oil Field Industry

Oilfield waters can vary a great deal from reservoir to reservoir. The produced water (PW) can have a wide variety of contaminants that vary in severity. The technology today is focused on mitigating both corrosion and scale, and helping with water clarification so that the water can be recycled or reused. Water will continue to play an important role in the future of the oilfield, as this resource continues to be scarce. Many technologies exist today that can help turn oilfield brine into water that can be returned to the environment.

Theory of Oil Formation

The organic theory, which is the most generally accepted hypothesis for the origin of oil, presumes that microscopic plant and animal life from the sea and tidal areas provided oil's raw materials (hydrogen and carbon). According to this theory, rivers transported great volumes of mud, sand, and products of surface erosion to the sea floor for millions of years, which were spread by tides and currents. Under the increasing weight of this accumulating debris, the ocean floors slowly sank and were compressed to form the sedimentary rocks that contain petroleum—sandstone, shale, porous limestone, and dolomite (a mixture of calcium and magnesium carbonates).

The organic components of trapped microscopic organisms were changed over time to petroleum, through chemical, physical, and biological influences (Fig. 34.1).

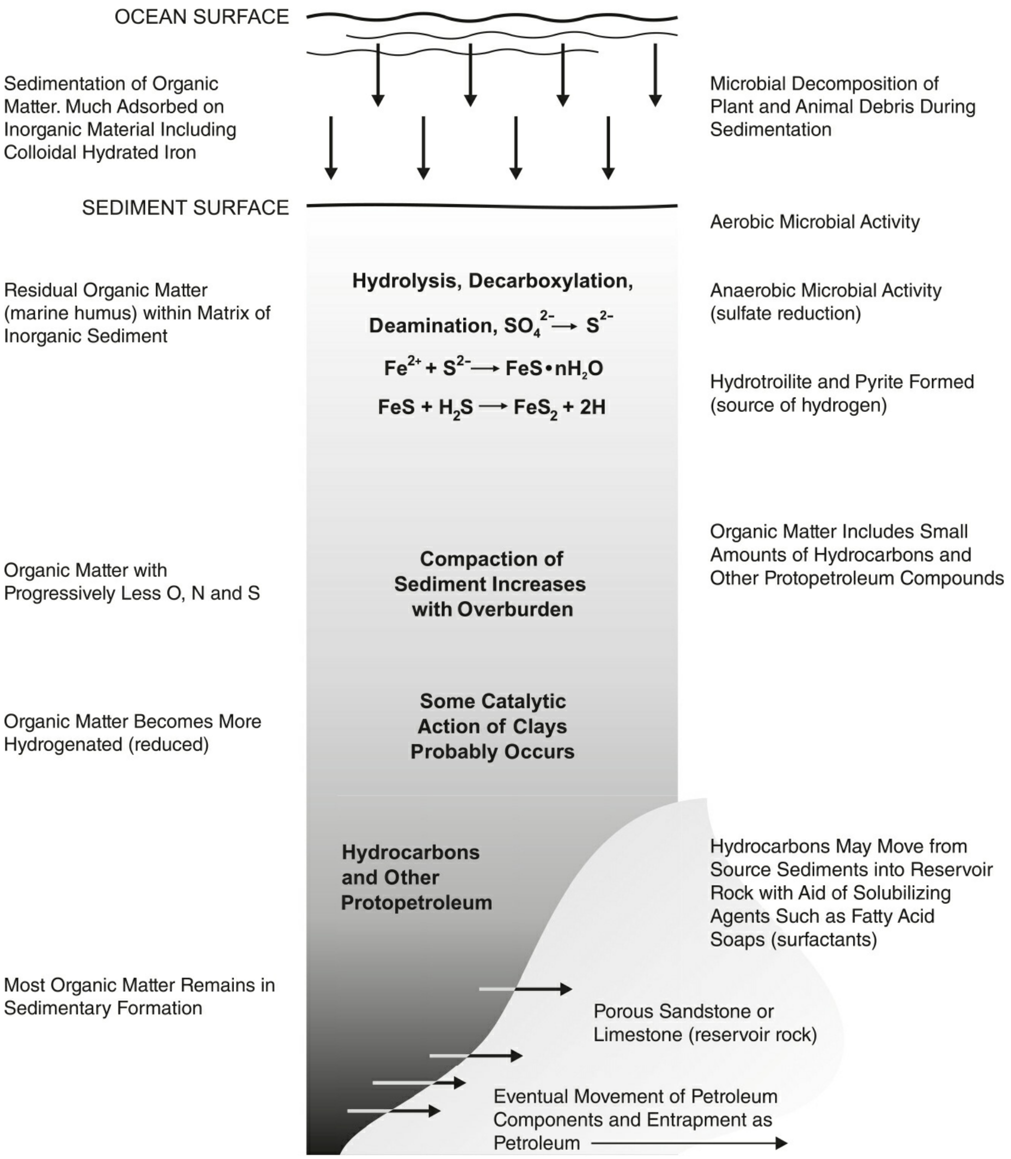


FIGURE 34.1 Events in the formation of petroleum from organic debris. (*Adapted from Davis, J. B., Petroleum Microbiology, Elsevier, Amsterdam, 1967*.)

A less prevalent theory proposes that methane and possibly other related hydrocarbons originate in the earth's mantle and work their way to faults and traps in the crust. This theory has gained support because of recent findings of hydrocarbons in meteorites and in the more distant planets.

A Few Basics about Petroleum

Naturally occurring petroleum is complex and variable in chemical composition. Its color ranges from light greenish brown to black. It may be fluid or so viscous as to be nearly solid. Although most people are familiar with the terms petroleum and crude, they may not quickly recognize the specific industry terms used to describe oils such as "conventional or unconventional oils, heavy oil and bitumen." In general, oil is called unconventional when it cannot be recovered by the conventional means of simply drilling a well. Unconventional oils are recovered by a variety of methods including surface mining, water flooding, steam stimulation or assistance, solvent extraction, gas injection, and others.

Crudes are commonly identified by American Petroleum Institute (API) gravity, a number that is inversely related to specific gravity (SG).

$$\text{API gravity} = (141.5/\text{SG}) - 131.5 \tag{34.1}$$

API gravity can be confusing to those unfamiliar with petroleum terminology. In the oil industry, a high-gravity crude is rich in volatile materials and has a low SG (0.75–0.84), so the API gravity is in the range of 35 to 55°. Some heavy crudes have a SG close to that of water, and the API gravity may be as low as 15° at the standard temperature of 60°F (15.6°C).

Figure 34.2 provides a graphical definition for heavy oil and bitumen relative to API gravity and viscosity. Crude bitumen is a thick, sticky form of crude oil that is so heavy and viscous it will not flow unless heated or diluted with lighter hydrocarbons.

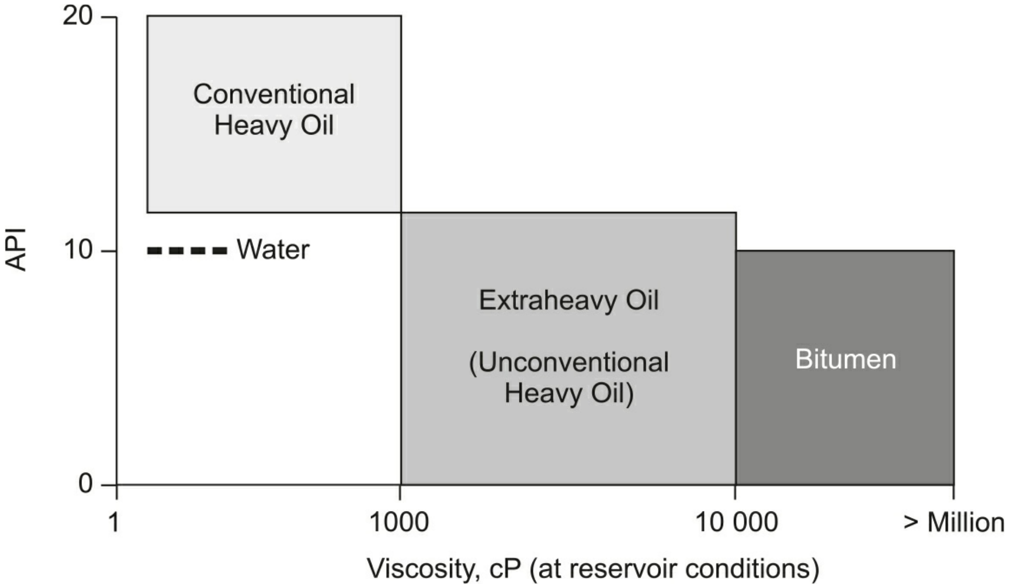


FIGURE 34.2 Definition of heavy oil and bitumen.[1]

Accumulations of Petroleum

Petroleum is found only in porous sedimentary rock. It migrates horizontally and vertically, reaching a local structure or trap having a caprock seal, which contains the oil and creates the reservoir. In some instances, the oil ends up incorporated within shale or near the surface incorporated within loose sand or a partially consolidated sandstone mixture of sand, clay, water, and bitumen.

Many different shapes, sizes, and types of geologic structures form oil reservoirs. These include domes and anticlines, fault traps, unconformities, dome and plug traps, lens-type traps, and combination traps. An anticline type of folded structure is shown in Fig. 34.3, and a trap resulting from faulting is shown in Fig. 34.4.

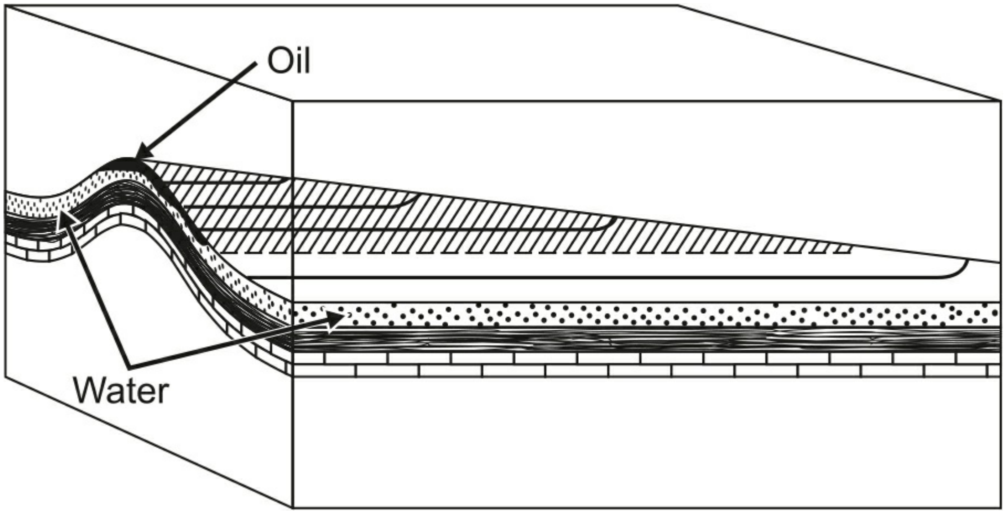


FIGURE 34.3 The separation of water and oil in an anticline, a folded structure topped by an impervious hood. (*Courtesy of API, from Primer of Oil and Gas Production.*)

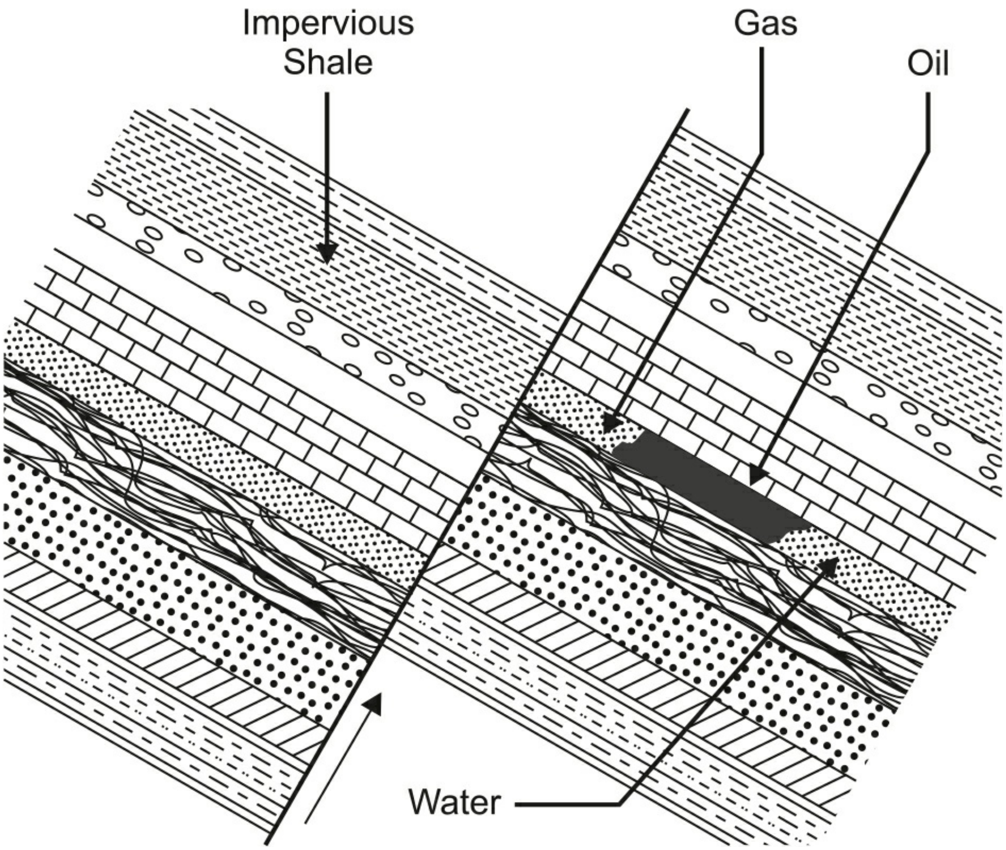


FIGURE 34.4 The separation of water and oil in sections of a fault, the displacement of layers along a slip plane. (*Courtesy of API, from Primer of Oil and Gas Production*.)

The length and width of a reservoir can vary from one to several miles (kilometers), and the depth from a few feet (meters) to several hundred. A 1 acre (4000 m^2) reservoir with a depth of 10 ft (3 m) would contain 10 acre · ft, a common U.S. unit of measure. To estimate its petroleum content, the total pore volume (porosity) and percentage oil saturation (10–99%) must be known. The remaining fluid is interstitial (or connate) water. The U.S. standard measurement of volume in the petroleum industry is the barrel (42 gal, 5.6 ft^3, 0.16 m^3).

A 10 acre · ft reservoir contains 435 600 ft^3 (12 300 m^3). With a porosity of 20% and an oil saturation of 80%, the reservoir would contain:

U.S. Units: (435 600 ft^3)(0.2)(0.8) =70 000 ft^3 or 12 000 barrels of oil

Metric Units: (12 300 m^3)(0.2)(0.8) = 2000 m^3

Oil Sands and Heavy Oil Reserves

Major oil sands and heavy oil reserves are found extensively in the Athabasca deposits of Alberta, Canada, and in Venezuela along the Orinoco River. Numerous other counties including Kazakhstan, Russia, and the United States hold oil sands deposits which are orders of magnitude smaller in size.

In the late 1940s, Sidney Ellis and Karl Clark developed processes to enable valuable oil to be extracted from oil sands. Pilot plant operations initiated in the 1950s led to commercial scale construction of a synthetic oil facility in the Athabasca region in 1965 by Great Canadian Oil Sands, Ltd. The plant went into operation in 1968. Syncrude Canada, Ltd., began operating a commercial facility in 1978. Synthetic oil production from oil sand processing in Canada has developed into the largest industry of its type in the world.

Petroleum Production

When the drill penetrates the reservoir, oil, and gas are forced to the surface by natural reservoir pressure. The period during which oil is produced by natural reservoir pressure is referred to as primary production and is typically a period of a few months or several years.

The flowing well is constructed of “strings” of concentric vertical pipes called casings and a smaller pipe, usually 2 to 3 inches (51–76 mm) in diameter, called tubing, through which produced fluid flows. The largest diameter casing (the surface string) extends to a depth of 200 to 1500 ft (61–460 m); the intermediate string may reach a depth of 5000 ft (1500 m); a third casing (the oil string) may reach the producing zone. Some producing zones are at depths of 20 000 ft (6100 m) or more. The tubing into the producing formation is secured by a packer, which seals the space between the tubing and the final casing (Fig. 34.5). Occasionally, intermediate level strings are perforated, allowing production to flow simultaneously from shallower producing zones. A series of valves and flanges at the wellhead (called a Christmas tree) includes a small orifice plate (called a choke) to control flow.

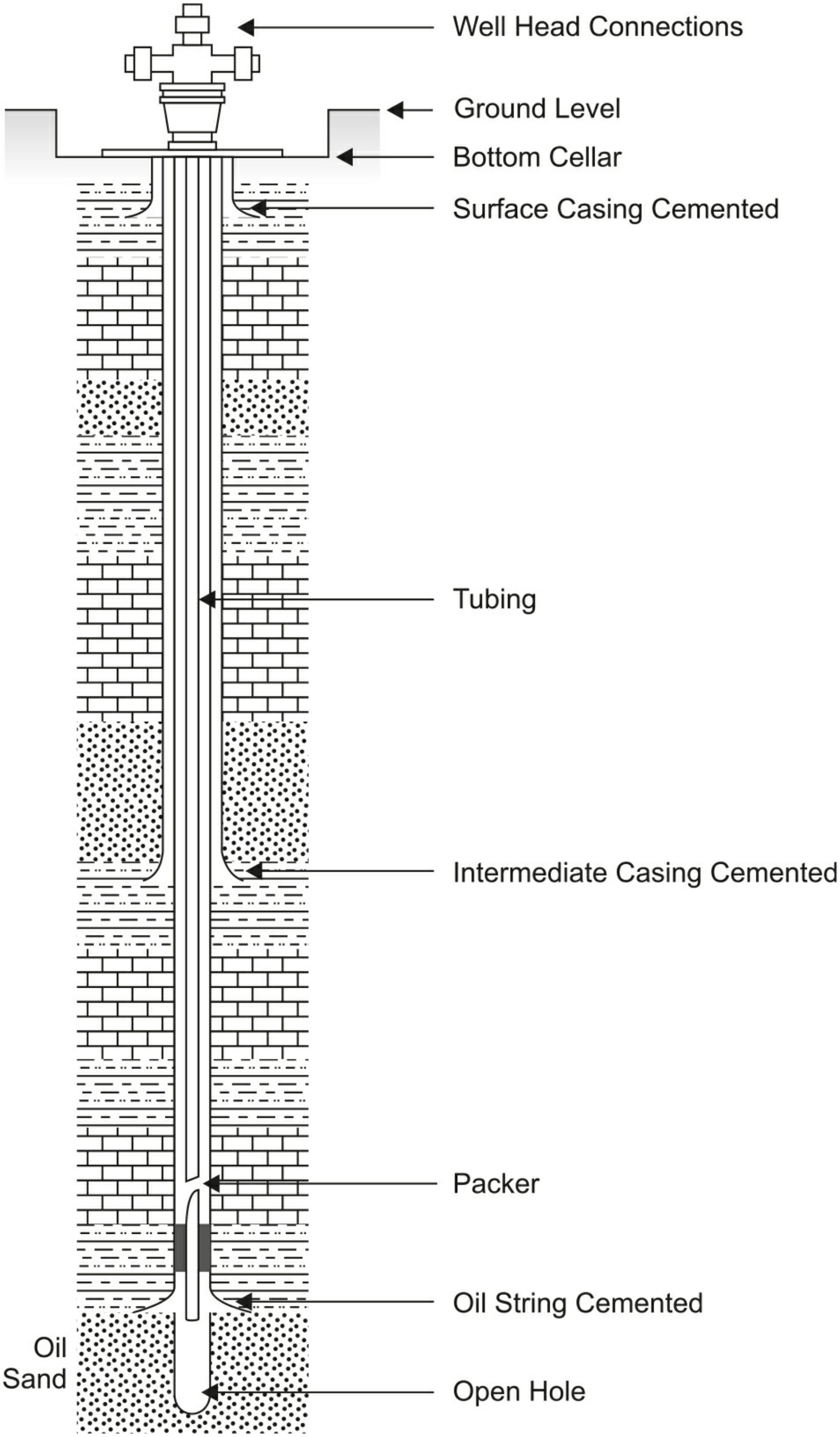

Well Head Connections
Ground Level
Bottom Cellar
Surface Casing Cemented
Tubing
Intermediate Casing Cemented
Packer
Oil String Cemented
Oil
Sand
Open Hole

FIGURE 34.5 Typical arrangement of casing, string, and tubing in an oil well. (*Courtesy of API, from Primer of Oil and Gas Production*.)

Oil Dehydration

Oil leaving the producing well is a mixture of liquid petroleum, natural gas, and formation water (Fig. 34.6). During early primary production, water may be insignificant. Most production, however, contains sizable proportions of PW (up to 90%). This must be separated from the oil, since pipeline specifications stipulate maximum water content (as low as 1% but up to 3 to 4% in some locations).

FIGURE 34.6 Oil is almost always produced as an emulsion, very different in appearance from finished oil products.

The initial separation vessel in a modern treating plant is called a free water knockout (FWKO) drum (Fig. 34.7). Free water, defined as that which separates within 5 minutes, is drawn off to a holding tank, to be clarified before reinjection or discharge. The remaining oil usually contains emulsified water and must be further processed to break the emulsion, usually assisted by heat, electric energy, or both.

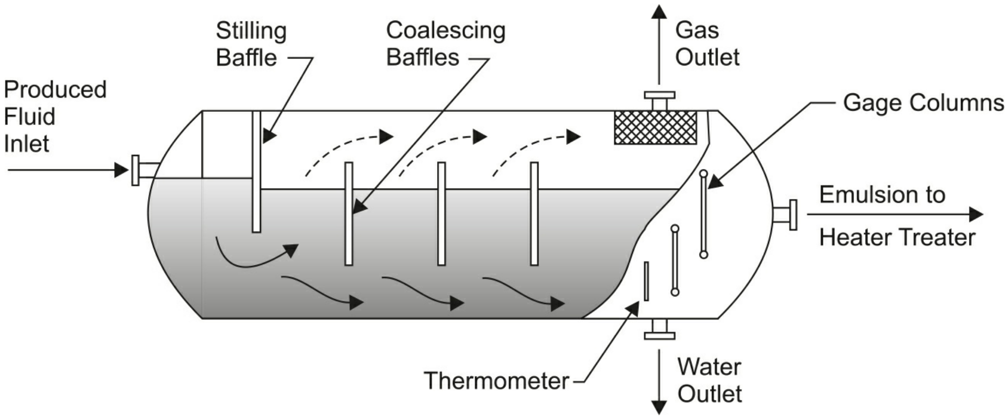


FIGURE 34.7 Free water and gas are separated from the produced fluid in this gravity separation vessel, simplifying emulsion breaking. (*Courtesy of API from Treating Oilfield Emulsions*.)

Heater treaters (Fig. 34.8) are vertical or horizontal vessels in which the water-in-oil emulsion is resolved, invariably with the assistance of emulsion breaking chemicals. The electrostatic treater employs heat, but also uses high-voltage alternating current to charge the water droplets, accelerating the process of coalescing smaller droplets into larger ones. The demulsified crude oil flows to a stock tank for pipeline shipment to a refinery.

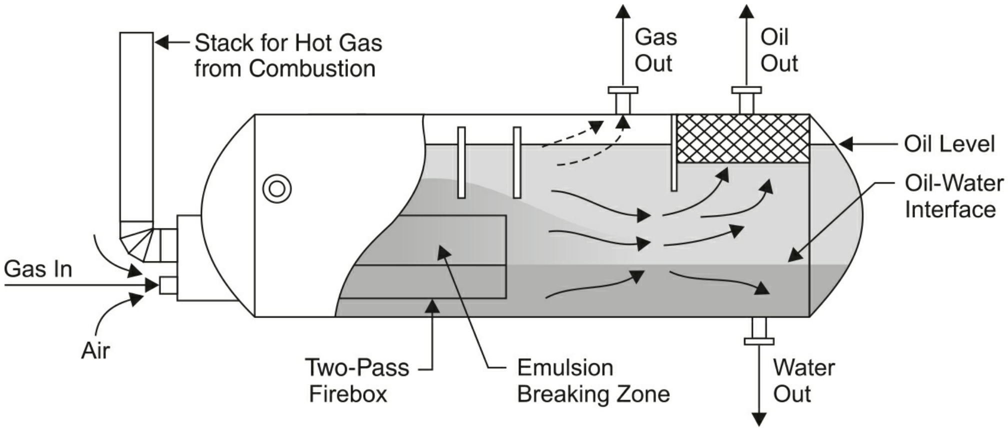


FIGURE 34.8 This heater treater uses the heat of combustion of gas or oil to heat the emulsion from the free water knockout drum, assisting chemical treatment to yield an oil of minimum water content. (*Courtesy of API from Treating Oilfield Emulsions*.)

Improved Recovery Techniques

In primary oil production, sufficient underground pressure exists to force the oil to the surface by natural mechanisms. As the well ages, its pressure naturally falls and at some point, introduction of artificial energy into the reservoir will be required to sustain production. This includes water flooding, gas injection, and other processing involving fluid or energy injection, whether for secondary or tertiary oil recovery.

Secondary recovery usually follows primary production, but may be conducted concurrently with it. Secondary recovery methods attempt to increase the degraded reservoir pressure by injecting water, natural gas, or other gases such as air or carbon dioxide. Waterflooding is the most common method of secondary recovery. A typical recovery factor from waterflood operations is about 30%.

Tertiary recovery is usually undertaken following secondary recovery, when production has dropped too low to justify continued operation. It is sometimes referred to as enhanced oil recovery (EOR). Tertiary methods attempt to increase the mobility of the oil in order to increase production. Tertiary techniques include thermal recovery (steam injection and in situ combustion), chemical injection or flooding, and carbon dioxide flooding. Steam injection is the leading form of both thermal recovery and EOR. Tertiary recovery techniques can add an additional 5 to 15% to the reservoir’s total recovered production.

EOR techniques of some sort are usually required when the oil is heavy or extra-heavy (extremely low API gravity), is part of natural bitumen deposits (oil sands), or is extra viscous because of an extremely cold reservoir location (e.g., Alaskan north shore). Steam injection is the most commonly practiced EOR technique for extracting heavy, extra-heavy, and bitumen-based oil.

Waterflooding

As noted, waterflooding is the most common method of secondary recovery practiced in traditional oilfields. In waterflooding, water is injected as a uniform barrier through the producing formation from a series of injection wells toward the producing well. Such injection wells can either be converted producing wells or new wells drilled specifically for injection of flooding water.

Proper spacing of the injection wells is important. Most reservoirs are flooded through wells distributed uniformly throughout the reservoir, peripheral injectors may flood others.

The permeability of the reservoir rock has a great bearing on its suitability for waterflooding. Rock is considered permeable if a significant fluid flow will pass through it in a short time; it is impermeable if the rate of passage is negligible.

The unit of permeability is the *darcy*, standardized by the API as follows: "A porous medium has a permeability of one darcy when a single-phase fluid of one centipoise viscosity that completely fills the voids (or pores) of the medium will flow through it at a rate of one centimeter per second per square centimeter of cross-sectional area under a pressure or equivalent hydraulic gradient of one atmosphere (760 mm of Hg) per centimeter."

The permeability of formation cores is generally in the range of 5 to 1000 millidarcies (md) (1 md = 0.001 d). A rough practical example of 1 d would be 1 ft^3 (0.028 m^3) of sandstone passing approximately one barrel (0.16 m^3) of oil per day with a pressure drop of 1 psi (6.9 kPa).

Permeability and porosity vary greatly both laterally and vertically in the typical reservoir rock. A rock whose permeability is 5 md or less is called "tight sand" or a "dense limestone" according to its composition. The following are rough permeability ratings:

- 1 to 10 md (fair permeability)
- 10 to 100 md (good permeability)
- 100 to 1000 md (very good permeability)

It is imperative for efficient flooding that the water be compatible with the reservoir formation. A desirable water for this purpose is that produced from the formation, after separation from the oil and gas. However, the amount of water required for flooding far exceeds the volume produced, so supplemental water is needed.

PW and supplemental surface waters must be clarified to remove residual oil accumulations, sand, and dirt washed from the producing formation, oxidized inorganic or organic suspended solids (SS), and corrosion products. Quality required for waterflooding is dictated by the permeability restriction of the reservoir. Currently, the most popular equipment for clarification is the flotation cell employing gas diffusion to produce clear effluent.

Where injection water must include surface or well water of lower salinity than the original formation water, chemical incompatibility with the formation rock may result. This may cause swelling of clay in the rock, blockage of the reservoir pores, and loss of oil production. Historically, the suitability of injection water has been determined through analyses of the waters in question, membrane filtration, or laboratory work with formation cores. All of these procedures have the disadvantage that the waters have been removed from the actual reservoir environment and may have changed.

Most injection waters are passed through some type of filter, with the media and design depending on the reservoir permeability. The filters must clean the water and remove any impurities, such as shells and algae. Typical filtration is to 2 micrometers, but really depends on reservoir requirements. The filters are fine enough to remove potential impurities which would block the pores of the reservoir. Types of filters include mixed media beds, individual well cartridges, or septum filters using diatomaceous earth (DE) as a filter aid. In some cases, more sophisticated treatment such as clarification or lime softening may be needed.

Deaeration may be required to reduce corrosion or to prevent iron oxidation and growth of certain bacteria. This may be accomplished by a deoxygenation tower which is a form of degassifier—dry gas, typically air, is passed counter current to the filtered water as it splashes onto a series of trays. Oxygen is stripped into the gas stream by this process and exits out the unit through a vent. An alternative method of deoxygenation, which may actually be used in addition to deoxygenation towers, is to add an oxygen scavenging agent such as sodium or ammonium bisulfite

Polymers or surfactants may be added to aid waterflooding. Polymers function by thickening the water used in the waterflooding process, resulting in improved fluid-flow patterns. Surfactants lower the interfacial tension of oil, facilitating oil flow to the well.

Steam Injection/Thermal

Waterflooding is not effective for recovery of low API gravity oil from relatively shallow formations with reservoir temperatures below about 120°F (49°C). This situation responds, however, to steam injection. Steam injection is a form of tertiary recovery, specifically a form of thermal recovery. There are different forms of the technology, with the two main ones being cyclic steam stimulation (CSS) and steam flooding.

With CSS the well is taken out of service and steam is injected for a period of several weeks to heat the oil-bearing rock. Next, the well may be allowed to sit for days to weeks to allow heat to soak into the formation. Finally, the oil well is returned to service until stimulation may be required again. A single well is used throughout the process. This method is also known as the huff-and-puff method of steaming.

The most common method of steam injection, however, is steam flooding which may also be known as a steam drive. With this method, some wells are used as steam injection wells and other wells are used for oil production.

The steam used is generated by a once-through steam generator or once through heat recovery steam generator (HRSG) and may be either wet or dry. When wet steam is used, approximately 10 to 40% of the mass sent downhole is present as hot water. The water phase doesn't contain as much thermal energy as the steam phase, so this method requires more mass downhole than when dry steam is used. Steam is injected into one of a group of centrally located displacement wells, with the steam and hot water then radiating outward toward the peripheral oil wells served by each of the injection wells.

Dry steam is produced by putting the wet steam through a steam separator prior to sending it to the well.

A form of steam flooding that has become popular in the Alberta oil sands is steam assisted gravity drainage (SAGD), in which two horizontal wells are drilled, one a few meters above the other, and steam is injected into the upper one. The intent is to melt the bitumen and reduce its viscosity to the point where gravity will pull it down into the lower producing well.

As time passes at any steam-flood site, there is a gradual increase in temperature of the produced fluids to about 160 to 180°F (71–82°C). The wells produce 6 to 8 bbl of water per barrel of oil (1–1.3 m^3/m^3). The oil and water are separated in dehydration tanks using emulsion breakers, and the water must then be processed to render it suitable for feed to the steam generators or for disposal. The salinity and chemical characteristics of the PW vary greatly from one site to another. Table 34.1 includes the analysis of several PWs after the dehydration tanks.

State	County	Formation	Constituents, mg/L							
			Na	Ca	Mg	Cl	SO$_4$	SIO$_2$	HCO$_3$	TDS*
Oklahoma	Kingfisher	Oswego	56 250	8300	260	98 300	180		50	166 652
Kansas	Ellis	Arbuckle	16 800	2630	690	30 500	2880		315	54 072
New Mexico	Lea	San Andreas	9150	1500	500	17 800	2000		1000	32 329
Texas	Hopkins	Paluxy	5640	630	40	8350	120		500	15 417
California	Kern		3936	124	66	5800	216		73	10 159
California	Kern		6725	235	115	10 714	216		52	18 382
California	Kern (Kern River)		184	25	5	170	65		234	620
Alberta	Cold Lake		800	5.3	< 1.6	1200	29	200	370	2620
Alberta	Fort McMurray		2500	50	< 4.2	4100	< 10	110	190	6900
Saskatchewan	Lloydminster		3400	140	52	5100	55	180	144	10 200
Saskatchewan	Lloydminster		1800	110	13	3000	22	150	380	6400

*Total dissolved solids.

TABLE 34.1 Analyses of Several PWs

Figure 34.9 shows a typical flow diagram of a water treatment plant servicing a steam flooding facility. After dehydration, oil is removed in dispersed gas flotation units, assisted by cationic emulsion breakers. The skimmings are recovered, and treated water is discharged to storage. The flotation unit and storage tanks are gas blanketed to avoid pickup of oxygen. An oxygen scavenger is usually applied at this point. If the Stiff-Davis Index is strongly scaling, a stabilizing inhibitor is applied here to prevent problems with calcium carbonate scale formation. Gypsum (calcium sulfate) may also be a problem. The water is then polished through septum filters. A variety of filter aids can be used, including specially processed cellulose, DE, and vermiculite. The filter is first precoated by recirculation; then it is put on stream, with a continuous application of filter aid (body feed) of 2 to 3 mg/L per mg/L oil.

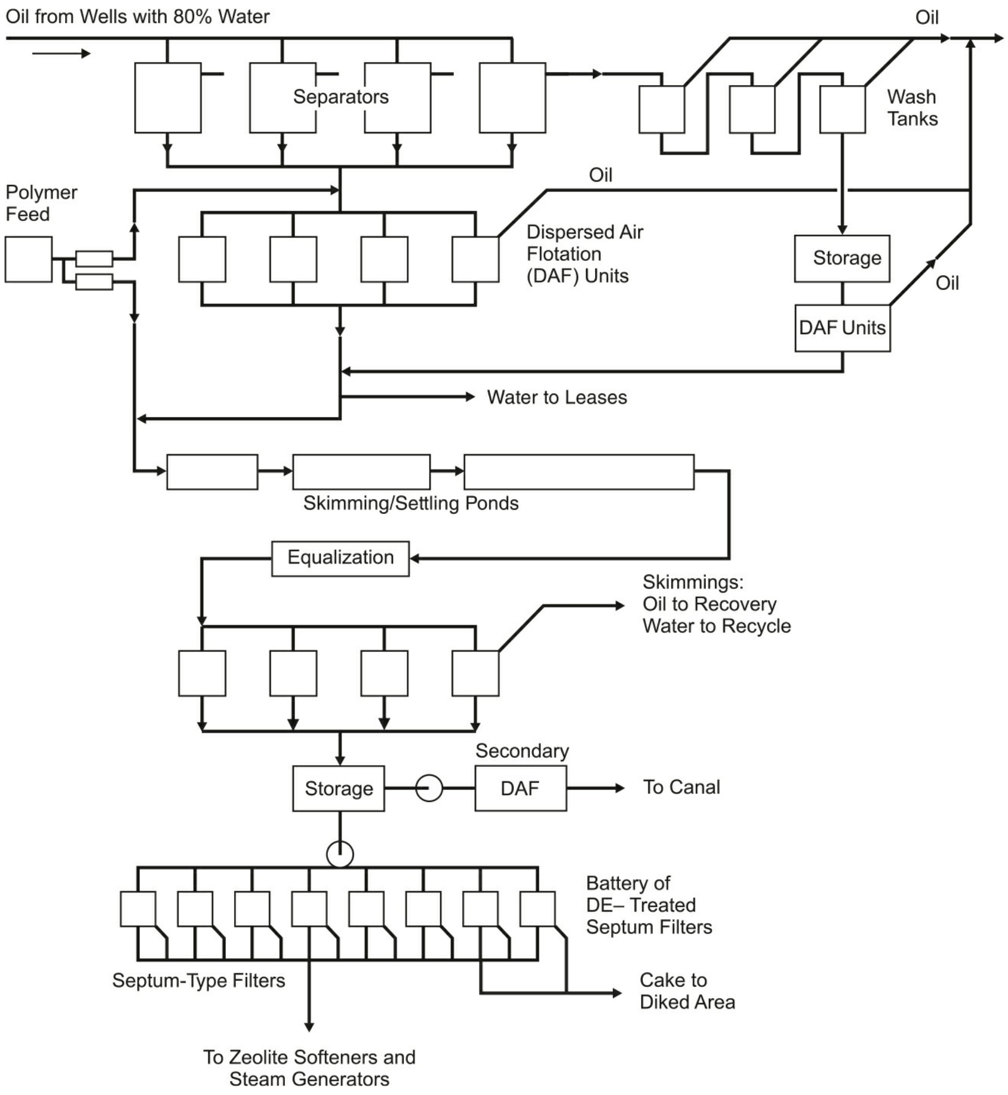


FIGURE 34.9 Treatment of PW for steam flooding.

The filtered water is then softened through sodium zeolite ion exchange softeners (Fig. 34.10). The high salinity of the PW makes softening difficult, so almost universally, a polishing softener follows the primary unit to assure low hardness in the finished water. The softened water is then sent to the various steam generators in different areas of the oilfield, sometimes several miles away. Alternatively, filtered water may be softened using warm or hot lime softening followed by sodium zeolite softening.

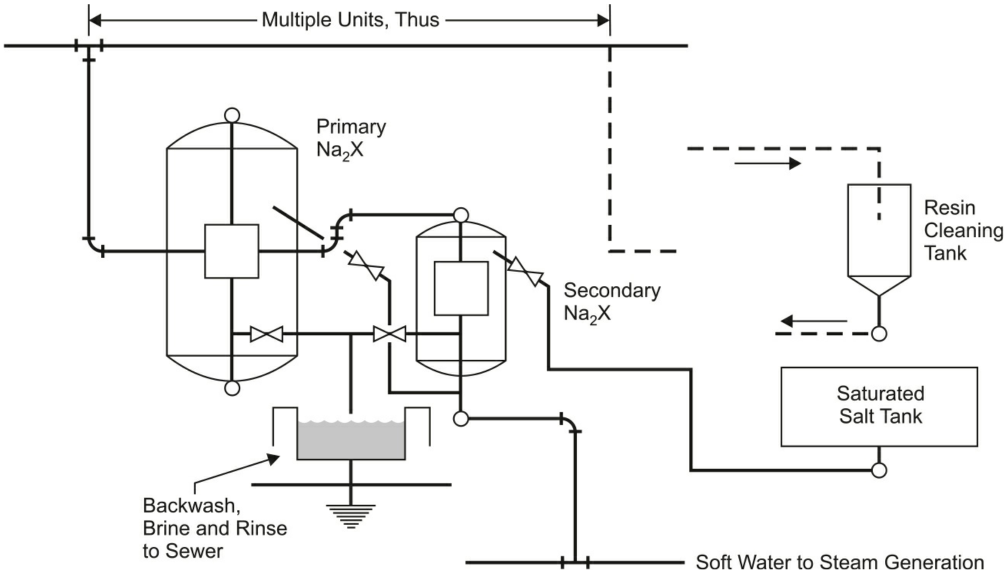


FIGURE 34.10 Two-stage sodium softening of de-oiled, filtered, produced PW to render it suitable for high-pressure boilers.

The typical steam generator is unusual in that it is a once-through unit (Fig. 34.11). Feedwater is preheated to avoid acid deposit attack of the economizer, and then flows through the economizer to recover heat from the stack gas. The feedwater then passes through the radiant and convection sections of the steam generator, where steam is generated. However, unlike conventional drum-type boilers, the fluid leaving the generator has a quality from 65 to 90% (commonly 75–80%); for example, at 80% quality the fluid contains 80% steam and 20% water by weight. Because the steam specific volume at 900 psig (6.2 MPag) is 0.49 ft^3/lb (0.031 m^3/kg), while the specific volume of water is only 0.021 ft^3/lb (0.0013 m^3/kg), the discharged fluid contains 99% steam and only 1% water by volume.

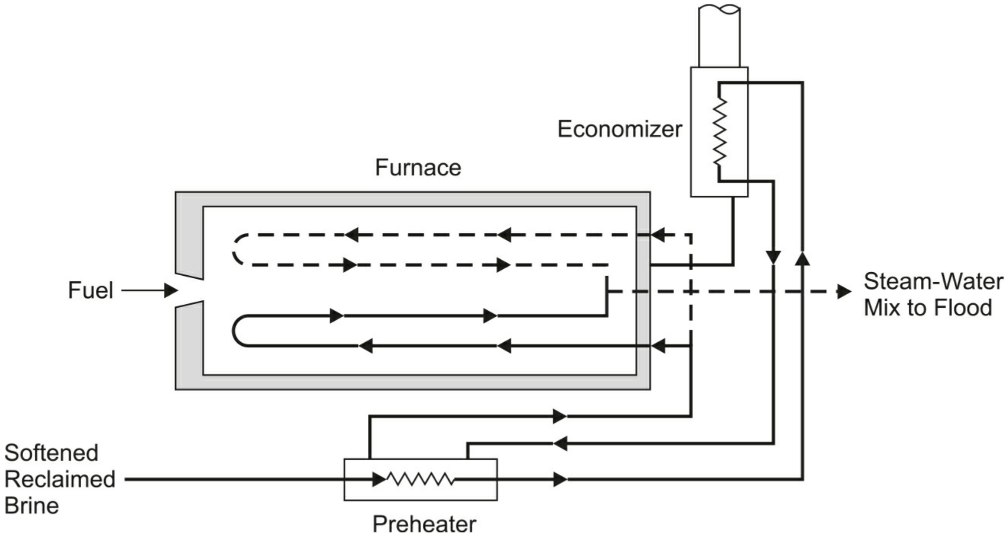


FIGURE 34.11 Once-through high-pressure steam generator designed for steam flooding and recovery of the low API gravity viscous oils of Lower California.

The water in the discharged steam contains all of the solids present in the feedwater. At 80% quality, 5 lb (2.3 kg) of feedwater produces 4 lb (1.8 kg) of steam and 1 lb (0.45 kg) of water, so the solids have been concentrated 5 times. The relationship between steam quality and concentration is:

$$\text{Concentration Ratio (CR)} = 100 - \text{quality} \tag{34.2}$$

Even though these waters are softened, chemically deaerated, and treated, it is still surprising that such high-salinity waters could be suitable feedwater for steam generators that frequently operate at pressures over 1000 psig (6.9 MPag). High fluid velocity and low heat flux relative to traditional boiler designs have been identified as the main reasons why more scale doesn't form in the once-through steam generators commonly used for steam injection.

In recent years, once-through HRSGs, traditional boilers, and hybrid boilers have also been used to generate steam for steam injection. Traditional and hybrid boilers require a better-quality feedwater and typically operate using evaporator distillate.

Depending on the depth of the injection well, and the permeability of the formation, the steam generators may operate at a pressure as low as 300 psig (2.1 MPag) and as high as 1500 psig (10.3 MPag). This pressure is maintained by the boiler feed pumps.

Chemical Flooding

Chemical injection uses dilute solutions of various chemicals to aid mobility and reduce surface tension of the oil. Injection of alkaline or caustic solutions into reservoirs that have naturally occurring organic acids in the oil may lower the interfacial tension enough to increase production. Injection of a dilute solution of a water-soluble polymer to increase the viscosity of the injected water can also increase the amount of oil recovered in some formations. Dilute solutions of surfactants may be injected to lower the interfacial tension or capillary pressure that impedes oil droplets from moving through a reservoir. Use of these methods is usually limited by the cost of the chemical program. Chemicals are commonly injected in separate batches or slugs into several wells and production occurs in other nearby wells.

Underground Combustion

The process of recovering bitumen by underground combustion is accomplished by drilling two wells into the oil sand deposit, one for injection and one for recovery. Bitumen at the base of one of the wells is ignited. Injected air feeds the combustion process and moves it through the reservoir as temperatures of 660 to 840°F (350–450°C) are attained. The bitumen is thermally cracked and vaporized. The cracked oils, gases, and vapors are driven toward the production well by injected air and collected.

Hydraulic Fracturing

Hydraulic fracturing is a recovery technique in which rock is fractured by a pressurized liquid. It may also be known as fraccing, fracking, hydrofracturing, or hydrofracking. The process involves the high-pressure injection of fluid into the well to create cracks in the deep-rock formations through which natural gas, petroleum, and brine can flow more freely. Such treatment is generally necessary to achieve adequate flow rates in shale gas, tight gas, tight oil, and coal seam gas wells. Some hydraulic fractures can form naturally in certain veins or dikes.

The injection fluid is typically water containing small grains of sand, aluminum oxide, ceramics, or other small particulates used in hydraulic fracturing, called proppants, suspended with the aid of thickening agents. When the hydraulic pressure is removed from the well, these small particulates hold the fractures open. Hydraulic fracturing is highly controversial in many countries.

Oil Shale

Extracting oil from oil shale requires conversion of solid hydrocarbons found in the rock to liquid form, so that they can be pumped or processed. This is done by heating the rock to a high temperature, and separating and collecting of the resultant liquid. This heating process is also known as retorting. Oil shale processing may be done in one of two ways: surface retorting and in-situ retorting.

Surface Retorting

The processing of oil shale by surface retorting involves large-scale mining operations, since the amount of oil in economically treatable shale is usually only 10 to 15% of weight of the native shale. At 15%, the production of 100 000 barrels (16 000 m^3) of oil would produce a residue of about 100 000 tons (91 000 tonne) of spent shale.

The release of oil is accomplished by heating the raw shale in a device like a kiln, although there is hope that in situ retorting may prove practical in the future.

Since the heat capacity of the shale is high, this process consumes a great deal of energy, which is one reason for its rather slow development. The hydrocarbons released from the shale may be processed by fractionation and extraction, to yield light ends and heavy fractions that may be used as refinery feedstock or fuel for retorting and steam generation.

Wastewater problems are similar to those of the refineries and coal-fired utility stations, the major one being the runoff from the large volumes of spent shale residue.

In-Situ Retorting

In-situ retorting processes oil shale underground. This eliminates the problems of mining, handling, and disposing of large quantities of material, which occurs for above ground retorting. With in-situ processing, the oil shale is slowly heated underground and the resulting liquids and gas extracted directly from the reservoir much like crude oil. Various technologies differ by the method used to introduce heat underground, but follow the same basic principle.

Bitumen Recovery from Surface Mining

Raw oil sand is collected in open pit mines using massive bucket wheel excavators and electric draglines. To obtain one barrel (0.16 m^3) of recoverable, synthetic crude oil from oil sand, about 1.6 tons (1.5 tonne) of oil sand must be mined and processed. It is estimated that 10% of the energy obtained from the final synthetic crude is required for oil sand mining. Once mined, methods such as hot water extraction, cold-water extraction, solvent extraction, direct coking, and fluid coking are employed to recover the oil sand hydrocarbon for fuel processing.

Hot Water Processing

Hot water processing requires mixing the sand with water at a temperature of about 195°F (90°C), to form a pulp containing 60 to 85% solids. Sodium hydroxide (NaOH) and other conditioners can be added to control pH and aid in separation. Conditioning is carried out in a rotating, steam-heated drum. Large quantities of water are added, and the layers disintegrate. The conditioned pulp is pumped to separation cells, where the sand settles and the bitumen oil froths to the surface on the rising bubbles. The sand is separated, and the bitumen oil mixture is collected for further processing.

Direct Coking

Direct coking is a pyrolysis process utilizing a fluidized bed reactor to distill and remove bitumen from the oil sand matrix. Oil sand is heated in a coker to about 900°F (482°C). At this temperature, the volatile synthetic oil separates from the sand matrix and is recovered from the coker as a condensed liquid. Coke deposits form on the sand as a result of thermal cracking of bitumen. The coke bearing sand is then fluidized with air and transferred to a burner operating at 1400°F (760°C) to drive coke from the sand, producing flue gas, and hot clean sand. A portion of this sand supplies heat for additional coking.

Upgrading Bitumen and Heavy Oil to Produce Synthetic Fuels

Heavy and extra-heavy crude oils and crude bitumen are viscous semisolid forms of oil that do not easily flow at normal temperatures. They must be upgraded to lighter synthetic crude oil, blended with diluents to form dilbit, or heated to reduce their viscosity in order to flow through oil pipelines.

In the Canadian oil sands, bitumen produced by surface mining is generally upgraded onsite and delivered as synthetic crude oil. Upgrading may involve multiple processes including vacuum distillation, de-asphalting, cracking, and hydrotreating.

In-situ producers do not have the ability to upgrade their bitumen in the same manner. This bitumen is typically diluted to improve flow characteristics using either conventional light crude or a cocktail of natural gas liquids. The resulting diluted bitumen, or dilbit, has the consistency of conventional crude and can be pumped through pipelines to upgraders or refineries.

The Nature of Oilfield Waters

After establishing injection and feedwater quality requirements, steps must be taken to eliminate or control scaling, corrosion, and fouling of surface equipment, tanks, lines, and steam generators to prevent interruption of water or steam injection and a decrease in oil production.

It is necessary to conduct several types of analyses to identify and evaluate these potential problems. Analyses must be run at points throughout the water system, because changes through the system provide data for proper control. In waterflood systems, the job of injection system control starts at the producing well, for it is here that water begins to change. As water enters the production tubing, a pressure drop occurs that could cause precipitation, either in the tubing string or in the formation. As the produced fluid approaches the surface, further pressure drop causes loss of gases and a reduction in temperature. In steam injection systems, scaling, fouling, and corrosion can occur anywhere there is a significant change in water temperature, heat input, or concentration of the water by evaporation.

Substances in oilfield waters are classified as dissolved ionic solids, SS, dissolved gases, problem-causing bacteria, dissolved organic material, and residual oil.

Total Dissolved Solids

In oilfield brines, total dissolved solids (TDS) ranges from less than 10 g/L to over 350 g/L, of which sodium chloride (NaCl) constitutes 80% or more. Troublesome cations found in oilfield waters are calcium (Ca^{+2}), magnesium (Mg^{+2}), barium (Ba^{+2}), strontium (Sr^{+2}), ferrous iron (Fe^{+2}), and lithium (Li^{+}). Commonly encountered anions are chloride (Cl^{-}), sulfate (SO_4^{-2}), bicarbonate

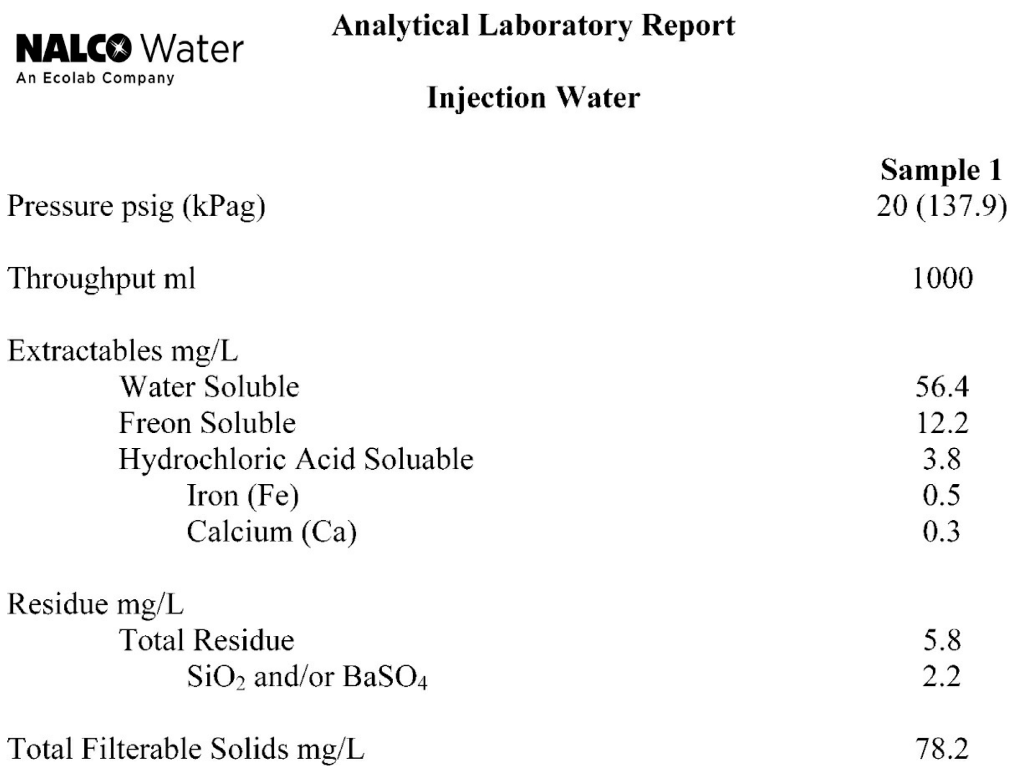
(HCO_3^-), bisilicate ($HSiO_3^-$), and sulfide (S^-).

Potassium (K^+), boron (B^{+3}), zinc (Zn^{+2}), and copper (Cu^{+2}) are also frequently measured. Soluble organic acids and ammonium (NH^{+1}) compounds can also be present at high concentrations. A few typical brine combinations were shown in Table 34.1.

Suspended Solids

Various inorganic and organic solids are found in petroleum waters. These may be particles of metal oxides from well casings or oxidized iron or manganese originally in the water. Other SS may be silt, sand, clay, or bacterial bodies. Lime softening solids, primarily calcium carbonate ($CaCO_3$) and magnesium hydroxide [$Mg(OH)_2$], from precipitated solids carryover are common in systems using lime softening.

SS particulates can be collected on a 0.45 μm membrane filter for identification. The filtered solids are analyzed separately (Fig. 34.12). A high concentration of solvent extractables usually indicates the need for better demulsification or clarification of the water. Hydrochloric acid soluble materials include carbonates of calcium, magnesium, and iron, as well as oxides and sulfides of iron. Residue remaining after treatment could include silica, barium sulfate, calcium sulfate, or heavy hydrocarbons such as asphaltenes, which are insoluble in most solvents. The residue could also include bacteria.



NALCO Water
An Ecolab Company

Analytical Laboratory Report

Injection Water

	Sample 1
Pressure psig (kPag)	20 (137.9)
Throughput ml	1000
Extractables mg/L	
Water Soluble	56.4
Freon Soluble	12.2
Hydrochloric Acid Soluable	3.8
Iron (Fe)	0.5
Calcium (Ca)	0.3
Residue mg/L	
Total Residue	5.8
SiO_2 and/or $BaSO_4$	2.2
Total Filterable Solids mg/L	78.2

FIGURE 34.12 Analysis of SS.

Dissolved Gases

The gases of greatest concern are hydrogen sulfide (H_2S), carbon dioxide (CO_2), and oxygen (O_2).

PWs containing hydrogen sulfide are called sour waters. Oil reservoirs can become sour through the activity of sulfate-reducing bacteria (SRB) in the producing formation. H_2S concentrations can reach several hundred milligrams per liter. H_2S can also be produced in the water handling system by the same bacteria. Any increase in H_2S concentration along the water system which is not caused by blending should be considered an indication of bacterial activity.

As H_2S is extremely poisonous, all sour oilfield operators post conspicuous signs at tanks or vessels, cautioning against inspection without the use of breathing equipment.

H_2S in contact with iron produces iron sulfide (FeS), which can accelerate corrosion and cause serious scale. The sulfides of most metals are insoluble in water. H_2S in contact with dissolved oxygen (DO) can produce elemental sulfur, also a potential foulant.

$$H_2S+\frac{1}{2}O_2 \rightarrow H_2O+S^0 \tag{34.3}$$

Carbon dioxide is an ionizable gas, forming carbonic acid (H_2CO_3) when dissolved in water at pH below 8.3. Although carbonic acid is a relatively weak acid, it is one of the greatest contributors to production well and waterflood system corrosion. Production well concentrations of CO_2 can exceed 200 mg/L, much of which is lost to the atmosphere when the produced fluids leave the well. Carbon dioxide is also responsible for dissolving limestone reservoir rock, increasing both hardness and alkalinity.

DO is rarely present in produced fluids coming from the reservoir, unless entrained through leakage, but it is perhaps the most serious corrodent participating in oilfield water corrosion mechanisms. Oxygen is a highly active element. Even in small amounts, it can cause serious corrosion in lines, heat exchangers, and steam-operated equipment. Corrosion increases with increasing oxygen content.

Problem-Causing Bacteria

Of several types of bacteria responsible for corrosion and formation of plugging type solids, the most serious offender is the anaerobic sulfate-reducing bacterium *Desulfovibrio desulfuricans*. SRB are bacteria that can convert sulfate to sulfide. The SRB are anaerobic bacteria and as such do not require free oxygen for their metabolism. Their presence in water systems is most problematic since these anaerobes are likely to reside in areas where oxygen depleted regions exist. Additionally, the product of sulfate reduction is hydrogen sulfide (H_2S), an undesirable corrosive species.

SRB can easily be determined with laboratory and field testing of fresh sample. Analysis takes a minimum of 48 hours for results and may not differentiate between multiple microorganisms present.

Residual Oil

Problems with oil water separation equipment and chemistry can lead to higher residual oil present in water stream. Residual oil contributes to fouling of heat exchangers, evaporators, and steam generators.

There are a great number of test methods and online monitors for various forms of oil in water which may or may not provide similar values. For a qualitative determination of residual oil, solvent extraction followed by weighing is recommended. This procedure requires time, limiting its use for monitoring.

Mineral Scales

The mineral scales of greatest concern to oil producers are calcium carbonate, calcium sulfate, and barium sulfate. Strontium sulfate, a less common scale, can also cause problems. Several iron compounds are of concern, related to corrosion or to oxidation of ferrous iron because of oxygen intrusion. Table 34.2 lists common scales with system variables that affect their occurrence.

Name	Chemical Formula	Primary Variables
Calcium carbonate (calcite)	$CaCO_3$	Partial pressure of CO_2, temperature, TDS
Calcium sulfate		
Gypsum (most common)	$CaSO_4 \cdot 2H_2O$	Temperature, pressure, TDS
Anhydrite	$CaSO_4$	
Barium sulfate	$BaSO_4$	Temperature, TDS
Strontium sulfate	$SrSO_4$	
Iron compounds		
Ferrous carbonate	$FeCO_3$	Corrosion, dissolved gases, pH
Ferrous sulfide	FeS	
Ferrous hydroxide	$Fe(OH)_2$	
Ferric hydroxide	$Fe(OH)_3$	
Ferric oxide	Fe_2O_3	

TABLE 34.2 Most Common Scales

Mineral scales can form in many areas:

- Supersaturation can occur in the formation face as the produced fluids enter the production tubing.
- Scale can form throughout the length of the production tubing, on sucker rods, and in downhole pumps.
- In the heater treater, scale can form in surface vessels and on the heating surfaces.

- In the water handling system, scale can form in injection water pumps, surface lines leading to injection wells, and rock surfaces in the injection formation.
- In the feedwater system for steam injection, scale can form at heat exchangers, evaporators, evaporator and radiant sections of the steam generator, and steam separator.

Mineral Scales in Water Injection Systems

Calcium Carbonate

Calcium carbonate equilibria are frequently upset in oilfield waters, due to changes in temperature, pressure, and pH. Since calcium carbonate solubility decreases with increasing temperature, injection from the surface to a warm formation increases the chance of calcium carbonate deposition. Its solubility increases as the TDS content increases. For instance, the addition of 200 g/L NaCl increases $CaCO_3$ solubility by over 100%. Prediction of calcium carbonate scale potential has been the subject of much research. The Langelier Saturation Index (LSI) attempted to relate calcium and alkalinity concentrations to pH, temperature, and TDS. However, this had limited value in oilfield brines.

The Stiff–Davis Index is now widely accepted for predicting calcium carbonate deposition in oilfield systems. To be useful, the analytical data must be determined on freshly drawn samples; analyses determined in a laboratory are not reliable, since the character of the water may change substantially. The Stiff–Davis Index ranges from –2.0 to +2.0. Positive numbers indicate a progressively severe supersaturation; negative numbers indicate an under saturated solution. The validity of the index depends on the accuracy of the analysis.

Calcium Sulfate

Most calcium sulfate deposits found in the oilfield are gypsum ($CaSO_4 \cdot 2H_2O$), the predominant form at temperatures below 100°F (38°C); above this temperature, anhydrite ($CaSO_4$) may be found. Gypsum solubility increases with temperature up to about 100°F (38°C), and then decreases with increasing temperature. Sodium chloride increases the solubility of anhydrite, as it does for calcium carbonate, up to a salt concentration of approximately 150 g/L. Higher salt concentrations decrease calcium sulfate solubility. The addition of 150 g/L NaCl to distilled water triples the solubility of gypsum.

One of the more recent predictive indexes for gypsum are that developed by Skillman, McDonald, and Stiff. Calcium sulfate precipitation usually results from the mixing of two waters, one of which has a high calcium or sulfate concentration. A solubility graph relating calcium and sulfate concentration to total brine concentration is shown in Fig. 34.13.

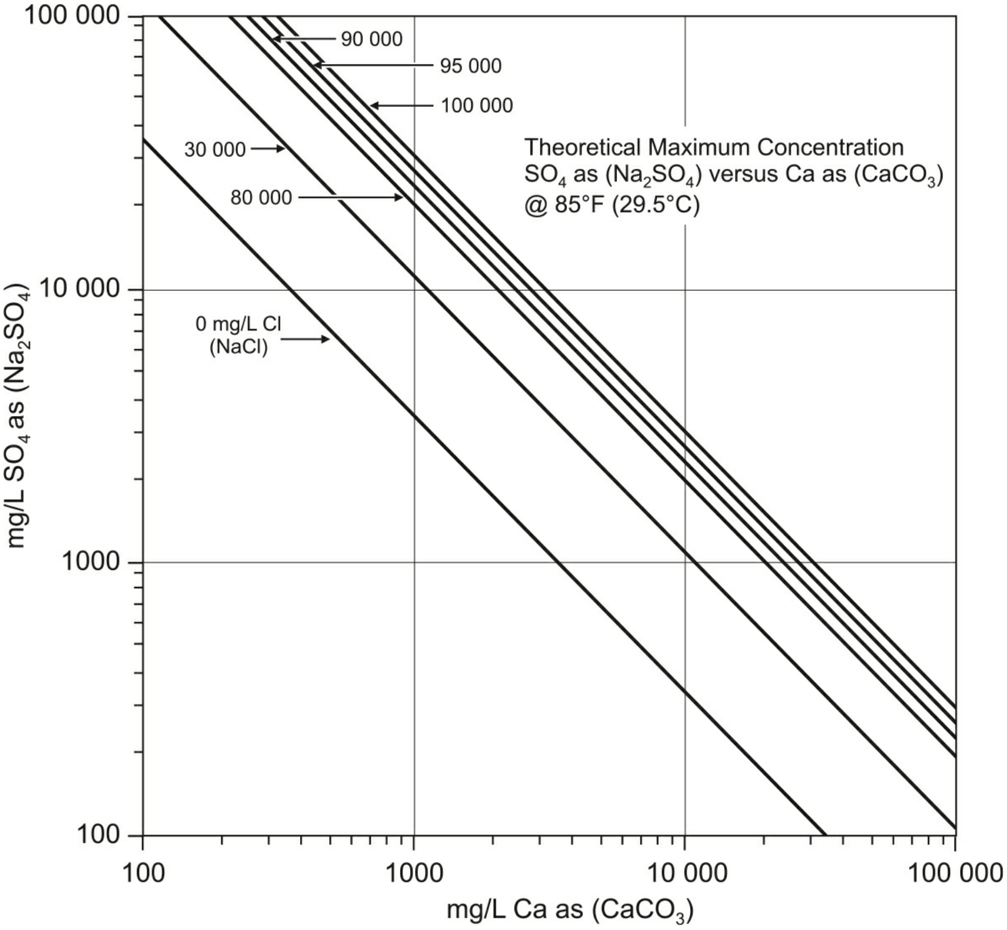


FIGURE 34.13 Calcium sulfate solubility at various brine levels.

Barium Sulfate

Barium sulfate solubility is the lowest of the usual scales, approximately 2.3 mg/L in distilled water. Increasing salt concentration increases the solubility of barium sulfate. The addition of 100 g/L NaCl to distilled water, increases the solubility of barium sulfate from 2.3 mg/L to approximately 30 mg/L at 77°F

(25°C).

The solubility of barium sulfate increases with temperature. The combined effect of temperature and sodium chloride concentration can increase solubility to approximately 65 mg/L at 203°F (95°C).

Barium sulfate deposition usually results from the mixing of barium-rich water with sulfate-rich water. Such a combination should be avoided, but where mixing is unavoidable, chemical inhibitors may control deposits.

Scale Removal and Prevention

Most scales are typically removed by some form of mechanical cleaning, but can also be removed by chemical cleaning. Scales such as barium sulfate, which cannot be removed chemically, may require replacement of surface lines or abandonment of the well.

The first scale inhibitors were the inorganic polyphosphates, but their limitations were quickly discovered. Above 140°F (60°C), they revert to orthophosphate, as they do at acidic pH or over a long residence time. The orthophosphate form does not inhibit scale. Present day oilfield scale inhibitors are of three types:

1. Esters of polyphosphoric acid
2. Phosphonates
3. Organic polymers, such as polymers or copolymers of acrylic or methacrylic acid

The phosphate ester formulations are versatile for most oilfield water applications. Phosphonates and polymer products have definite advantages where water temperatures exceed 200°F (93°C). Dosages vary with temperature and the concentration of SS, since solids adsorb the inhibitor, requiring higher concentrations for effective inhibition. Dosage is directly proportional to the degree of supersaturation.

When applying scale inhibitors to producing wells, the "squeeze" technique is frequently used. This involves injection of a scale inhibitor into the producing formation through the production tubing string under pressure. The scale inhibitor molecules adsorb to the formation, to be gradually released with the produced fluids. Scale inhibitor squeeze applications can last for periods up to six months. The need for renewed treatment is determined through tests for inhibitor residual in the produced fluids.

Mineral Scales in Steam Injection/Thermal Systems

Once through steam generators (OTSGs) for oil field use is designed to tolerate higher boiler feed water dissolved solids and the resulting deposit formation than conventional drum boilers. In addition to the challenges created by the feedwater chemistry, the high cycles of concentration (COC) at which these systems operate create very high levels of super saturation with a greater tendency to form deposits. OTSGs and HRSGs tend to operate at 3 to 5 COC (using poorer feedwater quality compared to a conventional boiler at comparable pressure) while evaporators can operate from about 6 to 50 COC.

Composition and nature of deposits formed during operation of OTSGs can be identified from samples obtained from pigging operations or from tube samples received for metallographic analysis. Deposits obtained from heat-transfer tube surfaces and pigging samples are measured by X-ray fluorescence (XRF), X-ray diffraction (XRD), and C/H/N analysis. Those tests are used to determine percent levels of chemical ions (inorganic and organic) and any crystalline mineral species present in the deposit. Tables 34.3 and 34.4 summarize analyses from several tube and pigging deposits found in systems using high silica feedwater.

Composition by XRF	Location Number			
	1	2	3	4
SiO_2	15	17	12	45
CaO	4	7	2	1
MgO	9	10	5	6
Na_2O	< 1	2	1	2
Fe_3O_4	15	5	2	14
P	3	5	0	0
S	4	5	1	2
Carbonate		< 1	< 1	< 1
Total Inorganic	54	49	24	72
Loss at 925°C	46	51	76	28
Total Organic (C,H,N)	42	42	67	26
Sample Source	Pigging	Tube	Pigging	Tube

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[*] HRSG, heat recovery steam generator operating as once-through system.
[†] Lithium species are not directly detected by XRF.

TABLE 34.3 % Composition of Tube Deposits and Pigging Samples (OTSGs, HRSGs[*], by XRF[†])[2]

Mineral Species (observed by XRD)	Location Number			
	1	2	3	4
Lizardite [$Mg_3Si_2O_5(OH)_4$]	X	X		
Ferrorichterite [$Na_2CaFe_5Si_8O_{22}(OH)_2$]			X	
Sodium Magnesium Silicate Hydroxide [$Na(Na,Mg)Mg_5SiO_8O_{22}(OH)_2$)]			X	
Lithium Silicate (Li_2SiO_3)				X
Alpha-quartz (SiO_2)	X			
Magnetite (Fe_3O_4)	X	X		
Hematite (Fe_2O_3)		X		
Wustite (FeO)			X	
Iron Sulfides ($Fe_{(x)}S_{(y)}$)	X			
Hydroxylapatite [$Ca_5(PO_4)_3(OH)$]	X	X		

TABLE 34.4 Mineral Composition of Tube Deposits and Pigging Samples (OTSGs and HRSGs by XRD)[3]

Hardness, Iron, and Silica Scales

By their very nature, thermal processes used to remove bitumen result in large volumes of silica-laden PW that must be treated for reuse [2-to-9 volumes of steam (cold water equivalent) are injected per volume of bitumen recovered with a cumulative steam-to-oil ratio ranging from about 2:1 to 9:1][4]. The majority of the feedwater are a direct result of recycling the PW, however, supplemental water containing high hardness levels (calcium, magnesium) are needed to maintain the correct water balance. The mixing of waters containing hardness and silica in conjunction with equipment operating conditions can directly lead to silicate-based deposits forming inside plant equipment. Iron salts, also present in under-ground formations or from system corrosion, adds the potential for iron based silicate deposit formation during transferring and storing water.

Aluminum ions (Al^{+3}) and high salinity (Na^{+}) can be present, often leading to their incorporation into the silicate deposits. Also, low concentrations (mg/L) of nonhardness ions (e.g., lithium, Li^{+}) can form insoluble silicate-based deposits.

Several unit operations in thermal plants (boilers, OTSGs, HRSGs, evaporators, and waste-disposal) typically run at high COC, which dramatically increases the possibility that silicate-based deposits will form. Once silicate-based deposits form inside plant equipment, those deposits are tenacious and prove to be very difficult to remove. Deposit formation often reduces heat-transfer efficiency/equipment output. In many cases, this may lead to tube failures and unexpected equipment shutdown. The result is a negative impact on steam generation and ultimately oil production.

Even when unit operations are generally running within specification, deposit forming conditions can still exist due to high levels of silica/hardness/iron occurring from upset conditions. This can occur over relatively long periods of time or may occur as numerous short episodes at random times.

Oil and Other Organic Components

One additional complication to the deposit formation in thermal systems is that the feedwater can contain organic constituents such as bitumen, oil, and organic carbon. Often the deposits formed are primarily inorganic with a significant percentage of organics present. This organic portion of the deposit is often generically referred to as coke.

We know from conventional drum boilers that when oil gets into a boiler, it will stick and cause all kinds of problems. Looking at free oil is a good way to monitor how the oil separation process is going and predict if oil-related coke formation may occur. Soluble organics appear to be involved too, although not all water-soluble organics will form coke. The chemical and mineral composition of coke deposits is exceedingly complex.

Scale Removal and Prevention

OTSGs and once-through HRSGs for oil field use are designed to tolerate higher levels of deposit formation, as they are relatively easy to clean by mechanical methods (pigging). Evaporators typically rely on chemical washes and mechanical cleaning once deposition becomes sufficient to impede system operation. Whether it's an OTSG, HRSG, or evaporator; mechanical cleanings can be expensive and time consuming. Downtime for the cleanings results in substantial lost production. In many instances, continuous treatment of the water stream with polymers or chelant treatments can prevent or reduce scale formation.

Corrosion

Water Injection Systems

The primary corrodents in oilfield water systems are carbon dioxide (CO_2), hydrogen sulfide (H_2S), and oxygen (O_2).

Oxygen is corrosive even at low concentrations because of its participation in creating differential cells beneath deposits on metal surfaces, which become anodic to adjacent deposit-free areas. Control of oxygen corrosion in oilfield water systems requires a conscientious effort to exclude air from all surface tanks and vessels and from the casings of producing wells. Field gas is used to maintain a positive gas blanket in these areas whenever possible.

After establishing control over oxygen exposure, it is then practical to use an oxygen scavenger to react with trace quantities of remaining oxygen. Several types of sulfite are commonly used, including sodium bisulfite ($NaHSO_3$), ammonium bisulfite (NH_4HSO_3), sodium sulfite (Na_2SO_3), and sulfur dioxide (SO_2).

The chemistry is the same with all forms; the sulfite reacts with oxygen to form sulfate:

$$SO_3^{-2} + \frac{1}{2}O_2 \rightarrow SO_4^{-2} \qquad (34.4)$$

The sulfite–oxygen reaction is influenced by temperature and pH. Optimum pH for quick reaction is above 7. Most oilfield waters will range in pH from 6.0 to 7.5.

Catalysis of the reaction is necessary. Sometimes, naturally occurring metal ions in the PW act as effective catalysts, but usually the catalyst is provided in the sulfite formulation.

Whenever H_2S is present, iron sulfide will deposit. The resulting deposits are cathodic to base metal, so it usually follows that severe pitting occurs beneath iron sulfide deposits, all because of the H_2S. Where O_2 intrudes into a sulfide system, the rate of corrosion can become uncontrollable. Carbon dioxide mixed with H_2S is also much more aggressive than either of the gases alone. Where H_2S is present, an efficient film-forming inhibitor must be used to prevent severe, localized corrosion. Hydrogen sulfide is corrosive because it ionizes to form a weak acid:

$$H_2S \rightarrow H^+ + HS^- \qquad (34.5)$$

Invariably, corrosion inhibitors used in oilfield applications are organic film formers. The molecules adsorb onto metal surfaces to shield the metal from corrodents. Since the film-forming corrosion inhibitors must be added to a wide range of brine concentrations and in many cases to a mixture of water and hydrocarbon, inhibitors with a wide range of solubility must be used. In the producing well, where a mixture of crude oil and brine must be treated, an inhibitor that is oil soluble and only slightly water dispersible is often required. This will film metal from the oil phase, providing long-term persistency to the metal surface, that is, the film will be maintained even when the inhibitor feed is discontinued. This allows batch treatment of producing wells in many instances. One of the most common methods of treating producing wells is using a treating truck to pump inhibitor down the tubing or into the annulus, followed by a flush of PW. The application is repeated periodically at intervals depending on the aggressiveness of the corrodents.

In injection water systems where water is the predominant phase, inhibitors must be either water soluble or highly water dispersible in order to carry through the surface line and tubing system. These inhibitors are not persistent, and it is necessary to feed continuously, always maintaining a residual in the system. Loss of inhibitor residuals results in desorption of inhibitor film and loss of protection.

In monitoring the chemical program, inhibitor residuals are determined through field extraction tests.

Corrosion monitoring is usually accomplished through a combination of metal weight-loss specimens, corrosion meters, pipe spools or nipples (which have the advantage of duplicating flow conditions), and iron counts. Residual iron concentrations are valid in systems without hydrogen sulfide, where H_2S is present, iron is deposited as iron sulfide.

Steam Injection/Thermal Systems

The most common corrodents in oil field thermal systems is oxygen (O_2). Less commonly, hydrogen sulfide (H_2S) may become a corrosion issue. Some metal surfaces may also experience erosion–corrosion.

Oxygen is a highly active element. Even in small amounts, it can cause serious corrosion in lines, heat exchangers, and steam-operated equipment. Corrosion increases with increasing oxygen content. The corrosion rate of oxygen dissolved in water is significant as temperature rises above approximately 120°F (49°C) and doubles for each 18°F (10°C) increase. In addition, portions of a system that are exposed to high flow rates or turbulent flow conditions are more susceptible to oxygen attack. Oxygen is also responsible for creating scaling agents through oxidation of ferrous iron and hydrogen sulfide. It is important to try to exclude oxygen from all vessels, casings, and surface supply lines. Sulfite based oxygen scavengers are typically used to chemically treat residual oxygen in OTSG feedwater, but low solids alternative scavengers are more commonly used in evaporated feedwater.

Recently published data suggests that an erosion–corrosion mechanism may be operating across steam generator passes. Iron pickup can be highly variable and is thought to be affected by layered, porous, coke-rich deposits that form near the point where boiling begins and are intermittently released at varying rates over time. When released, these solid deposits are accelerated by the fluid flow in the steam generator and provide the abrasive force needed for the erosion–corrosion mechanism. The presence of hard silicate minerals within the coke matrix of the deposits makes the particles far more abrasive than pure coke without inorganic mineral inclusions.[5]

Pigging is performed widely in OTSGs to mechanically remove the scale and fouling material that decreases heat transfer efficiency. A pig is a scraping device designed to closely fit inside a boiler tube. The pig abrasively removes deposit from the internal surface of the tube when it is forced through the length of the tube. The pigging process generally cleans the tubes down to bare steel. The bare metal is initially more susceptible to corrosion and an OTSG will generate more corrosion products over a steam generating pass shortly after a pigging operation. Over time a bare steel surface exposed to the high temperature and high pH conditions of steam generation will spontaneously form a surface film of magnetite, Fe_3O_4, which is more protective against further corrosion.

Bacteria Control

Control of bacteria is important in oilfield water operations because bacteria can cause plugging of the injection water formation and serious corrosion. Bacteria are seldom an issue in thermal systems.

The most troublesome of these organisms is the anaerobic sulfate-reducing bacterium, *Desulfovibrio desulfuricans*. Present in many oil-bearing formations, it is involved in the chemical changes which occur during the formation of petroleum. It reduces inorganic sulfate (SO_4^{-2}) to sulfide (S^{-2}), which leads to iron sulfide precipitates.

Clostridia, another anaerobic sulfate-reducing organism, are not as prevalent as *Desulfovibrio*. *Clostridia* are reported to be thermophilic, preferring a temperature range of 131 to 158°F (55–70°C).

Several species of aerobic bacteria are also important, most of which are found in surface waters used to supplement PW in a waterflood. Some of the more important organisms are *Pseudomonas*, *Flavobacterium*, *Aerobacter*, *Escherichia*, and *Bacillus*. These form slime masses, which can cause plugging or which shield the anaerobic *Desulfovibrio*.

Iron bacteria are occasionally found in some waterfloods, the two major species being *Sphaerotilus* and *Gallionella*. These oxidize the ferrous ion (Fe^{+2}) to ferric ion (Fe^{+3}). Iron bacteria are identifiable through a microscopic analysis following staining.

Beggiatoa oxidize sulfide to sulfate and usually grow in open PW systems, where a gathering line dumps into an open pit. They are often responsible for filter plugging.

Microbes are controlled by chemical application. The concentration of chemical and the contact time vary among systems. Normally, chemical is fed at a selected dosage for a period of 4 to 8 hours. Following application, samples are withdrawn from the system, and microbial population is determined. The frequency of biocide application is dictated by such control tests.

In many situations, physical system cleanup is necessary to gain proper microbial control. Low spots in lines or tanks with bottom accumulations of sediment or debris protect bacteria from chemical contact.

Raw Water, Utility, and Cooling Water Systems

Raw water, utility, and cooling systems used by in-situ producers and upgraders are similar to those found in refineries with continuous operation incorporating a number of interrelated process units. They are discussed in detail elsewhere in the handbook and will not be discussed here.

Automation and Control of System Chemistry

Automation and control of steam and water system chemistry are still relatively new in oilfield systems. A limited number of sensors tolerant of oilfield conditions and chemistry currently exist. Development of reliable and accurate instrumentation has been hampered by the oil and color present in the feedwater, which consists largely of recycled PW. Traditional sensors are often fouled by oil and typical contaminant concentrations are often out of range for commercially available monitors.

Current trends appear to focus more on data management and analytics for system modelling and prediction. Canada’s Oil Sands Innovation Alliance (COSIA) and others have various projects in progress to supplement system operation predictive analytics.

Recycle and Reuse

Examples of recycle and reuse are plentiful and varied in oilfield steam and water systems. Common reasons include water scarcity at remote locations, legislative restriction on fresh water usage, and economics of operation.

Produced Water

PW is by far the largest byproduct of oil and gas exploration and production. It is estimated that 15 to 20 billion bbl/year of PW are generated from nearly 1 million wells in the United States. Globally the estimates are more than 65 billion bbl/year.[6] In these cases the producer is faced with basically two choices when dealing with PW:

1. Reuse or recycle
2. Discharge it to the environment (including down-hole discharge)

PW can be a complicated mixture containing some or all of the following; dispersed oil, dissolved or soluble organics, residual treatment chemicals, produced solids (clays, sand, and dirt), scaling metals (Groups 1A, 2A, and 3B in the Periodic Table), other metals, pH effects, sulfates and naturally occurring radioactive materials (NORMs). To release water to the environment, National Pollutant Discharge Elimination System (NPDES) discharge permits must be met. For environmental discharge, irrigation or water for livestock, BOD, salinity, TDS, oil content, heavy metals, and all must meet the NPDES permit.

To reuse the water in drilling applications, certain specifications must be met to ensure that it does not corrupt the well or other areas of potential use. In certain areas like fracturing, the water content plays a critical role in the choice and performance of fracturing chemistries.

In hydraulic fracturing operations, huge volumes of water are needed for well completion. Due to the enormous volumes of water needed for well completion there is a large economic incentive to reuse as much PW as possible during the fracturing, instead of relying on all freshwater. When reusing PW for hydraulic fracturing two major concerns in water quality are the amount of bacteria and iron in the PW. Bacteria in the PW are of concern as introducing SRB to the well during hydraulic fracturing can lead to souring of the well, creating a safety risk and decreasing the worth of the oil. High iron levels in the PW can lead to precipitates downhole that plug the well. PW can be treated with a peracid based biocide to control both bacteria and iron levels in PW. Peracid biocides are broad spectrum oxidizing biocides that kill bacteria by oxidizing proteins in microbial cells. The oxidizing nature of peracid biocides also will oxidize soluble iron in the water, producing particulate iron that can separate from the PW before it is used to formulating fracturing fluid.

Steam injection is a method of extracting heavy oil. There are at least three types of steam stimulation, CSS, Steam flooding, and the SAGD. The first two are most common and practiced throughout the world. The latter is practiced in the oil sands of northern Alberta. CSS is a 3-phase process consisting of steaming, soaking, and production. Steam flooding effectively uses steam to chase the oil from a steam well to a production well. SAGD uses two horizontal wells, the upper steams, while the lower collects the emulsified oil. The latter two use steam continuously, while CSS uses steam intermittently. In all cases, the emulsified oil is returned to the surface for processing where the oil is separated from the PW. In a majority of cases, the PW is further treated and then used to produce steam. In SAGD, PW is first treated with chemistries to break the oil out of the water, and then further treated to remove any residual oil. In Canada, the major scaling component is silica, so it is common to see a warm lime softener using magnesium Oxide to reduce Si concentration. In some cases, evaporators are used in place of the lime softener and effluent can be used for an OTSG or conventional boiler.

Transportation and Storage

The Midstream sector is an industry unto itself, linking the producers in the oil fields to the processers at the refineries. The modes of transport used to move these products include pipeline, marine tankers and barges, and rail and truck. Pipeline is the most common method of transport requiring compression pump stations to provide the motive force to move the products over thousands of miles of varying terrain and conditions.

The characteristics of the various crudes moved through these distribution systems often requires some remediation especially with the increased production of the unconventional oils. High wax or asphaltine content crudes typically will have flow problems such as poor pumpability or cold flow issues related to the viscosity of the oil. The use of additives such as viscosity modifiers, flow improvers, pour point depressants, and wax dispersants is critical to ensure that the products can be moved and stored in an efficient manner. In addition, corrosion inhibitors, biocides, and H_2S scavengers are also used to maintain the integrity of the distribution system or safety during handling. Some of these additives can be problematic at the end user especially in the treatment of the resulting waste.

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[1] Banerjee, D.K., Oil Sands, Heavy Oil, and Bitumen: From Recovery to Refinery, PenWell Corp., 2012.

[2] Ralph, C.K., Hoots, J.E., Batton, C.B., Silicate Deposit Control in Steam-Assisted Gravity Drainage (SAGD) and Produced Water Applications, Nalco an Ecolab Company, IWC paper 12–40, 2012.

[3] Ralph, C.K., Hoots, J.E., Batton, C.B., Silicate Deposit Control in Steam-Assisted Gravity Drainage (SAGD) and Produced Water Applications, Nalco an Ecolab Company, IWC paper 12–40, 2012.

[4] Tristone Capital Inc., SAGD: Looking Beneath the Surface, Energy Investment Research, 2007.

[5] Godfrey, M.R., Desch, P., LaRocque, L., Erosion-Corrosion in Oil Field Once Through Steam Generators, Nalco Champion an Ecolab Company, IWC paper 14–53, 2014.

[6] Veil, John A., Pruder, Markus G. Elcock, Deborah, Redwelk, Robert, A White Paper Describing Produced Water from the Production of Crude Oil, Natural Gas and Coal Bed Methane (2004).

CHAPTER 35

The Refining Industry

Refining

Petroleum refining is a continuous operation incorporating several interrelated process units, each designed to either produce or enhance a finished product. Since water is used in the refinery for heating, cooling, and processing, it represents an integral component of the refining process. A refinery may draw water from a variety of sources, and the treatment processes used to condition this water vary accordingly. Little or no treatment may be required for some well waters, while other water sources may require extensive treatment incorporating clarification, softening, and filtration. The types of water treatment problems here are much the same as in other industrial applications. In general, the basic water flow scheme is illustrated in Fig. 35.1.

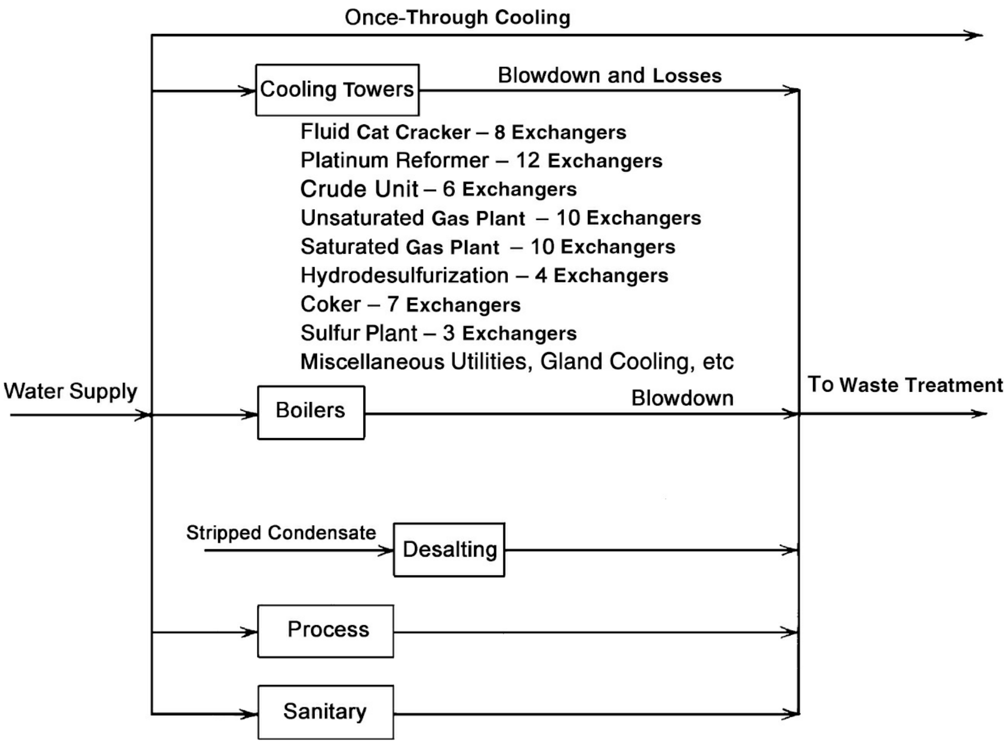


FIGURE 35.1 Water uses in a typical 150 000 bpd (23 800 m^3/d) refinery.

After initial processing, the water is usually divided into several streams for use throughout the refinery. At most locations, this water can be used directly as cooling tower makeup, with little or no further pretreatment. However, an extensive treatment scheme is usually necessary to produce the high-quality water required for boiler feed. Figure 35.2 shows a typical water system designed for a large refinery utilizing a surface water source as plant makeup. Although each refinery is unique in their water usage, it is not unusual for 70% or more of the water brought into the refinery to be used for the cooling of processes and the generation of steam. Consequently, these two systems are the first to be scrutinized closely when water conservation is desired.

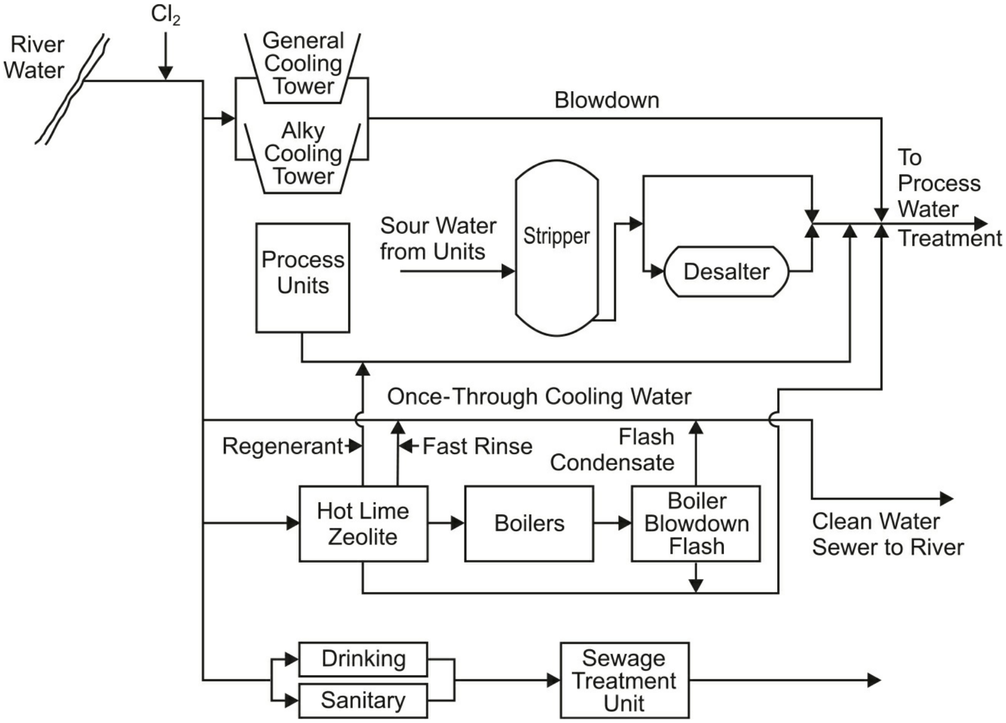
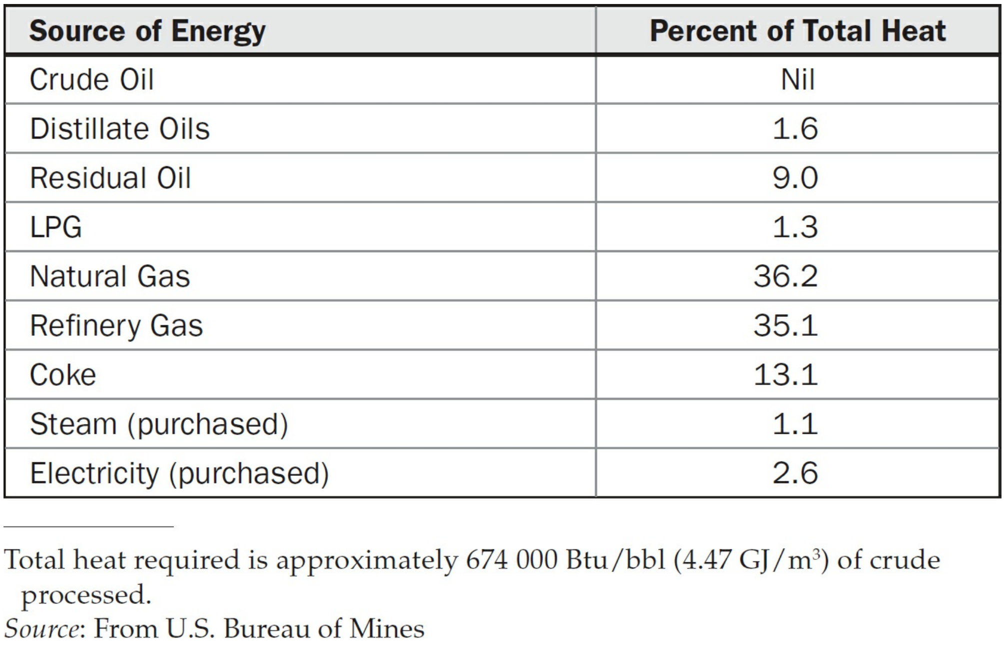


FIGURE 35.2 Water system treating surface water for refinery uses.

Refinery processes are net consumers of heat, to the extent that 10 to 15% of the heat equivalent of the incoming crude is used in the refinery operations. This is provided by refinery by-products, including off-gases, residual oil, and coke, and in many cases supplemented by natural gas. A typical process heat balance is shown in Fig. 35.3. This does not include heat recovered in waste-heat boilers.



Source of Energy	Percent of Total Heat
Crude Oil	Nil
Distillate Oils	1.6
Residual Oil	9.0
LPG	1.3
Natural Gas	36.2
Refinery Gas	35.1
Coke	13.1
Steam (purchased)	1.1
Electricity (purchased)	2.6

Total heat required is approximately 674 000 Btu/bbl (4.47 GJ/m^3) of crude processed.

Source: From U.S. Bureau of Mines

FIGURE 35.3 Refinery heat balance.

Process Operations

The refining of petroleum products and petrochemicals involves two basic operations: physical change (separation processes) and chemical change (conversion processes). A refinery is a conglomerate of manufacturing plants, the number varying with the variety of products produced. The bulk of these products (kerosene, fuel oils, lubricating oils, and waxes) is fractions originally present in and subsequently separated from the crude petroleum. Some of these are purified and supplemented with nonpetroleum materials to enhance their usefulness. A refinery with half a dozen processes, including distillation and cracking, can produce gasoline, kerosene, and fuel oils. The manufacture of solvents requires two or three more processes; lubricating oil production requires at least five more; waxes require another two or more. Asphalts, greases, coke, gear oils, liquefied petroleum gases, alkylate, and all the other kinds of products that can be made would require as many as fifty different processes. Figure 35.4 is an overall flow diagram for a generalized refinery production scheme.

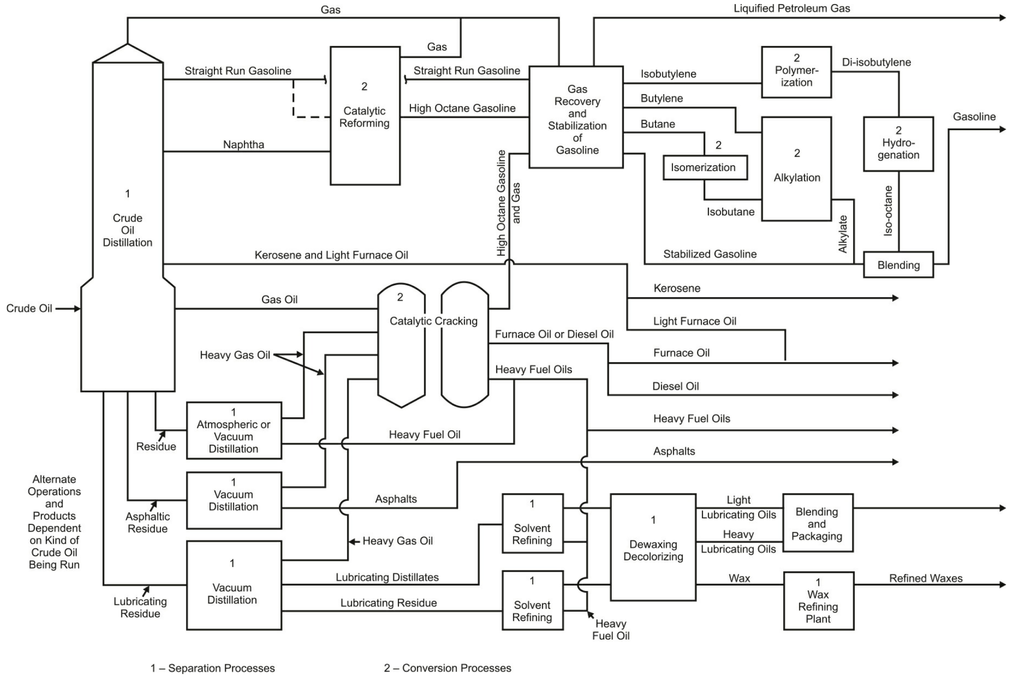


FIGURE 35.4 Generalized flowchart for petroleum refining. (*From Shreve, R. N., Chemical Process Industries, Third Edition, McGraw-Hill, New York, 1967.*)

As previously mentioned refining is concerned with separation and conversion processes, carried out by individual unit operations. Basic to most of them are furnaces, heaters, heat exchangers, as well as distillation and extraction columns. Heat exchangers are typically of shell-and-tube design, often utilizing incoming hydrocarbon feedstock as a cooling medium for hot products. If additional cooling (trim cooling) is required, water is used.

Distillation and extraction are usually the principal techniques in product separation. Distillation separates various hydrocarbon mixtures into components having different boiling points. In extraction, hydrocarbons are separated based on their different solubility in a specific solvent. In some unit operations, filters are used to remove suspended contaminants from the hydrocarbon stream, such as catalyst fines and inorganic precipitates.

Distillation

Figure 35.5 illustrates a typical distillation column (pipe still). Preheated crude is charged into the bottom of a distillation column at a pressure slightly above atmospheric; the vapors rise through the column, contacting a down flow stream (reflux). As a result, the lightest materials concentrate at the top of the column, the heaviest materials at the bottom, and intermediate materials in between. Desired products are withdrawn at appropriate points. Because the lighter products (as vapor) must pass through the heavier products (as liquid) and must be in equilibrium with them at each point in the column, each stream contains some very volatile, low molecular weight components (light ends).

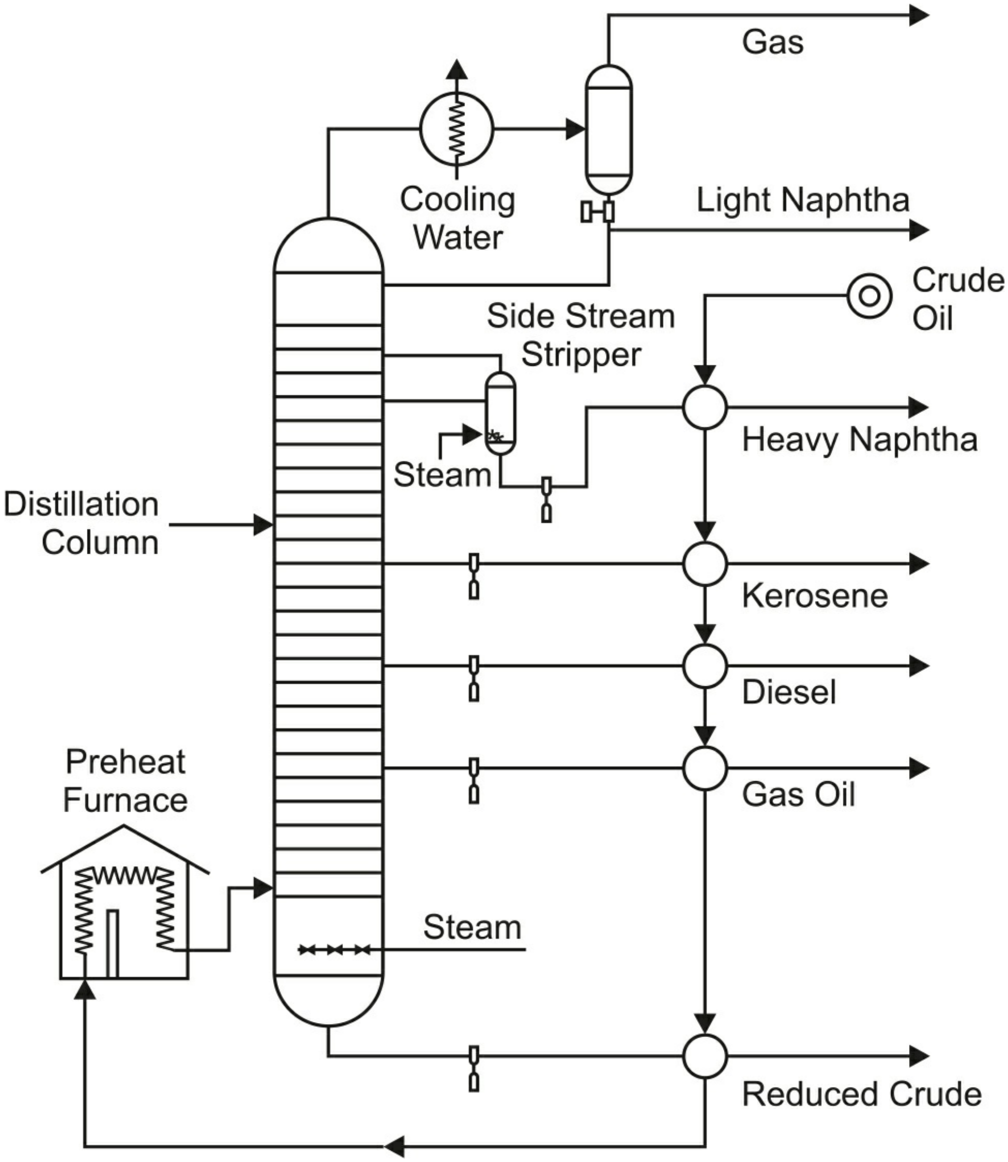


FIGURE 35.5 Distillation column with sidestream steam stripper.

As indicated in Fig. 35.5, steam strippers are sometimes used to remove light ends from a sidestream. The sidestream is fed to the top of the stripper; counter-current steam strips out the light ends and carries them back to the main column.

The wastes from crude oil fractionation, and in general from most distillation columns, come from three sources. The first is the water drawn from the overhead accumulator before recirculation or transfer of the hydrocarbons to another fractionator. The water that separates from the hydrocarbons in these accumulators is usually drawn off and discharged to the wastewater treatment system. This water can be a major source of sulfides, especially when sour crudes are being processed; it may also contain significant amounts of oil, chlorides, mercaptans, and phenols. In addition to naturally occurring contaminates, there are many contaminates that are added during production of the crude oil, or added to reduce harmful existing crude oil contaminates such as hydrogen sulfide (H_2S). Some of these additives or additive byproducts are water soluble and can impact the wastewater treatment unit, such as amines and methanol. A second significant waste source is discharge from oil sampling lines; this oil should be separable, but may form emulsions in the sewer. A third waste source is the stable oil emulsion formed in barometric condensers used to produce a vacuum in some distillation units (Fig. 35.6).

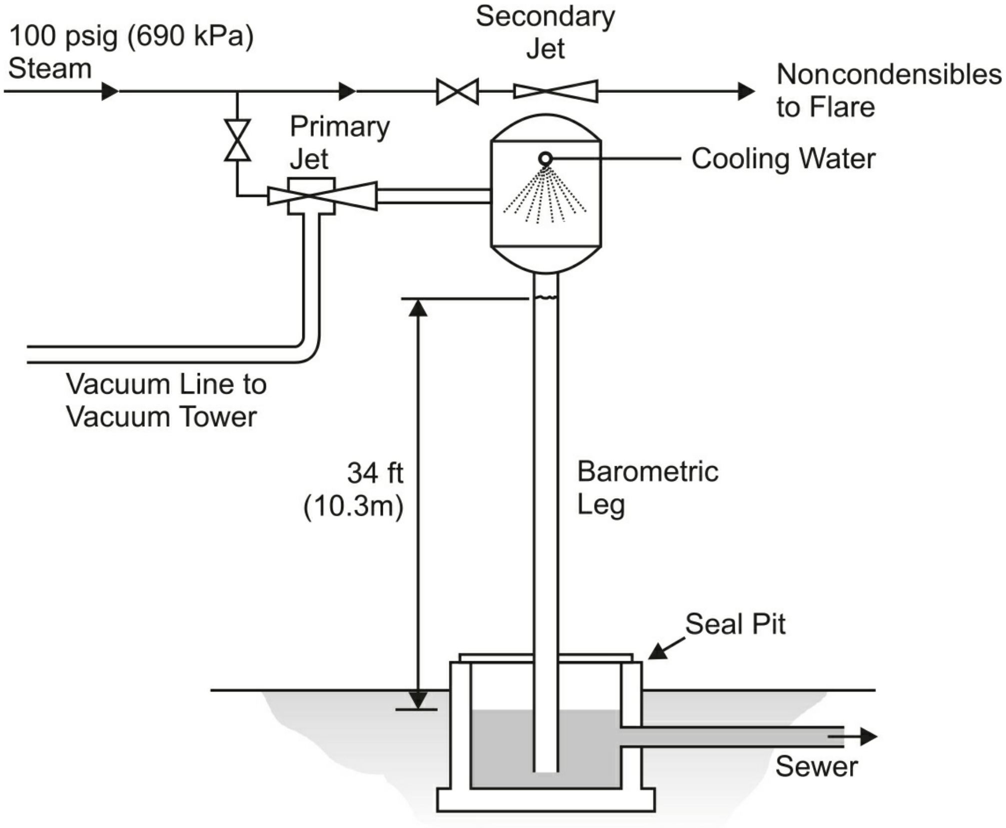


FIGURE 35.6 Barometric condenser.

Desalting

A refinery's desalting process is one of its most valuable assets. The desalter removes water-soluble contaminants and oil-insoluble particulates. It provides more protection to refinery equipment than any other single piece of process hardware (Fig. 35.7).

FIGURE 35.7 Desalter unit.

Contaminants found in crude come into the refinery from several sources. They may be inherent to the crude itself or to the producing field or they may have been introduced by the equipment and methods used to produce the oil in the field. They may have arisen as corrosion or erosion products when the oil was in transit from the field to the refinery. Contaminants also may be introduced in recovered oils and waste streams added to the crude for processing. Desalting is a two-step process, consisting of contacting and separation.

- Contacting mixes fresh water (4–10 vol%) with the crude so that the water contacts and dilutes all of the salts. Other solids also adhere to the water through a process called water wetting.

- Separation separates the diluted brine and solids from the oil as completely as possible, leaving the oil dehydrated, desalted and the water "de-oiled." The heavier water is then drained away to waste treatment. In many cases, the desalter brine effluent is processed through a sour water stripper before being discharged to waste treatment.

In vacuum towers, a steam jet ejector is the most widely used method for creating a vacuum. The steam and other vapors removed from the fractionator must be condensed, and the liquid removed before discharge of the vapor to the atmosphere.

The barometric condenser condenses the steam jet by use of a water spray in a closed chamber, and the water drains down the barometric leg. The organics, oils, and steam condensate are intimately mixed in a large volume of cooling water, which tends to form difficult to handle emulsions. Most refineries use surface condensers instead of barometric condensers. These units consist of a series of shell-and-tube exchangers in which the condensables are removed, and the water for cooling does not come into direct contact with the condensate (Fig. 35.8). The water discharge from the distillation operation is sent to the refinery waste plant, sometimes through a separate oil separation unit.

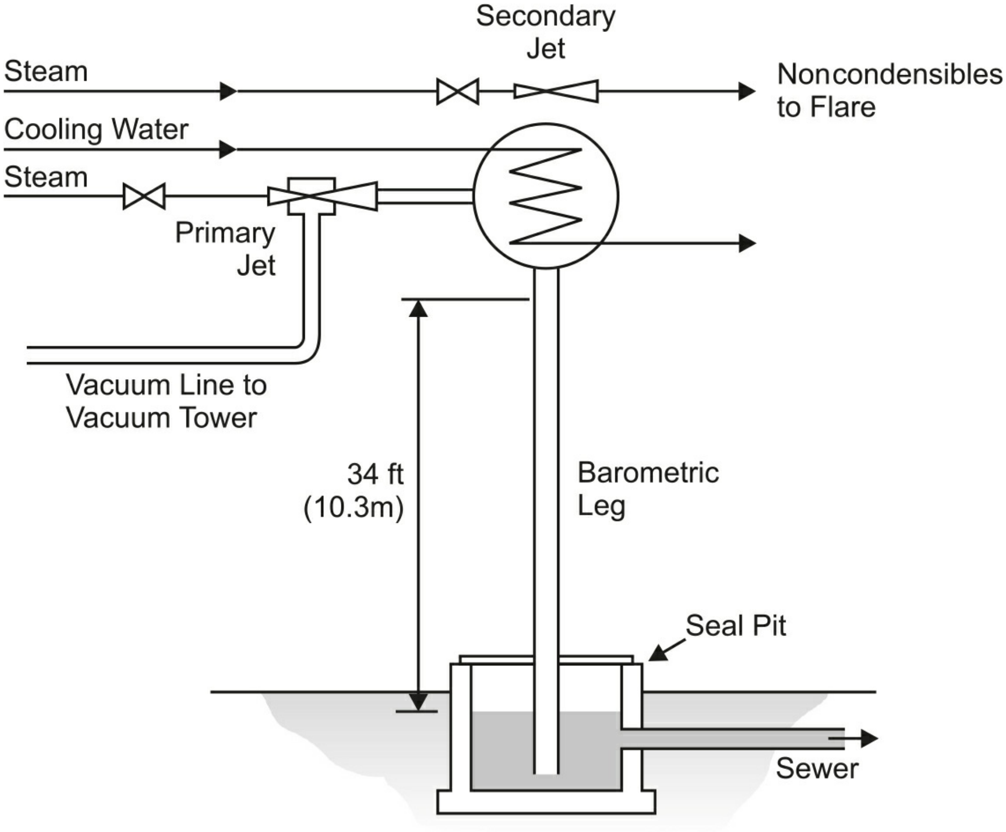


FIGURE 35.8 Tubular steam condenser.

Thermal Cracking and Related Subprocesses

In thermal cracking units, heavy oil fractions are broken down into lighter fractions by application of heat, but without the use of a catalyst. Production of gasoline is low, but middle distillates and stable fuel oils are high. Visbreaking and coking, the two major types of thermal cracking, maximize the production of catalytic cracking feedstocks, indirectly increasing gasoline production.

Oil feed is heated in a furnace to cracking temperatures, and the cracked products are separated in a fractionator (Fig. 35.9). The heat breaks the bonds holding the larger molecules together, and under certain conditions, some of the resulting smaller molecules may recombine into larger molecules again. The products of this second reaction may then decompose into smaller molecules, depending on the time they are held at cracking temperatures.

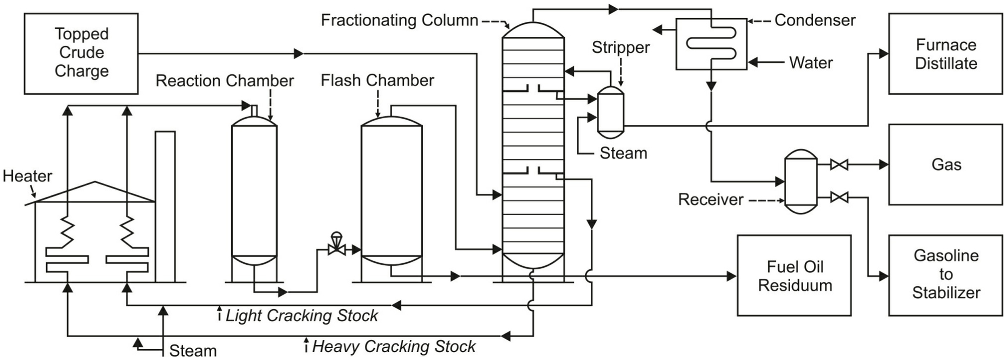


FIGURE 35.9 A thermal cracking process treating topped crude (Universal Oil Products process). *(From Shreve, R. N., Chemical Process Industries, Third Edition, McGraw-Hill, New York, 1967.)*

Visbreaking is a mild form of thermal cracking; it causes little reduction in boiling point, but significantly lowers viscosity. The feed is heated, cracked lightly in a furnace, quenched with light gas oil, and flashed in the bottom of a fractionator. Gas, gasoline, and furnace oil fractions are drawn off, and the heavier fractions are recycled.

Residual oils may be cracked to form coke as well as the usual gaseous and liquid products. The most widely used process, known as delayed coking (Fig. 35.10), accounts for about 75% of the total oil coking capacity.

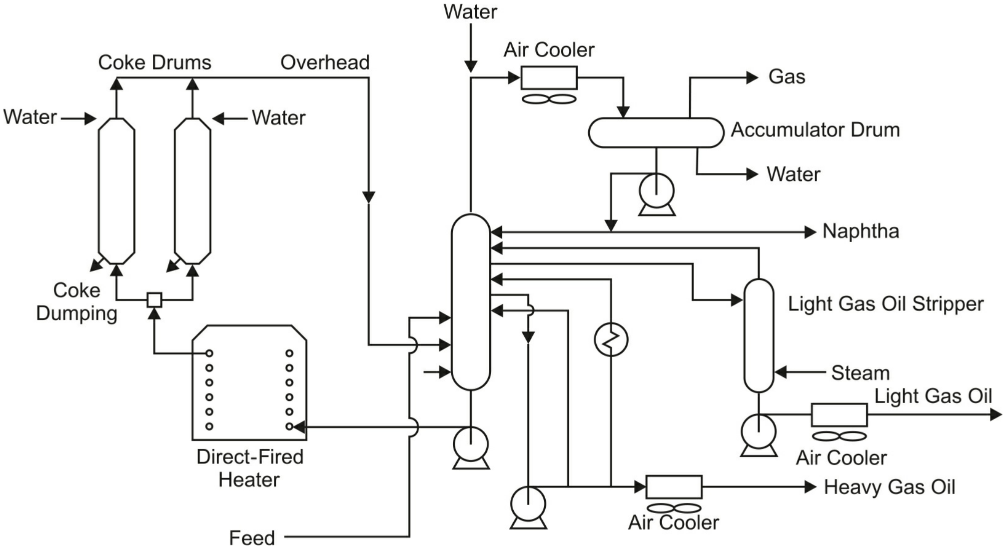


FIGURE 35.10 Delayed coking process.

Thermal cracking units require cooling water and steam on the fractionating towers used to separate products. Some towers employ steam stripping of a sidestream to remove light ends, requiring an overhead condenser and accumulator system for product/wastewater separation. Wastewater usually contains various oil fractions and may be high in pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia (NH_3), phenol, organic acids, and sulfides. Another important water use area is the high-pressure water sprays used for coke removal in delayed coking. Several refiners have instituted water recycle clarification systems to minimize water discharge from these coking units (Fig. 35.11).

FIGURE 35.11 Coker unit.

Catalytic Cracking

The fluid catalytic cracking process is the most widely used refining process (Fig. 35.12). A large mass of finely powdered catalyst contacts the vaporized oil in the processing unit. The catalyst particles are of such a size that when aerated or “fluffed up” with air or hydrocarbon vapor, they behave like a fluid and can be moved through pipes and control valves.

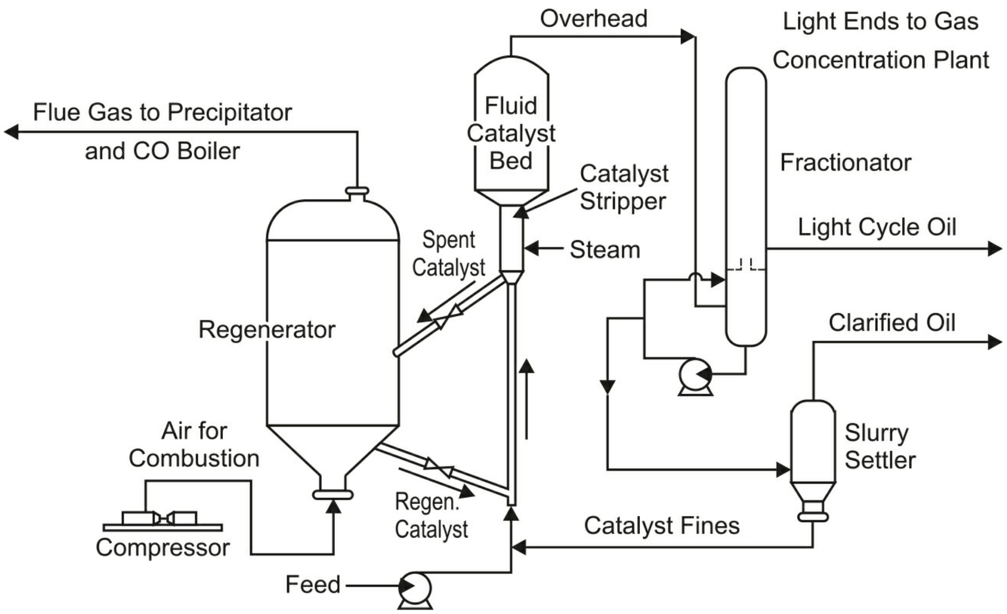


FIGURE 35.12 Fluid catalytic cracking unit.

In the catalytic cracking process (Fig. 35.13), feed and regenerated equilibrium catalyst flow together into the riser reactor. The cracked vapors from the reactor pass upward through a cyclone separator, which removes entrained catalyst. The product vapors then enter a fractionator, where the desired products are removed and heavier fractions recycled to the reactor. Spent catalyst passes from the separation vessel, downward through a stream stripper, and into the regenerator where carbon deposits are burned off. The regenerated catalyst again mixes with the incoming charge stream to repeat the cycle. On units using a carbon monoxide (CO) boiler, partial combustion in the regenerator is used. This incomplete combustion produces a preponderance of CO over carbon dioxide (CO_2). Significant amounts of hydrocarbons and other substances also remain unburned in the combustion gases. The CO and hydrocarbons in the exhaust make it a useful fuel. Most refineries burn this exhaust gas in specially designed CO boilers to generate steam. The gas burned in the CO boiler carries a significant amount of residual catalyst fines, which can cause furnace deposits.

FIGURE 35.13 Fluid catalytic cracking unit.

Today, most units operate in a complete combustion mode in the regenerator. This reduces carbon on regenerated catalyst, improves product yields, and helps reduce preheat fuel requirements.

Most fluid catalytic cracking units process vacuum and coker gas oils as feed. These feeds contain low levels of nickel (Ni) and vanadium (V), which are serious catalyst poisons. Heavy oil units, which use part heavy oil for feed, may operate with more than 2000 mg/L Ni and V on the equilibrium catalyst. This is made possible by using a metal passivator, which decreases the dehydrogenation poisoning activity of Ni and V.

The catalytic cracker is one of the largest producers of sour water in the refinery, coming from the steam strippers and overhead accumulators on the product fractionators. The major pollutants resulting from catalytic cracking operations are BOD, oil, sulfides, phenols, ammonia, and cyanide.

Catalytic Reforming

In catalytic reforming (Fig. 35.14), the object is to convert straight chain organics into cyclic molecules (aromatics of high octane). Reforming is essential to production of high-octane gasoline. Platforming, the most widely used reforming process, includes three sections:

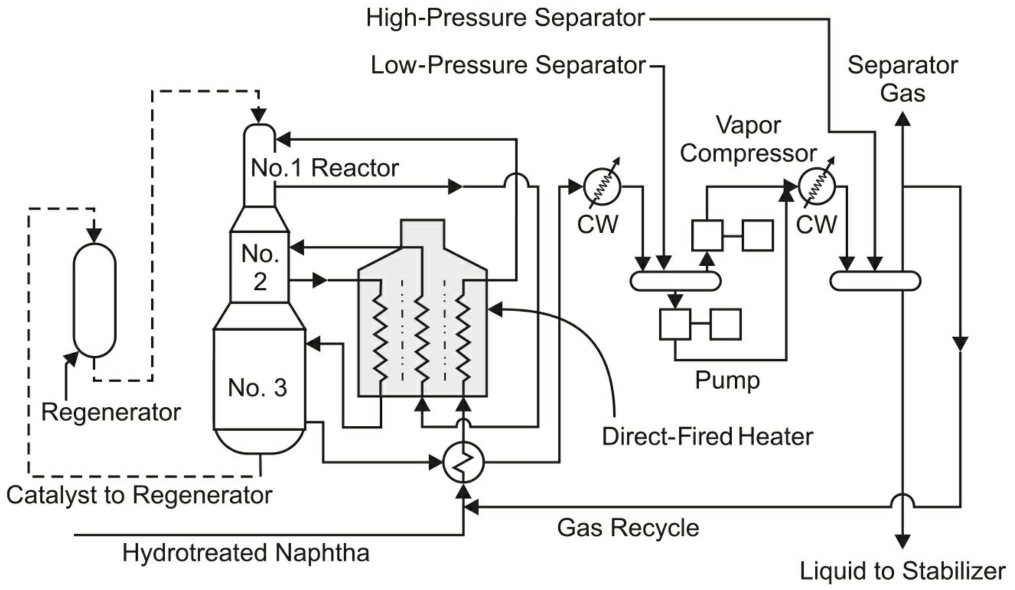


FIGURE 35.14 Catalytic reforming process.

1. In the reactor heater section, the charge plus recycle gas is heated and passed through reactors containing platinum catalyst.
2. The separator drum separates gas from liquid, the gas being compressed for recycling.
3. The stabilizer section corrects the separated liquid to the desired vapor pressure.

The predominant reforming reaction is dehydrogenation of naphthenes, or removal of hydrogen from the molecule. Important secondary reactions involve rearrangement of paraffin molecules. All of these result in a product with higher octane ratings than the reactants. Platinum and molybdenum are the most widely used catalysts, with platinum predominating because it gives better octane yields.

Because platinum catalysts are poisoned by arsenic, sulfur, and nitrogen compounds, feedstocks usually are treated with hydrogen gas (hydrotreated) before being charged to the reforming unit. This produces hydrogen compounds, such as H_2S, which can be removed from the hydrocarbon stream.

Reforming is a relatively clean process. The volume of wastewater flow and the pollutant concentrations are small.

Alkylation

The amalgamation of small hydrocarbon molecules to produce larger molecules is known as alkylation (Fig. 35.15). In the refinery, this reaction is carried out between isobutane (an isoparafin) and propylene, pentylenes, and in particular, butylenes (olefins). The product is called alkylate. The olefin–isobutane feed is combined with the fractionator recycle. It is then charged to a reactor (contactor) containing an acid catalyst at a controlled temperature. The two predominant acid catalysts used are sulfuric acid and hydrofluoric acid. The contents of the contactor are circulated at high velocities to expose a large surface area between the reacting hydrocarbons and the acid catalyst. Acid is separated from the hydrocarbons in a recovery section downstream and recirculated to the reactor. The hydrocarbon stream is washed with caustic and water before going to the fractionating sections. Isobutane is recirculated to the reactor feed, and alkylate is drawn from the bottom of the last fractionator (debutanizer).

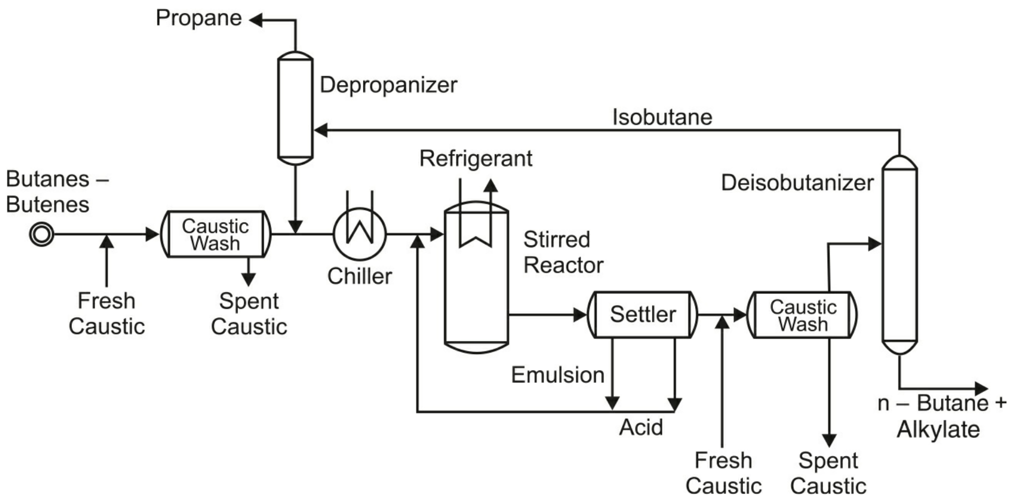


FIGURE 35.15 Alkylation process using sulfuric acid. (*Adapted from Hengstebeck, R. J., Petroleum Processing, McGraw-Hill, New York, 1959.*)

Acid may contaminate the cooling water should heat exchangers leak. Water drawn from the overhead accumulators contains varying amounts of oil, sulfides, and other contaminants, but they are not a major source of waste in this sub process. The wastes from the reactor contain spent acids, which refineries may process to recover clean acids or may sell. Occasionally, some leakage to the sewer or cooling system does occur. The major contaminant entering the sewer from a sulfuric acid alkylation unit is spent caustic from neutralization of the hydrocarbon stream leaving the reactor.

Hydrofluoric acid alkylation units do not have spent acid or spent caustic waste streams. Any leaks or spills that involve loss of fluoride constitute a serious and difficult waste problem.

Sulfuric acid alkylation units usually have a chilled water refrigeration system with several compressors, which have critical shell-side cooling water on inter- and after-coolers.

Hydrotreating

Hydrotreating is mild hydrogenation (Fig. 35.16) that removes sulfur, nitrogen, oxygen, and halogens from a hydrocarbon feed and convert olefins (unsaturated hydrocarbons) to saturated hydrocarbons. Petroleum feedstocks ranging from light naphthas to lubricating oils are hydrogen treated. The major application of hydrotreating has been removing sulfur from feeds to catalytic reformers to prevent catalyst poisoning. Each of the different types of hydrotreaters, which vary in the selection of catalyst, incorporates a reactor and a separator. The oil feed, preheated to 400 to 700°F (204–371°C), passes through a fixed-bed reactor, where it combines with hydrogen in the presence of a regenerable metal oxide catalyst at 200 to 500 psig (1.4–3.4 MPag). The product stream is cooled before entering a separator, where excess hydrogen gas is separated for use in other operations. After separation, the product is steam stripped for removal of residual hydrogen sulfide (Fig. 35.17).

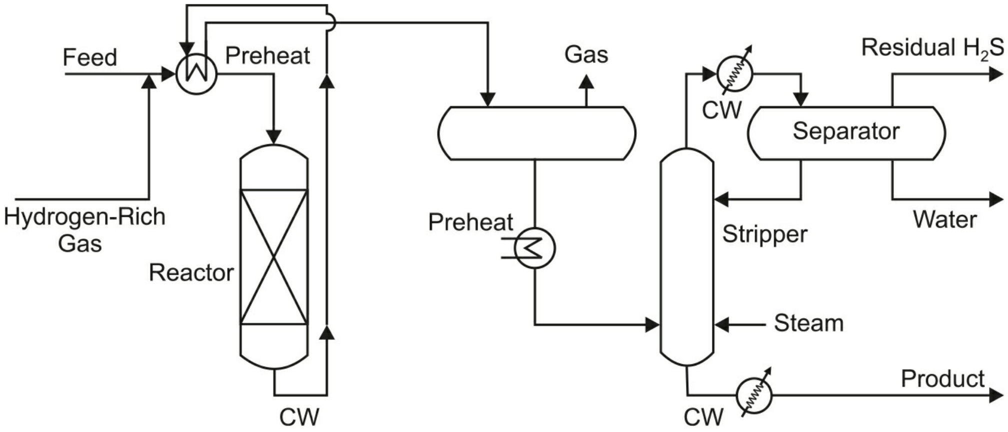


FIGURE 35.16 Hydrotreating process.

FIGURE 35.17 Vacuum residue hydrotreater reactors.

Major wastewater streams come from overhead accumulators on fractionators and steam strippers and sour water stripper bottoms. The major pollutants are sulfides and ammonia. Phenols may also be present, if the boiling range of the hydrocarbon feed is high.

Utility Systems

The steam generating system is the heart of the refinery operation, since steam is a major source of energy in the refinery. It is used to drive pumps and compressors, to heat process streams, to strip sour water and can represent up to 35% of the water use in an average refinery. A typical steam system is shown in Fig. 35.18.

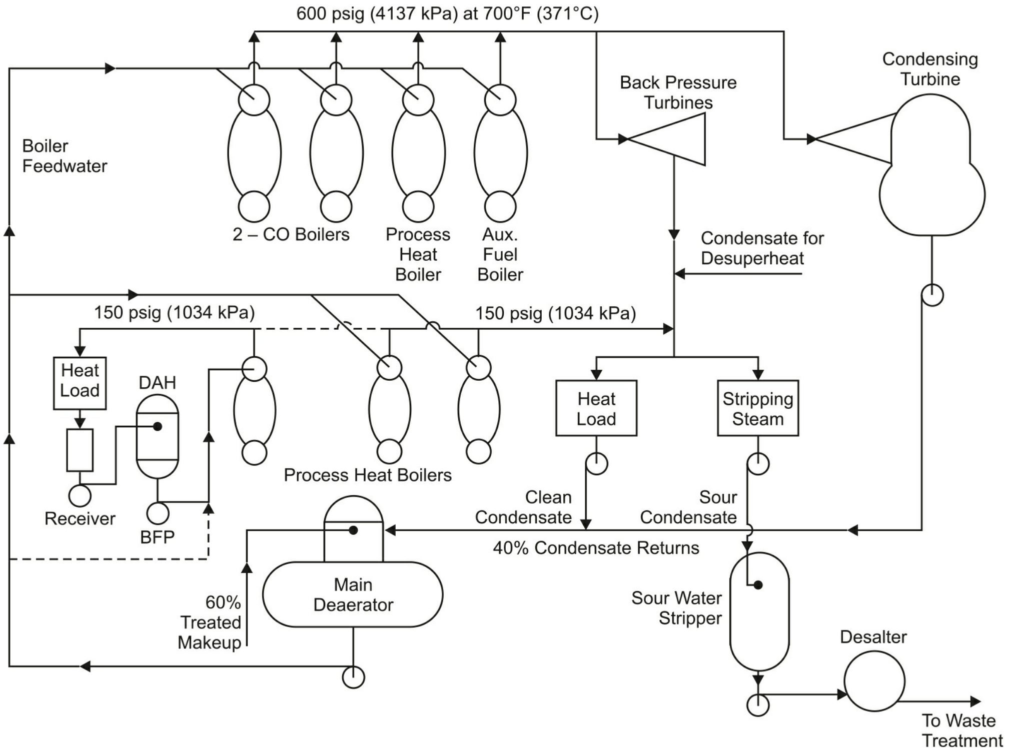


FIGURE 35.18 Process steam uses and condensate recovery in a typical refinery.

The pretreatment of boiler feedwater is one of the most important steps in efficient boiler operation. The specific pretreatment scheme for a steam generating system is dependent on such factors as boiler design, steam requirements, heat balance, outside power costs, and future expansion. Many refineries use hot process softeners, filters, ion exchange trains, and reverse osmosis units to prepare their boiler makeup. The selection of the appropriate pretreatment equipment will ensure that the steam generators can operate at optimum cycles of concentration with a low risk of failure. Incorrect matching of pretreatment with the boiler water requirements will result in lower cycles of concentration, higher water usage, and high operating costs.

Additional steam is generated in heat recovery and process heat boilers. These boilers can be found throughout the refinery in the various process units. Process heat boilers or kettles often resemble shell-and-tube heat exchangers in design but without the more sophisticated steam separation equipment found in conventional boilers. These small boilers can represent a significant volume of low pressure steam but can also be a major source of steam contamination. In most refineries, the steam generated by the process usually condenses as an acceptable quality condensate for return to either the boiler that produced it or to the general condensate return system. The major concern in these systems is prevention of corrosion in the condensate systems, particularly at the point of initial steam condensation. Depending on the pressure of the system, a condensate polishing unit may be installed to remove oil, corrosion products, or both, before returning this water to the boiler.

One source of condensate that is problematic is condensate being returned from a methane reformer or hydrogen plant. Excess steam used in this process is recovered as condensate and returned to the boiler feedwater system. Traditionally, the returned condensate is laden with carbon dioxide, typically resulting in a pH of approximately 4.3. In addition, this condensate is also rich in organics and organic acids. This process condensate is mechanically treated for CO_2 removal prior to use as boiler feedwater. Even after CO_2 stripping, the residual CO_2 content as well as the organic acid content of this condensate results in unacceptably low pH conditions for the typical carbon steel feedwater system. Untreated, this feedwater condition will result in unacceptable preboiler corrosion. Due to the organic acid content, the preferred pH adjustment treatment is the use of dilute caustic feed of high purity caustic with feedback on feedwater pH for monitoring/control. Amines can also be used but at the expense of more ammonia generation in the system.

Cooling Water Systems

The cooling requirements of a refinery demand a large volume of water. It has been estimated that 50 to 60% of the total water requirements in a refinery are for cooling. The cooling systems in a refinery are similar to those found in many manufacturing plants, involving once-through, open recirculating, and closed cooling circuits. While each of these systems can be found in the refinery, the open recirculating system serves the greatest demand for process cooling. Once-through cooling, while not common can be found in refineries adjacent to large bodies of water, be it fresh, brackish or seawater.

Waste Treatment Systems

Refinery wastewater treatment systems separate pollutants from the water by physical, chemical, and biological means. Primary treatment consists of physical, and often chemical, processes where the gross waste load of oil and suspended solids are separated from the water. Secondary treatment removes much of the remaining organic and dissolved solid pollutants by biological treatment, which consumes and oxidizes organic matter.

There are a few physical, chemical, or biological methods known as tertiary treatment, including activated carbon adsorption and filtration. As pollution control regulations become more stringent, tertiary treatment methods will become more common.

Broadly speaking, a refinery wastewater system consists of:

- A drainage and collection system
- Gravity oil–water separators and auxiliaries to remove oil and sediment
- Treatment units or disposal facilities to handle segregated chemical solutions and other process wastes, and to control the effects of pollutants that have toxic properties

Figure 35.19 is a generalized list of wastewater sources; it also shows how they are segregated into various sewer systems to optimize reuse, and reduce overall treatment volumes to a minimum.

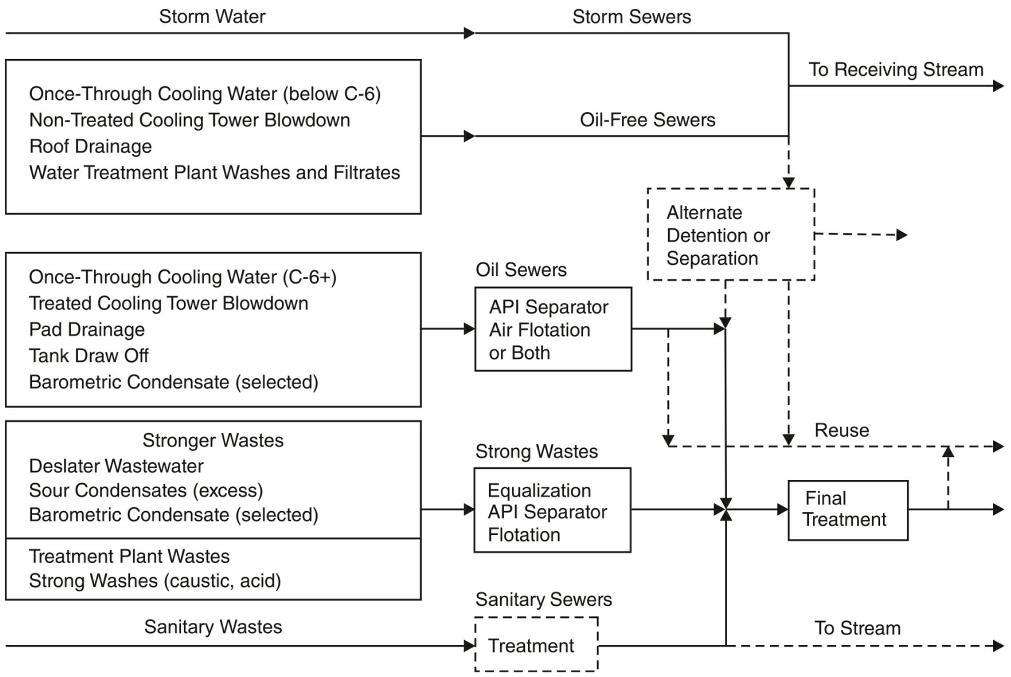


FIGURE 35.19 Suggested scheme for collection and treatment of refinery wastewaters.

The oil-free sewer collects wastewaters that have not contacted oil and that are not subject to any other contamination for which treatment must be provided. Since these waters seldom contain significant oil contamination, they may bypass primary treatment and some may discharge directly into the refinery outfall. However, if collected in a common sewer, this flow may be mixed with oily waste after primary treatment to reduce the hydraulic load on the primary treatment system.

The oily cooling water sewer system is intended to handle waters that are expected to be subject to minor oil contamination from leaks in heat exchange equipment or from spills. In the absence of contamination by chemicals or fine solids, which tend to cause emulsions, separation of any oil from the water can be readily accomplished. Barometric condenser cooling waters that are subject to contamination by easily separable oil, but not containing emulsified oil, may also be included in this system.

The process water sewer system collects most wastewaters that come into direct contact with oil, or that are subject to emulsified oil contamination, or chemicals limited by the plant discharge permit. Water from the process water sewer system can be treated in a variety of ways. It is not uncommon for the waste to pass through an API separator where solids are settled by gravity and insoluble oil is floated and removed. A polishing step, utilizing a floatation process such as induced air floatation (IAF) or dissolved air or gas floatation (DAF/DGF) often follows to ensure up to 90% removal of insoluble material. Pollutants remaining after gravity and floatation separation are reduced by secondary treatment methods.

Separator skimmings, which are generally referred to as slop oil, require treatment before they can be reused because they contain an excess of solids and water. Solids and water contents in excess of 1% generally interfere with processing.

The sanitary sewer system collects only raw sanitary sewage and conveys it to municipal sewers or to a separate refinery treatment facilities. State or local regulations usually determine the sanitary disposal requirements. Raw sewage can be used for seeding refinery biological treatment units.

Special systems include those required for the separate collection and handling of certain wastes, having physical or chemical properties that cause undesirable effects in the refinery drainage system, oil-water separators, or secondary treatment facilities. Spent solutions of acids and caustic, foul (sour) condensates, and degraded solvents are examples of such wastes.

Sour Water Stripping

Many wastewater effluents from petroleum refining processes originate from the use of steam within the processes. The subsequent condensation of the steam usually occurs simultaneously with the condensation of hydrocarbon liquids, and in the presence of a hydrocarbon vapor phase that often contains, H_2S, NH_3, hydrogen cyanide (HCN), phenols, and mercaptans. After separation from the hydrocarbon liquid, the condensed steam contains oil and a mixture of these contaminants. These wastewaters are typically called sour waters or foul waters, because of the unpleasant odor characteristic of dissolved hydrogen sulfide.

The amounts of these contaminants in a sour water stream depend on the type of refining process from which the stream originated, as well as the feedstock to that process and the pressure at which the steam was condensed within the process. The contaminant concentrations in typical sour waters will usually be 50 to 10 000 mg/L H_2S, 50 to 7000 mg/L NH_3, and 10 to 700 mg/L phenolics.

The principal contaminants in sour waters are hydrogen sulfide and ammonia, ionized as HS^- and NH_4^+, respectively. These can be removed by single-step steam stripping, which is a simple form of distillation for the removal of dissolved gases or other volatile compounds from liquids. Stripping is rather inefficient and requires large volumes of steam, because these ionized substances exert very little gas pressure unless the pH is adjusted. Stripping also removes phenolics to some extent, but the amount of phenolics removed may vary from 0 to 65%.

Effluent water from a sour water stripper is often reused as wash water makeup to the desalter.

Spent Caustic Treatment

Alkaline solutions are used to wash refinery gases and light products; the spent solutions, generally classified as sulfidic or phenolic, contain varying quantities of sulfides, sulfates, phenolates, naphthenates, sulfonates, mercaptides, and other organic and inorganic compounds. These compounds are often removed before the spent caustic solutions are added to the refinery effluent. Spent caustics usually originate from batch operations, and the batches may be combined and equalized before being treated or discharged to the general refinery wastewaters. Precautions must be taken when disposing of any high pH material into a waste stream as the pH balance can change dramatically resulting in the potential for scale formation in the lines and equipment downstream of the injection point. Chemical treatment and/or neutralization will often be needed to prevent this from occurring.

Spent caustic solutions can be treated by neutralization with spent acid or flue gas, although some phenolic caustics are sold untreated for their recoverable phenol value. Neutralization with spent acid is carried to a pH of 5 to ensure maximum liberation of hydrogen sulfide and acid oils.

In the treatment of spent caustic solutions by flue gas, hydroxides are converted to carbonates. Sulfides, mercaptides, phenolates, and other basic salts are converted to hydrogen sulfide, phenols, and mercaptans at the low pH conditions caused by the flue gas stripping. Phenols can be removed and used as a fuel or can be sold. Hydrogen sulfide and mercaptans are usually stripped and burned in a heater. Some sulfur is recovered from stripper gases. The treated solution will contain mixtures of carbonates, sulfates, sulfides, thiosulfates, and some phenolic compounds. Reaction time of 16 to 24 hours is required for the neutralization of caustic solutions with flue gas.

CHAPTER 36

The Chemical Industry

The chemical industry manufactures more than 50 000 different products, making it the largest and most varied of all industries. The massive scope of chemical products ranges from alkali to xylene, and touches markets from fibers to pharmaceuticals. Most are used as basic materials in other industries, and some are used directly by consumers. This industry includes such diverse products as industrial gases, chlorine, resins, fibers, film, synthetic rubber, pharmaceutical ingredients, soaps, detergents, paints, coatings, and agricultural chemicals like fertilizers, herbicides, and pesticides.

Figure 36.1 shows the extensive interrelationships of chemical products using petrochemical processing as an example. Basic building blocks like monomers, ammonia, and hydrogen are derived from feedstock such as natural gas and petroleum. These basic building blocks are strictly sold on the basis of their chemical composition. The commodity chemical product of one supplier is readily interchangeable with that of any other. Organic intermediates represent the next step via further chemical conversion of the bulk petrochemicals. Sometimes, multiple steps are required to produce an intermediate of the desired chemical composition. All of these products in turn are used in downstream “fine chemical” derivatives. Fine chemicals are sold on the basis of their performance rather than their composition. They are produced batch-wise and not in a continuous process. Depending on the end use application, chemical compositions can vary between subgroups, and they are not considered interchangeable. Table 36.1 lists the major high-production chemicals produced in the United States under the classification of inorganic and organic compounds.

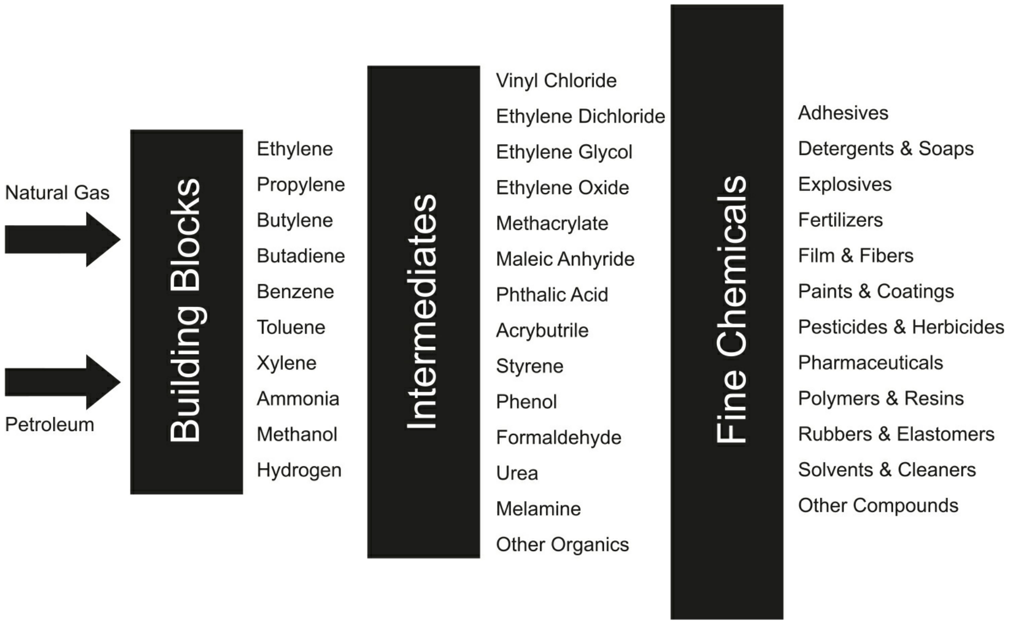


FIGURE 36.1 Chemical industry overview.

Organic		Inorganic	
Chemical	**Output**	**Chemical**	**Output**
Ethylene	24.0	Sulfuric acid	36.5
Propylene	15.3	Phosphoric acid	11.6
Urea	5.8	Chlorine	10.2
Ethylbenzene	5.3	Ammonia	9.8
Styrene	5.0	Sodium hydroxide	8.4
Ethylene oxide	3.2	Ammonium nitrate	6.4
Vinyl acetate	1.3	Nitric acid	6.3
Acrylonitrile	1.3	Hydrochloric acid	4.4

Source: Abstracted from Chemical Engineering News, July 10, 2006.

TABLE 36.1 2005 U.S. Production of Chemicals (Millions of Metric Tons)

Process Cooling Is a Major Water User

The chemical industry has the potential to use more than 324 million acre · ft (400 km^3) of water each year, with the vast majority used for cooling purposes. Water use varies widely within the industry. At the higher end, the manufacture of silicon nitride requires more than 15 000 lb (kg) of water to produce 1 lb (kg) of product. Several other products require in excess of 1000 lb (kg) of water to produce 1 lb (kg) of product. A number of the major commodity chemical products, including ammonia and ethylene, require 100 to 200 lb (kg) of water to produce 1 lb (kg) of product.

Table 36.2 shows the water usage by unit operation for several industry segments. The greatest use of water is for cooling process equipment. Many reactions generate heat, and the reaction vessel is cooled so that the temperature is controlled at the desired limit for production efficiency and product quality. Other chemical reactions require heat, and most chemical plants provide this with steam. If the steam is used only for low-temperature process heat, the plant may operate a low-pressure boiler; but if the plant requires a great deal of electric energy as well as heat, it is common to install high-pressure boilers to generate power through steam turbines, with the turbines exhausting into a process steam line, with perhaps some of the steam going directly to a turbine condenser. Chemical production is the second largest consumer of water treatment chemicals in North America. Many chemical plants are converting to cogeneration using high-pressure process steam to generate electricity for resale to the power grid.

	Water Used [lb/lb (kg/kg) of Product]				
Segment	**Cooling Water**	**Process Water**	**Steam**	**Total Water Use**	**Typical Consumptive Use**
Ethylene	198	3.6	14.5	216.1	10–30
Phosphoric acid	135	4.2	1.3	140.5	10–20
Propylene	135	2.4	0.8	138.2	9–18
Polyethylene	82	0.5	0.4	82.9	4–9
Chlorine	70	3.0	1.8	74.8	6–12
Sulfuric acid	66	0.4	0.4	66.0	3–7

Source: 2002 Process Economics Program (PEP) Yearbook International, published by SRI Consulting.

TABLE 36.2 Water Usage by Chemical Industry Segment

Cooling water is usually reclaimed by the use of cooling towers, so the requirement for makeup water is minimized. Most heat exchangers use water on the tube side. However, in some chemical processes, it is more suitable to have water on the shell side, with process fluid on the tube side. In this latter design, the cooling water is more likely to create deposit problems, due to the lower velocity.

Another large use of water is for process applications, which may include hydraulic conveying, classification, washing, and equipment cleaning. Some water may become part of the finished product. Finally, provision is made in most chemical plants for fire protection. This usually requires water applied either directly as a fog, or as a component in foam.

Chemical plant operations are classified into unit operations (such as evaporation, drying, and crystallization) and unit processes (such as monomer production, sulfuric acid production, or catalytic cracking—all involving a number of unit operations). Because each chemical manufacturing plant differs so much from its neighbors, it is simpler to assess water and steam requirements for different classifications of chemical manufacturing plants.

In most chemical operations, there are a number of processing steps involved, in preparing raw materials for the reaction that produces the finished product. The raw materials may be crushed and then conveyed by water to classification devices such as screens, which may be operated either wet or dry. Soluble raw materials may be dissolved in water, or if gases, absorbed in water to facilitate the chemical reaction. The quality of water may be important; for example, the water may contain iron, which could catalyze a reaction, discolor the finished product, or precipitate to produce a turbid product.

After preparation, the ingredients may be charged to a reactor. This may be done batch-wise or continuously, depending on the volume of throughput, the value of the products being handled, and the economics of the alternative designs. If the reaction is endothermic, the reactor is usually heated with steam. If the reaction is exothermic, the reactor is designed so that the mixture is heated to a certain temperature before the reaction initiates. Thereafter, cooling is required to maintain the desired reaction temperature. Figure 36.2 illustrates a reaction vessel designed for both heating and cooling. The polymerization of organic materials is an example of a reaction requiring initial heating, followed by cooling to maintain a specified temperature. The chemical reaction does not always take place in a sophisticated reactor; it often occurs in a simple sedimentation vessel, similar to that used for lime softening of water.

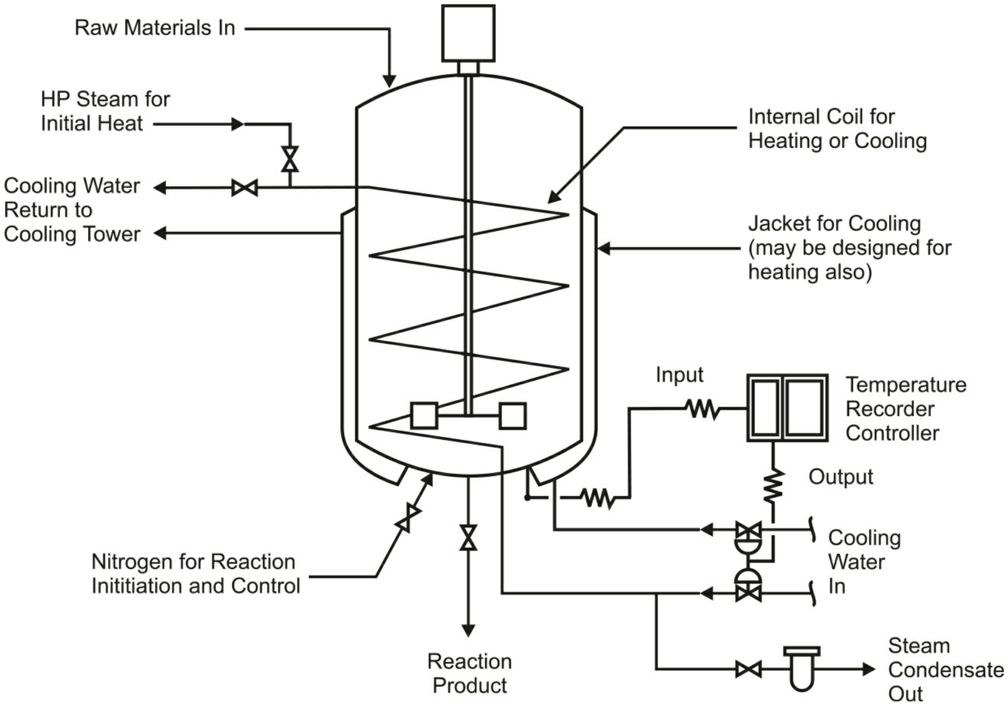


FIGURE 36.2 A reaction vessel designed for both heating and cooling of process materials.

Once the chemical reaction has taken place, additional processing is usually required to remove the unreacted raw materials or unwanted products. When these impurities are solids, typical solids/liquids separation processes are used. Depending on the nature of the solids to be removed, the choice may be sedimentation, filtration, or centrifugation. The solids removed are often washed for recovery of valuable residues (Fig. 36.3).

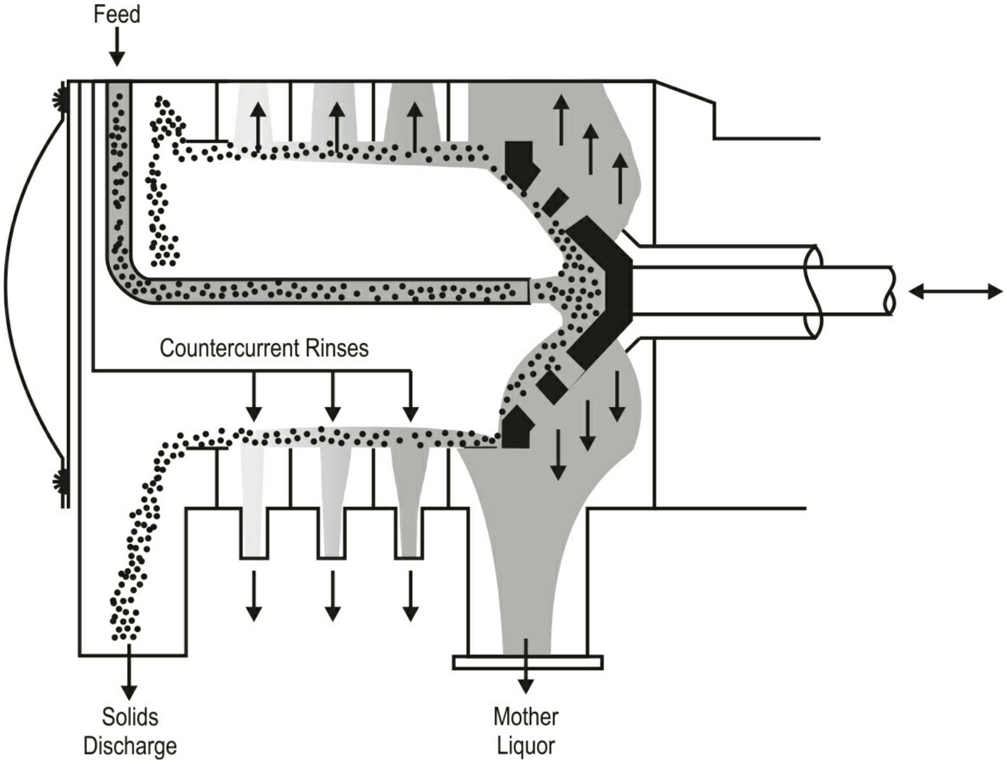


FIGURE 36.3 A pusher-type centrifuge designed for counter-current rinsing of solids for liquor recovery. (*Courtesy of Sharples-Stokes Division, Pennwalt Corporation.*)

Reactors can be mild steel, stainless steel, or glass lined. Mild steel is used for noncorrosive and low purity products, such as polyvinyl chloride (PVC). Stainless steel jacketed reactors are used in many fermentation systems. Typically stainless steel vessels are used in biopharmaceutical manufacturing.

Glass-lined reactors are used when reactants are very corrosive or high-purity products are critical, such as pharmaceuticals. Jackets may be full or segmented plates, half pipe coils, or spirals wrapped around the outside of the vessel. Jackets may have nozzles that allow to increase fluid velocity and reduce fouling while improving the temperature profile and performance. Figure 36.4 shows fluids that may be present in a jacketed vessel. Figure 36.5 shows a typical full plate jacked reactor.

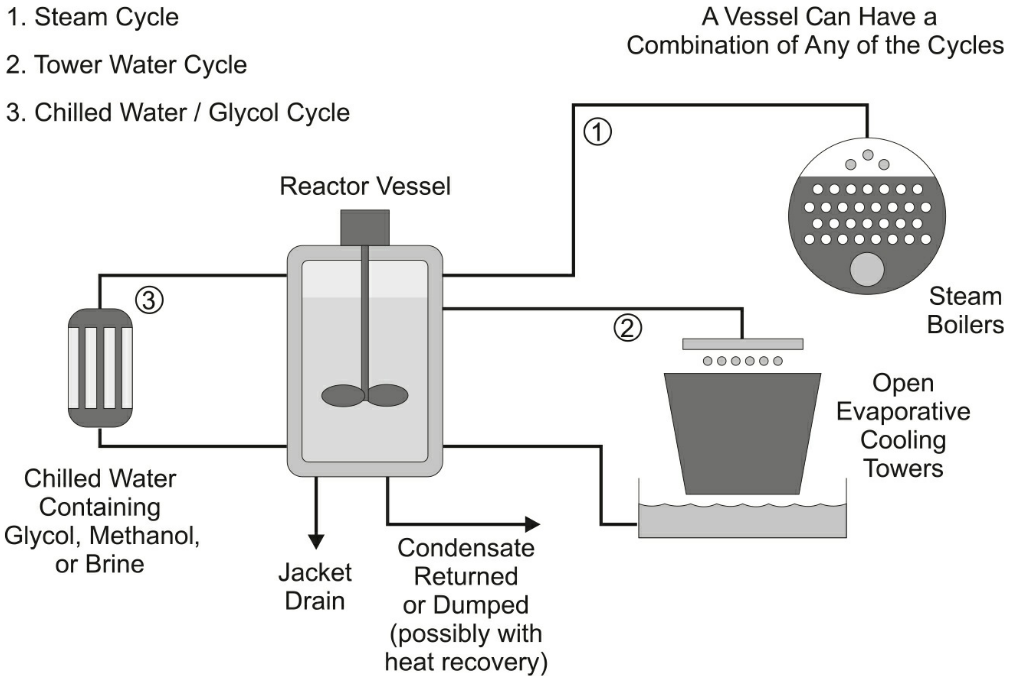


FIGURE 36.4 Possible series of fluids in a jacketed vessel.

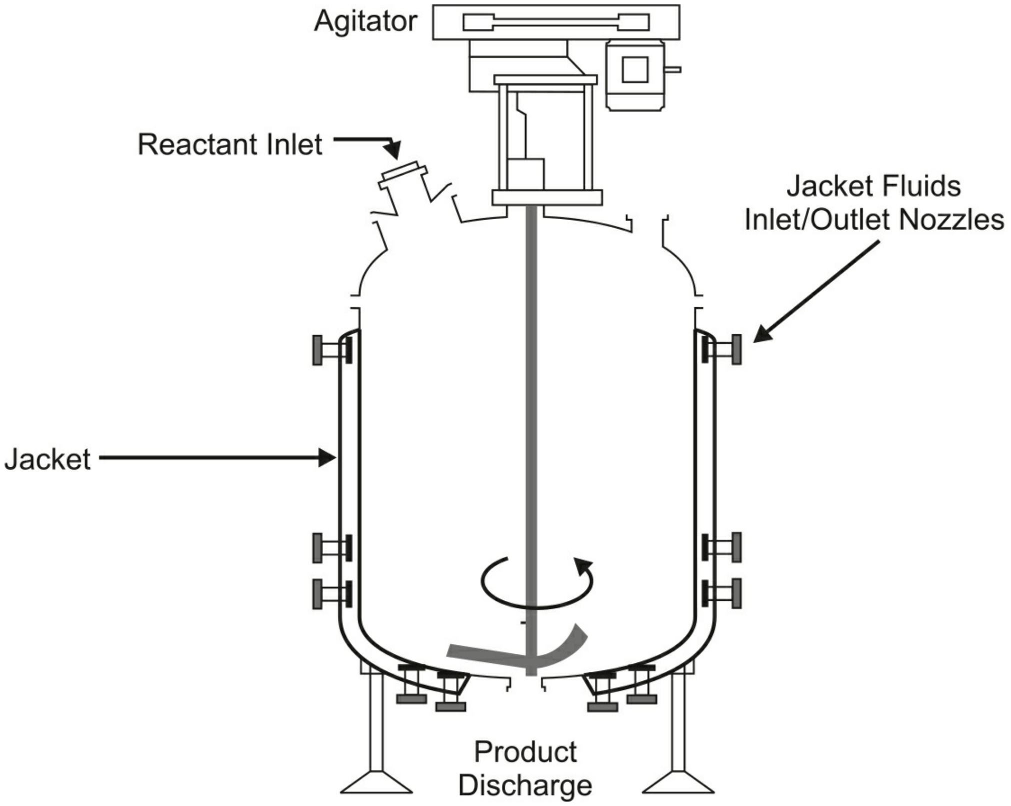


FIGURE 36.5 This is a typical jacketed reactor showing the reactant inlets, agitator, jacket product discharge, and jacket inlet and outlet nozzles for the heating and cooling fluids.

Many of the manufacturing processes using glass-lined jacketed vessels require heat to initiate the reaction. Once the reaction starts, it is exothermic, meaning the reaction generates excess heat, which must be removed to obtain the desired product quality and yield. The most aggressive corrosion and scaling conditions occur within the jackets when steam and cooling waters mix. Steam creates very high temperature, which leads to scaling when cooling water is added. The high temperature also increases the corrosion potential. Mixing steam and cooling water dilutes the corrosion and scale inhibitors in the cooling water, increasing the potential for corrosion and scale within the jacket. Water losses from the cooling tower and chilled water systems complicate effective treatment. The treatment programs for the two cooling water systems must be compatible.

Typically, the steam cycle is first to heat the reactants and start the chemical reaction. The steam condensate might be recovered for boiler feedwater or discharged if not suitable to return to the boiler. If recovered, the steam condensate may be contaminated with cooling water containing hardness, which would cause scale in the boilers.

Cooling water might be used subsequent to the steam cycle in order to remove some of the heat of reaction and provide the desired temperature for optimum product quality and yield. Significant corrosion and scaling can occur as cooling water is added to the hot jacket containing steam condensate.

Chilled water or brine (glycol, alcohol, or salt) might be used as the next step if the reaction generates too much heat for the cooling water to maintain the desired reaction temperature. This step can result in mixing cooling water with chilled water or brine, having the undesirable effect of contaminating both systems. Figure 36.6 shows a typical jacketed reactor with both chilled water (CWR) and cooling tower (TWR) waters present.

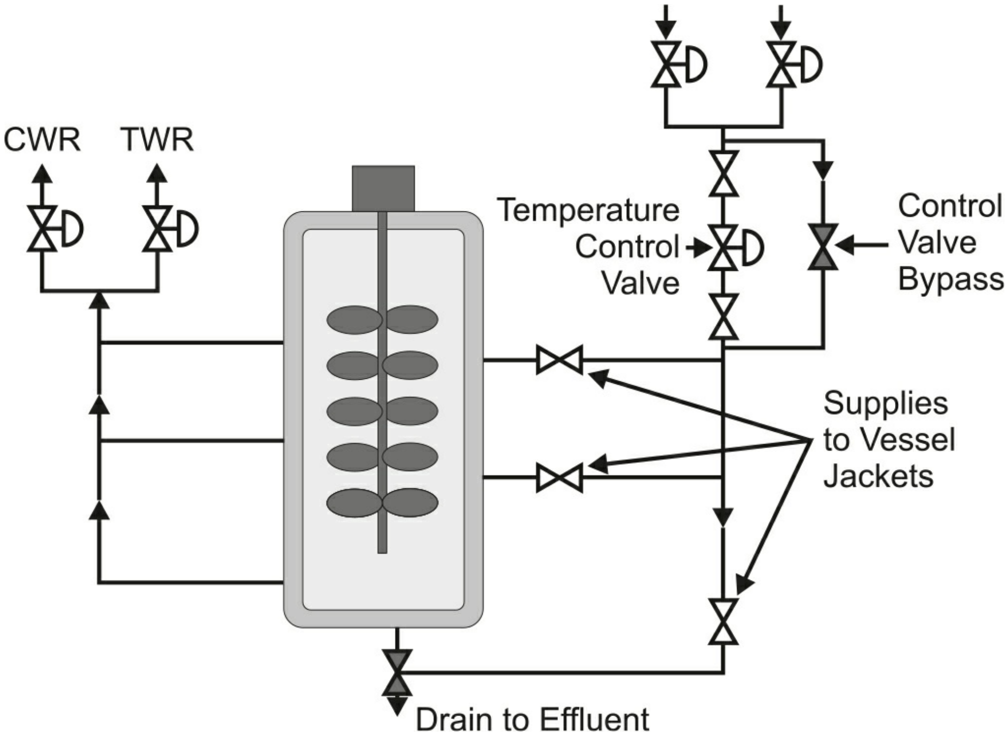


FIGURE 36.6 This schematic shows a typical glass-lined jacketed vessel with two different fluids used in the jacket—cooling tower water (TWR) and chilled water (CWR).

Ideally, for good corrosion, scale, and biological control, the two waters should not mix, but this schematic shows that the two waters can mix.

Rather than mixing fluids within the jacket, some systems maintain a single fluid within the jacket, typically a synthetic heat transfer fluid like, Dowtherm, Syltherm, Therminol, closed loop water, or the like, and use heat exchangers to control the fluid temperature (Fig. 36.7). This arrangement prevents fluid mixing and subsequent severe corrosion and scaling issues in the jacket. Depending on the heat transfer fluid used, treatment, monitoring, and control might still be needed. The major disadvantage of this approach is the high capital cost for the extra heat exchangers and possibly additional pumps. Designing and installing these types of systems initially are gaining favor in new systems, but very few retrofits to an existing system are undertaken.

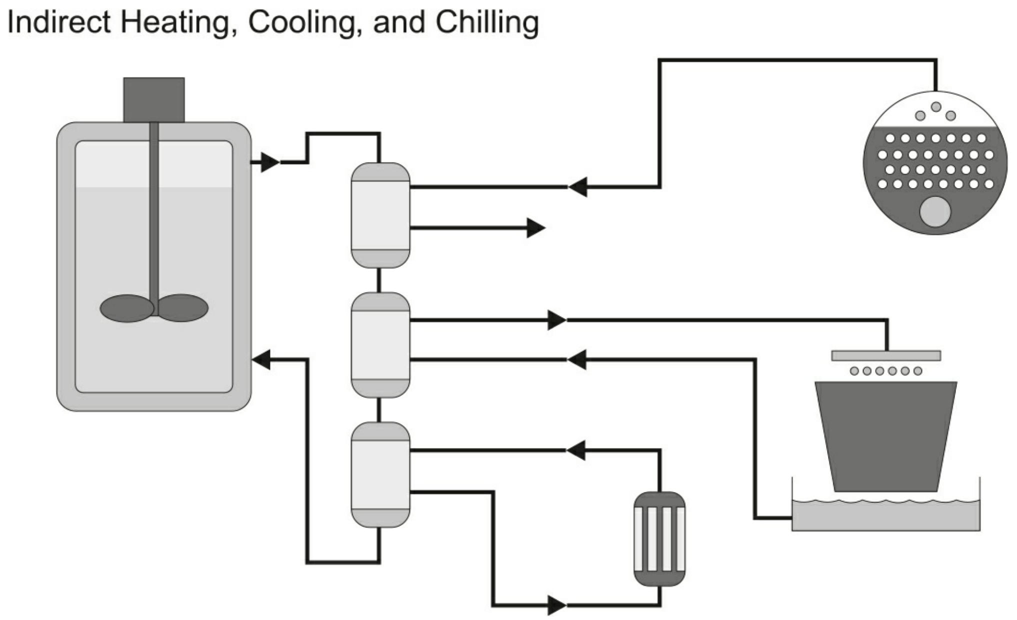


FIGURE 36.7 Indirect heating/cooling.

Contamination of the steam condensate with cooling water can force the disposal of valuable condensate or risk scale and corrosion problems in the boilers. Installing a heat exchanger can allow recovery of most of the heat from the steam condensate, but the water value, including the effect on the boiler cycles of concentration, is still lost.

Steam condensate, chilled water, and brine entering the cooling water periodically from batch reactor operations creates a difficult situation for maintaining good corrosion and scale control in the cooling water system. Any single condition can be handled, but variable conditions require automated feed and control systems to keep up with the constant changes.

Organic contamination, such as amines from steam and glycol or alcohol from brines, creates increased biological activity in the cooling water system, requiring an aggressive approach to biological control programs and adaptable feed systems.

Even with nozzles, as seen in Fig. 36.5, fluid flow within jackets is inherently low, increasing the potential for fouling and poor corrosion control.

Care must be taken when treating fluids, such as steam and cooling water, going to jackets. If treatment programs are not chosen and controlled correctly for all of the streams entering a jacket, a number of problems can develop, such as:

- Incompatible treatment products can react, deactivating both products. For example, neutralizing amines in the steam can react with halogen-based biocides in the cooling water.
- Direct injection of steam into cooling water dilutes the corrosion and scale inhibitors in the cooling water, reducing the treatment protection.
- Heating cooling water with steam, either directly by injection or indirectly with heat exchangers, raises the cooling water temperature beyond normal conditions, increasing the corrosion and scale potentials.

To provide good overall control, monitoring must be conducted on the outlet streams from the reactor jackets, not the bulk water systems. The goals in jacket water treatment should include:

- Start with clean reactor jackets. Clean metal surfaces are easier to control than dirty ones.
- Pretreating the clean jackets to minimize flash rust.
- Evaluating all fluid streams entering the jacket, including dilution effects and chemical interactions.
- Additionally, one water treatment supplier should treat all fluid streams entering the jackets so that all mechanical, operational, and chemical effects can be adequately evaluated and addressed.

If the impurities are not solids, then the final separation may require solvent extraction. This extraction may be accomplished with water if the process fluid is a hydrocarbon. Alternatively, the separation may be achieved by an operation involving a phase change such as evaporation, distillation, crystallization, or drying. In all of these operations, energy is applied to produce the separation, and cooling water may be used on the condensers or reflux heat exchangers (Fig. 36.8).

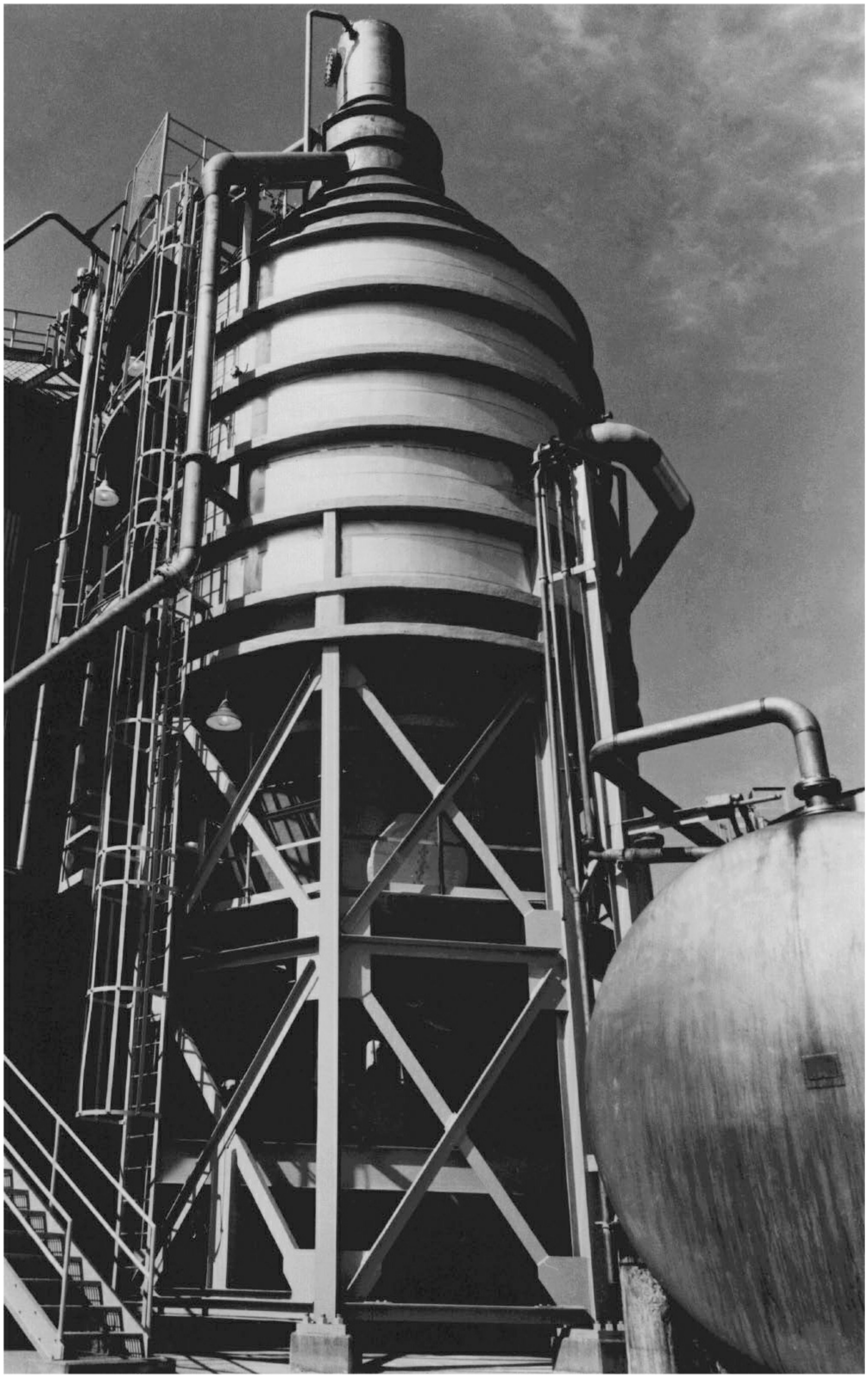


FIGURE 36.8 A large crystallizer producing ammonium sulfate. (*Courtesy of Whiting Corporation*.)

Process Flow Sheets

Many of the heavy chemicals listed in Tables 36.1 and 36.2 are used in water treatment processes. They are used in various pretreatment processes (softening, dealkalization, coagulation, disinfection, etc.), and their costs are minimal. Their use in pretreatment allows specialty water conditioning chemicals needed for cooling systems, steam generators, and other special applications, to perform at a reasonable maintenance cost. Without these less expensive pretreatment chemicals, the increased use of the more expensive specialty chemicals would not be cost-effective. The following brief look at the processes used for the manufacture of some of these chemicals, introduces the chemical industry to those not familiar with it.

Some of the processes in the chemical industry seem more mechanical in nature than chemical. For example, nitrogen and oxygen are produced from air by a combination of compression, distillation, and refrigeration. Solutions such as brine or even water are evaporated, sometimes in solar evaporation ponds, to produce salt.

Other simple processes used in heavy chemical manufacture depend on a phase change. Native sulfur is melted underground by hot water and brought to the surface in molten form. Salt and sodium carbonate are dissolved and brought from underground strata to the surface in solution form.

Simple processes that rely on combustion include:

Sulfuric acid—Sulfur is burned over a catalyst to produce sulfur trioxide (SO_3), and this is dissolved in sulfuric acid (H_2SO_4) and concentrated to market strength by recycle.

Lime—Limestone is heated in a kiln, producing quicklime (CaO), which is converted to hydrated lime [$Ca(OH)_2$] by slaking with water. By-product carbon dioxide (CO_2) may be recovered from the kiln gases.

Phosphoric acid—In one process, phosphorus is burned to phosphorus pentoxide (P_2O_5) and dissolved in water. Sodium orthophosphates are produced by neutralizing this acid with sodium hydroxide (NaOH).

The major water treatment chemicals manufactured electrically, sodium hydroxide and chlorine, are made by electrolysis of sodium chloride (NaCl) brine, producing sodium at the cathode and chlorine at the anode. The sodium is then reacted with water to yield sodium hydroxide. Since they are coproducts, the price of one is affected by the market and price of the other.

Chlorine and sodium hydroxide are used in many products and processes such as PVC, pharmaceuticals, nylon, paint, herbicides, adhesives, and catalysts. Most of the chlorine produced is used for manufacturing vinyl chloride monomer (VCM). Chlor-alkali plants are typically positioned close to VCM manufacturers and other chlorine derivatives.

Some heavy water treatment chemicals are byproducts or waste products. Ferric chloride, a coagulant, is a byproduct of the manufacture of titanium dioxide (TiO_2) and a waste product from hydrochloric acid (HCl) pickling of steel plate in a steel mill; hydrated lime is available in some areas as a byproduct of acetylene manufacture; hydrochloric acid is often a byproduct of the chlorination of organic compounds.

Alum (hydrated aluminum sulfate) is one of the water treatment chemicals produced in a multistage operation. The process flow sheet is shown in Fig. 36.9. In the preparation of raw materials, the bauxite is crushed and ground in the dry form and fed into the first reaction vessel, where it meets concentrated sulfuric acid and is diluted with washings from later operations. The mixture is heated with steam so that the reaction can take place rapidly; iron is removed as an impurity; and the liquor is fed to a clarifier, where a flocculant is added. The underflow solids are pumped to a two-stage washing system, where the alum liquor is recovered by having these solids washed with the condensate. The overflow is further concentrated in an open evaporator, and the concentrate is then discharged onto a cooling floor, where crystallization occurs. As seen in this flow sheet, the reaction takes place in relatively simple and compact vessels, and the balance of the equipment is for preparing the raw materials and finishing the product to meet the required specifications. Steam is required for the operation, and the condensate produced is used as the wash water in processing the waste solids.

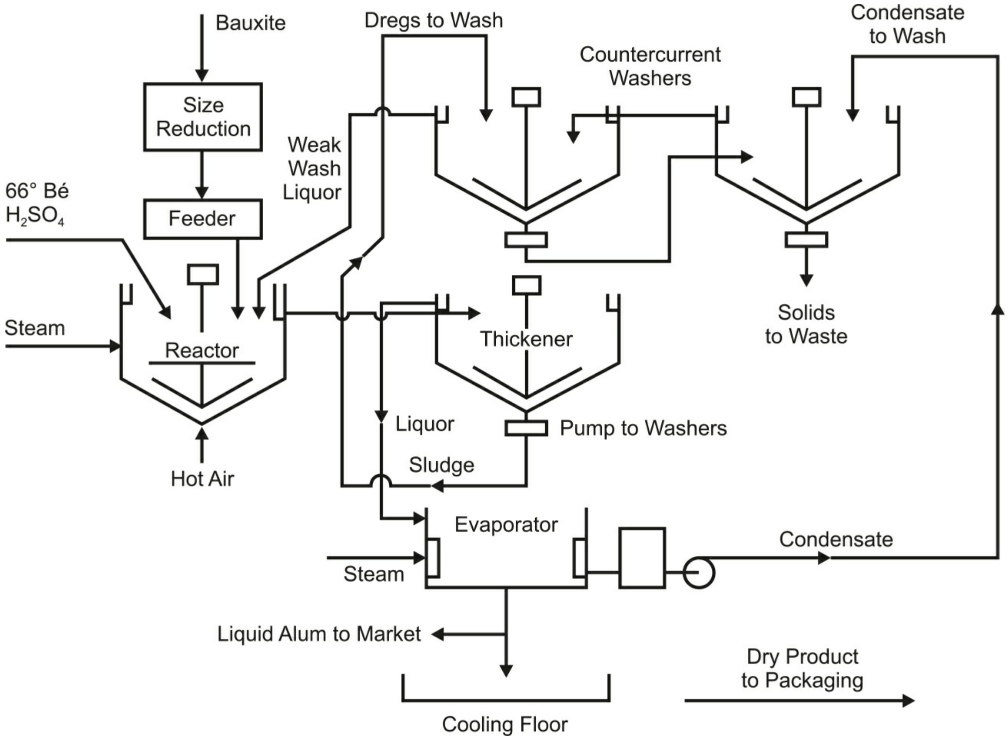


FIGURE 36.9 Simplified flow sheet of alum manufacture using several unit processes.

Beyond the confines of water treatment chemicals, a good example of the complexity of the petrochemical industry is the manufacture of synthetic rubber, illustrated in Fig. 36.10. The raw materials are intermediates or specialty chemicals; the equipment for carrying out the reaction is quite complex; and the final processing steps are equally complicated. There is extensive use of steam and water throughout the process.

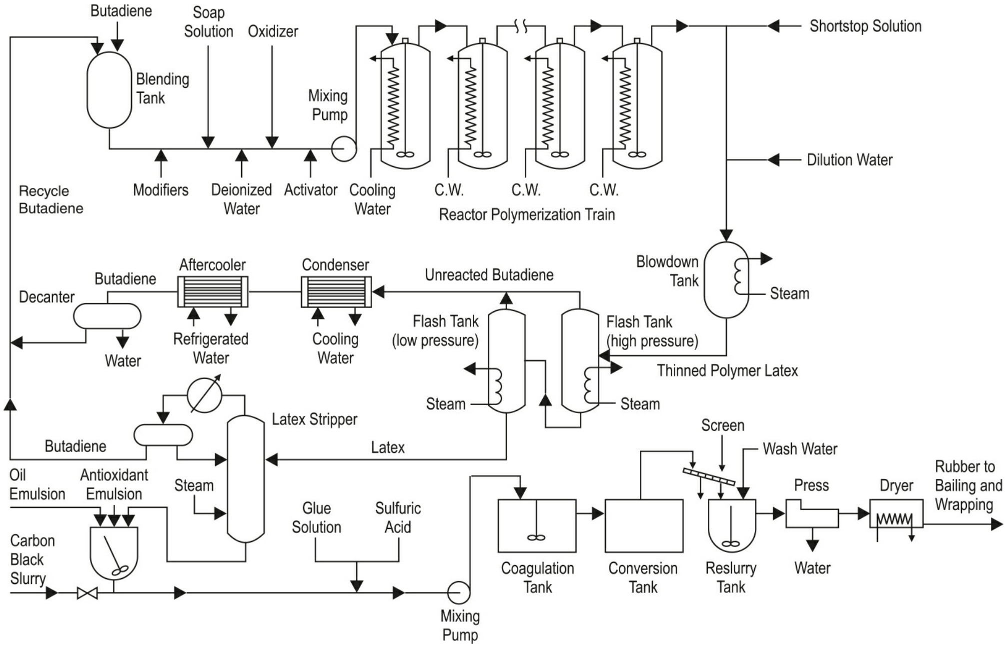


FIGURE 36.10 In petrochemical processes, a large variety of sophisticated units may be required, as in the manufacture of synthetic rubber. (*From Chemical Engineering, February 22, 1960, pages 121–126*.)

Ammonia and Fertilizers

Several factors have influenced the growth in demand for nitrogen-based fertilizer products. Population growth and global dietary changes, combined with a corresponding decrease in arable land (Fig. 36.11), require increasing yields from available agriculture through the use of fertilizers. Additional factors affecting demand for nitrogen products include mandated use of urea solution to reduce nitrous oxide emissions from diesel engines, and anticipated expansion of ethanol from corn.

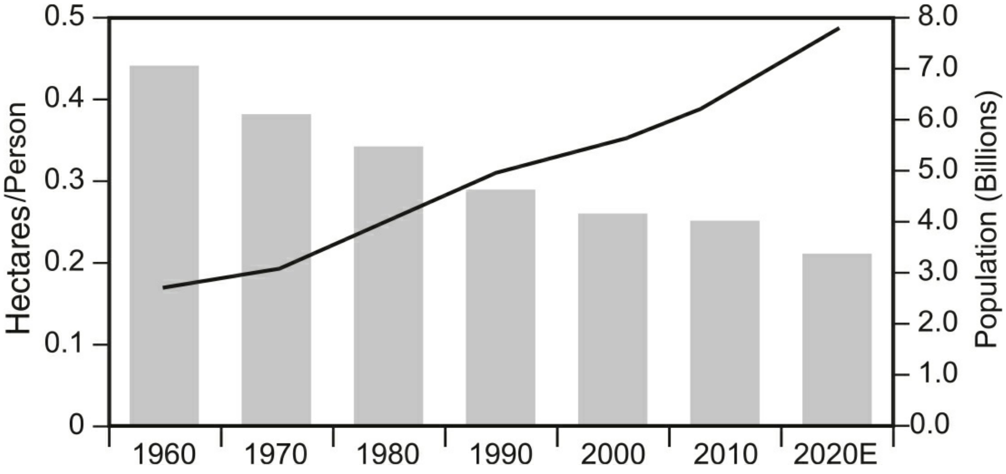


FIGURE 36.11 Arable land versus population. (*Compiled utilizing information from Potash Corporation, http://www.potashcorp.com/.*)

Nearly, all ammonia currently is produced by the Haber–Bosch steam reforming process. In areas where methane (natural gas) is available, hydrogen is separated out from the gas feedstock with steam in the presence of a catalyst. If natural gas is not an available feedstock, hydrogen is usually supplied by gasification of coal or coke. Nitrogen is drawn from the atmosphere via air compressor prior to adsorption in the presence of a catalyst. The process is outlined in Fig. 36.12.

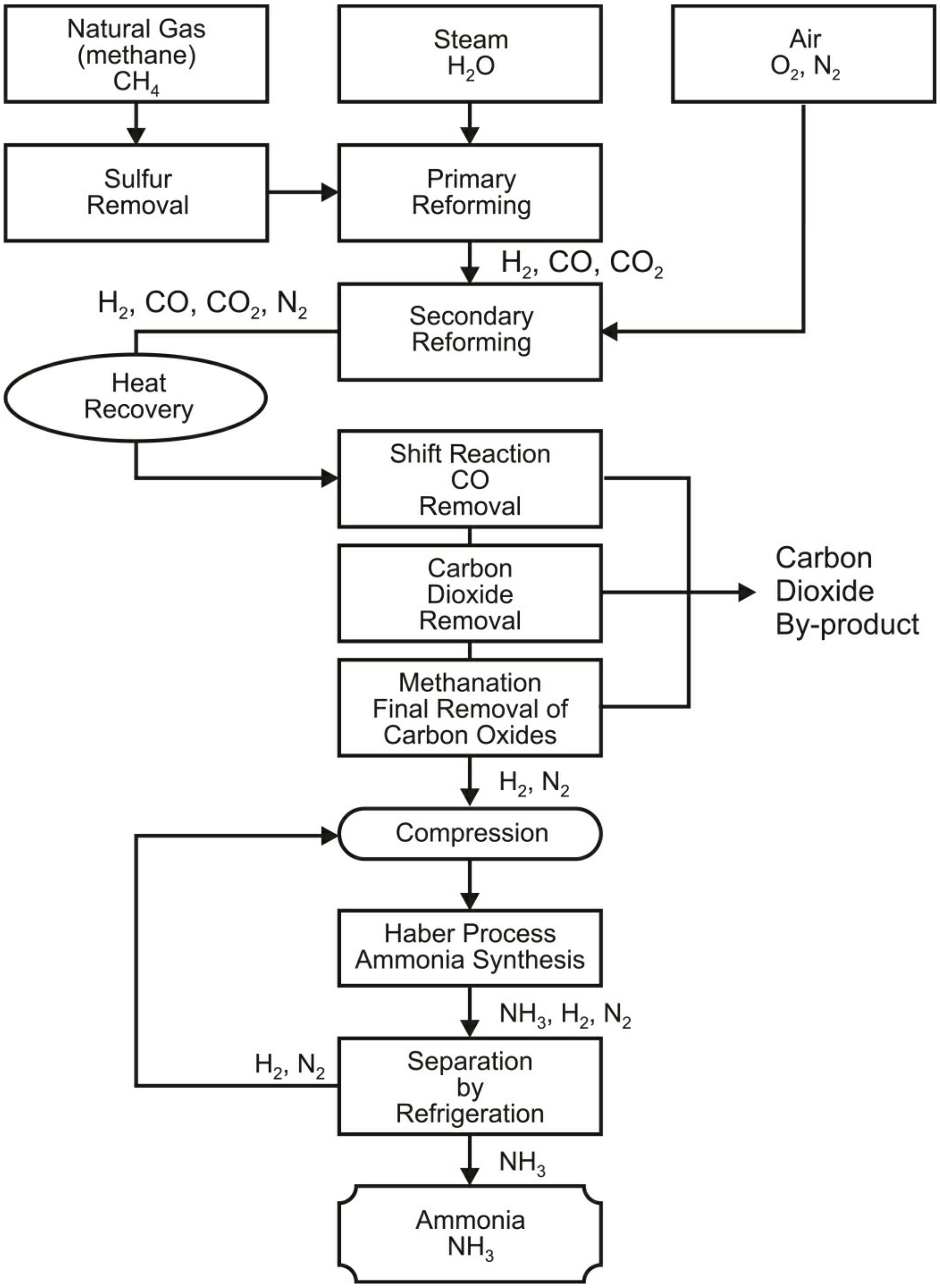


FIGURE 36.12 Haber–Bosch steam reforming process for producing ammonia.

Ammonia is the basic building block for a number of derivatives, such as urea, ammonium nitrate, nitric acid, and urea ammonium nitrate (UAN).

Efficient use of water for steam generation and process cooling is essential to the production of ammonia and upgraded products. Most plants produce high pressure steam requiring excellent purity of makeup water and reused condensate. In addition, proper treatment of cooling water is in order to maximize heat transfer in critical heat exchangers and surface condensers. Insufficient attention to water treatment may adversely affect overall plant efficiency due to inadequate process cooling, or negative effects on plant equipment such as gas compressors and the like. Fouling or scaling of heat exchangers may negatively impact plant production rates, shortening the time between major maintenance outages.

Environmental Effects

The problem of water pollution control is particularly complicated in the chemical industry. The flow charts have shown how widely water and steam are used in numerous operations, and each point of use represents a possibility for contamination with the raw material, intermediate, or finished product.

It is usually less expensive to design the process to prevent contamination and to install equipment to recycle and recover chemicals, than it is to remove or neutralize the contamination after the fact in a waste treatment plant. For example, if the waste solids produced in the alum process (Fig. 36.9) still contain too much liquor to be acceptable in a landfill, a third washing stage may be added. In the removal of unreacted raw materials from a finished liquid organic compound, the installation of additional trays in the distillation column to recover the unreacted material may be much more practical than permitting the material to be discharged as a vapor or condensed in a barometric condenser, either of which represents a pollution problem.

Generally, if a chemical plant is producing inorganic chemicals, precipitation and separation equipment are usually used for the waste treatment operation. If handling organic chemicals, removal of organics by adsorption on activated carbon or by digestion in an activated sludge system is usually required. The organic residues present a difficult problem in that many of them are not easily digested by bacteria, and sometimes a combination of bacterial digestion plus activated carbon adsorption is required.

Table 36.3 lists a few organic compounds found in wastes from chemical plants. For the organic acids and alcohols shown on this list, the biochemical oxygen demand (BOD) is usually over 50% of the chemical oxygen demand (COD) or the theoretical oxygen demand (TOD), and such wastes are amenable to biological digestion in an activated sludge system. Benzene and its close relatives are usually impervious to biological attack, and must be removed by stripping, adsorption, or both. Therefore, in many organic chemical plants, if a wide variety of compounds across the spectrum of active groups is present, the waste may require both biological and activated carbon treatments.

Chemical	BOD*	COD†	TOD‡
Acids			
Acetic	0.34–0.88	1.01	1.07
Benzoic	1.37	1.95	1.97
Formic	0.15–0.27	–	0.35
Maleic	0.38	0.83	0.83
Alcohols			
n-Amyl alcohol	1.6	–	2.72
n-Butyl alcohol	1.5–2.0	1.9	2.59
Ethyl alcohol	1.0–1.5	2.0	2.1
Methyl alcohol	0.6–1.1	1.5	1.6
Phenol	1.6	–	2.4
Isopropyl alcohol	1.45	1.61	2.4
Aldehydes			
Formaldehyde	0.6–1.07	1.06	1.07
Furfural	0.77	–	1.66
Ketones			
Acetone	0.5–1.0	1.12	2.2
Ether			
Ethyl ether	0.03	–	2.59
Cyclic Compounds			
Aniline	1.5	–	3.09
Benzene	0	0.25	3.07
Monochlorobenzene	0.03	0.41	2.06
Toluene	0	0.7	3.13
Xylene	0	–	3.16

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*Biochemical oxygen demand
†Chemical oxygen demand
‡Theoretical oxygen demand

TABLE 36.3 Waste Profiles of Selected Organics in Water (g O_2/g chemical)

In any case, the pollution control engineer must be aware of all raw materials, intermediates, and finished products produced, recognizing that they may be found in the effluent. He should be familiar with the toxicological properties and tolerance levels of each, and their potential effect on the receiving stream, the waste treatment plant, the land surface, and subsurface aquifers. Pollution control in the chemical industry is unique in that the industry is responsible not only for its own wastes, but also for the ultimate fate in the environment of products it sells to others. One of the most difficult problems is monitoring the end use of containers in which products are supplied to customers.

CHAPTER 37

The Aluminum Industry

Aluminum is the most common metallic element in the earth's crust, comprising about 7.3% expressed in the elemental form (Al) or about 15% in the commonly occurring oxide form (Al_2O_3). Unlike iron, the next most common element, aluminum was unknown to the ancients, and it was only a century ago that the metal became available in commercial quantity.

As indicated by its position in the electromotive series, aluminum is a reactive metal. Because of this, reduction in aluminum oxide by carbon in a furnace, a process that easily produces iron from its ore, is unsuccessful because the aluminum metal produced is vaporized and quickly returns to the oxide form, when the reaction is reversed on cooling. Success in producing aluminum from the oxide was finally achieved in 1889 by the discovery of a unique electrochemical process. Hall in the United States and Heroult in France discovered the process simultaneously.

Aluminum manufacture has four distinct phases of production from raw ore to finished products: mining, bauxite refining, reduction, and fabrication. Another category is secondary production by independent scrap reclamation plants, but this is similar to recovery operations in the remelt section of the fabrication plant.

Mining

Bauxite is the ore used in the production of aluminum. It is a mixture of aluminum oxide trihydrate and monohydrate, with iron oxides, aluminum silicates, and titanium oxide impurities. The ore usually contains 5 to 25% moisture, which is removed from imported ores to reduce shipping weight and improve handling. In the United States, most ore is imported, but some Arkansas bauxite is processed. Lower grade aluminum minerals, such as kaolin and refuse from coal preparation, are being investigated in a variety of research programs attempting to extract alumina from such alternate sources.

Open pit mining accounts for almost all bauxite production. The overburden is stripped and the ore recovered by draglines and shovels. The ore is then sized and sent to the bauxite plant, where it is stored for blending and later use.

Bauxite Processing

To utilize the aluminum, the alumina in ores must be extracted and purified. This is done in alumina refineries, which produce a finished product of calcined alumina (Al_2O_3) necessary for the electrolytic reduction process, which is used to produce primary aluminum metal.

Of the nine basic alumina refineries operating in the United States, two are in Arkansas utilizing domestic bauxite. The others use ores imported from Australia, Jamaica, Africa, and other areas.

In an operation called the Bayer process, raw bauxite is digested by caustic solutions at temperatures as high as 475°F (246°C) and at pressures up to 500 psig (3.4 MPag), to yield a slurry containing sodium aluminate ($NaAlO_2$) and suspended waste solids called red mud. A process flow sheet is shown in Fig. 37.1. To allow efficient recovery and reduction in waste, the red mud is settled or filtered from the dissolved liquor, using natural and synthetic flocculants to produce a clear sodium aluminate solution.

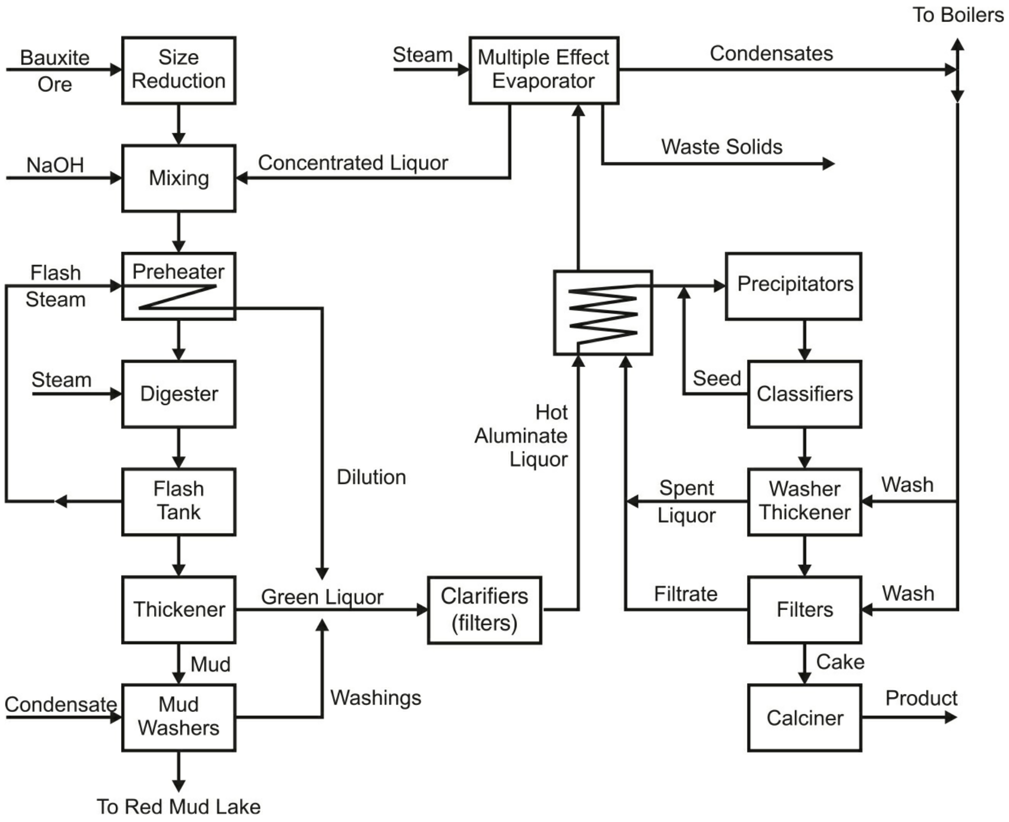


FIGURE 37.1 Simplified flow sheet of Bayer process for refining bauxite ore.

The red mud from the first separation step is reslurried with weak liquor in a washing operation to extract more of the aluminum and alkali. The most common practice uses a continuous counter-current decantation arrangement with as many as seven washing stages to recover almost all significant alumina and alkali. The red mud waste is finally discharged to a large mud lake (tailings pond).

After filtration, the pregnant liquor, rich in sodium aluminate, is cooled through heat exchangers to about 120 to 140°F (49–60°C) before entry into precipitation tanks. Here, seed crystals of previously precipitated alumina trihydrate are added and the tanks agitated for a day or two. This hydrolyzes the aluminate to yield aluminum trihydrate [aluminum hydroxide or $Al(OH)_3$], which grows on the seed material. This process is allowed to continue until about half of the alumina is converted. Further precipitation may result in excessive dropout of impurities, such as silica. The aluminum trihydrate slurry is then sent to classification and thickening tanks to separate the trihydrate from the spent liquor. The trihydrate is filtered and calcined to produce anhydrous alumina. Following the removal of the trihydrate crystals, spent liquor is concentrated by evaporators and returned to the beginning of the circuit.

Many Uses for Water

Water enters the process stream primarily as steam or condensate. A small amount of water may be introduced as purified makeup to prepare process reagents, such as flocculants or cleaning solutions. Storm water and waste surface water may enter the process as return water from the mud lake. Noncontact cooling water is used for equipment cooling and finished alumina product cooling. This water may be from an outside source or from the mud lake reservoir (Fig. 37.2).

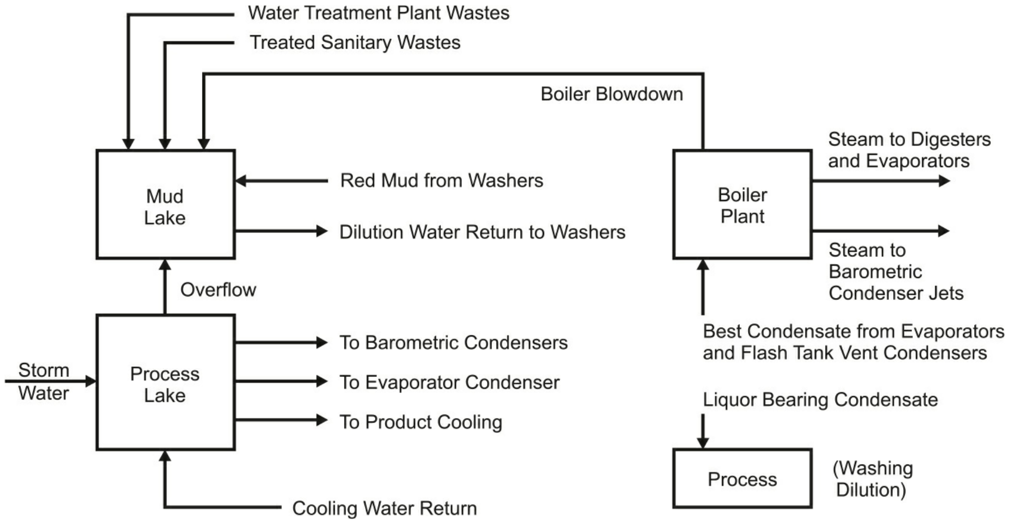


FIGURE 37.2 Water and steam uses in Bayer process.

Once in the process stream, water is used repeatedly as a solvent, to transport heat or slurry, wash away impurities, create vacuum, generate electricity, and prepare chemical makeup solutions.

A major input of steam comes from the digestion tanks, where the alumina is dissolved from the ore. As pressure is relieved in flash tanks, the lower pressure steam is liberated with its heating potential. This is used to heat the spent liquor before it joins the fresh bauxite in the digester, thereby recycling heat in a closed loop. Other uses for the steam from the digester flash tanks are in the evaporators concentrating the spent liquor.

Wash water streams vary in composition, depending on the product purity required. Condensate is used to wash the precipitate on the trihydrate filters to remove residual impurities. This wash water or other condensate may be used to wash the thickened trihydrate before going to filtration dewatering. Excess condensate beyond that required in steam generation may be used in final red mud washing along with mud lake return water.

Mud lake return water consists of overflow from gravity thickening as well as storm water inflows. The amount varies depending on local conditions. The water contains a low concentration of alumina and caustic from mud leaching. This proceeds to the last mud thickener, where it washes mud underflow from the previous thickener. Increased in alumina and caustic content, it joins mud from the second previous washing, and so on through the circuit. As it progresses up through the wash train, alumina and caustic values increase correspondingly. Finally, it joins the partially cooled digester discharge, where the final increase in alumina content is achieved. This counter-current decantation process is designed to provide economical recovery of as much alumina and alkali as possible.

In addition to its use as an effective solvent, water serves to transfer solids from unit to unit within the process. This includes not only bauxite slurry, but trihydrate and red mud as well. It also provides a medium for wet grinding of the bauxite ore to the proper particle size for digestion. The use of water as a means of contact cooling of the overhead vapors and barometric condensers allows both the extraction of needed condensate water and the concentration of process streams. Water use in these barometric condensers may reach 5000 to 10 000 gal/ton (21–42 m^3/tonne) of product.

Because of process economics, the bulk of the unit process contact effluent streams, becomes intermediate feed streams to the other units as described. Noncontact streams represent a loss of heat rather than chemicals, and heat is recovered wherever practical. Even though no significant discharges are planned, water may be lost from any of the following production areas:

- Drying and calcining
- Red mud (evaporation and seepage from lakes or contained as part of the in-place mud content)
- Evaporation of liquor streams
- Sand disposal
- Evaporation of wash down water streams

The complete water use scheme, including the Bayer process circuit, is shown in Fig. 37.2.

Aluminum Reduction

Alumina produced by the Bayer process previously described is dissolved in a molten bath composed chiefly of cryolite ($3NaF \cdot AlF_3$), to which is added fluorspar (CaF_2) and aluminum fluoride (AlF_3). The molten mixture is prepared in an electrolytic cell, called a pot, illustrated by Fig. 37.3. A series of carbon anodes project into the bath from above. The amorphous carbon pot lining, with metal collector bars embedded in it, serves as the cathode. The pot lining is encased in insulation and refractory brick surrounded by an outer steel shell. The exact reactions in the cell are not completely understood, but the important result is a reduction in the aluminum oxide by carbon, according to the following reactions:

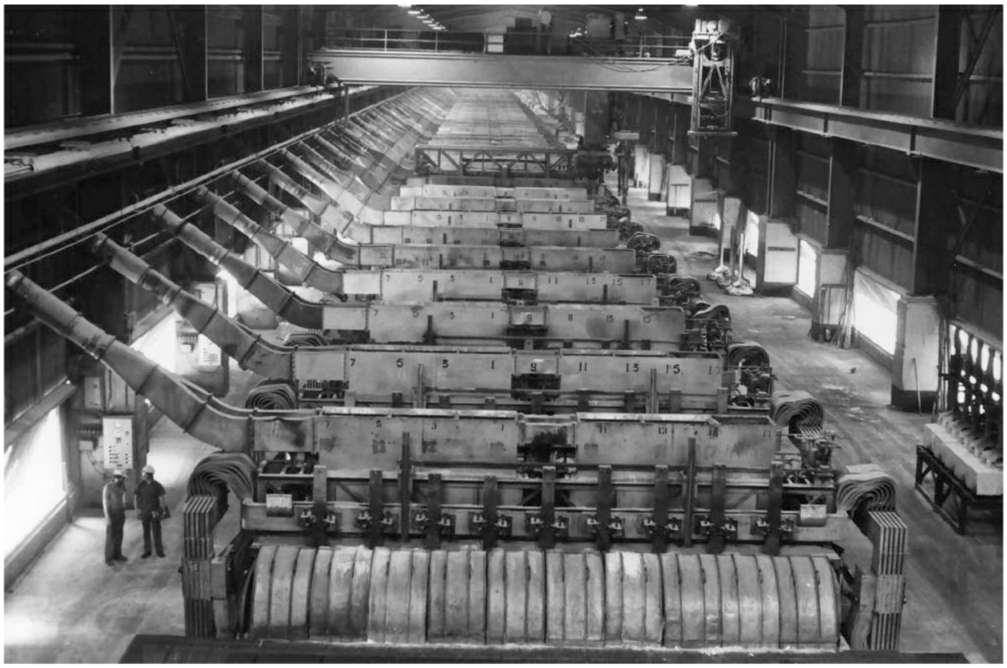


FIGURE 37.3 A pot line in an aluminum reduction plant. Fumes are withdrawn from each cell and delivered to a scrubber. Fresh anodes are in the rack at the right. The crane moves the tapping device and crucible from cell to cell. (*Courtesy of Kaiser Aluminum and Chemical Corporation*.)

$$Al_2O_3 + 3C \rightarrow 2Al + 3CO\uparrow \tag{37.1}$$

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \uparrow \tag{37.2}$$

The oxidation occurring at the anode produces a mixture of about 25% carbon monoxide (CO) and 75% carbon dioxide (CO_2), and this exiting gas mixture carries with it certain volatile fluoride compounds. Carbon is consumed at the rate of about 0.5 lb per lb of aluminum produced (0.5 kg/kg). Aluminum is produced by reduction at the cathode, and a pool of aluminum metal collects on the bottom of the cell. The passage of current through the cell generates sufficient heat to keep the bath molten and at a temperature of about 1650 to 1740°F (900–950°C).

Frequent Feeding Necessary

The heat is contained by the insulation of the pot lining material, plus a crust, which forms on the surface of the bath. Although aluminum oxide is the basic raw material, it makes up less than 8% of the bath and must be continuously added. A supply of alumina is maintained on the crust, where it heats and dehydrates. The crust is broken periodically, and some of the alumina is stirred in to replenish what has been consumed by the reduction process.

Molten aluminum is periodically withdrawn (tapped) from the pot and cast into pigs or into any of the various types of ingots. The usual power consumption for aluminum reduction is in the range of 8 to 10 kWh per pound (18–22 kWh/kg) of aluminum produced, so that a pot line of perhaps 200 to 240 cells producing about 100 000 ton/year (91 000 tonne/year) of aluminum would have a power requirement of about 200 to 250 MW. Because of this high electric power requirement, aluminum reduction plants are usually located near low-cost sources of power. Typically, these plants use hydroelectric power or have contracted with nearby utility stations for a significant block of their electric output. Because direct current is needed for electrolytic cells, a substantial investment is required for electrical facilities to convert the alternating current available from public utilities to direct current.

Due to the high consumption of carbon electrodes, each plant has its own facilities for producing these from mixtures of petroleum coke and pitch. Rather extensive facilities are required for materials handling and processing of the electrodes. A flow sheet of an aluminum reduction plant and an electrode processing plant are shown in Fig. 37.4.

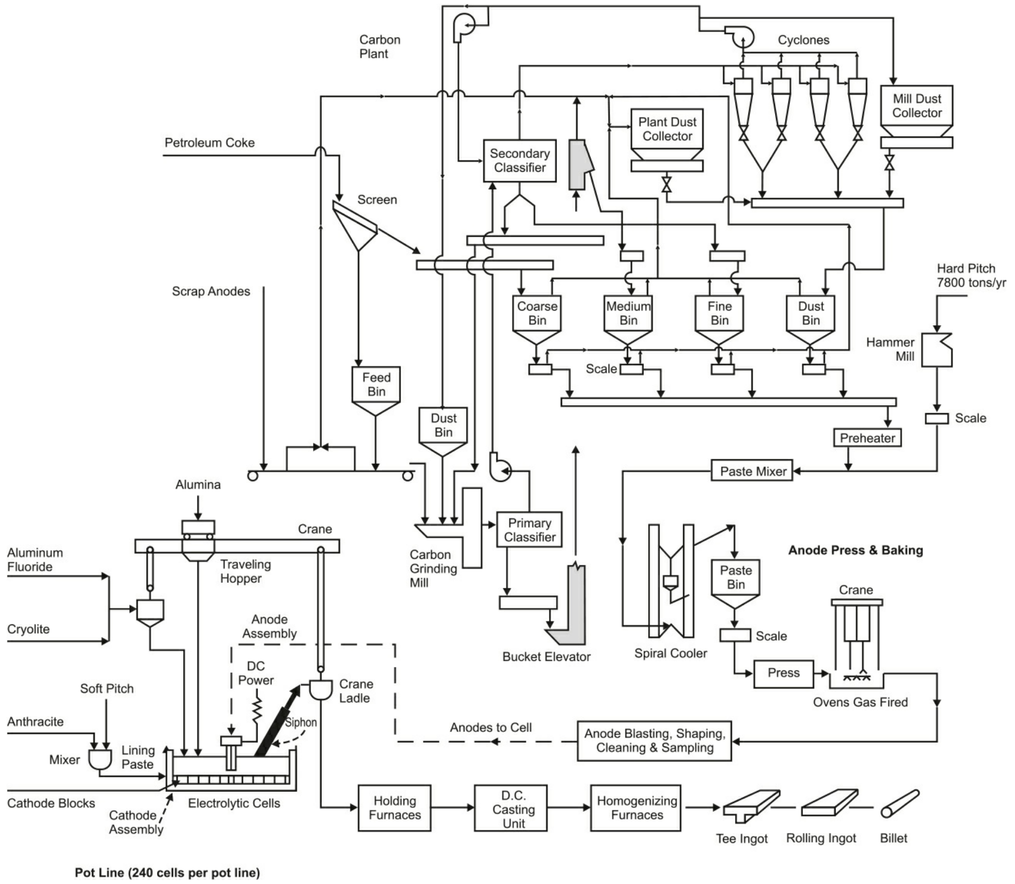


FIGURE 37.4 Flow sheet of aluminum reduction plant and electrode processing plant.

Exhaust Gases

In the reduction process, as indicated by the chemical equations shown earlier, consumption of the carbon electrodes produces a mixture of carbon monoxide and carbon dioxide. These gases leave the cell and carry with them certain volatile components from the bath, including fluoride compounds. Particulates from the surface of the pot are also entrained with the escaping gases. To control air emissions, hoods are positioned over each cell, and suction is applied to collect the gases. The gases are routed through wet scrubbers to remove both gaseous and particulate materials. Since the fluoride content of the gas stream is valuable, the scrubbing water is often fortified with reactive chemicals, such as sodium aluminate, to produce various mixtures of sodium and aluminum fluorides. These can be returned to the bath after concentration and drying.

For air emission control in the electrode processing plant, wet scrubbers are sometimes used, and the scrubber water becomes a significant part of the total waste treatment load. However, it is more common to control these emissions with dry collectors.

Following the reduction in aluminum in the pot line, the metal is cast either by a continuous casting process, such as a small ingot casting machine, or by conventional casting into cast iron sow molds on a casting floor. In continuous casting units, spray water is used for external mold cooling. In a roll caster, water is used to cool the molds internally and as a spray to cool belts. The need for water of consistent quality and temperature is much more important for semi-continuous casting operations [Direct Chill (DC) and Horizontal Direct Chill (HDC)], than for conventional small ingot and sow operations.

The semi-continuous casting operations typically produce cast metal in the shape of rectangular ingots and cylinders called billets. In this operation, water is critical because it is contacting the finished shape and is thus part of the process. To cast these shapes utilizing sophisticated aluminum casting molds requires water providing optimized heat extraction, that is, quenchability. The cooling water is normally recirculated over evaporative cooling towers to remove heat from the process and to provide consistent year-round cooling water temperature. The systems can be difficult to operate because the water often is contaminated by casting lubricants, hydraulic oil, and plant cleaning materials. These materials provide food for microbes, making it difficult to keep the cooling system free of microbial masses. Precise chemical control of these cooling systems is necessary to optimize quenchability, while meeting the stringent plant environmental permits.

After casting, ingots are cooled by air or water spray. In some cases, the system is designed to produce a very fine spray so that the water evaporates completely to dryness, and leaves no residual wastewater for subsequent treatment. If an excess of water is required, it contains suspended solids and oil, and requires treatment before disposal. Air-cooling, either alone or combined with a water spray, will undoubtedly find increasing use as a way of minimizing wastewater discharge.

There are various other cooling water applications in the reduction plant. These include water for cooling hydraulic oil, green anodes, and compressors. The plant receives electric power from a nearby utility at high voltage, which must be reduced through transformers. The alternating current, at reduced voltage, is then converted by mercury arc rectifiers to the usable direct current. With the cells of the pot line being connected in series, this may be as high as 800 V, based on a loss of about 5 V at each pot. Cooling water is required for components of the rectifier.

There is a transformer and rectifier unit for each pot line. Cooling water may also be required for the chlorine compressors, which are used to supply chlorine gas for degassing molten aluminum.

The cast metal shapes produced in the reduction process proceed to further manufacturing facilities, where they are remelted and fabricated into finished products or extruded into structural shapes.

Metal Fabrication

The primary aluminum shapes produced in the reduction plants are remelted and converted into a wide variety of forms, including sheet, plate, structural shapes, rods and other bar stock, tubes, wire, and foil at various fabricating plants. Aluminum scrap is melted in reverberatory furnaces in operations quite similar to these in the primary smelter itself, where scrap must be reclaimed from butt ends and clippings. The same semi-continuous casting operation is used. In these operations, the nature of the impurities is unknown, so fluxing agents are added to eliminate them. The contaminants are removed as dross from the surface of the molten metal after casting. Some of the billets can be extruded by heating the metal to a temperature at which it becomes plastic, but the bulk of production is done in the rolling mill. Since initial rolling is done on hot metal, the hot ingot slabs may be sent directly to the rolling mill, but it is usually passed through furnaces to make certain that the temperature is uniform throughout. Cooling water is applied at the rolls to maintain the proper temperature for rolling, and lubricating oils (called rolling oils) are often applied to the hot mill system to facilitate rolling. The rolling oils also prevent the development of surface imperfections, caused by the friction of working through the rolls. The roll cooling water is recirculate and the debris from the rolling operation settled, with facilities provided to reclaim the rolling oil wherever possible.

In addition to the cooling water used on rolls, water may be required for cooling furnace doors and for typical utilities operations, such as compressor jacket cooling and bearing cooling.

Some fabricated shapes may be finished by special chemical treatment, such as the anodizing of aluminum sheet or tube by chromic acid treatment. These finishing operations may generate wastes that require separate treatment before discharge to the final waste treatment plant.

Most reduction plants purchase power from utilities and have no need for high-pressure boilers. Power may be generated in the bauxite plants, where turbines exhaust into the steam line supplying the evaporators. However, in the reduction plants, low-pressure boilers are operated for space heating in the winter, coolant and lubricant heating, and for electrode paste heating. The water treatment systems for these operations are usually quite fundamental.

The aluminum industry is very environmentally sensitive, and there is a major effort to minimize aqueous wastes and to tightly control water usage.

CHAPTER 38

The Steel Industry

Archeologists have used the terms Stone Age, Bronze Age, and Iron Age to delineate successive stages of civilization. During the Bronze Age, humans learned to use charcoal as a reducing agent, as well as a fuel, to convert mixed ores of copper and tin into molten bronze in clay furnaces. Iron ores were not so easily reduced, and the same process that yielded molten bronze from copper and tin minerals, produced instead a spongy mass when iron ores were processed. The metal smith had to learn to beat this mass into a solid, and in the process, most of the slag fell away, but some was retained in the iron to produce what is known as wrought iron. Eventually, metal workers learned how to reheat this mass in the forge, so that it dissolved some carbon from the charcoal and was thereby converted to steel. Such secrets were carefully guarded as they provided the balance of power in warfare and commercial trade.

It was not until the late Middle Ages that relatively large-scale production of iron was achieved with the development of the blast furnace. However, iron produced by the blast furnace (pig iron) contained high carbon content; it was excellent for casting into shapes in molds, but it was not malleable. Processes were developed to convert pig iron into wrought iron or steel that is more malleable, and today, over 50% of steel produced still follows the two-step process of blast furnace followed by the converter that burns carbon out of molten iron to produce steel.

However, in developing countries that have fossil fuel reserves, direct reduction processes are being developed that turn back the clock of history and produce “sponge iron.” This product is mixed with scrap steel, and the charge is melted in electric furnaces to produce steel. In the United States, “mini-mills” have sprung up to compete with large integrated steel mills, and their major source of raw material is steel scrap. Almost one-third of the world’s steel production now comes from these electric furnaces, creating a large demand for scrap steel. This has raised the price of scrap to the point that sponge iron [direct reduced iron (DRI)] is widely used in electric arc furnace charging, with the likelihood that DRI production and processes will continue to grow.

Water usage rates in a steel plant can vary widely from 150 to 6600 gal/ton (0.63–27.5 m^3/tonne) depending on the type of steel plant, water quality, environmental restrictions, cooling system design, and numerous other factors.

A summary of water consumption rates by major process is shown in Table 38.1. With the use of best available technologies (BAT), water consumption rates can be reduced to less than 240 gal/ton (< 1 m^3/tonne) in electric arc furnace steel plants (mini-mills) and to less than 1200 gal/ton (< 5 m^3/tonne) in large integrated steel works.

	gal/ton	**m^3/tonne**
Blast furnace	350	1.5
Basic oxygen furnace (BOF)	2100	8.8
Direct reduction	290	1.2
Electric arc furnace	250	1.0
Continuous casting	1000	4.2
Hot strip mill	3100	13

TABLE 38.1 Water Usage Rates by Steelmaking Process

Blast Furnace Operations

The blast furnace is the heart of the iron-making process. Iron ore, coke, and limestone are charged by a skip car to the top of a furnace. Most furnaces range from 16 to 28 ft (4.9–8.5 m) in diameter and may be 100 ft (30 m) tall. Raw materials, fed in layers to the furnace are iron ore or pellets, coke, and limestone. In the lower portion of the furnace, hot blast air is injected through a series of circumferential openings called tuyères, at about 30 to 90 psig (207–621 kPag) and 1800 to 2000°F (982–1093°C). Air flows upward through the burden of raw materials in the furnace, and gas exits the furnace top at 5 to 30 psig (34–207 kPag).

Coke (carbon) reacts with magnetite (Fe_3O_4) and hematite (Fe_2O_3) in the furnace, releasing iron (Fe^0) and producing carbon monoxide (CO) and carbon dioxide (CO_2) gas. Iron sinks to the furnace hearth, where the original impurities in the charge combine with the lime, forming slag, which floats to the top of the iron. Gas leaving the top of the furnace carries fine dust, which is separated and recovered in collection equipment. The combustible exhaust is used in reheating stoves and in generating steam at boiler houses. Iron and slag are periodically tapped and collected in special railcars every 2 to 6 hours, depending on furnace conditions.

To keep this large furnace working efficiently, much of the equipment connected with the furnace uses cooling water at various points. Figure 38.1 illustrates the overall dimensions and general cooling water utilization for a typical blast furnace. This generalized drawing shows that the blast furnace may be constructed in two ways. In older furnaces, water sprays provide cooling water on the outer shell of the furnace, as illustrated on the left side; in more modern furnaces, as illustrated on the right side, the furnace contains copper plates, which have hollow passages for cooling water built into the furnace wall. The primary task of the cooling water in the stack and bosh is to prolong the life of refractory inside the furnace and extend overall campaign life of the blast furnace.

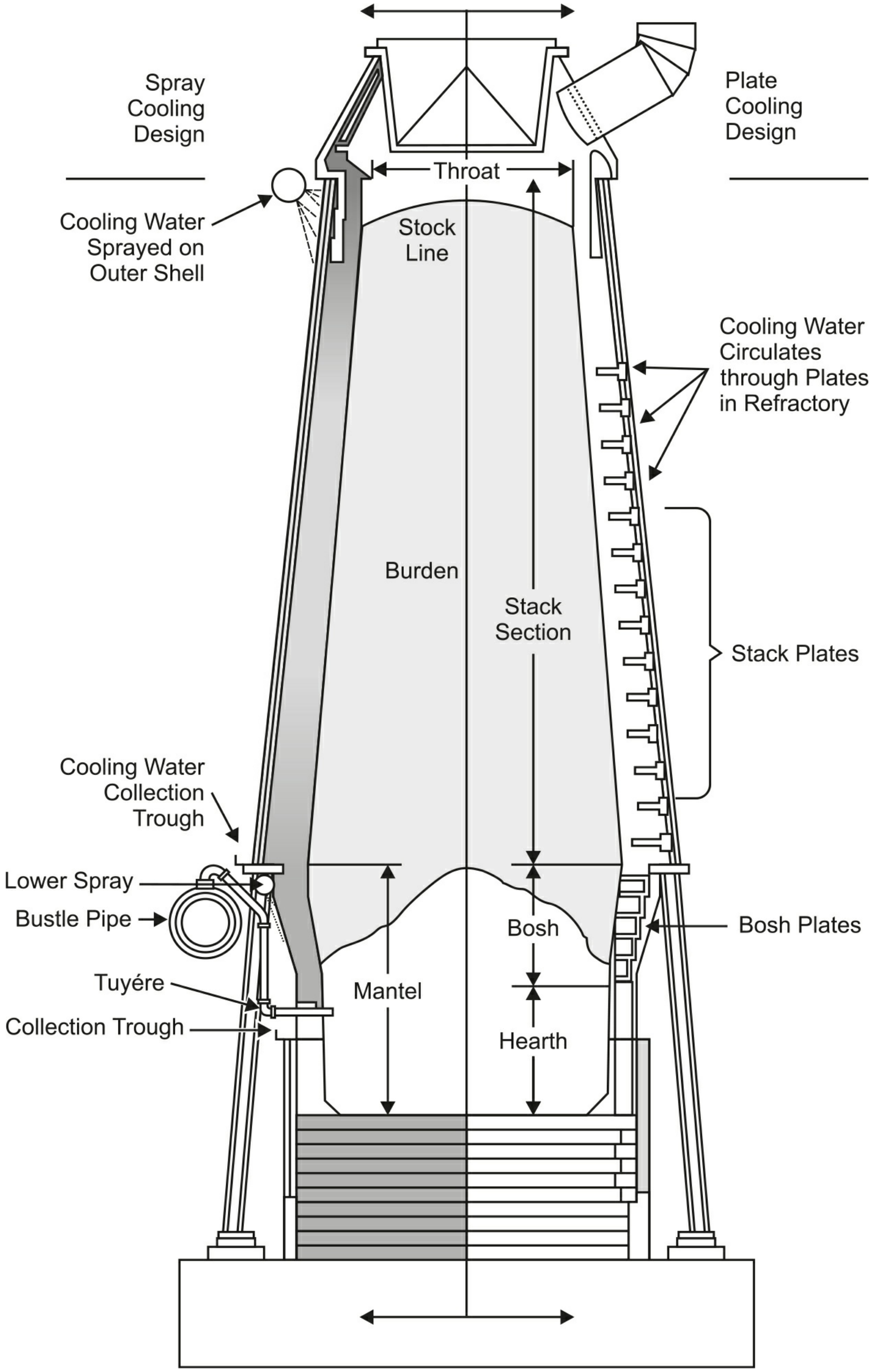


FIGURE 38.1 Blast furnace schematic showing two types of cooling water systems.

Where plates are used, these are generally connected vertically in a series of 4 to 7 plates with water flow of 15 to 50 gpm (3.4–11 m^3/h) in each series. Temperature rises 12 to 25°F (7–14°C) throughout the series. Cooling demand for the refractory decreases as height above the ground increases.

Figure 38.2 shows a hearth and bosh section of the blast furnace. The bosh area reaches the maximum furnace temperature, ranging up to 4000°F (2200°C). At this point, cooling requirements for the furnace are most critical. The bosh area can be cooled with sprays, copper plates, or staves, which are blocks of copper or cast iron containing cooling water passages. The hearth or lower section of the furnace is typically cooled with sprays or staves.

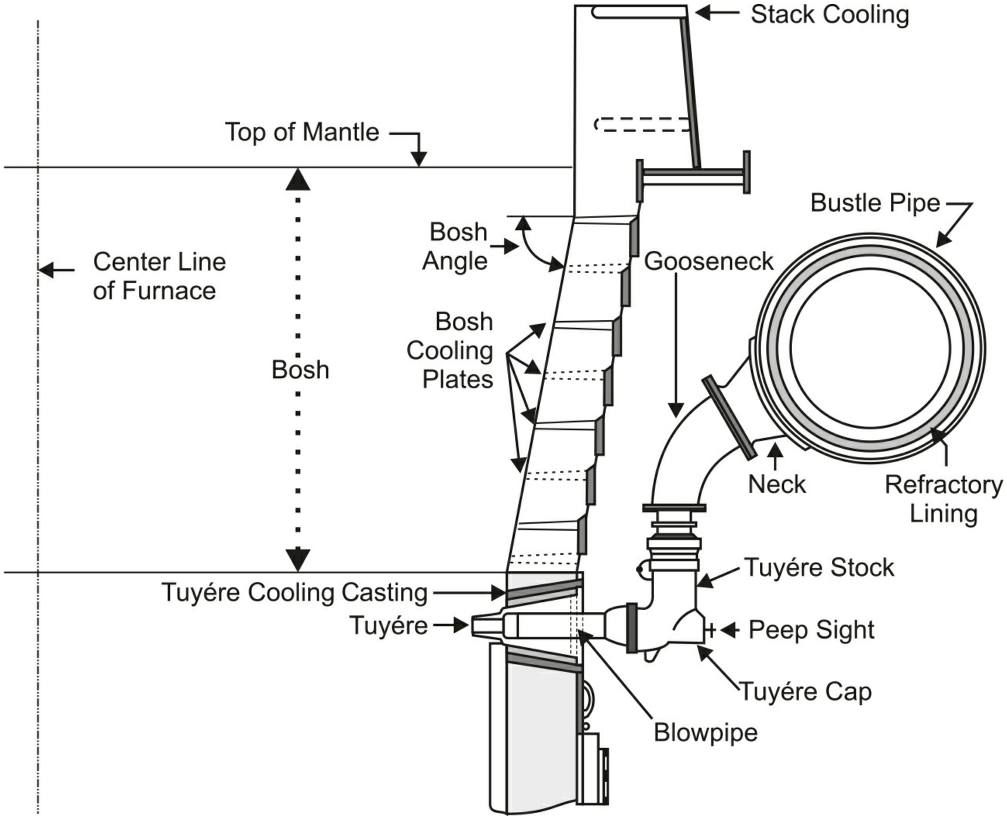


FIGURE 38.2 Blast furnace wind blowing area with plates for bosh cooling. (*Copyright 1971 by USS Corporation.*)

In the tuyère area, air preheated in stoves is blown into the furnace. The tuyères are copper-jacketed nozzles with cooling water in the jackets. Heat exchange rates are extremely high, and it is important that the cooling system be protected from fouling or plugging to maintain adequate flow rates and heat transfer.

The large valves controlling the flow of hot blast air from the stoves to the furnace, must also be cooled to prevent failure or jamming.

The basic problem of water quality for all of these systems is protection from corrosion, scale, and fouling from silt or microbiological growths. Any of these problems can quickly lead to equipment failures and lost productivity.

Exhaust Gas Treatment

Hot air blown through the furnace changes in composition and expands in volume. Exit gas velocity is high and entrains solids, principally burden fines of ore, coke, and limestone. This dirty gas passes through a dry dust collector, where a majority of the heavier solids is removed, and then proceeds to a wet scrubbing system. Scrubbing water and dirty gas collide in a venturi or orifice system, where almost all suspended solids are removed (usually over 99%). The scrubbed gas contains 75 to 90 Btu per standard cubic foot (2.8–3.4 MJ/m^3) and is used for heating stoves or firing boiler house furnaces.

Scrubber water containing high suspended solids, from 500 to as high as 10 000 mg/L, is normally sent to a thickener or clarifier. Here, the solids are settled, and the effluent water is either discharged or recycled after appropriate treatment (Fig. 38.3).

FIGURE 38.3 Clarifier-thickener used to treat blast furnace gas scrubber water and to recover solids. (*Courtesy of Inland Steel Company.*)

The heaviest concentrations of solids settled from the water are normally iron, silica, and limestone. Soluble impurities usually include ammonia, phenols, and cyanide. Chemistry of scrubbing water continually varies as it is exposed to hot, dirty gas and then cooled and clarified before recycle. Cooling towers are often used to reduce temperature after the water contacts the hot gas. Evaporation of pure water vapor in the cooling tower concentrates dissolved solids within the water and affects its chemical balance. This must be considered when planning a proper cooling water program. Blowdown is required to control salinity of the recirculating water, and chemical treatment is needed for control of scale, deposition, and corrosion.

Additional water is used for slag granulation or for slag cooling. Where water is recycled within a slag pit area, there is usually a high potential for deposition occurring within recycling lines and pumps. The water chemistry of these systems must be continually monitored.

There are a number of boiler houses in an integrated steel mill complex, and the boiler house in the blast furnace area is one of the most important. A major use for steam is to operate turbines, which drive large compressors delivering air to blast furnaces. A typical compressor discharges 100 000 scfm (2830 m^3/min) of air at 30 to 35 psig (207–241 kPag), requiring a steam turbine using about 350 000 lb/h (160 000 kg/h) steam at 900 psig (6.2 MPag). These turbines operate on a condensing cycle, but some low-pressure steam may be extracted for operation of auxiliaries, such as fans, pumps, and compressors in the utility area.

Steel Production

Steel is manufactured from iron (the blast furnace product) by three different methods: the basic oxygen process (BOP), the electric arc process, or the much older open-hearth process. The objective of each is to reduce impurities; for example, the 4% carbon content of the iron is reduced to about 0.2% in the steel product, depending on the metallurgical specifications of individual orders.

Basic Oxygen Process

In the BOP method, the mixture of hot metal from the blast furnace (usually 50–60% of the total charge), scrap steel, and slag conditioning materials, such as lime and fluorspar, are charged to the furnace (Fig. 38.4). Oxygen at a rate of 15 000 to 20 000 ft^3/min (425–566 m^3/min) is injected through a lance lowered into the vessel only inches (millimeters) above the raw materials. The oxygen blowing period continues for 20 to 25 minutes to melt and burn off or react out impurities.

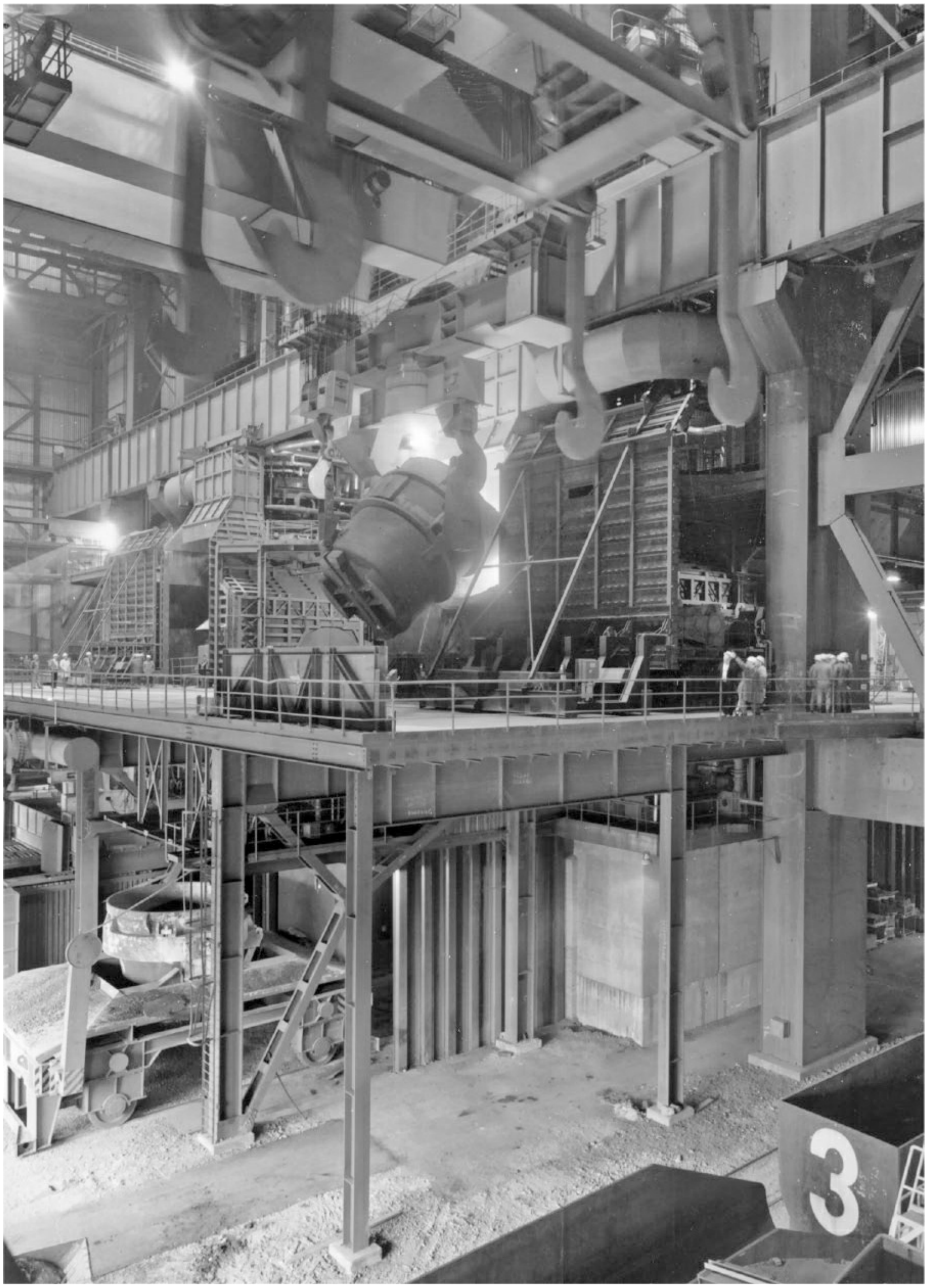


FIGURE 38.4 Hot metal is poured from the ladle into the tilted BOF as the first step in the steel making process. (*Courtesy of Baumco Gesellschaft fur Anlangenstechnik mbH, Essen, Germany.*)

A typical BOF vessel has 100 to 300 ton (91–270 tonne) capacity and produces steel in about 45 minutes. The vessel capacity is filled before the blowing of oxygen to allow space for the violent reactions to occur. In the quick basic oxygen process (Q-BOP) system, oxygen is blown through the bottom of the vessel, working through the materials and thus reducing the amount of violent splashing.

There are several water uses in the basic oxygen unit. First, the oxygen lance must be water-cooled. In most plants, this is a closed recirculating cooling water system. In most of these closed systems, lance water flows through the shell side of a heat exchanger, with cooling water on the tube side of the exchanger.

Because of the high heat release, gases leaving the furnace hood during the oxygen blow are very hot. The hood is usually cooled with water recirculating through the hood panels from both open and closed cooling circuits. A number of systems have boilers installed in the hood area for waste heat recovery and cooling of hot gases.

As gases leave the hood area, they can be further cooled by a wet scrubber and gas cooling system, which requires large volumes of water (Fig. 38.5). This water is then sent to clarifier–thickeners for sedimentation of solids, and water can be recycled or discharged. There is a wide swing in water composition through the entire heat, as shown by a pH record of the effluent from a gas scrubber. Those systems not using wet gas scrubbers normally have electrostatic precipitators.

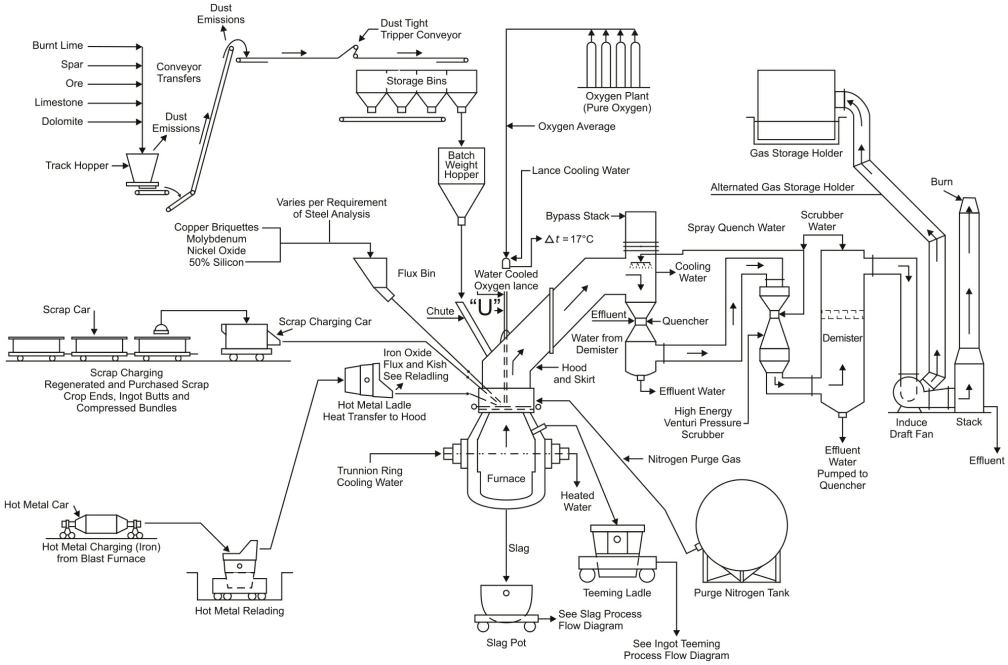


FIGURE 38.5 BOF showing major water uses for cooling and scrubbing. As different materials are added to the vessel during a heat, composition of scrubber water varies. (*From EPA 440/1-74-024a, "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category".*)

Electric Arc Furnace Process

The second method of steel making is the electric arc furnace process (Fig. 38.6), which can produce the common grades of low-carbon steel or, by charging with alloying materials, special steels such as stainless or tool steels. Electric furnaces normally operate on scrap and have the advantage of being adaptable to almost any part of the country close to special markets. Since they are not dependent on the hot iron from a blast furnace for their production, they are not tied down to the traditional steel centers.

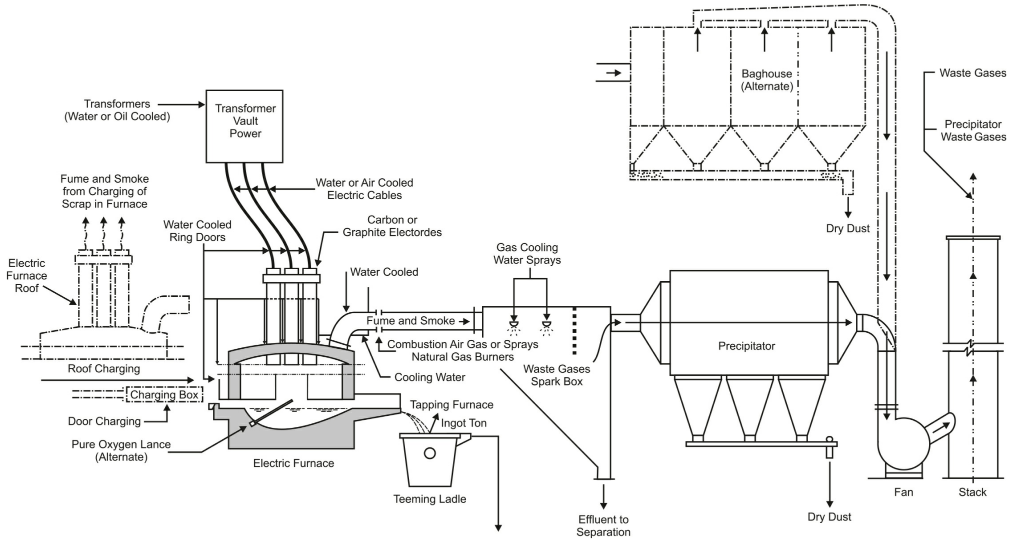


FIGURE 38.6 Electric furnace process for converting scrap to steel showing water circuits. (*Adapted from EPA 440/1-74-024a, "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category".*)

Most electric arc furnaces are equipped with water-cooled side panels or shells, roofs, off-gas elbows and ducts, electrode arms, cables, and clamps. While most electric furnace operations use baghouses to clean off gases, some plants use wet gas scrubbers.

Open-Hearth Process

The open-hearth process is the oldest of the steelmaking processes. In the open-hearth process (Fig. 38.7), the same basic materials used in the BOF process are charged to the open-hearth furnace. Hot metal is not as essential to the open hearth as to the basic oxygen unit. These furnaces normally produce 100 to 600 ton (91–540 tonne) of steel per heat over a period of 6 to 12 hours. In open-hearth furnaces, oxygen lance cooling is also required, similar to the BOF process.

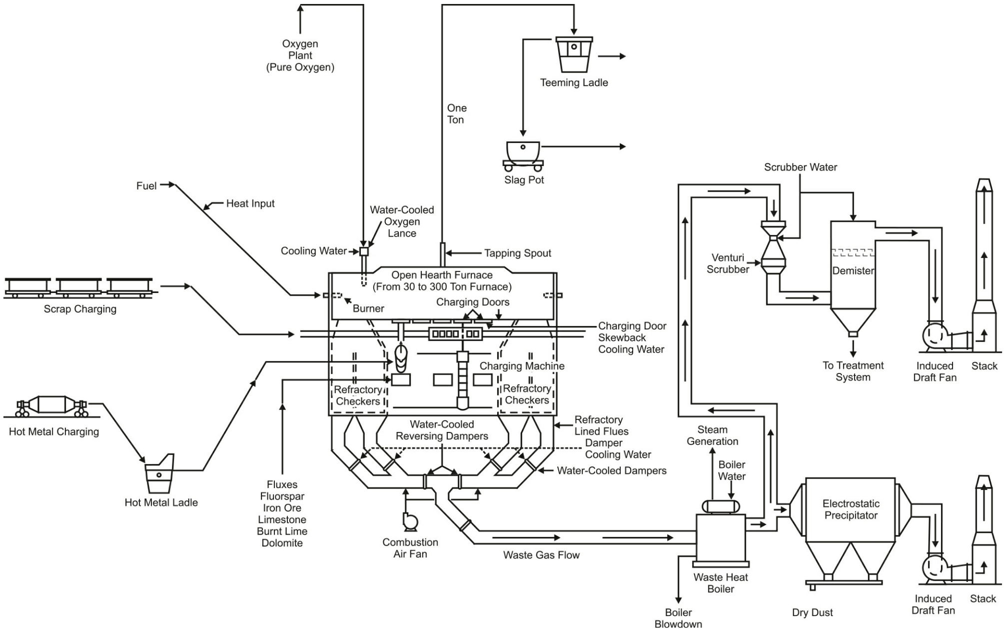


FIGURE 38.7 Open-hearth furnace operation showing water used for cooling and scrubbing. (*Adapted from EPA 440/1-74-024a, "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category".*)

The open-hearth process has been replaced with either the BOP or the electric arc furnace process in most steel plants around the world.

Direct Reduction Processes

As true of many developing technologies, a wide variety of processes is currently competing to determine which is best for the market of DRI. These processes are designed to handle a wide selection of reducing agents from solids (coke, as used in the blast furnace, coal, and lignite) to liquids (oil) as well as gases (coke oven gas, reformed natural gas, and producer gas). The largest DRI production rates are from gas-fired furnaces. The charge may include solid reductant, with supplemental fuel sometimes added, plus iron ore or pellets, and limestone or dolomite as a sulfur-reducing agent.

There are two furnace designs:

1. The horizontal furnace is essentially a tilted kiln (like a lime or cement kiln) with air and fuel fired into the discharge end countercurrent to the flow of solids. Air distribution to the kiln is critical to good temperature control to avoid clinker formation and poor control of

carbon content of the sponge iron. Coal can be used directly as a portion of the charge and as fuel, and this type of furnace favors coal-rich nations. However, production can be increased if the secondary fuel is oil or gas instead of coal.

2. The vertical shaft furnace has been designed for either fixed-bed or moving-bed operation. Reductant and fuel are usually both natural gas; however, coal can be a portion of the reductant, and coal can be converted to producer gas (coal gas), so indirectly coal could be used as both reductant and fuel.

Sponge iron discharged from the furnace can be crushed, screened, and separated magnetically from slag and char. The iron may be briquetted for easier transport and shipping, or go directly to a nearby electric furnace for charging.

Water is used for cooling in a number of operations, such as recycle gas cooling, product cooling or quenching, and machinery equipment cooling. Water is also used for gas scrubbing, and in the case of coal gas or reformer gas production, for steam generation.

Continuous Casting

Continuous casting (Fig. 38.8) was developed to reduce the overall cost of steel manufacturing by eliminating several steps in conventional steel preparation such as ingot teeming, soaking, and blooming. Continuous casting is the process of continuously pouring molten metal from a ladle into the complex casting equipment, which distributes the liquid, shapes it, cools it, and cuts it to the desired length. Casting is continuous as long as the ladle has available metal. Should one ladle follow another without interruption, the process is called “piggy-backing a cast.”

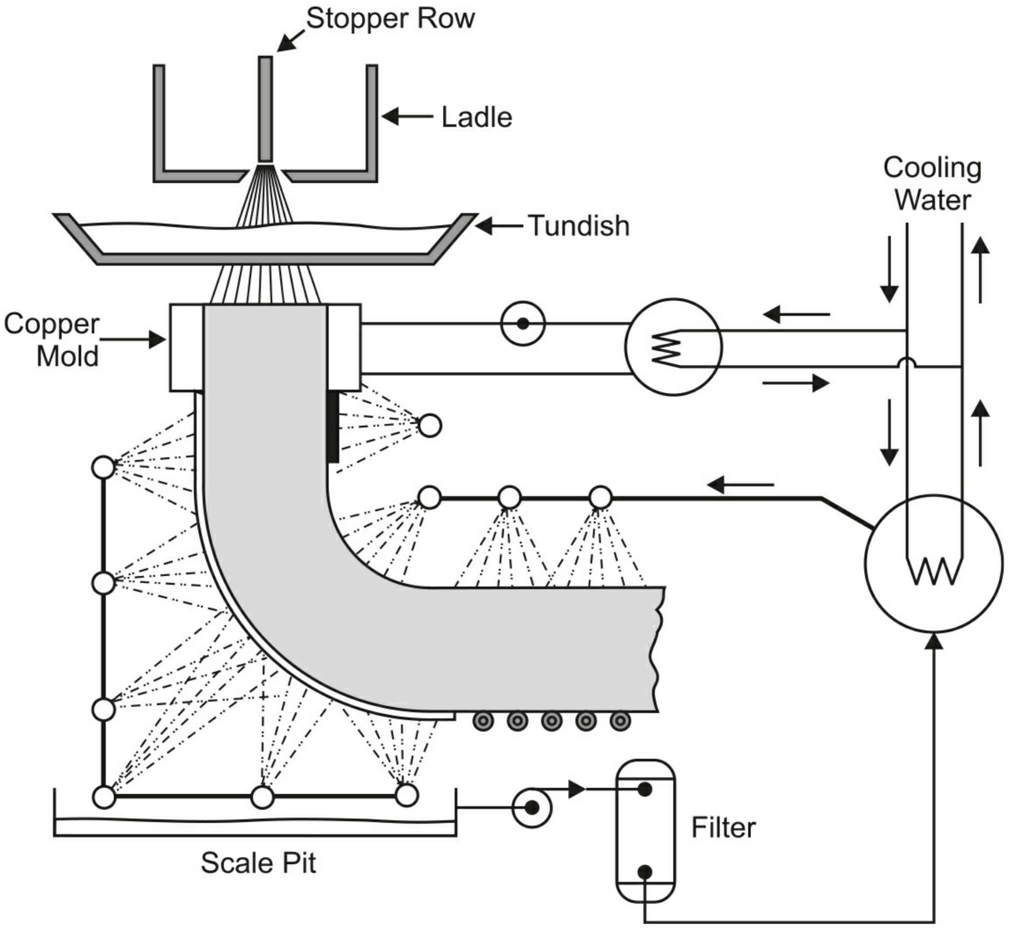


FIGURE 38.8 Continuous casting of slabs or billets.

Correct water treatment and distribution are critical to continuous casting. Steel leaving the ladle at about 2800°F (1540°C) is poured into a tundish. The bottom of the tundish has one or more openings through which molten steel is distributed to form slabs or billets in the forming area called the mold, which is a water-cooled copper jacket providing ultra-high heat exchange rate. At the start of a cast, a dummy bar is moved close to the top of the mold to completely seal the interior. As the cast starts, this bar is slowly lowered to receive molten metal, and the cooling effect of the water-jacketed mold starts the formation of a metal shell. Proceeding through the length of the mold a distance of 30 to 36 inches (about 1 m), the dummy bar and shell-contained metal are exposed to a series of direct-contact water sprays, which help to complete the job of solidifying the steel. As solidification is completed, the dummy bar is cut from the formed metal and removed. The continuously moving, solidified billet or slab then moves through guides to the straightening rolls and onto the runoff table for cutting to desired length.

The crucial point in this process is the copper water-cooled mold, which forms the initial shell. Unless the shell is formed quickly and uniformly, a product defect or breakout can occur. A breakout of liquid steel occurring below the mold is very costly and hazardous. The most reliable cooling water program uses the highest quality water available in a closed loop with a secondary open cooling loop. Condensate, high-purity boiler feedwater, or low-hardness waters have been used as makeup. Hardness levels should never exceed 10 mg/L. Since the system is closed, there is little water loss, and the best corrosion inhibitors and dispersants can be used.

Spray water that contacts the billet or the slab becomes contaminated with iron oxide particles, as the hot metal is oxidized, along with oil and grease. The water is normally processed in a filtration system for solids removal, recirculated over a cooling tower, and then recycled back to the sprays, which must be kept from plugging at all times, because the flow of water to the billet or slab being cooled must be uniform at all points.

Auxiliary mechanical equipment of the continuous caster such as machine rolls, bearings, segments, frame, and torch cut-off equipment are also water-cooled. This may have a separate cooling water system, or it may be consolidated with the spray cooling water.

Hot Mill Rolling Operation

The hot mill (Fig. 38.9) produces such products as sheets, plates, bars, rods, and structural shapes. The first step in rolling is heating the steel billet or slab in a reheat furnace to as high as 2350°F (1290°C). Cooling water must be used to cool the doors, frames, and other components of the reheat furnace, and this may come from a closed or open recirculating cooling circuit. As the heated billet or slab leaves the furnace, high-pressure water [2000 psig (14 MPag)] and even higher is blasted onto the surface to remove oxide scale, so that no imperfections are caused by rolling this debris into the metal.

FIGURE 38.9 Hot mill rolling plate for further reduction through hot strip mill. (*Courtesy of Tippins Machinery Company, Inc.*)

Water is used for roll cooling and for spraying directly onto the steel before being handled at the end of the mill. A high-speed sheet mill operates in the range of 4000 to 6000 ft/min (1220–1830 m/min); a high-speed rod or wire mill operates at 8000 to 10 000 ft/min (2440–3050 m/min). As water passes over hot metal from rolling station to rolling station, oxides washed from the metal are carried to a scale pit. There is a wide particle size range generated during descaling operations as the slab or billet travels through the mill. Larger particles are removed during initial rolling (the roughing end), and very fine particles are washed off in final rolling operations (the finishing end).

Much of the scale encountered in the scale pit can be removed with clam-type diggers, electromagnets, or traveling screen grates, but fine-sized particles are separated with coagulation in water clarification or filtration equipment. Most new plants recycle water used in the hot strip mill (Fig. 38.10).

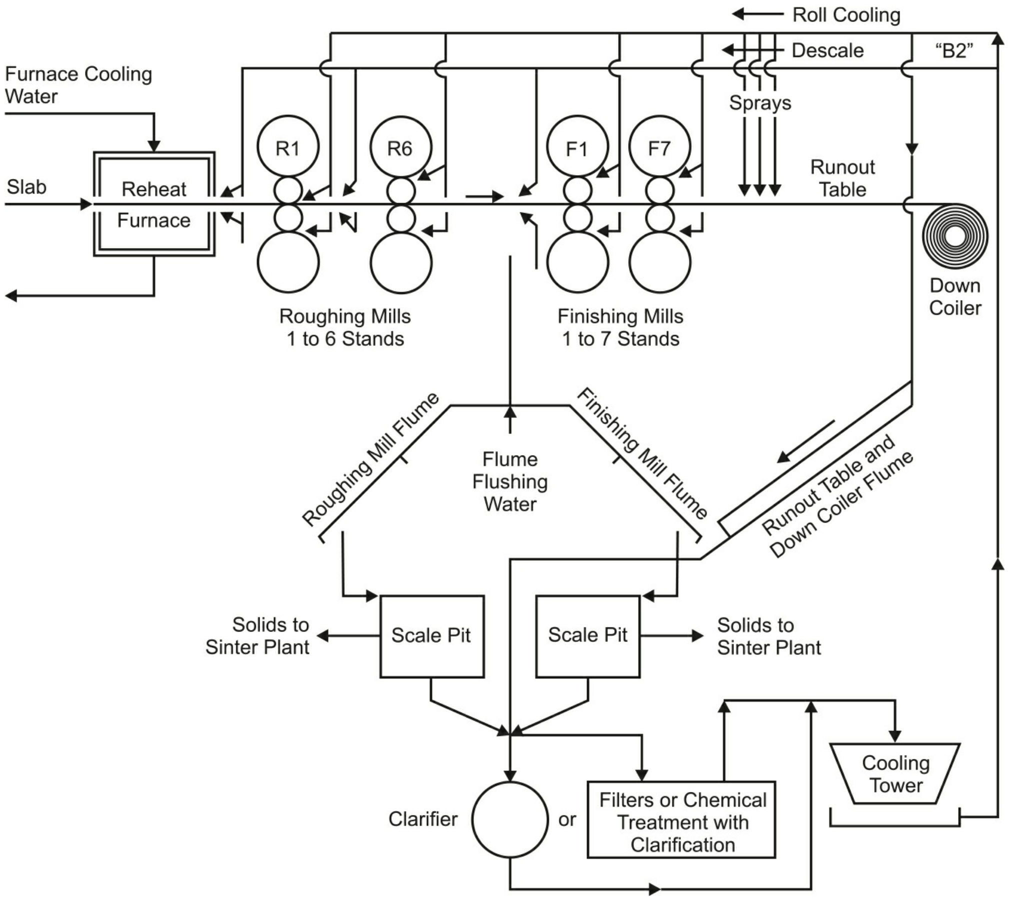


FIGURE 38.10 Hot strip mill showing recycle of clarified water for roll cooling and scale removal.

When water is recycled through the mill, attention must be given to potential problems of scale, corrosion, fouling, and microbial activity. This is especially true for water going to the high-pressure pumps and sprays.

Considerable amounts of water are used for cooling electric motor systems in many of these mills. Motor-driven rolls keep the product moving to its end point. There can be as many as 300 to 400 motors at an installation.

Cold Rolling Mills

Cold rolling mills are divided into two categories: single stand and multistand, where steel is rolled in tandem. Because the steel is cold, it is hard to work, and the cold rolling process requires lubricant (soluble oil) in the water not only to cool but also to give a good finish to the steel. Water properties to be controlled in this operation include total suspended solids, iron, and oil. There are two systems for feeding lubricant and water in a cold rolling operation:

recirculating and once through.

Recirculating System

In the recirculating system, a weak emulsion of oil and water circulates to the roll for cooling and lubrication of the sheet, collects under the roll, and then passes through to the treatment process. Emulsion is carried from the first stand to the second, third, and fourth. Spent liquid is normally collected, and an emulsion breaker is used to free the oil. Solids are settled and reclaimed for the iron content, and oil is reclaimed and reused (Fig. 38.11).

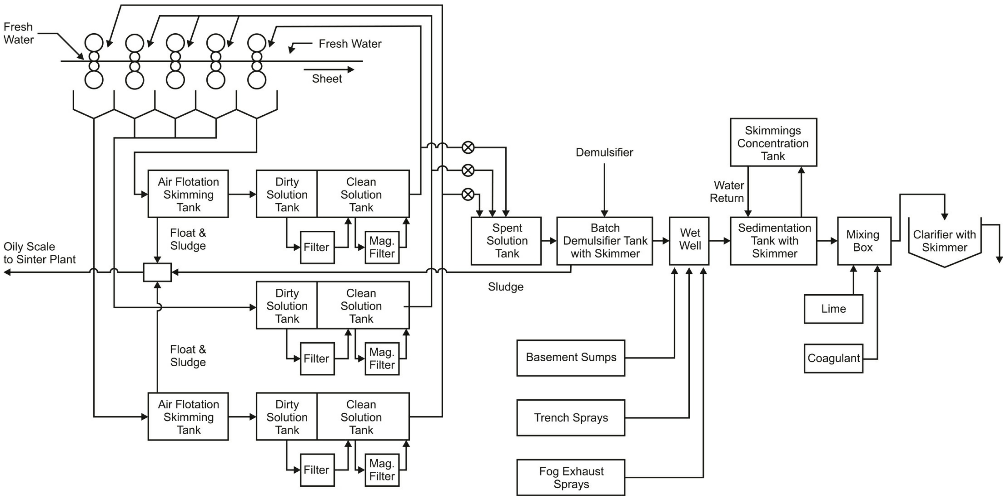


FIGURE 38.11 Cold rolling mill with recirculated water containing rolling oil emulsion. Provision is made for periodic treatment of spent rolling oil emulsions.

Water treatment for these systems consists of sedimentation, flocculation, filtration, and air flotation. Flows from these operations vary from 200 to 1500 gal/ton (0.83–6.3 m^3/tonne) of steel processed.

Once-Through System

Another cold rolling operation using direct application of oil is the once-through system, used on thin gauge material such as tin plate. The usual treatment system serves a multistand mill, having two to five stands. A 5 to 10% oil-in-water emulsion is applied to the steel at the first four stands, while a detergent solution is applied at the last stand. A once-through system is often used for this service, since the water must be kept extremely clean.

Wastewater, which contains a significant amount of oil, goes to a treatment system that includes an air flotation unit with oil skimmer, chemical treatment, aeration tanks, flocculating tank, and a settling basin or clarifier. Emulsion breaking chemicals may be required for efficient treatment of this waste. Oil is reclaimed and reused, while sludge is typically sent to a landfill.

Heat Treatment

To produce special physical properties in certain grades of steel, the metal passes through a series of heat treatment operations including heating in a furnace, annealing at a carefully controlled temperature for a specified period, quenching in water or oil, and final cooling in air.

Generally, temperatures in annealing furnaces are not so high as to require water-cooling of furnace elements, but some cooling may be needed in special cases. Temperature of the quench oil or water quenching tank must be carefully controlled, and the coolant in the quench tank is usually recirculated through a heat exchanger to remove heat brought into the system from hot metal. Inadvertent discharge of oil, which could arise with overflowing of the quench oil tank, or by rupture of a tube in the oil–water heat exchanger, must be guarded against. Oil is generally the only likely contaminant in the heat treatment area.

Sintering

Sintering is a process that recovers valuable solid residues from scrubbers and clarifiers. This process includes collection of useful materials such as iron ore fines, mill scale, limestone, flue dust, and coke fines (Fig. 38.12).

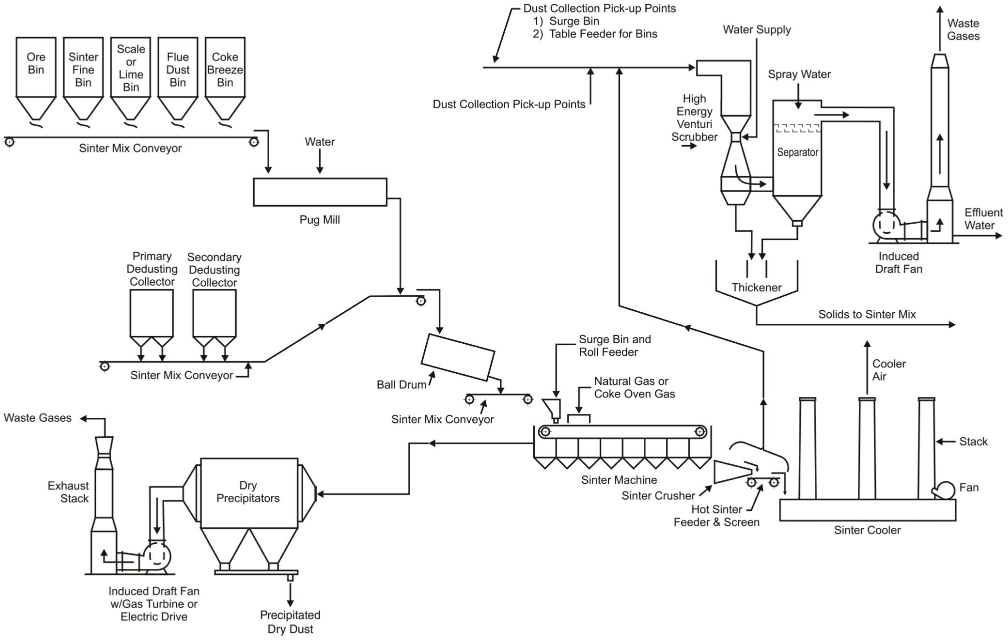


FIGURE 38.12 Sinter plant showing wet and dry dust collection. (*From EPA 440/1-74-024a, "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category".*)

The various materials are mixed in controlled proportions with a fixed amount of moisture, then distributed onto a permeable grate and passed through to a gas-fired furnace (ignition furnace). Combustion air is drawn downward through the bed. After a short ignition period, firing of the bed surface is discontinued, and a narrow combustion zone moves downward through the bed, with each layer in turn heating to 2200 to 2250°F (1200–1232°C). In advance of the combustion zone, moisture and volatiles vaporize. In the combustion zone, bonding of the particles occurs, and strong agglomerate is formed.

Most heat from the combustion zone is absorbed by drying, calcining, and preheating the lower layers of the bed. When the combustion zone reaches the base of the sinter mix, the process is complete. Sinter cake is tipped from the grate and broken up. After screening, undersized material is recycled, and the remaining sinter is sent to the blast furnace.

Water is added to the sinter mix to control moisture at 5 to 8%. Water is also sprayed for dust control in the plant and at the many conveyor transfer points, where raw materials are moved from storage areas to the sinter line (strand).

Many plants scrub sinter furnace exhaust gases to remove entrained solids. Scrubber water usually requires treatment by coagulation or flocculation to remove suspended solids. Additional chemical treatment may be required to control scale, corrosion, and fouling and removal of pollutants before discharge.

Acid Pickling

Treatment of steel in an acid bath, known as pickling (Fig. 38.13), removes oxides from the metal surface and produces a bright steel stripped down to bare metal and suitable for finishing operations, such as plating, galvanizing, or coating. Both sulfuric and hydrochloric acids are used, with the latter growing in popularity as more by-product hydrochloric acid becomes available from the chemical industry. With either acid, disposal of spent pickle liquor can be a serious problem.

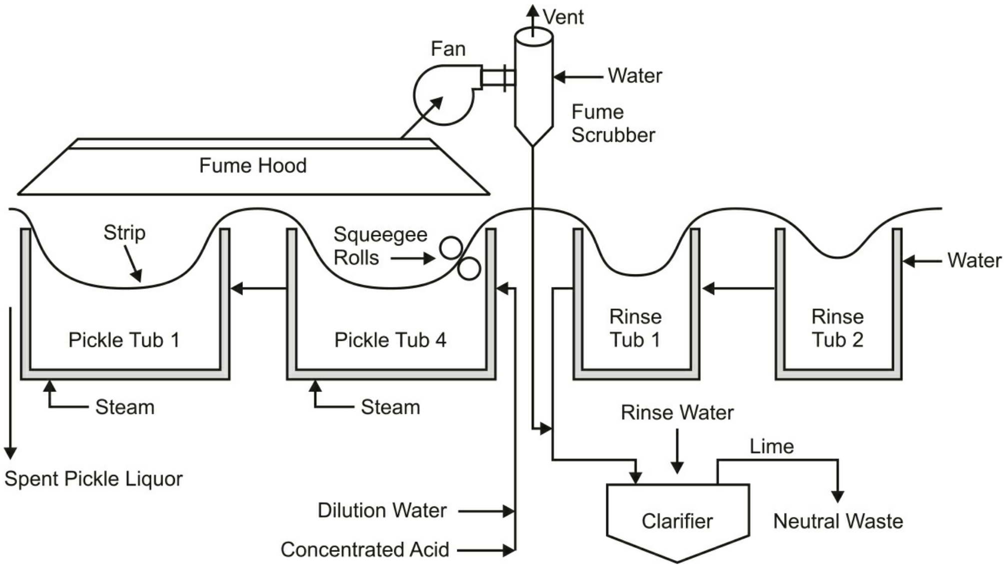


FIGURE 38.13 Acid pickling of steel sheet.

Pickling may be either batch or continuous. Usually, acid is prepared at about 5 to 15% strength, depending on the work to be processed in the pickle tank and the type of acid used for pickling. As acid works on the oxide surface, there is gradual buildup of iron in the pickle solution and depletion of acid. When the iron content reaches a level that slows the pickling operation, the bath is either dumped or reprocessed. In some pickling operations, acid is continually withdrawn in order to hold a constant ratio of iron to free acid in the pickle bath, thereby maintaining uniform pickling conditions. Metal leaving the pickle bath carries some liquor with it into the subsequent rinsing and neutralizing operations. Loss of acid varies with the type of work, shape of the products being pickled, and speed of the operation. Appreciable rinse water must be added to the rinse tank and withdrawn continuously for discharge to a treatment facility.

Slag Plant

Various useful products are recovered from slag; some being produced from slag in a molten form and others after solidification.

Molten blast furnace slag can be quenched with water to produce lightweight expanded aggregate for the manufacture of cinder block. It can also be spun into mineral wool insulation. Solid air-cooled slag is crushed to various sizes for use as track ballast, highway foundation, and similar structural material.

In plants handling slag, airborne dust normally tends to cake onto conveyor belts or interfere with proper operation of mechanical equipment. Water washing of air is sometimes practiced. Water may be used for washing conveyor belts, thereby creating high suspended solids wastewater.

BOF, open-hearth, and electric furnace slags are very high in iron. Therefore, they are usually broken up and reclaimed for charging to the blast furnace.

Utilities

Because of useful combustible gases produced at coke ovens and blast furnaces, steel mills are able to produce a large percentage of their total power requirements by burning these fuels in boiler houses. In addition to boilers directly fired with these by-product fuels, other boilers can reclaim heat from gases discharged from basic oxygen and open-hearth furnaces. Steam generated by these boilers is used throughout the mill for driving turbines, powering water pumps, presses, and forges, and providing heat wherever it may be required.

In addition to production of power from steam, some by-product gases are used in gas engines to produce electric power or mechanical energy directly for such uses as compressing air for blast furnaces. Other utilities include air compressors, vacuum pumps, and pump stations to supply the enormous quantities of air and water needed.

Water requirements for these utilities in the steel mill are similar to those of other industries. High-quality water must be produced for makeup to steam generators, and these in turn concentrate the water, which is then removed at a relatively high salinity level. Water treatment facilities required for producing this high-quality water generate their own wastes, such as lime sludge from lime softening operations, brine from ion exchange softening operations, and spent acid and caustic from demineralizer regeneration.

Cooling water is used by these utilities for such purposes as condensing turbine exhaust, cooling compressor jackets, cooling bearings on various types of powerhouse auxiliaries, and conveying ashes from coal-fired furnaces.

CHAPTER 39

The Institutional and Commercial Sectors

Many universities, hospitals, office buildings, hotels, resorts, and shopping centers use water-based heating, ventilation, and air conditioning (HVAC) systems for controlling internal environment. These facilities use hot water systems or steam boilers for heating, and refrigeration systems for air conditioning. While the individual equipment might appear quite different from one application to another, the basic systems for either heating or cooling are quite similar.

The problems encountered in water-based heating and air conditioning systems in buildings and institutions are similar to those in industrial plant systems (corrosion, scale, fouling, and microbial growth), but the impact of these problems on the operation of the facility can be quite different. First, the consequences of improper water treatment may be more critical to a hospital or residential complex, than to a large industrial plant, since human health, comfort, and even survival may be at stake. Second, heating or cooling is often required intermittently or on an instantaneous basis, so the system may be severely stressed physically, from a water treatment perspective.

Heating and cooling systems in modern commercial, institutional, and residential facilities require good water treatment to maintain efficiency and maximize value. Sophisticated chemical treatment and control systems can help provide the needed system control. This chapter will discuss the various types of heating and refrigeration systems found in these applications.

In a typical institutional or commercial facility, the HVAC system is usually one of the largest consumers of electricity. Figure 39.1 shows the relative distribution of the typical utility costs for building operation. Energy for heating, ventilation, and cooling is the largest cost component. Energy needed for building lighting is a distant second. Chemical treatment cost variations have an insignificant effect on the overall utility budget. A treatment program designed to help maintain the efficiency of the heating and cooling systems will provide far greater value to a facility than a cheap treatment program. The efficiency of the heating and cooling equipment will become more important as energy demand and fuel costs continue to rise.

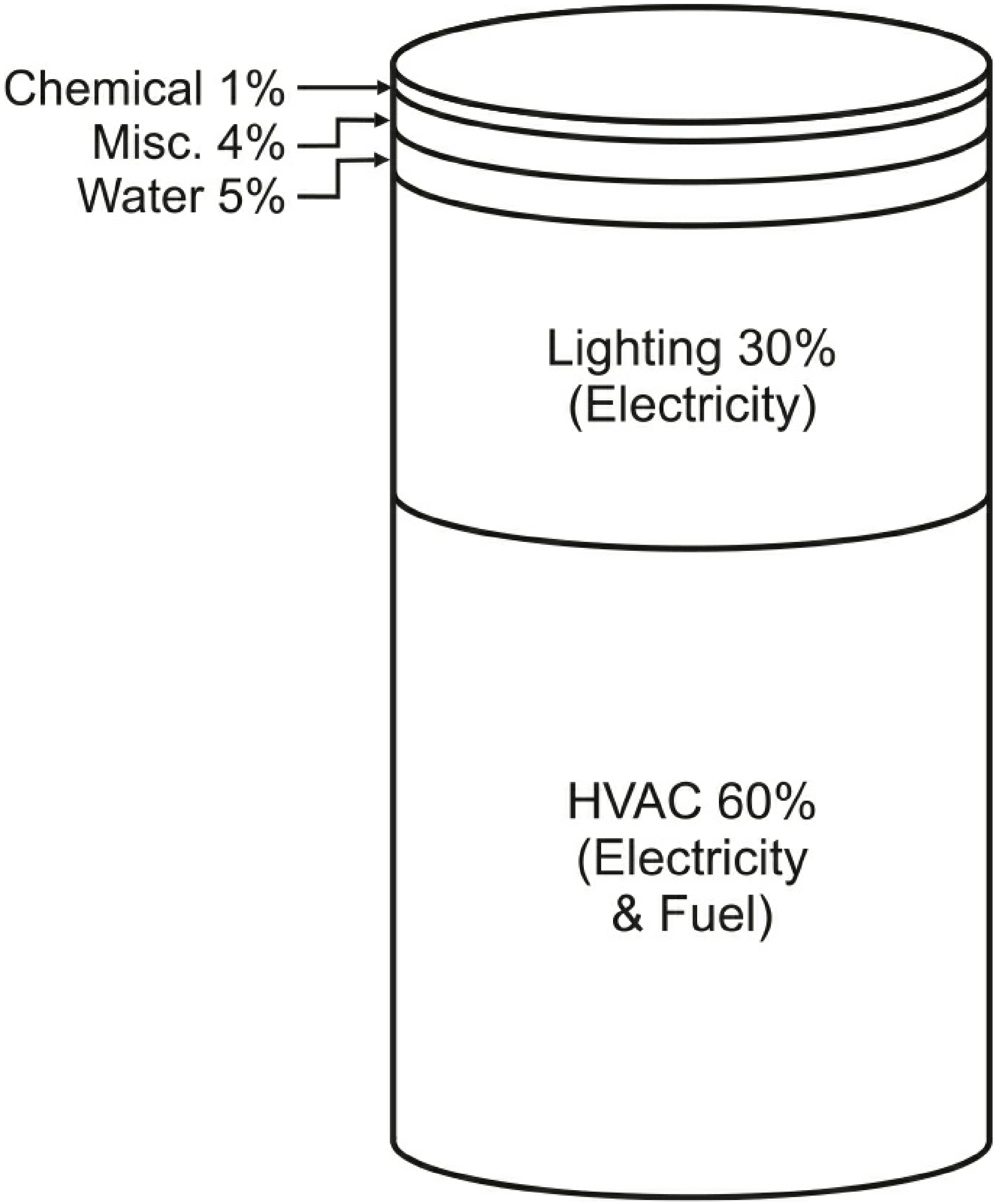


FIGURE 39.1 Typical utility budget distribution for a commercial building.

Heating Systems

The two basic types of water-based heating systems are steam boilers and hot water “boilers,” which are more appropriately called hot water heaters. Steam boilers are usually packaged firetube or watertube design operating below 200 psig (1.4 MPag) (Fig. 39.2). However, in more sophisticated installations, such as an energy supply complex for a large medical center or a large university campus, cogeneration systems with high-pressure [900–1200 psig (6.2–8.3 MPag)] boilers may be used. The high-pressure steam from the boiler drives a turbine to produce electrical energy, and the discharge steam [approximately 100 psig (0.69 MPag)] is used in the heating system. In areas where air conditioning is required in summer, the steam can be used to power an absorption chiller. In this way, energy efficiency is maintained throughout the year.

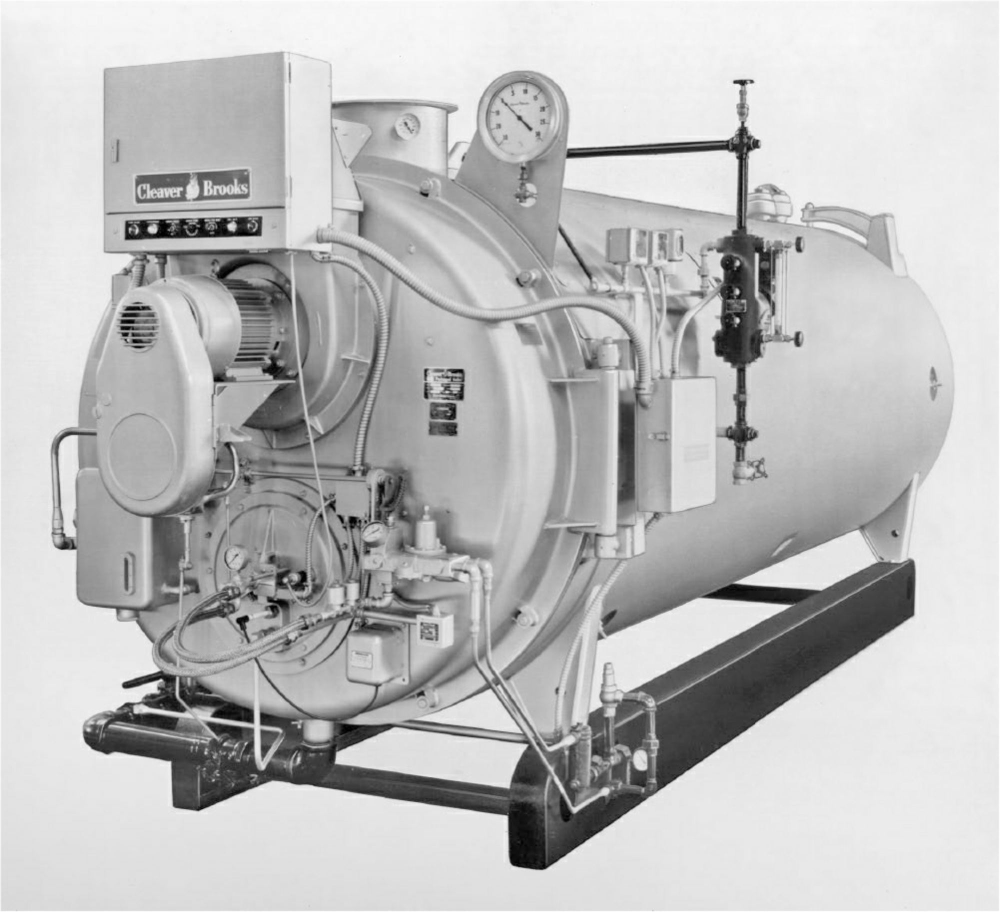


FIGURE 39.2 Typical packaged steam generator with complete fireside and waterside controls. (*Courtesy of Cleaver Brooks, Inc.*)

Most small institutional boilers are usually gas or oil fired, but occasionally, an electrically heated boiler is found. Fuel oils can range from No. 2 to No. 6, including mixtures of several grades. Many boilers contain burners designed to burn gas or fuel oil, a useful feature in areas where fuel shortages can occur. Coal-fired boilers in commercial buildings and institutions are rare, but can be found in some larger cogeneration systems.

Steam Boilers

In heating applications, the steam generated in these boilers is used in one of two ways. First, steam may be directly circulated throughout the building, where the heat is extracted through radiators or fan-coil units, and the condensate is returned to the boiler to be used as feedwater. In the second method, steam is used indirectly to heat a closed hot water loop that circulates hot water to the fan-coil units throughout the building. The heat exchanger for heating the hot water loop is located relatively close to the boiler, and the condensate returns to the boiler. Steam can also be used for humidification, sterilizing, kitchen, and research purposes.

Boiler Operation and Potential Problems

The boiler operation depends on the boiler design and the quality and pretreatment of the makeup water used to produce the feedwater to the boiler. Refer to Chap. 9 on Boiler Systems for more details on boiler operation. Ideally, low hardness, low oxygen, and low alkalinity water is used. The requirements of the feedwater depend on the size and operating pressure of the boiler. In a low-pressure boiler [<1000 psig (6.9 MPag)], the water may be only softened to reduce the hardness, leaving alkalinity and other dissolved solids in the feedwater. In a high-pressure boiler [>1000 psig (6.9 MPag)], the water may be demineralized or utilize reverse osmosis technology to remove the majority of dissolved solids. Most steam boiler systems use a deaerator to remove dissolved gases from the feedwater before it enters the boiler.

Boilers can experience scale formation, corrosion, and metal oxide deposits, depending on the operating characteristics, feedwater quality, and treatment practices. Any residual hardness in the feedwater can produce scale on the boiler internals. Hardness scales, like calcium and magnesium carbonate, occur due to the decreasing solubility of these minerals as temperature increases. These scales can form in the feedwater system and in low-pressure boilers, where no feedwater pretreatment or poorly maintained softening is used. Silica-based deposits can be found in low-pressure boilers, where the pretreatment system is not designed for removal of silica from the feedwater, or the boiler is operating at excessive cycles of concentration. Scale deposits reduce thermal conductivity of the boiler, reducing thermal efficiency and reliability. As a result, more fuel may be required to produce the same amount of steam, increasing operating costs.

Corrosion can occur in various parts of a boiler system. If dissolved oxygen is not controlled, corrosion can occur from the deaerator to the final condensate system. However, oxygen corrosion is rarely found inside an operating watertube boiler. Oxygen corrosion found in watertube boilers is generally the result of improper lay-up procedures. Oxygen corrosion can be a greater problem in the condensate system.

The iron generated from corrosion in other parts of the system can cause metal oxide deposits in the boiler. Corrosion of the feedwater piping and iron entering with the makeup water contribute to iron deposits. Most of the corrosion products that deposit in the boiler originate in the steam condensate system. These metal oxide deposits can cause under-deposit corrosion and overheating problems in the boiler.

Condensate Systems

The goal of the condensate system is to recover the hot pure water after the steam condenses and return this water to the boiler (see Chap. 13 on Condensate Systems for more detail). The system design depends on the type and size of the heating system. The condensate return system of a university can be complex and is subject to unusual corrosion problems, because of the stress of seasonal changes. Condensate is ultra-pure water and is very aggressive to most metals used in these systems. The main contaminants that can increase corrosion in the condensate system are gases, like carbon dioxide (CO_2) and oxygen (O_2). Carbon dioxide results from the thermal decomposition of alkalinity in the boiler water. The CO_2 dissolves in the condensate and produces carbonic acid (H_2CO_3). This acid decreases the pH of the condensate and increases corrosion of steel and copper alloys.

Dissolved oxygen can enter the system from either the feedwater or ingress of air into the condensate system. Oxygen inleakage can be difficult to control due to the many potential sources, such as condensate tanks, pump seals, and vacuum breakers on steam coils. The result is oxygen pitting in the condensate system, which can be quite severe, as shown in Fig. 39.3.

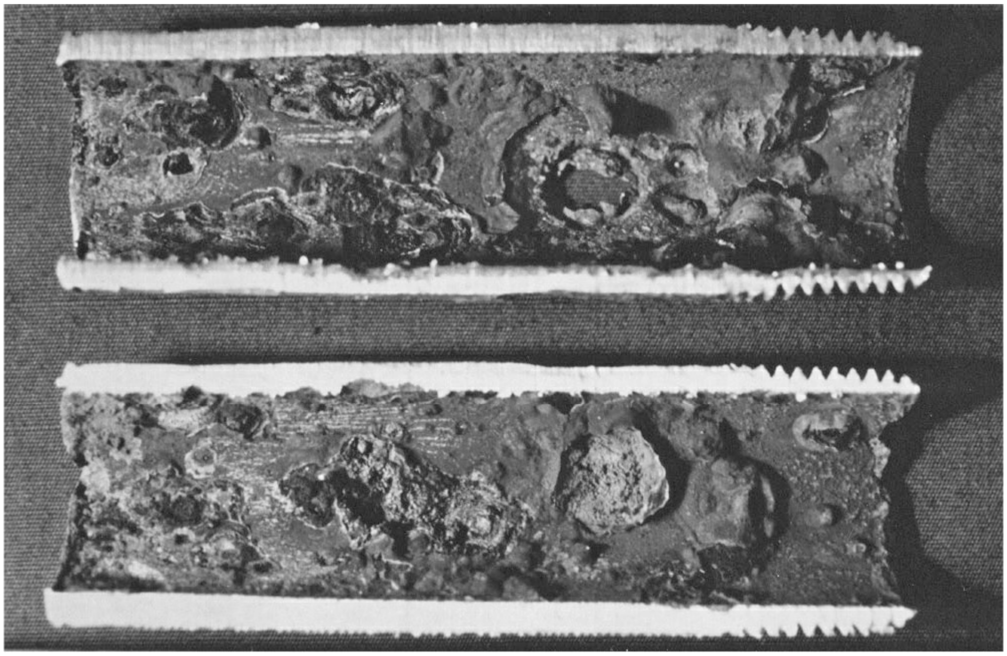


FIGURE 39.3 Severe oxygen corrosion on the internal surface of a condensate line.

In HVAC systems, a common source of air inleakage is the vacuum breaker found on heating coils in air handlers. The vacuum breaker allows air to enter the coil to eliminate a potential vacuum inside the coil when the steam flow stops. If the vacuum is not relieved, the coil could collapse. In a large HVAC system, there may be hundreds of fan-coil units, each with a vacuum breaker. Intermittent operation of the entire system can cause inleakage as a vacuum is created during idle conditions. This is particularly true during spring and fall heating seasons, when heat may be required at night but not during the day. A steam heating system under these conditions is subject to oxygen corrosion during the daylight hours, when condensate receivers cool and draw in air.

Boiler Lay-Up

A boiler may not need to be operated continuously, depending on the building and the need for steam. When boiler operation is stopped, air can leak into the boiler as the internal pressure decreases. Oxygen corrosion, which often occurs as pitting corrosion, can occur during out-of-service periods. Oxygen corrosion can be a major contribution to reduced equipment service life. During idle periods, proper lay-up procedures must be followed to minimize corrosion problems and ensure the boiler is ready to start up again when needed. Two different methods for boiler lay-up are wet lay-up and dry lay-up. In wet lay-up, the boiler is left full of water, and this water must be treated to maintain low oxygen content and appropriate pH. In dry lay-up, the boiler is drained of all water and typically maintained dry with either nitrogen or desiccant.

The choice of lay-up method generally depends on the length of time the boiler will be offline. Wet lay-up is most often used for short outages (30 days or less) and when the boiler may need to be started again on short notice. Dry lay-up is generally used for longer outages and is practical only if the boiler can be drained when it is hot.

For specific boiler lay-up methods and procedures, the reader is directed to "Consensus for the Lay-up of Boilers, Turbines, Turbine Condensers, and Auxiliary Equipment" published by the American Society of Mechanical Engineers (ASME).

Boiler and Condensate System Treatment

Water treatment in these steam plants is similar to that used in most industrial boilers. The chemical products should control scale, corrosion, and fouling in the boiler, as well as corrosion in the condensate system (see Chap. 11 for more details on boiler treatment methods). The types of products used are similar to those used in industrial systems; however, treatments may be blended and packaged so as to be convenient and easy to handle, feed, and control. Automated monitoring and control programs can make chemical treatment programs more effective and reliable.

The steam generated in these boilers can have other uses, such as humidification, dishwashing, food preparation, and sterilization in autoclaves (as in hospitals and research laboratories). A careful study must be made of the uses to which the steam is put so that acceptable and safe treatment chemicals can be used. If any part of the steam contacts food, for example, U.S. Food and Drug Administration (FDA) approved treatment chemicals are required.

In extensive condensate systems, where oxygen inleakage may be a common problem, complex feed systems may be required. In addition to a central chemical treatment station in the boiler house, satellite systems are sometimes installed to supply additional steam treatment to correct for seasonal upsets or depletion of the treatment. The quality of the condensate must be under constant surveillance to minimize any negative impact to the boiler. Continuous monitoring and control systems can be a significant benefit in large systems. Ion exchange condensate polishers are commonly installed in the boiler house to remove condensate contaminants, and prevent having to discard large amounts of valuable hot condensate. Monitoring conductivity at significant condensate return junction points helps to locate and isolate the failure promptly. Installation of sample coolers should be utilized to ensure safe sampling habits and maintain sample integrity.

Hot Water Systems

Hot water "boilers" are really misnamed, since they do not boil water and produce no steam. They can heat water to 500°F (260°C), but typically operate at temperatures of 180 to 250°F (82–121°C) in a vessel similar to a steam boiler. The heated water is circulated through the building to various heat exchangers and radiators and back to the boiler. The heat source for these boilers may be natural gas, fuel oil, or electricity. Electric boilers use either enclosed clad-type immersion heaters or resistance heaters, which operate by a flow of current between electrodes in the boiler water. The boiler water is conductive because of its mineral content.

Hot water systems are designed to be closed. Theoretically, there should be no makeup water required, but normally, a small amount is required to replace water lost by leakage of liquid or vapor. In these systems, the primary concern is prevention of corrosion caused by oxygen in the water. In a system with little leakage, the oxygen will be depleted, and corrosion will be minimized at this low oxygen concentration. However, corrosion can be a problem in systems where leakage causes continuous makeup demand. Scale formation, although not usually a major factor, can also occur in hot water boilers. This may be caused by a combination of hard water used to fill the system initially, continuous makeup to replace losses, and the high temperature of the boiler tube surfaces. The gradual accumulation of calcium and alkalinity precipitates calcium carbonate ($CaCO_3$) scale. In addition, foaming can occur, which can cause cavitation corrosion on recirculating pump impellers. Cavitation is loss of metal caused by the impingement of bubbles on the metal at high velocity.

Standard treatment programs for closed systems are the preferred chemical treatment in hot water systems. Such products contain a mixture of corrosion inhibitors to protect steel, aluminum, copper, and admiralty brass, and possibly a scale control agent. This treatment is initially charged at high dosage levels for maximum protection. For those systems containing aluminum, special caution should be applied to maintaining the system pH between 8.0 and 8.5 due to the amphoteric properties associated with that metal. Since hot water systems have little makeup and treatment chemicals are relatively stable, only small additions of treatment are required thereafter to maintain protection.

Cogeneration Systems

Because energy efficiency is increasingly important, many large facilities, especially universities, are installing cogeneration power plants. Systems that generate electrical power and use the excess heat for heating or cooling purposes are called cogeneration or combined heat and power (CHP) systems. The goal of these systems is to improve the energy efficiency of the basic power generation cycle. Production of electricity by the best conventional power plants converts only 40 to 50% of the fuel energy into electricity. The remainder is lost as heat. This heat, in the form of low-pressure steam, can be used to heat buildings, produce hot water for general use, or power an absorption chiller for air conditioning additionally, the steam produce can be utilized to drive steam driven pumps. When used for electrical production, heating in winter, and cooling in summer, these systems can improve the efficiency up to about 80 to 90% of energy in the fuel being converted to useful power.

CHP systems are used in a variety of large building facilities, university campuses, or for district heating systems. Many universities have CHP systems, including the Massachusetts Institute of Technology and the University of California at Berkeley, both of which have 25 MW generation facilities. Denmark has a large number of CHP systems, some of which burn agricultural waste for fuel and the excess heat is used for heating greenhouses.

CHP systems are common in municipal district heating systems in large cities around the world. Some of the largest district heating systems are found in:

- St. Petersburg, Russia
- Prague, Czech Republic
- Warsaw, Poland

- Seoul, South Korea
- New York City, USA
- Stockholm, Sweden

Collection of condensate can be more challenging in these systems because of their size, but it is important due to the purity and energy content of the condensate.

Heating System Efficiency

Energy costs for space heating in U.S. commercial buildings can be 50 to 60% of the total energy costs for HVAC, according to the U.S. Department of Energy (DOE). The combined efficiency of all parts of the steam system must be considered when evaluating these costs. The efficiency of the heating system depends on the boiler type and design, operating characteristics, and the design of the condensate recovery system. Maintaining the efficiency of the boiler and condensate system can have a significant impact on the utility budget of any facility. Improvement in boiler efficiency by only 1% can provide significant energy savings.

The overall efficiency of the boiler is generally considered to be the fuel to steam conversion efficiency, also called the total thermal efficiency. This is calculated based on the total steam produced, divided by the fuel input, and multiplied by 100 to yield a percent value. This efficiency value is usually calculated using units of energy use per time, such as Btu/h (kJ/h). Accurate inputs are needed to give a meaningful result.

Boiler efficiency depends on the boiler design, operating conditions, and steaming rate. The efficiency for a given boiler will change as the steaming rate changes, as shown in Fig. 39.4. The blowdown rate also affects the efficiency of the system. Blowdown is water removed from the boiler to limit the concentration of ions in the boiler water. The amount of blowdown defines the cycles of concentration of the boiler. Generally, blowdown is in the range of 1 to 25% of the feedwater flow. Lower blowdown means higher cycles of concentration. Since blowdown is very hot water, heat recovery can improve system efficiency. In some systems, the blowdown is discharged to a flash tank, which produces low-pressure steam that can be used for heating. The greatest benefit from flash tanks can be achieved when the low-pressure steam can be used for other heating purposes, or in the deaerator. In addition to flash tanks, a heat exchanger can be used to preheat the makeup water with the unused heat in the blowdown commonly referred to as blow down heat recovery.

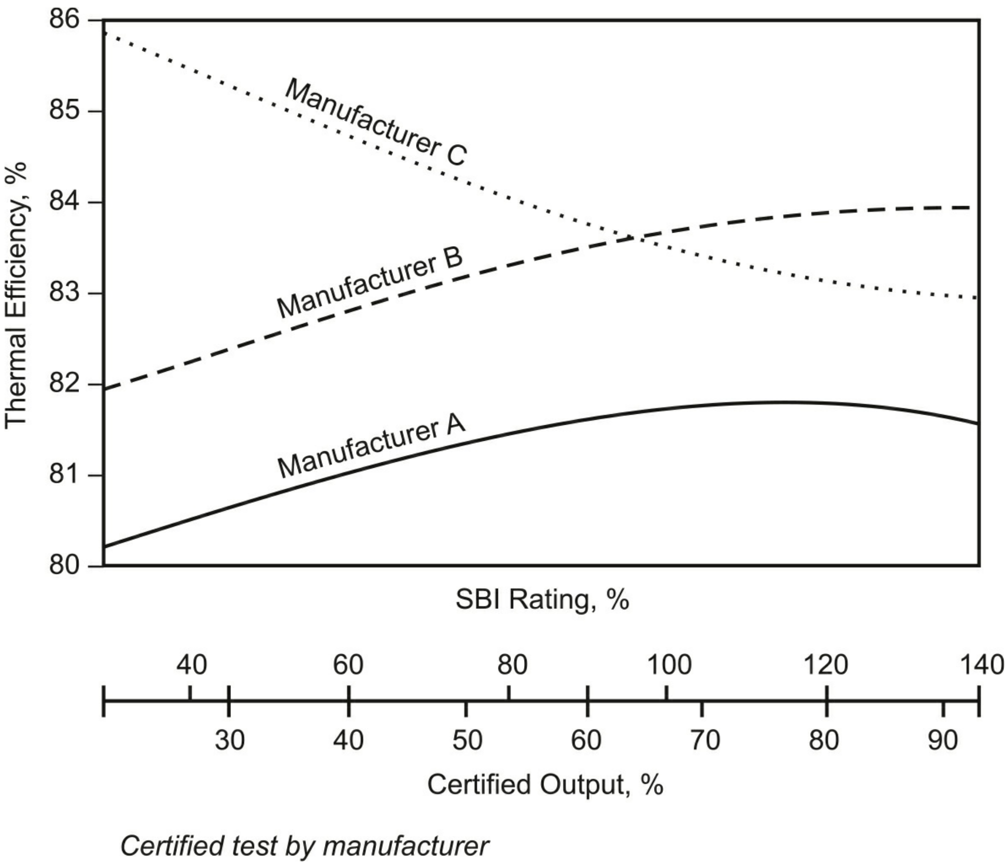


FIGURE 39.4 Typical packaged boiler performance curves illustrate the efficiency change as a function of steam output.

Return of condensate is important because of the heat content and purity of this water. Recovered steam condensate reduces the amount, pretreatment, and preheating of boiler feedwater. Heating systems in office buildings and institutions should return at least 80% of the steam as condensate.

Air Conditioning Systems

An air conditioning system is a mechanism designed to move heat from inside the building to the outside. When cooling below ambient temperature is desired, a refrigeration unit is needed. Air conditioners for households and small buildings use air-cooled refrigeration units. Most large buildings, shopping centers, data centers and similar installations use water-cooled air conditioning units, commonly referred to as refrigeration machines or chillers. Chiller systems have three component parts (Fig. 39.5). First, the chiller is in the center, consisting of the condenser, compressor, and evaporator, which produces chilled water. Second, the chilled water is circulated in a closed cooling water system to remove heat from the building. Third, the heat from the building, removed by the chiller, is generally rejected to the atmosphere by an open recirculating cooling water system. Treating and operating these systems is much like other closed and open recirculating cooling water systems. However, chiller systems have some differences from other cooling systems, because of the importance of efficiency in chiller operation.

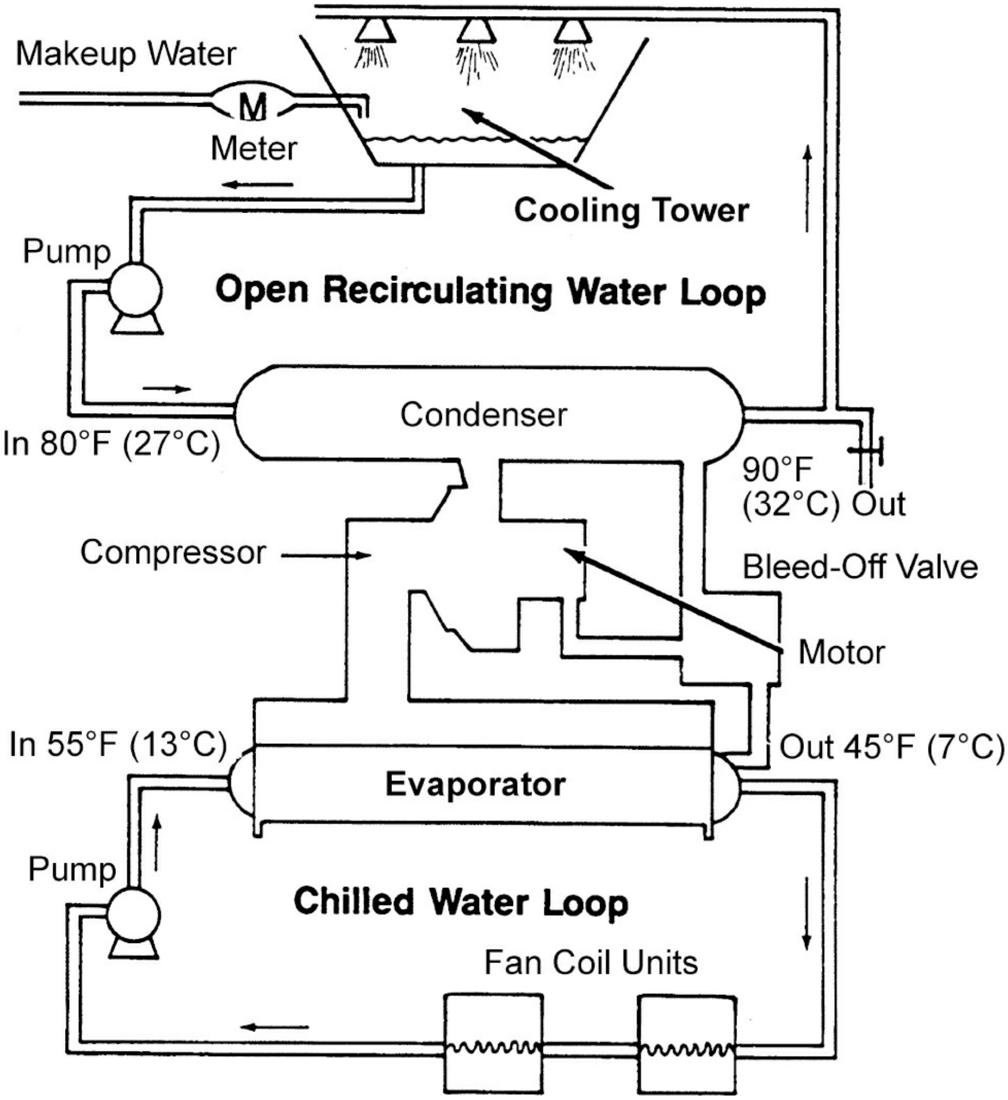


FIGURE 39.5 Complete air conditioning system schematic, showing the open cooling water system connected to the condenser and closed cooling water loop connected to the evaporator.

Servicing cooling systems on chillers requires an understanding of the operation and economics of these systems. Some chilled water systems are very small, with less than 1000 gal (3.8 m^3) volume. Others, especially those on large university campuses and thermal energy storage (TES) systems, can contain more than 7 million gal (26 500 m^3). While large chilled water systems are complex, the refrigeration equipment is the same as that for a small chilled water system, and the operation and control are quite similar.

Chillers generally fall into two categories—vapor-compression and steam-absorption units. In these chiller systems, a gaseous refrigerant is used within the chiller. There are two types of vapor-compression units—reciprocating compression units and centrifugal refrigeration units, which have similar cycles.

Vapor-Compression Units

Reciprocating compressor units are systems in which the refrigerant is compressed in a reciprocating compressor, which is driven by an electric motor. A complete system containing the compressor, condenser, and evaporator combined into one unit is shown in Fig. 39.6.

FIGURE 39.6 Reciprocating chiller in a packaged unit. (*Courtesy of the Trane Company*.)

Centrifugal refrigeration units compress the refrigerant by a centrifugal compressor driven by an electric motor, a steam turbine, a gas engine, or a gas turbine. Packaged units that contain the compressor, condenser, and evaporator are available (Fig. 39.7).

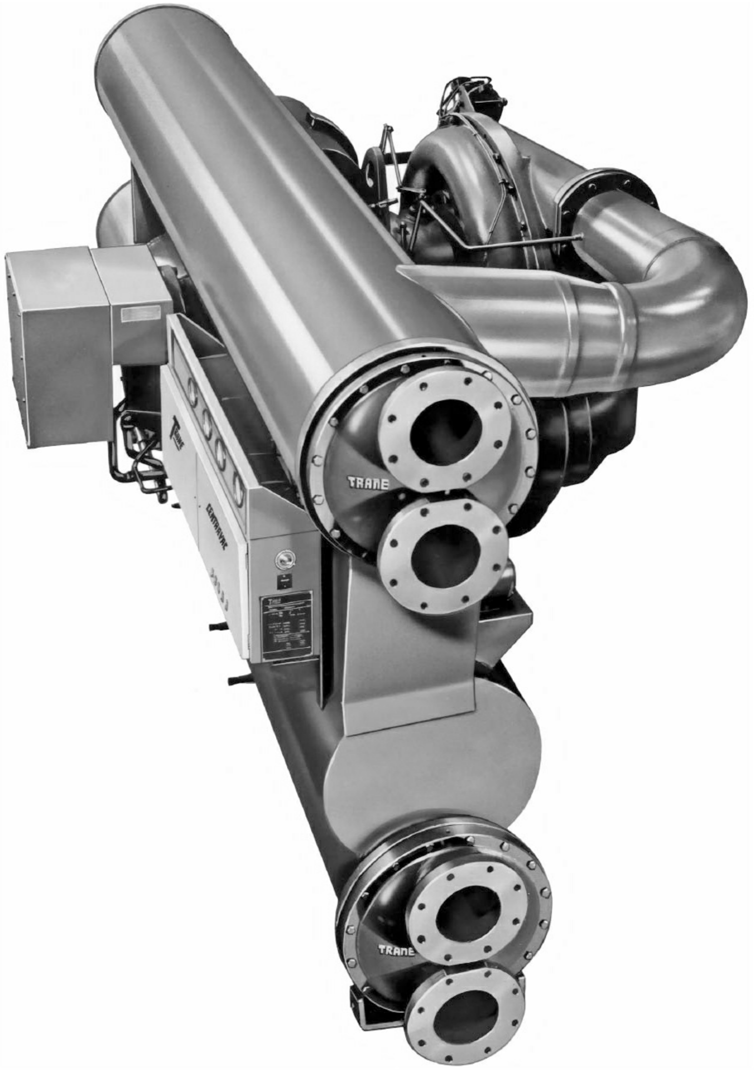


FIGURE 39.7 Packaged centrifugal refrigeration unit. (*Courtesy of the Trane Company*.)

The refrigeration cycle in a vapor-compression chiller is illustrated in Fig. 39.8. The description of the refrigerant cycle will start in the condenser, in the upper right of Fig. 39.8. In both reciprocating and centrifugal vapor-compression units, the hot compressed refrigerant vapor first passes through a water-cooled condenser. The condenser is usually a shell-and-tube heat exchanger, where the refrigerant is cooled and condensed into a liquid. From there, the liquid is sometimes stored in a reservoir. The flow of liquid refrigerant into the evaporator is controlled by a temperature-controlled valve, also called the expansion valve. When the liquid refrigerant enters the evaporator, the liquid rapidly expands under reduced pressure into a cool vapor, which absorbs heat from the chilled water loop on the other side of the evaporator tubes. The chilled water is generally cooled from about 55°F (13°C) to about 45°F (7°C) in the evaporator. The air being cooled in the building warms this chilled water back to 55°F (13°C) before return to the chiller. The refrigerant vapor is then drawn out of the evaporator by the suction of the compressor, where the vapor is recompressed, repeating the cycle. The compressor and the expansion valve separate the high-pressure and low-pressure sides of the refrigerant cycle.

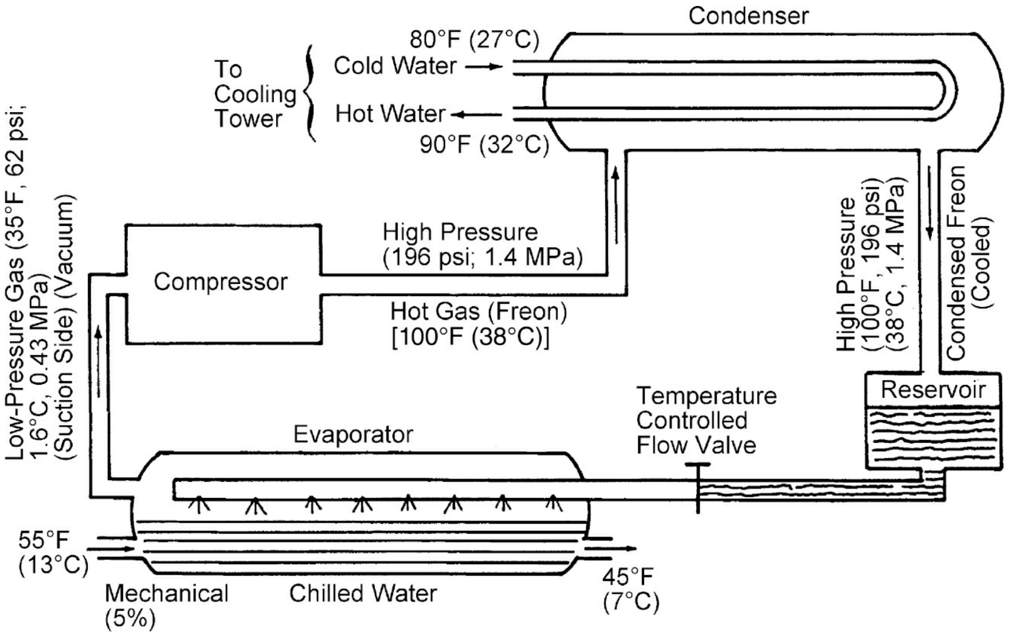


FIGURE 39.8 Typical vapor-compression chiller system schematic, illustrating the compression and expansion cycle of the refrigerant.

Typical open cooling tower water is used to cool the refrigerant in the condenser. In many cases, evaporative condenser towers are used for this purpose. In evaporative condensers, the condenser coils are placed directly in the cooling tower, and the open loop cooling water passes over the condenser coils as the water falls through the tower (see Chap. 14 on Cooling System Dynamics for more information on evaporative condensers).

Steam-Absorption Units

Regulations governing the use of refrigerants, and the increasing cost of electricity, have prompted many utility managers to consider alternatives to vapor-compression chillers. Steam-absorption refrigeration can be more environmentally friendly and economically appealing, even though it is one of the oldest technologies available. This is because it uses water as the refrigerant. In addition to the environmental issue, absorbers can allow a customer to utilize steam boilers more efficiently.

An absorption chiller may be constructed in one, two, or more shells or sections depending on the manufacturer and the application (Fig. 39.9). The steam-absorption unit cycle is more complicated than vapor-compression unit operation. Steam-absorption units use water as the refrigerant, a lithium bromide solution to create a vacuum by absorbing the water, and steam as a heat source to evaporate the water from the dilute lithium bromide solution. Absorption units use condensers cooled by water from a cooling tower and evaporators to provide chilled water for air conditioning. From the water treatment point of view, the operating principles of the open recirculating and closed chilled water systems are the same in all chillers.

FIGURE 39.9 A steam-absorption refrigeration system, illustrating the four different chambers required for the complete cycle. (*Courtesy of the Trane Company*.)

The absorption cycle (Fig. 39.10) consists of the following major components:

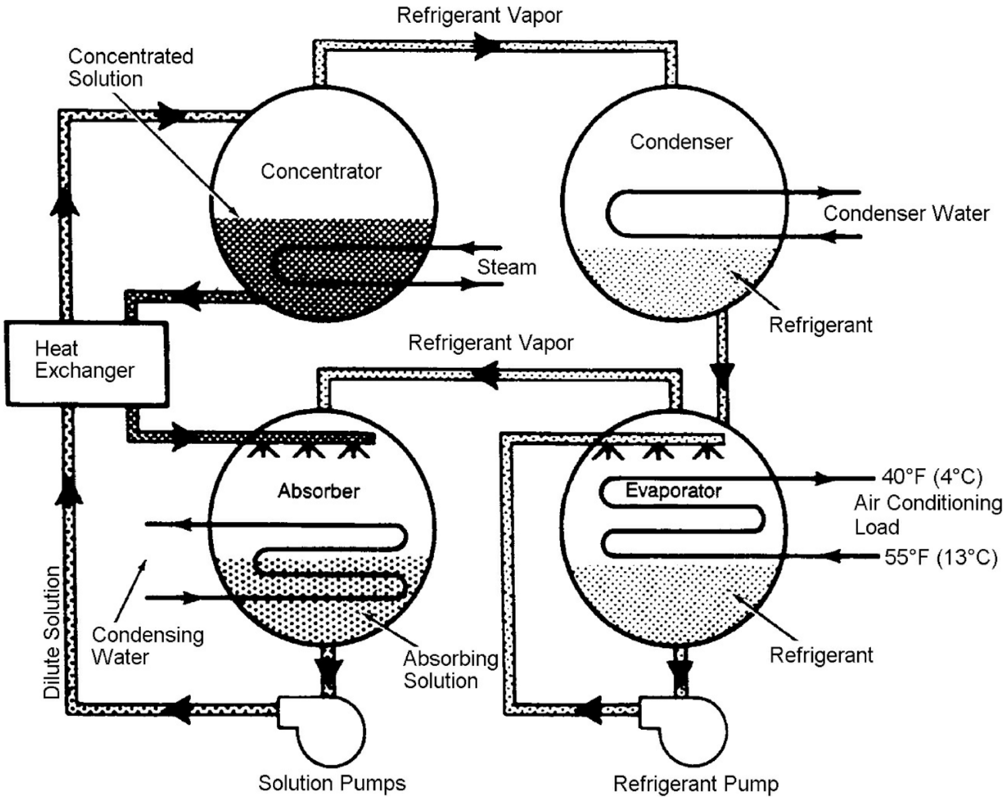


FIGURE 39.10 Flow diagram for the steam-absorption refrigeration cycle.

- Evaporator section, where the refrigerant (water) is sprayed over the chilled water tubes. The refrigerant picks up heat from the chilled water coils and flashes to vapor. The evaporation of the refrigerant cools the chilled water, which is contained in a closed cooling system. The evaporator is maintained at a vacuum, which causes the refrigerant to evaporate at a much lower temperature than at atmospheric pressure. This part of the process is essentially the same as that of an evaporator in a vapor-compression chiller.
- Absorber section, where the evaporated water vapor (refrigerant) is absorbed into a concentrated lithium bromide solution. The hot concentrated lithium bromide solution is sprayed into the absorber vessel. The water vapor coming from the evaporator is absorbed by the lithium bromide. The heat of absorption is removed by cooling tower water circulated through this section. Absorption of the water vapor produces the vacuum drawn on the evaporator. This vacuum is

maintained by controlling the temperature and concentration of the lithium bromide solution.

- Concentrator section, where heat is added by steam or hot water to boil off the refrigerant (water) from the absorbent to reconcentrate the lithium bromide solution. The steam demand is controlled by the temperature of the chilled water. When more cooling is needed, more steam is required.
- Condenser section, where the water vapor (refrigerant vapor) produced in the concentrator is condensed and cooled by condenser water (cooling tower water) circulated through this exchanger. The cooling water recirculation rate in an absorber condenser is usually higher than in a vapor-compression unit, and the cooling tower range or delta T (ΔT) is usually higher too. Higher skin temperature results, increasing the risk of scaling and microbial fouling on the cooling water side.
- Refrigerant pump, which pumps the refrigerant over the tube bundle in the evaporator section.
- Solution pumps, which pump the lithium bromide solution to the concentrator and to the spray header in the absorber.
- Heat exchanger, where the dilute lithium bromide solution being pumped to the concentrator from the absorber is heated by the hot concentrated lithium bromide solution, which is returned to the absorber.
- Heat recovery exchanger (not shown), may be used in some systems. This exchanger recovers heat from the refrigerant vapor leaving the concentrator, passing the heat to a closed hot water heating loop.
- Purge unit (not shown), which is used to remove noncondensable gases from the machine and to maintain a low pressure in the evaporator.

What is a Ton?

The cooling capacity of refrigeration units is often indicated in tons of refrigeration. A ton of refrigeration represents the heat energy absorbed when one ton [2000 lb (907.2 kg)] of ice melts during a 24-hour period. The ice is assumed solid at 32°F (0°C) initially and becomes water without changing temperature. The energy absorbed by the ice is the latent heat of fusion (melting) times the total weight (mass).

Refrigeration units can be rated in Btu/h, kcal/h, kJ/h, or kW instead of tons. The energy equivalent of one ton of refrigeration is:

- One ton of refrigeration = (2000 lb)(144 Btu/lb)/24 h = 12 000 Btu/h
- One ton of refrigeration = (907.2 kg)(80 kcal/kg)/24 h = 3024 kcal/h
- One ton of refrigeration = (907.2 kg)(334.7 kJ/kg)/24 h = 12 652 kJ/h
- One ton of refrigeration = 3.5145 kW

Unique Chiller Design and Operating Characteristics

New equipment designs and opportunities for more efficient operation can provide significant energy and cost savings. An example of new design includes chillers with enhanced tubes. Operating practices to improve efficiency include free cooling. A thermal storage system involves both design and different operating practices to obtain greater efficiency. These designs and operating practices can lead to unique or greater problems than with standard chiller designs and operation.

Enhanced or Rifled Tubes

Increasing energy costs and use of newer refrigerants are driving the move to high-efficiency chillers. Enhanced tubes are one way to make chillers more efficient. These tubes are usually rifled internally (typically the water side of the tubes), although the tubes can be rifled or finned on the external tube surface (Fig. 39.11). The grooves increase surface area and create more turbulent water flow, making heat exchange more efficient. Enhanced tubes require good water flow and effective water treatment programs, because deposition and fouling can occur more easily in the grooves of the tubes when low flow or inadequate water treatment occur.

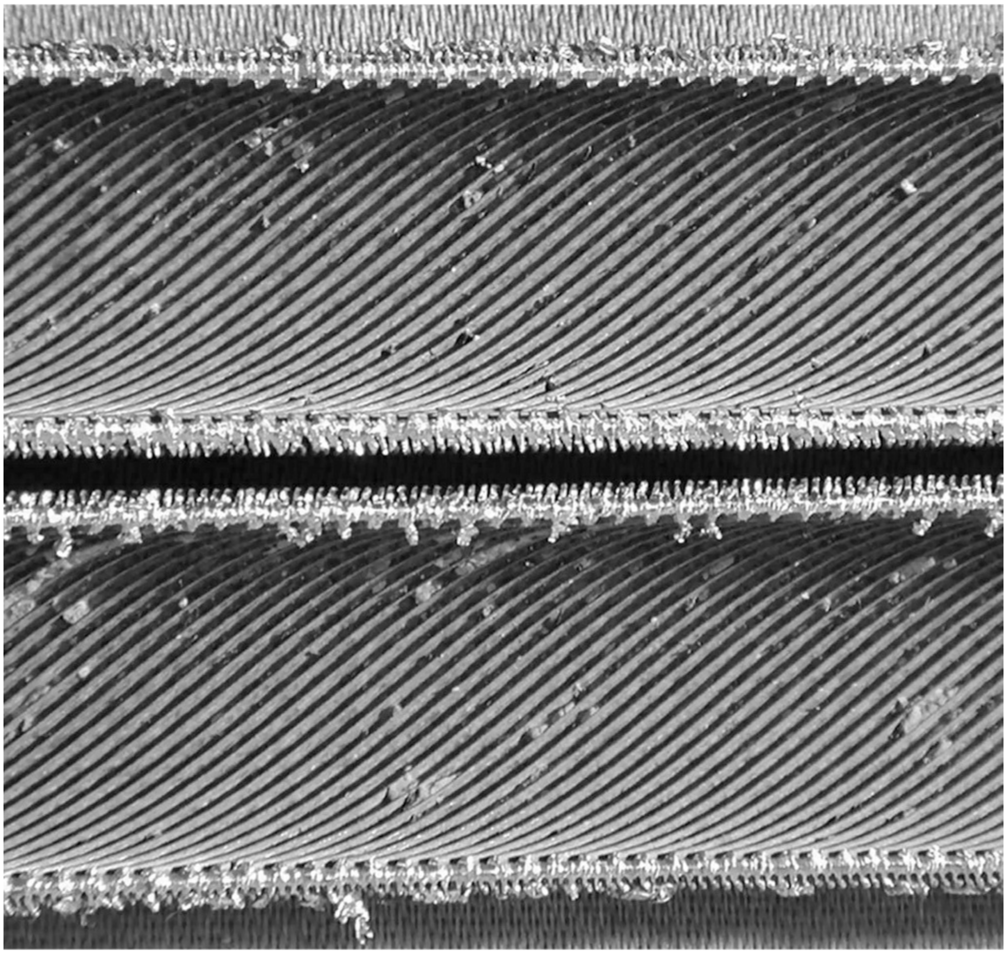


FIGURE 39.11 Rifled condenser tube split longitudinally. The deposits are the result of localized corrosion in the grooves.

Corrosion in copper tubes used in HVAC systems is generally uniform oxidation, pitting, stress corrosion cracking, or corrosion fatigue (see Chap. 16 on Cooling System Corrosion for more details on these forms of corrosion). Rifled chiller tubes can have additional failure modes, including erosion corrosion from flow variations over the groove, under-deposit corrosion from fouling of the rifled groove, and microbiologically influenced corrosion (MIC). A unique type of pitting that looks like an ant's nest when viewed in cross section is also seen in prematurely failed rifled tubes. This is sometimes called formicary corrosion. These pits can be branched, and the pinholes penetrating the copper walls are generally difficult to detect by the naked eye.

Several factors can influence failure of enhanced tubes, even before the tubes are installed. Lubricating oils used during tube manufacture can decompose into products that include carboxylic acids, acetates, and chlorides under the proper conditions of moisture, oxygen, and warmth. The presence of such corrosive chemicals initiates ant's nest corrosion, which can propagate before and after tube installation. Copper tubes may be stored under conditions of high humidity, which is known to worsen localized corrosion. In general, uniform copper dissolution occurs under total immersion in the water. However, in the presence of humidity, a thin layer of water molecules can occur in localized areas on a copper surface. This can increase the localized corrosion rate.

After tube installation, problems including deposition, low water flow, or poor treatment control can cause failure during normal operation. Corrosive substances can be present at the time of tube installation or develop over time by possible leaks (e.g., refrigerant). As mentioned above, there may be residual organics either from incomplete tube cleaning or from trace amounts of detergents and solvents. Suspended solids, scale, corrosion product, and microbial deposits will form more easily in the grooves of rifled tubes. Any of these deposits can cause under-deposit corrosion. Microbial deposits can also cause MIC. Prevention of these problems is more critical with enhanced tubes.

Intermittent operation of a chiller system can cause low or no cooling water flow. HVAC systems often do not operate on a continuous basis, and operators will shut chillers down periodically. This results in stagnant water inside the tubes, where suspended solids can settle and deposit easily on the tube surface. The situation is worsened when these deposits remain in the grooves of rifled tubes and eventually cause under-deposit corrosion.

Ineffective water treatment and poor system control can cause problems. Low dispersant levels allow mineral scale particles or suspended solids (silt and dirt) to deposit in the grooves of these copper tubes and initiate under-deposit corrosion. Low levels of copper corrosion inhibitor can lead to poor corrosion control, which can contribute to tube failures. In addition, poor microbial and system flow control will cause microbial colonies to develop and flourish. MIC will then become a factor in tube corrosion and failure.

Preventing problems in enhanced tubes requires many of the same practices that are required for smooth exchanger tubes. However, maintaining systems with enhanced tubes may require extra steps or require more careful monitoring. The practices for systems with enhanced tubes can benefit any system. The appropriate treatment program should be used in systems for both the condenser and evaporator cooling water systems. A standard closed system treatment program should be used to provide the necessary general corrosion, deposit, and microbial control. Maintaining the appropriate copper corrosion inhibitor concentration in the system is important.

For the open system serving the condenser, treatment can be more challenging. Any new system should be cleaned and passivated before starting a water treatment program. A treatment program should be selected based on the water chemistry, system characteristics, and operating temperatures to maintain control of corrosion, deposition, and microbial growth. Prevention of fouling by scale, corrosion, suspended solids, and microbial growth is essential.

Free Cooling—Opportunities and Challenges

Free cooling assumes that outdoor air temperature is low enough to provide cooling without running the chillers. This practice is useful when the outside temperature is below 45 to 48°F (7.2–8.9°C) and heating is not yet required in the building. In some parts of the world, free cooling is an option for 30 to 40% of the year.

In older free cooling systems, tower water was mixed with the chilled water system (direct injection) to provide free cooling. Both the chilled water system and the open cooling tower system will suffer when these waters are mixed. Examples of these problems include:

- Dirty tower water enters the relatively clean chilled water system.
- Microbial loading on the chilled water loop increases.
- Incompatible treatment chemistry mixes in the open and closed cooling water loops.
- Expensive closed loop treatment chemicals are lost.

As a result, costs for maintenance, downtime, water, chemicals, and energy can be higher when mixing open and closed system water.

Today, mixing the tower water with the chilled water is discouraged, because of the many operational problems that are created. A heat exchanger can be used to isolate the two water systems. Improvements in plate-and-frame heat exchanger performance have made modern free cooling a very desirable option. New plate-and-frame heat exchangers have design approach temperatures of less than 2°F (1.1°C). This means that when outdoor temperature is 48°F (8.9°C), chilled water temperature can be lowered to

50°F (10°C). The chiller operation is not necessary if outdoor temperature is at or below 48°F (8.9°C). The only energy cost is the energy needed to run the recirculating pump.

Lay-Up

Most chillers do not run continuously, and much of the water-side damage occurs during the offline (idle) periods. Allowing chillers to sit idle containing stagnant water for extended periods is a recipe for failure. Good offline practices are necessary to minimize corrosion and deposition. Maintaining flow with treated system water is the best approach. Dry lay-up is effective, but is inconvenient and does not allow rapid start-up of the idle machine.

Steam-absorption chillers have one unique characteristic concerning lay-up or idle periods. Since absorption chillers use steam as the energy source, condensate corrosion is a concern. The temptation is to valve off the steam side when the chiller is offline. However, steam valves often leak, and isolating the equipment can lead to condensate accumulation in the concentrator. Carbon dioxide can accumulate on the steam side, since CO_2 is a common contaminant in many steam sources. The combination of condensate and CO_2 can lead to highly corrosive conditions in localized areas. The best method to prevent steam-side corrosion during idle periods is to allow a small amount of steam to flow through the idle chiller. If desired, the steam discharge can be captured and reused, but the heat recovery system must not allow condensate to form in the chiller. All condensation must occur outside the chiller to avoid chiller corrosion.

Cleaning

Most closed loops will require cleaning eventually, unless sidestream filtration is used to remove debris. Sidestream filtration is often recommended in all closed loops to avoid the need for online or offline cleaning. Filtration equipment should be sized based on the ability to filter anywhere from 2 to 20% (as economics dictate) of the system volume per hour down to 0.25 microns in porosity. Online cleaning rarely removes more than 50% of the debris accumulated during operation of the system. Offline cleaning can remove most of the debris but is more expensive and time consuming. With offline cleaning, the system is not available for cooling during the cleaning, which can be impractical, impossible, or extremely expensive for the plant.

Cooling System Treatment

In any chiller system, careful attention must be paid to the treatment of both the open recirculating water system and closed chilled water system, whether the exchangers have enhanced tubes or normal, smooth tubes. This is necessary for water-cooled air conditioning systems to operate at design efficiency. A total treatment program for both the open cooling water system and closed loop chilled water system is necessary to minimize corrosion, deposition, and microbial growth.

Closed Chilled Water Systems

The primary goals in treating these systems are to prevent metal corrosion and fouling and to control microorganisms. Closed chilled water systems are generally less susceptible to scale formation, since no evaporation should occur in a properly operating system and water temperatures are low. However, leaks can increase the potential for scale formation from loss of treatment and continuous influx of scale forming ions. Standard closed cooling system treatment programs can prevent these problems and maintain system efficiency.

Microbial growth can be a problem in chilled water systems. Specific problems can be caused by denitrifying, iron and sulfate reducing bacteria (see Chap. 17 on Cooling Water Biology). These microbes cause corrosion of the system metal, which can become severe. Proper control is maintained by periodic analysis of the water and by the application of biocides, when necessary. Biodispersants and biodetergents might also be appropriate.

Open Recirculating Systems

Programs for cooling tower systems must emphasize cleanliness of the chiller condenser, good copper and mild steel corrosion control, and proper microbial control. The chiller condensers have copper-based tubes, in most cases. The copper corrosion and microbial control must be balanced, since oxidizing biocides can influence copper corrosion and impact some copper corrosion inhibitors.

Cooling System Efficiency

Figure 39.12 shows a typical distribution for the energy used by refrigeration systems to provide the desired cooling. Note that the chiller consumes about half of the total cooling energy, while the water circulating pumps (for both evaporator and condenser) consume most of the remainder.

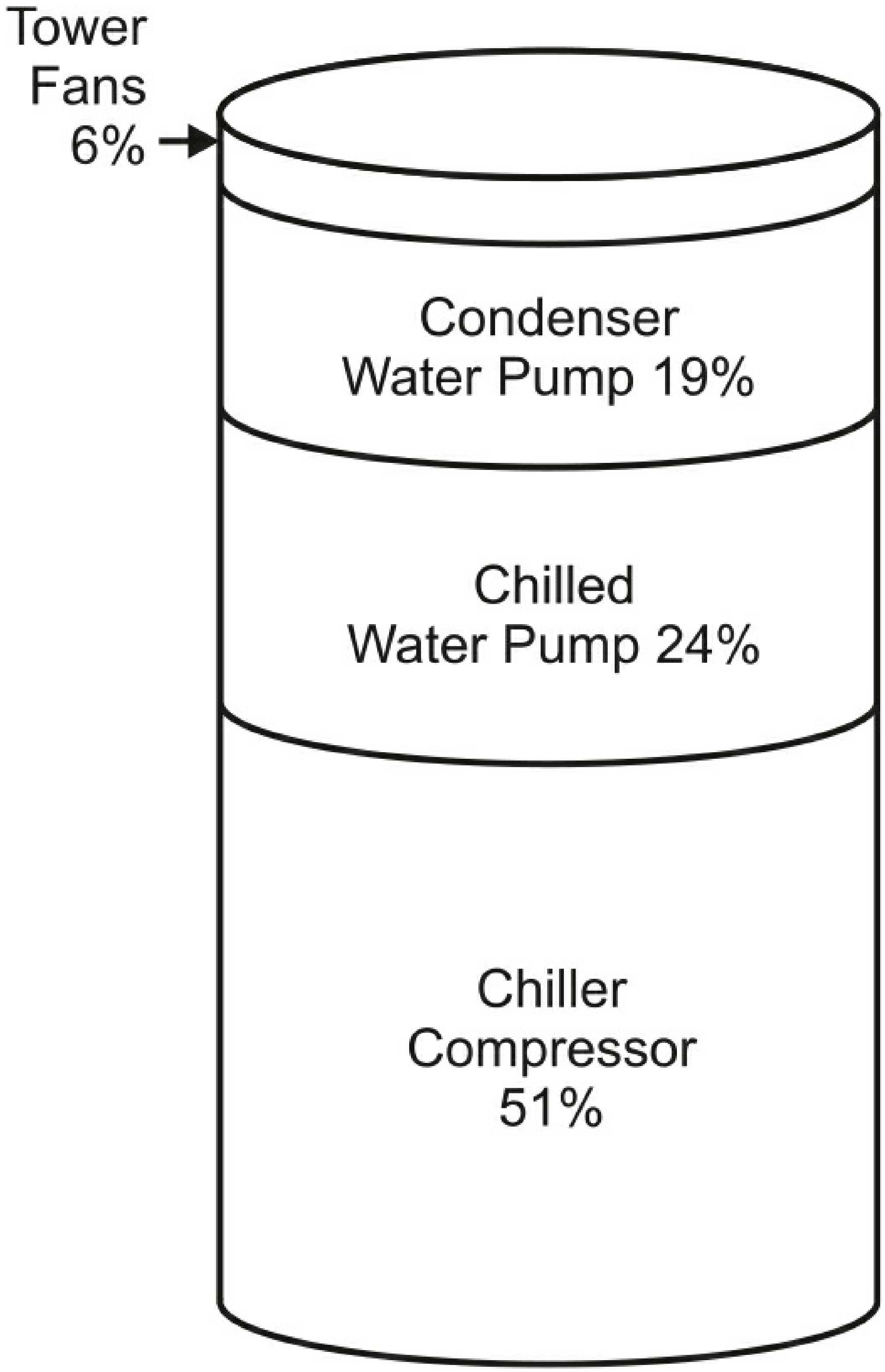


FIGURE 39.12 Typical chiller power consumption distribution.

Table 39.1 shows typical costs for refrigeration systems used in different applications. The lower cost for universities is due to the reduced demand in the summer when most students are not in attendance. An office building, like the Petronas Twin Towers in Kuala Lumpur, Malaysia, has 4.25 million ft^2 (395 000 m^2) of floor space. If the annual cooling operating cost were \$2.00/ft^2 (\$21.53/m^2), the total cooling bill would be about \$8.5 million/yr. Air conditioning is probably required all year in Kuala Lumpur because of the average temperature range of 72 to 90°F (22–32°C). While large facilities like this have a significant stake in maintaining peak performance to minimize cooling energy cost, even small facilities can benefit from good chiller maintenance and operation.

Type of Building	\$/Gross ft^2	\$/Gross m^2
College/University	0.5–0.7	5.4–7.5
Office building	1–3	11–32
Hospital	1.25–3	13–32

TABLE 39.1 Typical Annual Operating Costs for Chiller Systems

Unfortunately, chillers are often operated inefficiently or maintained poorly, resulting in higher energy costs, lower system performance and reliability, and shortened equipment life. The most common factors that contribute to reduced chiller efficiency include:

- Poor operating practices
- Ignored or deferred maintenance
- Poor cooling tower maintenance
- Oversized equipment
- Ignored energy saving features

Each of these factors affects chiller efficiency significantly, but all can be easily controlled or eliminated by proper operation and maintenance.

Thermal Energy Storage Systems

In some parts of the world, electric utilities offer lower electrical costs during off-peak hours, typically between 9:00 P.M. and 10:00 A.M. each day. One way to take advantage of lower off-peak electrical rates for comfort cooling is to produce and store chilled water or ice during the cheaper off-peak hours. During the day when the cost of electricity is higher, cooling is derived from the stored water or ice in the thermal storage tanks. TES cooling does not reduce energy usage, but the cost of providing cooling can be significantly reduced.

The two most common thermal storage designs are chilled water and ice storage. Chilled water TES systems require larger tanks than ice storage systems for equal cooling capacity. Chilled water at 40°F (4.4°C) can provide 20 Btu/lb (46.5 kJ/kg) of cooling, assuming it warms to 60°F (15.6°C) when cooling the building air. On the other hand, ice stores about 144 Btu/lb (334.7 kJ/kg) of cooling power, because of the latent heat of fusion at the freezing point. This makes ice storage more attractive from a system volume size. TES systems typically range from 10 000 to 4 million gallons (38–15 100 m^3) in capacity. Systems as large as 7 million gallons (26 500 m^3) have been used.

TES systems can be categorized as full-load or partial-load. The objective of full-load thermal storage is to shift the entire refrigeration load out of the period of peak electrical cost. The chiller must be sized to handle the entire capacity of the cooling load. The load profile in Fig. 39.13 illustrates full-load thermal storage, which is best utilized when cooling loads are short in duration, especially if they are high. In the partial-load leveling method, the chiller runs continuously, producing cooling capacity in the TES system at night and cooling the building directly during the day with help from the stored cooling. Figure 39.14 shows the load profile of a typical partial-load system. The chiller capacity can be smaller, because it does not need to handle the entire cooling load.

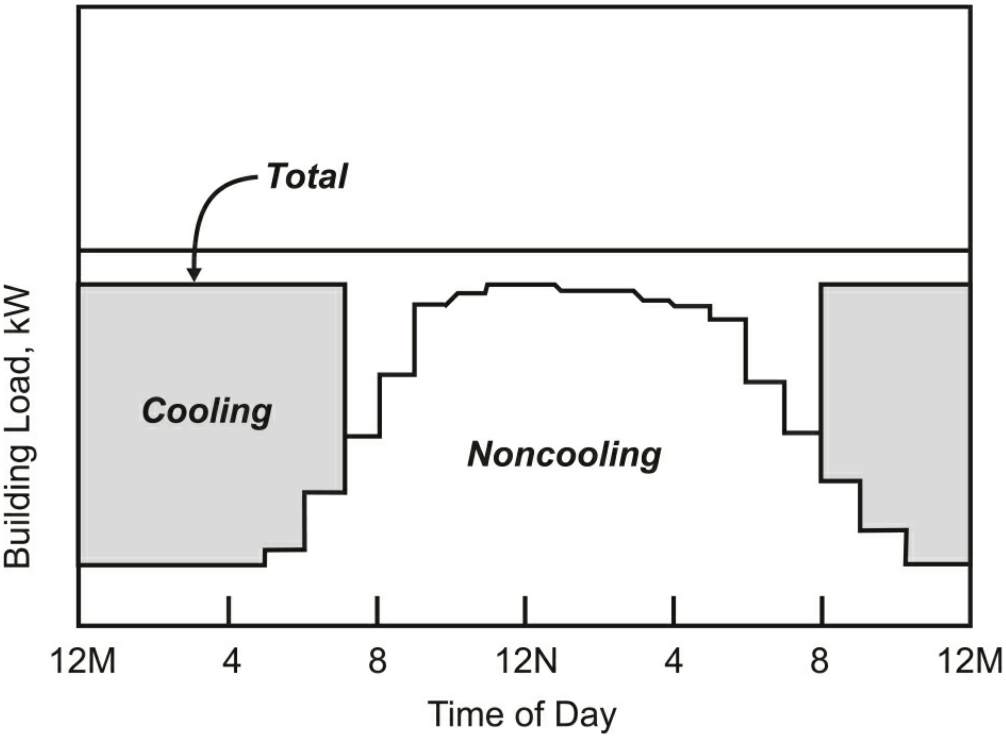


FIGURE 39.13 Full-load thermal storage runs the chillers only during off-peak hours for low electric rates.

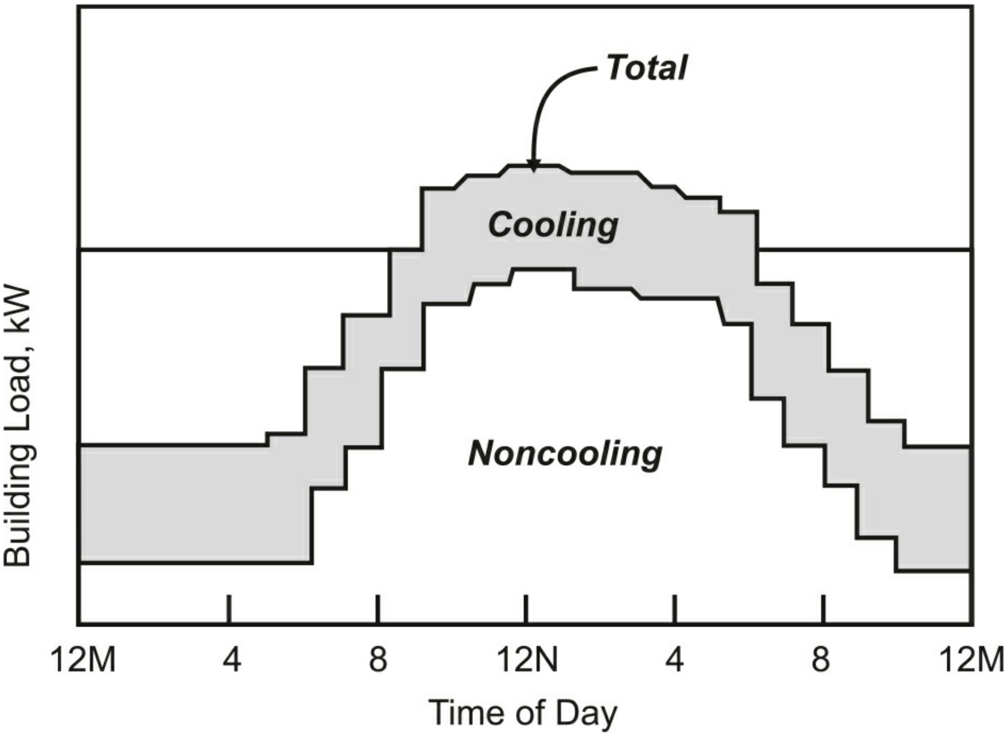


FIGURE 39.14 Partial-load thermal storage runs the chillers during off-peak hours to produce stored chilled water or ice to help minimize the chiller capacity needed during peak electric rates.

There are some important differences in the chilled water loops between on-demand and TES systems, from a water treatment perspective. The main difference is the storage tank in the TES system, which is not needed in on-demand systems. Therefore, TES systems are generally much larger. The on-demand chilled water system is typically completely closed and therefore a low oxygen environment. In most cases, the TES system storage tanks are open directly to the atmosphere, so the water can be constantly aerated. In-ground multiple-tank TES systems may be located in parking garages or other parts of a facility that allow contamination from dirt, rainwater, and other sources. Low flow or stagnant areas may exist in the tanks, where deposits can build up and create areas for microbial growth. Because of their open design, treatment options for TES systems must shift away from traditional closed loop inhibitors like nitrite, mainly due to degradation by microorganisms, which easily contaminate these systems.

Thermal Energy Storage System Problems

TES systems may experience a variety of operational problems due to their unique design. A multitude of factors can result in operational problems:

- Poor system design can cause problems with microbial contamination and sludge buildup in large single-tank systems, if the distribution headers are not designed properly. Deposits can occur in areas of the tank that do not have sufficient water velocity.
- Poor start-up (cleaning and passivation) can cause ongoing problems. Sometimes, only lines and equipment are cleaned and pretreated to remove debris, dirt, and mill scale. However, the storage tank must also be cleaned to allow the corrosion inhibitors to work properly and eliminate sites for deposition, microbial growth, and under-deposit corrosion.
- If water treatment is neglected, active corrosion, large amounts of iron in the water, and microbial growth can occur. These problems can foul the system and reduce energy efficiency.
- Intermittent operation can cause stagnant conditions for extended periods. Corrosion inhibitors can be locally depleted, leading to corrosion and the development of corrosion-based deposits. The lack of flow can affect the distribution of treatment programs throughout the

system.

- Inadequate mechanical removal of solids due to the lack of filters can cause sludge buildup in the tanks. Microbial growth in this sludge can contaminate the entire system.
- Lack of designed blowdown or replacement of water can lead to depletion of inhibitors and increased concentration of dissolved solids in the system.
- Open storage tanks can lead to contamination by a variety of materials, including dirt and microbial organisms.

TES offers the opportunity to reduce the cost of energy used for cooling. However, it increases the complexity of the system and its operation.

Thermal Energy Storage Treatment Programs

There is a variety of treatment programs available for TES systems. Control strategies from typical chemical treatment programs, to nitrogen blanketing and oxygen scavenger technology have been proposed. However, the more elaborate the program, the more difficult it is to control and maintain. Corrosion inhibitor treatments should be nondepositing in nature. Dispersant polymers should be included at times (dependent on iron removal ability from on-site side stream filtration) for dispersion of suspended material and iron. Economics of the biocide treatment program often restrict or minimize biocide use in TES systems. The use of nonoxidizers requires slug dosing of the material to achieve a sufficient biocide concentration to kill the bacteria. Typically, low-level feed of nonoxidizing biocides is ineffective for microbial control in TES systems and over use should be discouraged due to the potential for increased COD and TOC buildup from the bio-degradable nature of the products. Oxidizing biocides are not often used, because of the potential for corrosion from buildup of halogen and halides. However, the use of chlorine dioxide as alternate to the more commonly used oxidizing biocides (chlorine, bromine, and hydrogen peroxide) has shown to be effectively in reducing both planktonic and sessile micro-biological activity due to its persistent and elevated oxidative capacity without the related end product issues.

Data Centers

Data centers vary widely in size and design. In the past, computer servers would commonly reside in commercial multi use buildings and HVAC systems would closely resemble that of other commercial and institutional buildings. Past data centers would be a designated space within a building, sometimes as small as a closet or a few floors of a high-rise building.

With the emergence of the public cloud, social networks, mobile phones, and the Internet of things, computer server volume and density have continued to increase the amount of heat generated by the computing load. As densities have increased, so have the numbers and sizes of stand-alone data centers.

The evolvement of the data center industry has changed its cooling system landscape. Today, it is quite common for data center HVAC systems to be built for the single purpose of cooling computer servers and to be optimized for this single purpose. It is also common for servers owned by different tenants to be co-located in buildings occupied only by computer servers, requiring optimized cooling schemes to ensure reliability and efficiency.

Data center cooling systems can be tailored to the local daily outdoor ambient temperatures and humidity, and the cooling strategy aligned to the heat load. Most recently, there has been the emergence of mega data center campuses that contain thousands of servers and multiple cooling strategies at a single site based on the type of heat load being generated.

Water treatment in data centers has become increasingly complex. Design and operating practices can lead to unique water problems specific to a single system within the data center. Typically scale, corrosion, fouling, and microbiological growth are the greatest concern in data centers. These problems are solved with the same principals of water treatment that are utilized in other commercial and industrial HVAC systems. Also, because energy and water usage for cooling takes a significant part of data centers' utility bill, as the data centers grow bigger and bigger, treating water properly and efficiently has become more and more important for the data centers owners.

Data center cooling systems vary widely and are typically customized to the local prevailing climactic conditions. Broadly, the cooling approaches fall under air side economizer cooling strategies and water side economizer cooling strategies. These systems may be standalone approaches or combinations of several different cooling strategies depending on the individual data center needs. A typical evaporative approach involves running water over media with a crossflow of air (see Fig. 39.15).

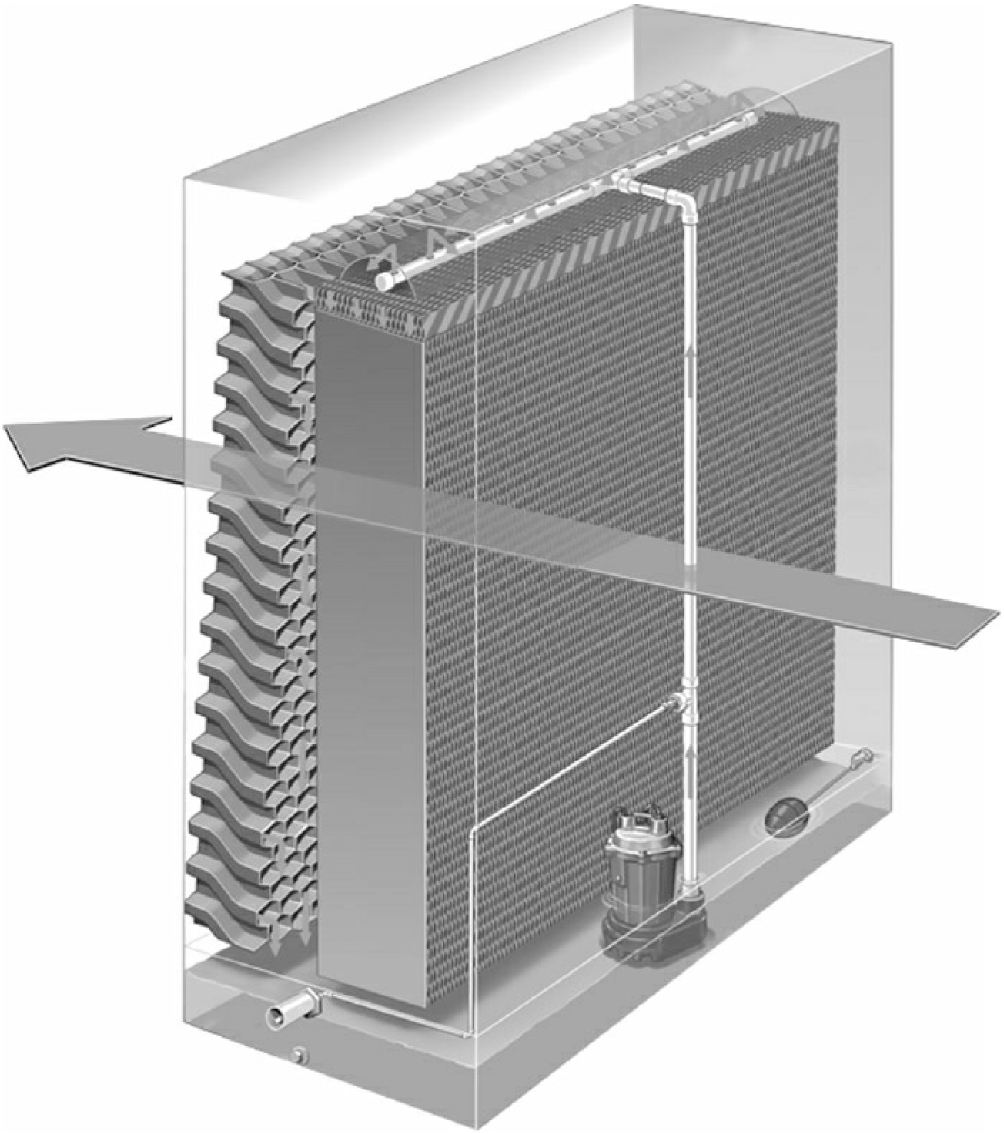


FIGURE 39.15 Typical data center direct air cooling utilizing evaporative media. (*Courtesy of Munters*.)

Air side economizer cooling typically takes the form of one of the following cooling configurations:

- Direct outside air system with direct evaporative cooling (DEC)
- Recirculating (closed) air system with indirect evaporative cooling (IEC)
- Recirculating (closed) direct outside air system, 2 stage indirect-direct evaporative cooling (IDEC)

- Indirect air to air heat exchange with direct evaporative cooling in secondary air (IOA + EC)
    - Mechanical cooling
    - Air cooled chiller coupled to chilled water coil in air handling unit (AHU)
    - Direct expansion packaged in AHU or separate direct exchange coil and remote condenser
- Cooling configuration options
    - Interior AHU—direct outside air with direct evaporative cooling
    - Exterior AHU—indirect outside air and indirect evaporative cooling

Water side economizer cooling typically takes the form of one of the following cooling configurations:

- Direct (open) evaporative cooling tower with flat plate (OCT + FP) heat exchange
- Indirect (closed) cooling tower with spray (CCT + spray)
- Mechanical cooling
    - Water cooled chiller (WCC) coupled with chilled water coil in AHU. Typically seen with OCT + FP
    - Air cooled chiller (ACC) coupled with chilled water coil in AHU. Typically seen with CCT + Spray
- Cooling configuration options
    - Computer room air handling unit (CRAH) is perimeter air delivery with chilled water coils
    - In-row unit has the cooling system in close proximity to the server rack with the cold air delivered via module fans and a cooling water coil
    - Rear door heat exchange (RDHx) is a passive form of cooling that combines the cooling coil sans fan within the server rack structure
    - Overhead coil heat exchange (OCHx) is a passive form of cooling

that combines the cooling coil sans fan within the server rack structure.

CHAPTER 40

The Food and Beverage Industry

Due to its intimate connection with public health, the food industry has a long history of surveillance of its activities by local, state, and federal agencies. The United States Congress passed the original Food and Drug Act in 1906. With subsequent legislation, that act controls the chemicals that are directly added to food such as salt, seasonings, and preservatives but also such chemicals as sizing in food wrap that may indirectly become food additives by contacting food.

In addition to the close control by the U.S. Food and Drug Administration (FDA), additional surveillance is imposed on meat and poultry processing plants through the U.S. Department of Agriculture (USDA). Chemicals cannot be brought into a meat or poultry processing plant unless approved by the USDA for its intended use, such as equipment cleaning or water treatment. Because of this close regulation, the choices of chemicals used in water and wastewater treatment, may be more limited in the food industry than in other major water-consuming industries.

One of the major long-term trends affecting the food and beverage industry is sustainable development. Sustainable development in the industry can generally be defined as corporate and individual plant performance initiatives with goals to reduce, conserve, reuse, or recycle those resources, which will reduce the corporation’s or plant’s environmental “footprint.” The aim is toward a goal where all the resources, whether they are natural, monetary, or human, are utilized to create, in essence, a zero-use system. Every resource would be fully replenished with a positive impact on individuals, communities, and the environment in which food-processing companies operate.

Sustainable development has three major components: social, environmental, and economic. The industry continues to focus on economic performance and improvement, but with vastly higher awareness and expectation for the total impact of its actions. This trend does not look to abate, and Nalco continues to develop and implement innovative, differentiated solutions that are financially, technically, and environmentally sustainable to contribute to industry and individual location improvements.

Although there are wide variations in the process steps in each of these industry segments, there are a number of common unit operations. The distribution of water in the plant can be put into three categories: process water, cooling water, and boiler makeup water. The percentage distribution varies considerably from a high of about 60% used for processing in the meat and poultry industry, to a low of only 15% in the sugar industry. However, 65 to 75% of the water used in the sugar and ethanol industries is for cooling purposes, with only 25% being used in the meat and poultry industry. Most food processing plants generate steam for cooking or processing, and water used for boiler makeup ranges from about 6% of the total usage in fruit and vegetable processing to about 15% in the fats and oils segment.

Process water uses include washing of raw product and process equipment, transporting product from one process area to another, and as part of the finished product. Cooling water may be used in refrigeration equipment, to condense steam from evaporators or turbines, or to cool process equipment such as compressors, process vessels, engine jackets, or sterilizer equipment.

Steam may be generated for cooking, sterilizing, heating evaporators, cleaning and sanitizing or comfort heating. In some industries, enough steam is required to justify installation of a turbine to extract power from the steam before it is sent to process (cogeneration). If the steam can come into direct contact with food, there are limits not only on what chemicals may be used for both steam and boiler water treatment, but also on their maximum concentrations.

Knowing the processing operations in a food plant is helpful to understanding water use; water may be used sequentially for several purposes. For example, the sugar industry has a very high requirement for condenser cooling water because of the evaporation and concentration of syrups. This cooling water is used for washing cane brought in from the fields before it is discharged, and it is categorized as cooling water rather than process water.

Because the problems of cooling water and boiler water treatment in the food industry are similar to other industries, this chapter will deal specifically with a regulatory review and process water, with some consideration of its contamination, control of foam generated during processing, and final treatment for disposal.

Regulatory Review

Since the beginning of time, people have been concerned with the quality and safety of food and medicine. King John of England put the first English food law into place back in 1202. His law prohibited the adulteration of bread with ground peas or beans. Over the centuries, the food industry has seen an increase in regulation on the local, state, provincial, and federal levels around the world, to ensure that products put on the market are safe, wholesome, and sanitary.

In 1906, the United States Congress put in place the original Food and Drug Act. This act has been amended over the years to increase its scope and depth, but the fundamental objective of this act, to ensure public safety and inform the public properly about products in the marketplace, remains constant. Under this act, manufacturers have a legal obligation to ensure products they market are safe to consume or use by the consumer. In addition, manufacturers have a legal obligation to ensure their products are promoted accurately and honestly based on scientific facts.

From a water treatment perspective, the FDA regulates the safety of all food products, except for meat, poultry, and egg processing. The FDA also regulates the safety of veterinary products, such as livestock feed and pet foods. In the industries where these products are produced, water treatment products are considered a food additive by FDA definition. The definition of food additive is any substance where the intended use results, directly or indirectly, in its becoming a component or otherwise affecting the characteristics of food. Livestock feed is controlled under this regulatory standard, because products used in livestock feed eventually end up in the human food chain.

Up until 1998, the USDA maintained the responsibility to approve products used in meat, poultry, egg, and processed meat product facilities. Registration of products with the National Sanitation Foundation (NSF) has now replaced the USDA approval.

Although many countries follow the USDA and FDA guidelines, a manufacturer must comply with all regulations specific to the region or country in which its products are sold.

Depending on the market, food manufacturers may also require additional approvals or certifications, such as NSF Standard 60, which regulates materials used in potable water, Kosher, or organic certification. These approvals/certifications require further raw material restrictions for the water treatment programs and ultimately for the end use manufacturer.

Fruit and Vegetable Processing

The purpose of processing fruits and vegetables is to stop or significantly slow down spoilage, prevent food-borne illness, and maintaining the nutritional value, texture, and flavor. Thermal processing is a method of food preservation, where a food and its container are rendered commercially sterile by the application of heat alone, or in combination with pH adjustment or chemical additives. The hermetically sealed container (cans, glass jars, pouches, and plastic containers) maintains the sterility of the food. Commercial sterility, which is synonymous with shelf stability, means the destruction of all viable microorganisms of public health significance, and those capable of reproducing under normal nonrefrigerated conditions of storage and distribution. Commercially sterile, aseptically processed and packaged foods are also considered thermally processed foods.

There are many different methods to meet commercial sterility criteria, including thermal processing, freezing, aseptic packaging, pasteurization, cooking, and vacuum sealing. Conventional thermal processing involves filling containers with hot or cold food, sealing them hermetically, and heating them in a temperature-regulated vessel, generally called a retort. The heating source may be steam, hot water, or a steam/air mixture.

A different and newer thermal processing method is aseptic processing. The number of systems and the variety of products being aseptically processed are rapidly expanding. This method involves the sterilization of the product and package separately and bringing them together in a sterile environment.

General Process Overview

Prior to being canned, food undergoes a variety of production processes, depending on its type. Vegetables, for instance, are graded, trimmed, washed, and blanched. The latter process inactivates the enzymes present, removes gas from the tissues causing some shrinkage, and softens the tissues, enabling more to be packed into the cans without damage. Whether it is steam generation, cooling, or fluming, water is used extensively throughout fruit and vegetable processing. Water has been the media of in-plant conveyance (fluming) of most fruits and vegetables in this industry segment. Not only has this choice been economical, but it provides additional benefits in prewashing and cooling. However, because of the pollution load that results from fluming, and the focus on water conservation, new methods of conveyance (air, vacuum, and mechanical) are now becoming more common, so washing and rinsing which may require as much as 50% of the total water used in process operations, is a separate step. Grading and sizing are sometimes accomplished simultaneously with washing.

After fruits and vegetables are washed, peels are removed in a variety of ways. Steaming or soaking in caustic solutions is the most common, but air and mechanical peeling are also used. Dry caustic peeling of potatoes is gaining acceptance within the industry as a means of greatly reducing pollution loads.

Water blanching is generally used for vegetable processing to remove air and to leach solubles before canning. Steam blanching of vegetables is usually used to destroy enzymes before freezing or dehydration. The blanching effluent stream contributes a significant portion of the total pollution load in canning operations.

The cans are filled, hermetically sealed, and then thermally processed to sterilize the contents prior to labeling, packing, and final dispatch.

After the sterilization step, cans are quickly cooled with water, causing steam in the headspace to condense, creating a partial vacuum inside the can. If there were to be a pinhole fault in the can seam, this could cause cooling water to be drawn into the can. Both *Salmonella* and *Staphylococcus* have been seen in cans contaminated via this route. This obviously dictates that only disinfected cooling water be used.

Thermal Processing

All types of natural food products (other than fresh food intended for immediate human or animal consumption) must be thermally processed.

The canning industry recognizes two categories of food products: high acid and low acid. The difference is in the degree of thermal processing needed and the influence of final product pH on long-term preservation of the food. Low-acid foods ($pH > 4.6$) require higher heat processing treatment. Examples of low-acid food products are carrots, beans, peas, meat, corn, and fish. High-acid foods ($pH < 4.6$), such as berries, sauerkraut, plums, pears, apricots, and tomatoes, require less heat processing, because bacterial spores are already partially inhibited by the low pH.

Hydrostatic Sterilizer

Hydrostatic sterilizers are designed to continuously process food products packaged in a variety of container types and sizes including metal, glass, and plastic containers. These sterilizers are specifically suited for processing products that require long cook and cool times, high throughputs (up to 2000 containers per minute), and from those deriving little or no benefit from agitation.

Sterilizers operate on the hydrostatic principle, with the pressure of saturated steam in the sterilizing zone, balancing heads of water. The temperature prevailing in the sterilizing zone depends on these heads, which are adjustable. The product in the containers is conveyed through the machine in carriers fitted between two endless steel chains. Automatic feed and discharge systems are used to introduce the filled containers to the machine and remove them from the machine, respectively.

Manufacturers of hydrostats claim the following advantages:

- Savings in floor space
- Reduced heating and water costs because of regenerative heating and cooling
- Capability of processing all sizes of cans, glass containers, and pouches
- Constant temperature operation due to hydrostatic control
- Minimal thermal and physical shock to containers because of low chain speed [1–6 ft/min (0.3–1.8 m/min)]

The main disadvantages of hydrostats are the large capital investment required. Also, maintenance costs are relatively high due to a greater number of moving parts. Hydrostats are usually preferred to continuous rotary cookers when the following conditions are involved:

- Year round operation
- When strict temperature control is required (where products may be

temperature sensitive, for example, product discoloration at high temperature)

- Filler speed at least 400 cans per minute on consumer sizes

A hydrostatic sterilizer process (Fig. 40.1) generally consists of four stages: a water-filled leg for can preheating; a steam pressurized cooking section called a steam dome where the sterilization process takes place, a water-filled leg for can precooling and a final atmospheric cooling section, usually consisting of a cascade or spray-type cooling tower (not to be confused with a standard evaporative cooling tower). In some cases, an additional pressure cooling zone is required.

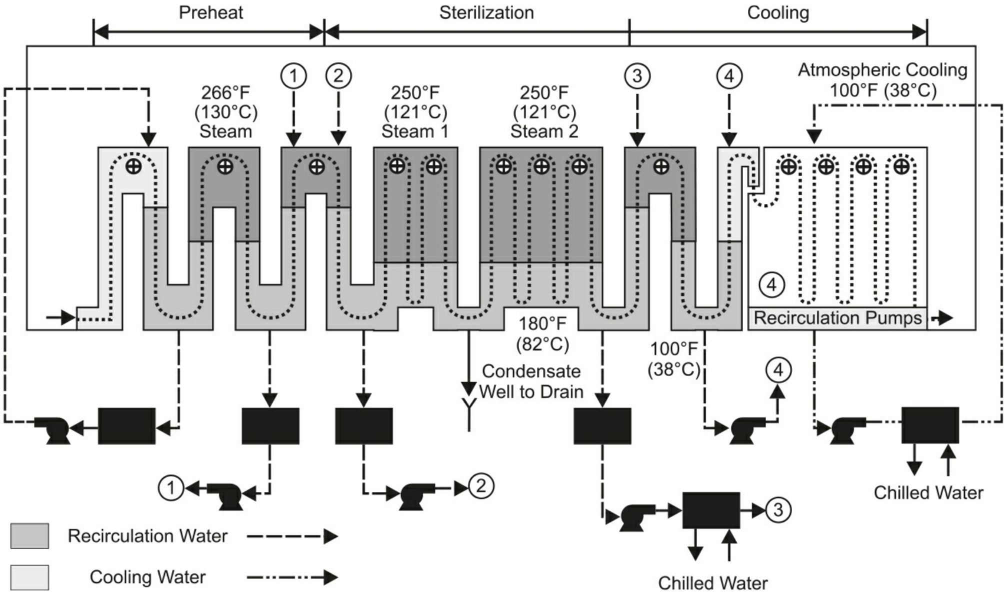


FIGURE 40.1 Hydrostatic sterilizer.

Hydrostatic In-Feed Leg (Preheat Section) This section contains a column of water to act as a hydrostatic water valve that allows the entrance of containers into the sterilizing chamber (steam dome) without the loss of pressure and temperature. As the cans are fed into this leg at temperatures of 185 to 194°F (85–90°C), they are exposed to increasing pressure as they pass through the column of water. If no means were taken to prevent it, rapid exposure of the container to processing pressure would crush it. In order to prevent this problem, the water in this leg is heated either by direct steam injection or a heat exchanger. In this way, the contents of the can are heated, and an internal can pressure is built up to withstand the external water pressure.

Sterilizing Chamber (Steam Dome) Cans enter the steam dome where appropriate temperatures of are maintained as required for the specific product being processed. The time containers remain in this section is controlled by both the number of chain passes built into the machine and by chain speed. This depends on the heat penetration characteristics of the product being sterilized. The objective here is to achieve the sterilizing temperature in the center of the can for the predetermined processing time required for complete sterilization.

Hydrostatic Discharge Leg (Precool Section) On discharge from the sterilizing chamber, the internal pressure in the container will be relatively high. With insufficient external pressure it would expand enough to lose the lid. To prevent this, the leg is cooled to ensure that the internal can pressure is reduced gradually and can integrity is maintained. This temperature control can be achieved by:

- Recirculation of water between preheat and precool sections
- Use of an exchanger with cooling water on one side
- Direct cooling water injection into the precool (discharge) leg
- A combination of methods

In some applications, it is not possible to remove the heat quickly enough from the cans during passage through the precool leg. In such cases, a pressure cooling leg is employed where compressed air (air-over pressure) is applied to maintain container integrity until they are further cooled by passage through the atmospheric cooling section (cooling tower).

Atmospheric Cooling Section The final stage of the process is to cool the cans to their final targeted temperature of 95 to 110°F (32–43°C) by making several passes through a series of water sprays or cascading cooling water in the cooling tower section. In some machines, this is followed by passage through an immersion tank (cooling trough) prior to discharge. Due to the possibility of “micro-leakage” of cooling water into the cans, bacteria counts must be maintained at a very low level, usually below 100 CFU/ml. The FDA requires a trace level of a sanitizer (usually chlorine or bromine) to be maintained in the water.

Rotary Horizontal Sterilizer

Rotary sterilizers provide continuous container handling with intermittent container agitation. These systems employ one or more processing shells for sterilization and one or more cooling shells depending on the product and process conditions. They are designed to take sealed containers continuously from the seamer equipment through the sterilizing and cooling operations. The rotary shells can be arranged in various configurations which may include preheating and/or pressure cooling shells in addition to the atmospheric cooling and sterilizing shells (Fig. 40.2).

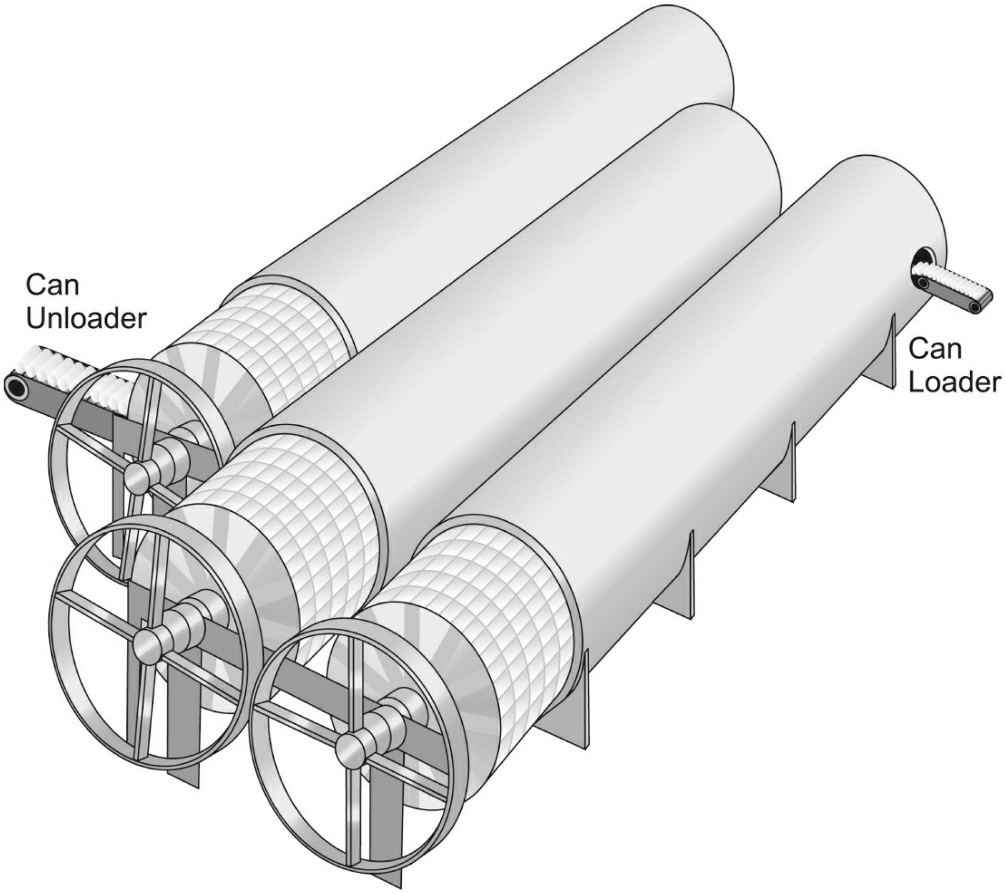


FIGURE 40.2 Rotary horizontal sterilizer.

Most of the rotary sterilizer shells are 58 to 112 inches (1.47–2.84 m) in diameter and vary in length from 15 to 52 ft. (4.6–15.8 m). Although variations can be found based on differing processing needs, the length required is dependent on the process time, production speed, and container size. Some models can operate at process temperatures as high as 292°F (144°C) and some at line speeds of 800 containers per minute.

Rotary sterilizers can be either pressurized or atmospheric. In pressurized sterilizers, steam is injected directly into the cooking shell. Steam is used in the cooking shell and in pressure cooling shells (directly injected to the water to control pressure and temperature), and water is used in the pressure and atmospheric cooling shell. For atmospheric cookers, water in the cooker shell is heated through direct steam injection or by recirculating the water through a heat exchanger. Atmospheric cookers are normally found only in vegetable and fruit processing facilities.

Inside the cylindrical processing shell is a rotating reel with "angles" to hold the containers. A fixed spiral "*T*" is permanently attached to the inside of the shell. The turning of the reel and the lead of the spiral *T* move the containers through the length of each shell.

As the containers advance through a sterilizer shell, they are subjected to a targeted temperature, which sterilizes the contents. The target temperature will vary depending on the product. When the containers reach the end of the processing shell, they are transferred to a cooler shell.

Continuous cooling can be accomplished in an atmospheric cooling shell, a pressure cooling shell, or both. Depending on the product, container size, and processing temperature, the pressure cooling may be necessary to prevent buckling of the containers (Fig. 40.3).

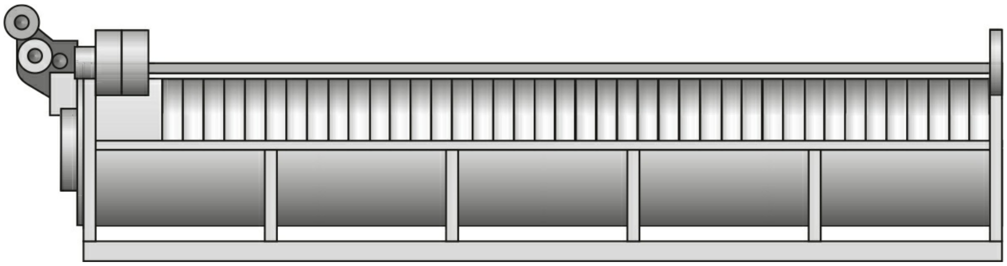


FIGURE 40.3 Rotary pressurized cooler.

Continuous rotary sterilizers offer several advantages over still retorts. One advantage is the reduced process time due to intermittent agitation. The agitation occurs when the containers roll on the bottom of a shell, resulting in product movement within the container. This movement increases the rate of heat penetration. The product agitation allows the use of high processing temperatures, and in some instances, product uniformity and quality are improved. Another advantage is the possibility of reduced production costs through savings in labor cost and steam consumption.

Some of the possible disadvantages associated with continuous rotary sterilizers include the initial and the fact that each system will accommodate only a limited range of container sizes.

Still Retorts

Retort sterilizers (often referred to as still retorts) work in a batch operation, with the cans normally held in carts or baskets. These systems use one processing shell for both cooking and cooling. They are designed to process sealed containers either stacked in layers separated by plastic divider sheets or simply dumped in metal baskets. In this process, the cans remain in the same shell for both the cooking and cooling processes.

All still retorts are of the pressurized type, but the method by which the cans are heated and cooled may vary. There are two distinct ways heat can be exchanged to cans in a retort sterilizer. The first is by direct steam injection, where the steam is distributed in the retort by means of steam manifolds. The second is by exchange of a recirculated body of water in the retort heated and cooled through a heat exchanger. The major difference between these two methods is that with direct injection of steam, there is very virtually no water in the retort during the cook cycle (only a small amount of accumulated condensate) when operated properly. When a heat exchanger is employed, there is water in the cooker throughout multiple cycles. This type of retort is sometimes referred to as a “Sterile Water” retort. Some retort systems utilize direct steam with retained cooling water cooled via a heat exchanger interfacing with an external cooling tower.

The cook cycle time period will depend on the size of the cans and the product being processed. Once the sterilizing process is completed, the steam is shut off.

Following the sterilization cycle, cooling water is either admitted to the retort (in direct steam injection-type systems) or circulated through a heat exchanger which is utilized throughout the duration of the cooling cycle. During the cooling cycle, air or steam pressure must be employed to allow for gradual external pressure reduction to counter the internal pressure of the cans while they cool. This prevents the cans from over-expanding and becoming misshapen or leaking. Since the water in “Sterile Water” retorts often remains in the machines for long periods of time, accumulation of product in the water or breakdown of water treatment chemicals must be considered when designing chemical programs.

A commonly used variation in the batch system is the Immersion Retort. These units utilize a water-cook system where recirculated water is heated via direct steam injection. The containers being processed are held in baskets which are rotated in the machine to agitate the contents. The cook water is dispensed from a holding tank normally located on the top of each unit (some systems utilize a common tank for a given number of retorts). This water is held at a high temperature between sterilization cycles to allow for more efficient processing.

The cooling cycle in Immersion Retorts has two phases. The first brings in cooling water (sometimes fresh makeup water) which displaces the hot water to the holding tank allowing some of the cooling water to migrate to the hot water vessel. After the first phase, the cooling water circulates through the lower drum with the baskets continuing to rotate. The cooling water temperature is controlled with a temperature control valve assembly that lets the cooling water enter and exit the lower drum or with a plate and frame heat exchanger interfacing with external cooling water.

The advantages of still retorts over continuous rotaries include:

- Lower capital cost
- Greater flexibility in container size due to carts as opposed to angles and flights in rotaries and hydrostats
- Equipment easier to monitor and control

The major disadvantages of still retort sterilizers are longer processing time due to lack of agitation and extra time associated with loading and unloading the retort and the amount of steam that must be vented in order to remove all the oxygen from the vessel at the beginning of the sterilization cycle.

Table 40.1 compares the steam and cooling water usage for the three types of retorts used in the food industry.

Type of Equipment		Steam Use lb/lb (kg/kg) of Product	Cooling Water Use gal/lb (L/kg) of Product
Still retort		0.3–0.4	0.6 (5)
Rotary sterilizer	Pressurized	0.15–0.2	0.2–0.3 (1.7–2.5)
	Atmospheric	0.3	0.2–0.5 (1.7–4.2)
Hydrostatic sterilizer		0.12–0.15	0.1–0.2 (0.8–1.7)

TABLE 40.1 Typical Steam and Cooling Water Requirements for Various Types of Sterilizers Equipment

Containers

The most common containers are steel cans. Steel cans used in food packaging are usually made of electro-tin plate steel (ETP) or tin-free steel (TFS). Organic coatings such as vinyl, epoxy, or enamel are used to protect both the inside and outside of all TFS cans. Tin cans typically require these coatings on the inside and sometimes the outside to protect the base metal from corrosion.

A trend toward reduced tin weight and changes in the chemistry of the organic coating as well as an increasing use of easy-open ends puts a far greater pressure on correct water treatment to maintain good container appearance and integrity.

Other types of packaging are also thermally processed. Aluminum cans, glass jars, glass or plastic bottles, plastic trays, and flexible pouches are other types of food containers that are becoming increasingly popular.

Water Treatment Objectives

Specific challenges found in processed and canned food plants include the following:

- Food safety
- Container appearance
- Equipment protection
- Sustainability
- Wastewater

Food Safety

Poor microbiological control in sterilizer cooling water is one of the primary causes of product spoilage. Best Practice calls for total bacteria counts to be maintained at less than 100 colony forming units per milliliter (CFU/ml). This is a challenging task as there is always a varying amount of contamination from lubricants and food product in this water. Unfortunately, the high halogen demand often employed to control bacteria in this water and relatively high temperatures can be corrosive to the equipment, particularly in the vapor space, and cans.

Container Appearance

The primary objective of a water treatment program in sterilizer systems is to minimize container spotting and staining due to equipment corrosion byproducts, organics in the water or mineral salts deposition. Most companies have a low tolerance for container spotting as it hurts "shelf appeal" for their products in the super market. Also metal cans may rust later in storage as a result of the hygroscopic nature of mineral or organic deposits on cans.

Another concern is that excessive deposits (scale and corrosion products) inside the equipment can actually block the pathway of the containers, in particular on rotary cooker spirals, and may scratch or dent the metal surface of cans. Once scratched, the container is more likely to experience postprocessing corrosion.

Can shelf life is a major concern for companies that maintain a large inventory of product that may ship to customers a relatively long time after it is processed. This is of also a concern for products intended for export, as corrosion, that can accelerate during overseas transit, may negatively impact the integrity of metal containers. There have been examples of entire shipments of cans refused by Asian customers, due to the presence of a very minor corrosion on cans.

It is important to be aware that lubricants are used to protect equipment and maintain smooth operation. Varying levels of these lubricants will be found in retort cooling water. This can leave a film on cans, making labeling difficult. With a well-designed water treatment program including the correct surfactant treatment, this film can be minimized.

Equipment Protection

The second most important water treatment objective in Thermal Processing plants is to prevent scale and corrosion in the processing equipment. Unplanned equipment failure during the season is very costly not only in the capital cost of repair but, more importantly, in production loss. Seasonal plants generally run 24 hours a day, seven days a week, and cannot afford any downtime. The cost of inadequate protection of sterilizer systems is a long-term depreciation problem affecting plant equipment amortization and capital plans.

A hydrostatic sterilizer can cost as much as 8 to 10 million U.S. dollars (chain replacement is typically over 1 million U.S. dollars with several months lead time for delivery). A Rotary sterilizer shell costs anywhere between 0.3 and 1 million U.S. dollars. Even though the equipment life is generally over 30 years, moving parts and “wear parts” such as chains, frames, chain guides, and rails are more directly affected by corrosion and scaling problems, leading to costly repair or replacement.

Sustainability

Most companies today are deeply concerned with sustainability in their factories. The cost of water both incoming and discharge is rising rapidly on a global basis. Also companies are increasingly concerned with their plant operations impact on the environment due to pressure from their customers who require documentation of the implementation of “green projects.” Recycling and heat recovery projects tied to sterilizer operations are great opportunities for impressive reduction in water and energy consumption. It is important that such project planning include the impact on water conditions as they tend to increase the holding time of contaminated process water. Proper filtration and offline cleaning and sanitation procedures must be included in such projects. Failure to do so will negatively impact container appearance and, more importantly, the ability to maintain low bacteria levels in the cooling water systems.

Wastewater

As with all other industries, food processors are now forced to reduce the pollutant loading of their effluent water. This pollution loading varies enormously from one type of product to another. For example, in the processing of asparagus, the biochemical oxygen demand (BOD) and suspended solids are usually below 100 mg/L, whereas in the production of whole kernel corn, the

BOD and suspended solids may be several thousand milligrams per liter. The solid wastes also vary considerably from one product to another.

Although many canneries are served by municipal sewage systems, a growing number operate their own waste treatment facilities. Those in farm areas where land is available have been successful in using spray irrigation as a means of disposal reducing the volume of water requiring treatment. However, changing environmental protection agency (EPA) regulations have reduced the volume of water that can be used in such applications. As a result, the demand for improved wastewater strategies has greatly increased.

Meat and Poultry

A packinghouse for beef or pork slaughtering will include holding pens for the animals, a kill floor, chilling coolers, and shipping facilities. There may be an inedible/edible rendering department, a hide cellar, and facilities for processing other by-products such as blood. The process is continuous, with animals entering in a steady stream in one end and product leaving at the other.

Live poultry are unloaded at the processing plant onto a moving chain and then taken to the killing station. The birds are then scalded with hot water to remove the feathers, assisted by mechanical beaters and manual pulling. Residual hair and feathers are singed off with a flame or by wax stripping, and the birds are then surface washed. The birds are eviscerated manually and washed internally and again externally. The carcasses are then chilled or frozen, packaged, and shipped to market.

Water Needs

One of the key water needs of the meat packing industry is centered around a requirement for reliable quantities of 140°F (60°C) and 180°F (82°C) “on demand” potable hot water. Internal deposition in the potable water system is likely. The three main causes of potable water system problems are:

1. Heat exchanger, direct steam/water heater, or hot water delivery lines scaling and being unable to produce enough hot water at the use point.
2. Chips and scale from the heat systems or water distribution system breaking off and depositing on the carcasses or meat being processed.
3. Contamination of the meat products due to “red water.” This results

from iron deposition in any point of the system being sloughed off and making its way to the processing lines.

All chemicals used in and around meat packing plants require regulatory approval. The approval may vary based on the process area or plant hazard analysis critical control point (HACCP).

Primary boiler steam load is for the operation of water heaters required for the 140/180°F (60/82°C) water systems. Hot water heat exchanger condensate is normally returned. If the plant has rendering cookers, they are typically operated at 20 to 30 psig (138–207 kPag), and condensate may be returned. If returned, contamination by grease can be an issue.

Defoamers

Defoamers are used in processes such as scalding water, wastewater, washing water, dehairing systems, rendering cookers, and protein recovery. Excessive foam may cause production slowdowns and increase the risk of product contamination. As a rule, defoamers should be FDA or USDA approved.

Ammonia Compressor

This unit is the heart of most meat processing cooling water systems. Warm ammonia gas comes to the compressor from the coil cooling units located throughout the plant. The compressor compresses this liquid into a superheated gas. The gas then travels to the shell-and-tube heat exchanger or the evaporative condenser, where heat is exchanged from the ammonia and the gas becomes a liquid. The liquid drains to an accumulator and is available to be sent back to the coil units, where it removes heat (and thus cools) by becoming a gas.

Major meat processing plants typically have a number of ammonia compressors, often specifically designated to certain plant areas, and staged on and off through computerized controls based on suction side head pressures.

A special type of system is found in a meat plant that practices rendering. This shell-and-tube rendering vapor heat exchanger, transfers the waste heat of the process vapors to the incoming process water. This system needs to be carefully monitored, because high and varying temperatures from the rendering cookers can cause deposition.

Odor Control

Odor control chemical additives can be grouped based on their mode of action. These include:

- Masking agents, deodorants, and perfumes
- Counteractants
- Oxidants and other microbiocides
- Enzymes or biological augmentation
- Chemical precipitants and scavengers

Biofiltration is an odor treatment process, where contaminants and odor causing agents are adsorbed and filtered through biologically active media compost. The main by-products of the breakdown are water and carbon dioxide. Biofilters are extremely effective when they are well managed, and can reduce odor emissions by 90%, hydrogen sulfide by 85%, and ammonia by around 50%.

Gas Scrubbers

The most commonly used scrubbers in the meat processing industry are preformed spray, packed bed, multistage wet scrubbers that are very effective for high intensity odor control. The plants use Venturi scrubbers to remove coarse solids loading before treatment in the primary multistage unit. Plants may treat process and fugitive emissions by ducting the plant ventilation air through a single-stage wet scrubbing system, in order to minimize odorous emissions. More plants are considering polishing scrubber exhaust with biofiltration.

Rendering

Rendering and waste product utilization are major factors in the economics of meat processing. Rendering plants process animal by-product materials for the production of tallow, grease, and high-protein bone meal. Plants that operate in conjunction with animal slaughterhouses or poultry processing plants are called integrated rendering plants.

Plants that collect their raw materials from a variety of offsite sources are called independent rendering plants. Independent plants obtain animal by-product materials, including grease, blood, feathers, offal, as well as entire animal carcasses. These materials come from butcher shops, supermarkets, restaurants, fast-food chains, poultry processors, slaughterhouses, farms, ranches, and feedlots.

Wastewater

Waste treatment systems in the meat packing industry and in further processing plants are used to remove suspended solids, oil and grease, blood, and BOD from the effluent water before discharge to a receiving stream, a publicly owned treatment works (POTW), or for agricultural irrigation use. Wastewater from slaughterhouses and packinghouses contain organic matter (including grease), suspended solids, and inorganic material such as phosphates, nitrates, nitrites, and salt.

Most meat processing plant wastewater treatment consists of equalization followed by dissolved air flotation (DAF) and some type of secondary biological system. Sludge from the DAF and biological system is then pressed or dried and disposed of via land application, landfill, or recycled to recover nutrient value. Recycling of DAF sludge requires the use of generally recognized as safe (GRAS) sanctioned polymers.

In older plants, located in the countryside, the secondary system is often a simple aerobic pond or anaerobic lagoon, followed by discharge of the water for irrigation use. The ponds are then dredged on a frequent basis (2–3 years) and the sludge dried before being land applied. In newer, modern plants, the secondary system may have a clarifier to process the spent biomass.

The Beverage Industry

The beverage industry is a major consumer of water, much of which becomes part of the final product. The balance is used for clean-in-place (CIP) operations, pasteurization, container warming or cooling, cooling of compressors and refrigeration equipment, and makeup to boilers producing steam used for cooking, evaporation, heating of pasteurizers, and space heating.

The water used in the product must, of course, be potable; in addition, the water quality can have a significant impact on the taste of the finished beverage. In the soft drink industry, for example, it has been historically common practice to lime soften the water for hardness and alkalinity reduction. However, membrane filtration processes, such as ultrafiltration (UF) and reverse osmosis (RO), are gradually replacing lime softening. In many facilities, the water is passed through activated carbon for the removal of chlorine and residual tastes or odors due to organic contamination. Most soft drink bottling plants have boilers to provide the heat required for CIP operations and potentially for bottle molding operations.

Bottled water is a large portion of the overall beverage market. There are many different types of bottled water operations. This includes facilities that bottle spring water and plants that simply bottle processed city water. Unit operations vary depending upon the company and the water source. However, it is common to see media filtration, carbon filtration, and membrane filtration. The goal is to provide water that is free of microbial and taste contamination. Regulations regarding the allowable concentration of specific contaminants in water are detailed and growing every year. Many of these facilities make their own plastic bottles. This typically involves blow-molding operations, which require heating (steam) and cooling with closed and open recirculating cooling loops.

Breweries, fruit juice bottlers, and distilleries operate their own steam plants, because steam is required for cooking raw product and pasteurization, and is the energy source for distillation and evaporation. Breweries generally pasteurize or warm the beer once it has been placed into containers (bottles or cans). This operation requires steam and cooling water. An increased emphasis has been placed on reducing overall water usage in every brewery. By 2007, the average water usage was five liters of water for every liter of beer produced. The unit operations in breweries and distilleries are quite similar to those found in the chemical industry in principle, but special designs enable the process equipment to be readily cleaned to prevent microbial contamination of the product, and to avoid risks to the public health.

Special designs of piping and fittings, such as long-sweep pipe elbows, are used throughout the food industry because of this need for sanitation (Fig. 40.4). Highly polished stainless steel, Monel, or chrome-plated steel eliminates scratches, nicks, and crevices, which could offer a home for bacterial growth. The careful cleaning of equipment after each use creates a special problem of pollution control in that spent chemical cleaners, especially those containing biocides, often interfere with the performance of pollution control equipment.

FIGURE 40.4 Typical filter installation in the food and beverage industry. Note the use of special stainless steel piping and fittings. (*Courtesy of Croll-Reynolds Engineering Company, Inc.*)

Two water-using systems are unique to the food industry and found in the beverage market: the bottle and container washing systems and the pasteurizer.

In the bottle washing operation, both cleaning and sterilization are required, and detergents and biocides are applied to match the severity of the problem. If the bottle washer is handling returnable bottles, it is important to use effective cleaning chemicals, since there is no way of knowing what might have been in the bottles when in the hands of the public. Typical cleaners are a mixture of sodium hydroxide and surfactants or chelants. Because of this, it is beneficial to have softened water for washing and rinsing, as this reduces the demand for detergents and greatly facilitates the drainage of the bottle after rinsing for spot-free surfaces.

When strongly alkaline cleaners are used, these provide a biocidal effect that depends both on the length of time the chemical is in contact with the bottle, and the causticity of the cleaning solution. Even with this protection, however, chlorine is often applied to the final rinse water to ensure sanitation.

In the tunnel pasteurizing operation, as practiced in breweries, the bottled product is moved through the pasteurizer to halt the growth of specific spoilage organisms. A controlled temperature water bath then slowly brings the beverage to approximately 140°F (60°C), and holds it for the required time to ensure that the entire contents of the bottle have been pasteurized. Multiple heating and cooling stages are used to prevent thermal shock to the product and container breakage. The goal for the final product temperature is to reduce it as much as possible without dropping below the dew point. If the container sweats, difficulties arise in the packaging operations. The temperature in the pasteurizing section is maintained by circulating hot water, and the chilling sections may be tied into a cooling tower and supplemented with a closed chilled water system (Fig. 40.5), although once-through cooling water is still widely used.

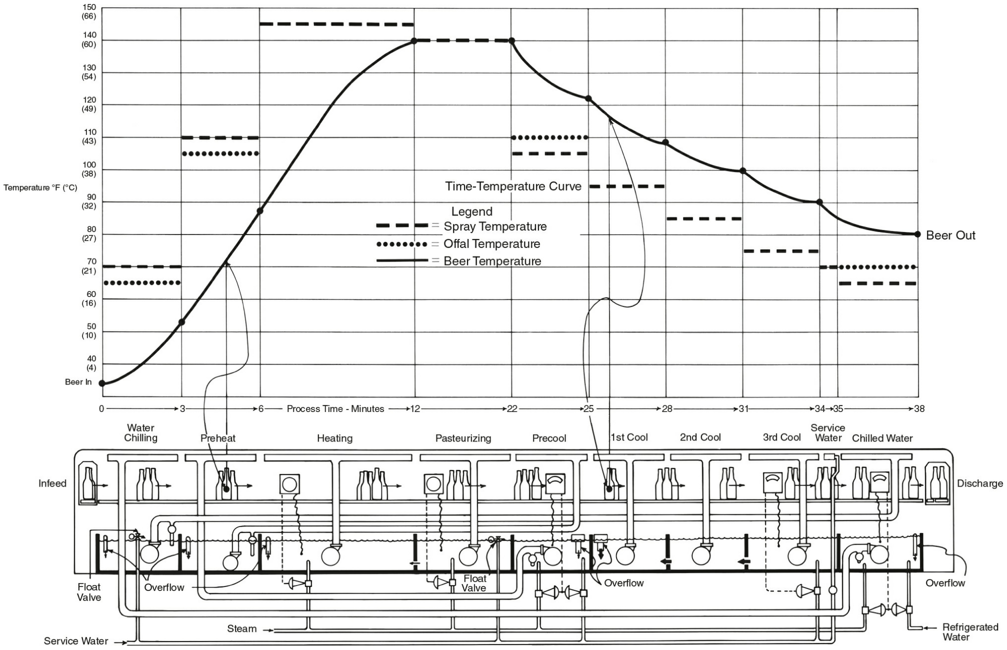


FIGURE 40.5 Flow of product and water through a pasteurizer for careful control of beverage temperatures. Flows are cascaded for energy recovery. (*Courtesy of Barry-Wehmiller Company*.)

In the event of bottle breakage, these water systems are inoculated with nutrients (the beverage), and microbial activity may quickly get out of hand. Common industry practice is to utilize chlorine or bromine treatment programs to keep this under control.

For the most part, beverage industry wastewaters are handled by municipal sewage systems. This may require the plant to install equalization facilities to unify the composition and flow rate and to adjust pH. In-house handling of strong wastes, such as chemical cleaners, may be necessary to make the equalization program effective.

A number of large breweries and distilleries operate their own waste treatment facilities. While conventional biological treatment had been the norm for many years, the last 15 years has shown a significant increase in the use of anaerobic pretreatment. The BOD loading in brewery waste is significant. This leads to high sludge volumes and high disposal costs. With BOD levels consistently at 2500 mg/L or above, brewery waste is ideal for operating anaerobic pretreatment facilities.

The Sugar Industry

There are many process steps in the sugar industry (some of which are similar to corn processing). As the largest food processing water user with a variety of process operations, the sugar processing industry offers a good example of water use in food processing.

Sugar (sucrose), a chemical classified as a disaccharide with the formula $C_{12}H_{22}O_{11}$, is derived from two major crops: sugar cane and sugar beets. Cane is cultivated in tropical and semitropical climates (Louisiana, Florida, Central America, and Brazil), while beets are raised in temperate climates (North Dakota, Minnesota, Montana, Michigan, Wyoming, Nebraska, Colorado, Idaho, and California). 51% of the U.S. sugar produced from beets comes from the Red River Valley which is in eastern North Dakota and western Minnesota.

Cane exceeds beet sugar production but in the United States 55% of total sugar production comes from sugar beets. Because these crops spoil rapidly, they cannot be stored for extended periods unless they are frozen, and the production of sugar is seasonal, with a mill operating a production campaign of about 120 days geared to the plant harvest. However, facilities that freeze the beets the production campaign are about 250 days. Sucrose, which constitutes up to 20% of the weight of the cane or beet, is readily degraded by bacterial action. The first step in the degradation is the production of invert sugars (fructose and glucose):

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{glucose}}{C_6H_{12}O_6} \tag{40.1}$$

The second step is the production of lactic acid ($C_3H_6O_3$) under the conditions prevailing in beet sugar manufacture, or dextran ($nC_6H_{10}O_5$) under the conditions common in cane sugar mills. Since bacteria primarily cause this degradation, it is important to maintain control of microbial organisms throughout the mill to avoid loss of sucrose production. Microbial activity also causes processing difficulties, such as filter blinding, slime formation, and odors.

Figure 40.6 shows a basic flow diagram for cane and beet sugar processing.

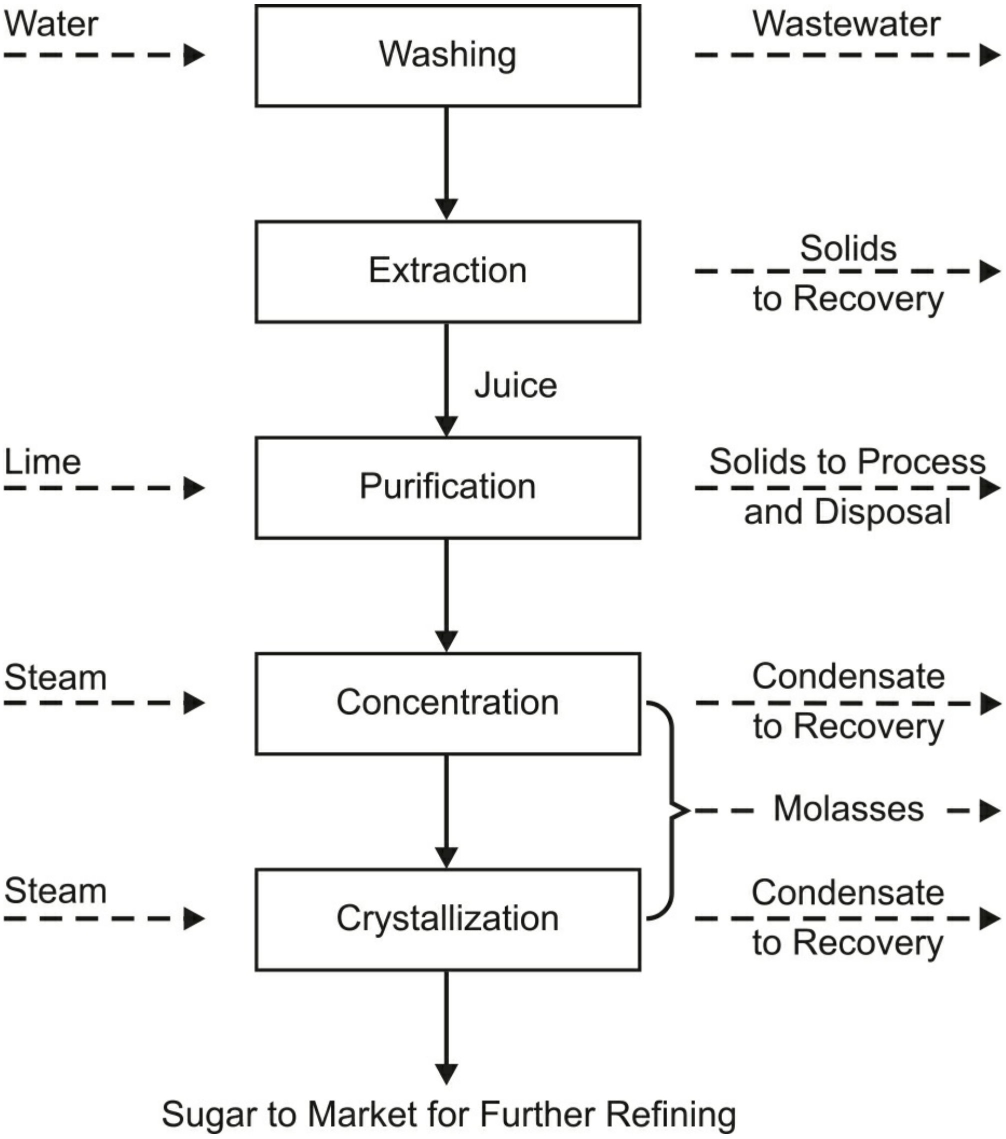


FIGURE 40.6 Sugar processing flow sheet.

As the crops arrive at the mill, they contain soil and trash accumulated during the harvesting operation. In the case of cane sugar harvested by pushers (similar to bulldozers), the refuse may constitute as much as 10 to 25% of the weight of material delivered to the mill. This is not merely inert material; it represents a major source of bacterial inoculation, since soil organisms are present with appreciable fecal matter from birds, rodents, and other small animals that live on the croplands. Because of this, washing is a critical operation to the preparation of raw materials going to further extraction processes. However, washing should not be excessive, as this leads to loss of sucrose in the wash water.

After washing, sucrose is extracted from the raw material. In cane sugar mills, this is usually done by crushing and milling the washed, cut cane stalks, producing a juice containing approximately 12 to 15% sucrose. In the beet sugar industry, the beets are sliced into long, narrow pieces, and the sucrose extracted by washing with water in diffusers at about 160°F (71°C). There is growing interest in the use of diffusers in place of crushers and mills in cane processing to reduce maintenance costs and improve yield.

The cane stalks are pressed after initial crushing and milling to reclaim as much sugar as possible, and the remaining solids (called bagasse) are usually burned in boilers to generate steam. Bagasse may also be used as a raw material for such products as insulation board or acoustical tile. In the beet sugar industry, the beet pulp residue is quite high in protein, and it may be mixed with some of the plant production of molasses for cattle feed.

As with most other natural products, there are a variety of chemicals other than sucrose in the cane and beets. These must be removed to maximize the yield of sugar, minimize the production of molasses, and reduce taste, color, and odor-producing impurities. Lime is used to precipitate these impurities, and conventional separation devices remove the lime mud. The mud is washed to reclaim as much sugar as possible, and it may then be:

- Used to produce fresh lime
- Returned to the fields for its fertilizer value (it often contains significant phosphate)
- Sent to landfill

The purified juice must be concentrated to produce thick syrup, the form of sugar often used by the beverage industry, or to produce a crystalline product. The juice is concentrated by evaporation. Since it contains calcium from the lime treatment, a common problem is the formation of scale in the pans (simple steam-jacketed evaporators) or in the multieffect evaporators. Another common problem is foaming, as the juices become concentrated during evaporation.

The flow sheet of a cane sugar mill producing raw sugar is shown in Fig. 40.7. There is widespread use of steam throughout the plant, so the boiler house is a significant factor in economical production of sugar. Many sugar mills operate intermediate pressure boilers and produce electric power, taking extraction steam from the turbines for operation of pans, evaporators, and crystallizers, and in many cases taking part of the steam through the turbine generator to a condenser. Cooling water from both turbine and evaporator condensers may then be used as process water.

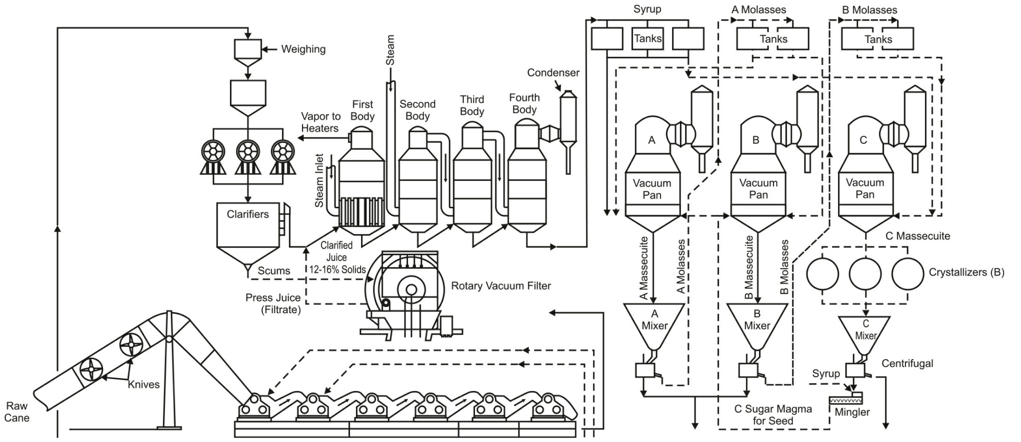


FIGURE 40.7 Process flow chart of cane sugar mill. (*Courtesy of Rio Grande Valley Sugar Growers, Inc.*)

Because the operation of a multieffect evaporator produces more water as condensate than it consumes as steam, there is usually an excess of condensate available as boiler feedwater. This condensate often presents special problems in that it is likely to be high in ammonia, and it may periodically contain sucrose or invert sugar. The introduction of sugar into the boiler quickly produces an acid condition, and careful monitoring of the condensate system for sugar content is important to the protection of the boiler system.

The pollution control problems of the sugar mills are unusual because of the seasonal nature of the industry. The campaign is usually during the dry months, when streams cannot assimilate excess organic loading. The mills minimize discharge flows by recycling as completely as possible, and the wastewaters are treated biologically and impounded for solar evaporation or controlled discharge, when stream flows return to acceptable rates.

The Grain, Oil Processing, and Biofuels Industry

This industry segment consists of corn wet milling, wheat processing, oil processing, and biofuels. Each will be discussed separately.

Corn Wet Milling

Corn refining began in the United States in the mid-19th century, with the development of the process for cornstarch hydrolysis. Before this time, the main sources for starch were wheat and potatoes. In 1844, the William Colgate and Company wheat starch plant in Jersey City, N.J., became the first dedicated cornstarch plant in the world. By 1857, the cornstarch industry reached significant proportions in the United States. Starch was the only product of the corn refining industry. Its largest customer was the laundry business.

Today, starch, glucose, and dextrose are still core products of the wet milling industry. However, the products of microbiology (fructose, ethanol, food additives, and chemicals) have overshadowed them. New technology and research have significantly expanded the industry's product portfolio. Advances in process engineering and biotechnology have enabled refiners to become low-cost suppliers of basic food and chemical ingredients, opening new markets in the food and industrial sectors. From one bushel of corn, a producer can get:

- 32 lb (14.5 kg) of starch
- 11.4 lb (5.2 kg) of gluten feed
- 3 lb (1.4 kg) of gluten meal
- 1.6 lb (0.7 kg) of corn oil

The wet milling process is broken into seven primary parts:

1. Cleaning
2. Steeping
3. Germ recovery
4. Fiber recovery
5. Gluten (protein) recovery
6. Starch washing
7. Co-product manufacture

In the mill, a series of solid/solid separation steps, separate the fiber, gluten, protein (germ), and starch from a signal kernel of corn. The oil is extracted from the germ and is sent for further processing. The starch is then moved to the refinery, where a multitude of products can be made. Over the past couple of decades, major developments of the industry include:

- Ethanol as a motor fuel
- High fructose corn syrup (HFCS) reaching a near par with sugar consumption
- Specialty sweeteners such as crystalline fructose
- Food and feed additives such as vitamins, lysine, tryptophane, and others
- Organic acids for industrial and food use
- Degradable replacements for chemical products

As the name suggests, the wet milling industry is an extremely water intensive process [30–40 gal (114–151 L) per bushel of corn ground, where a bushel is 56 lb (25.4 kg)]. This process is the largest user of energy and water in the food industry. It is within the mill (Fig. 40.8) where the majority of the water and energy is used. Balancing the water use in this process can be challenging. Freshwater enters the process to rinse the pure starch, and flows counter-current upstream to be used for washing various co-products, until it reaches the front of the mill where it is used for soaking the corn. This process is called steeping, which acts as an antimicrobial and prepares the kernel for the physical separation steps that follow. As the various co-products are separated, they need to be dried, and the water that was put into the process now needs to be removed through multieffect evaporation, as well as by natural gas and steam driven dryers.

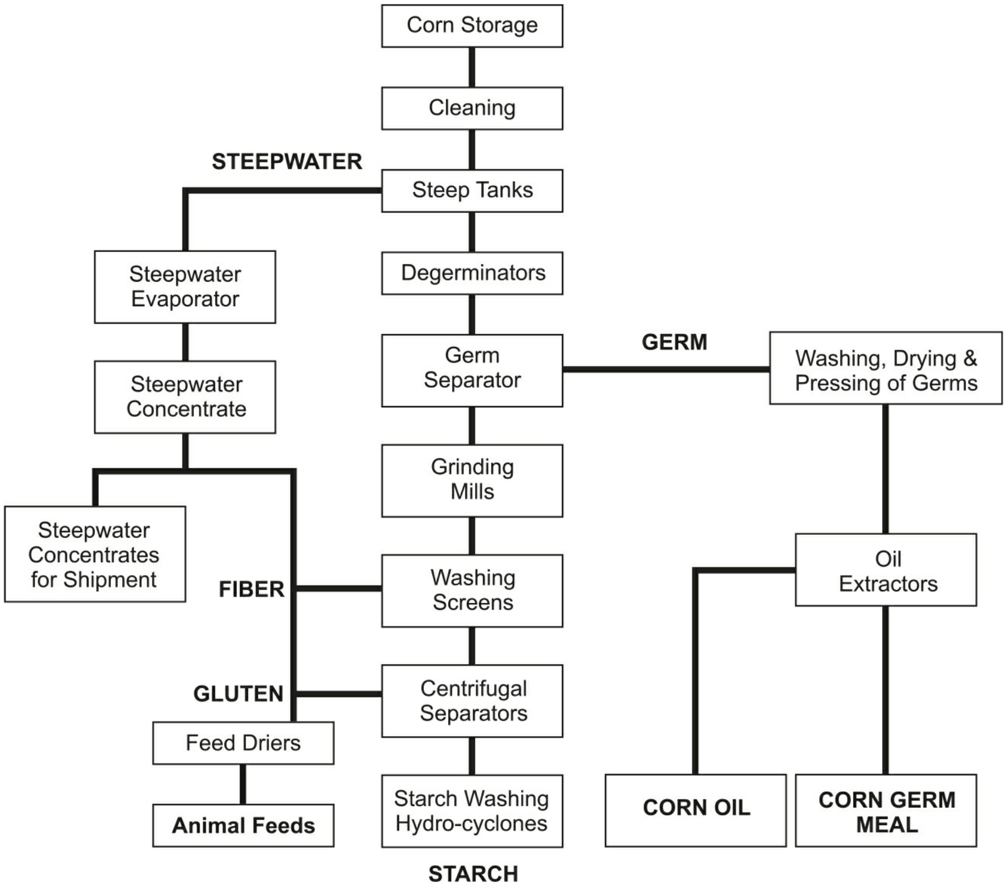


FIGURE 40.8 Wet corn milling process.

After the starch is extracted via the milling process, it is further processed into a variety of products. The standard starch refining process is shown in Fig. 40.9.

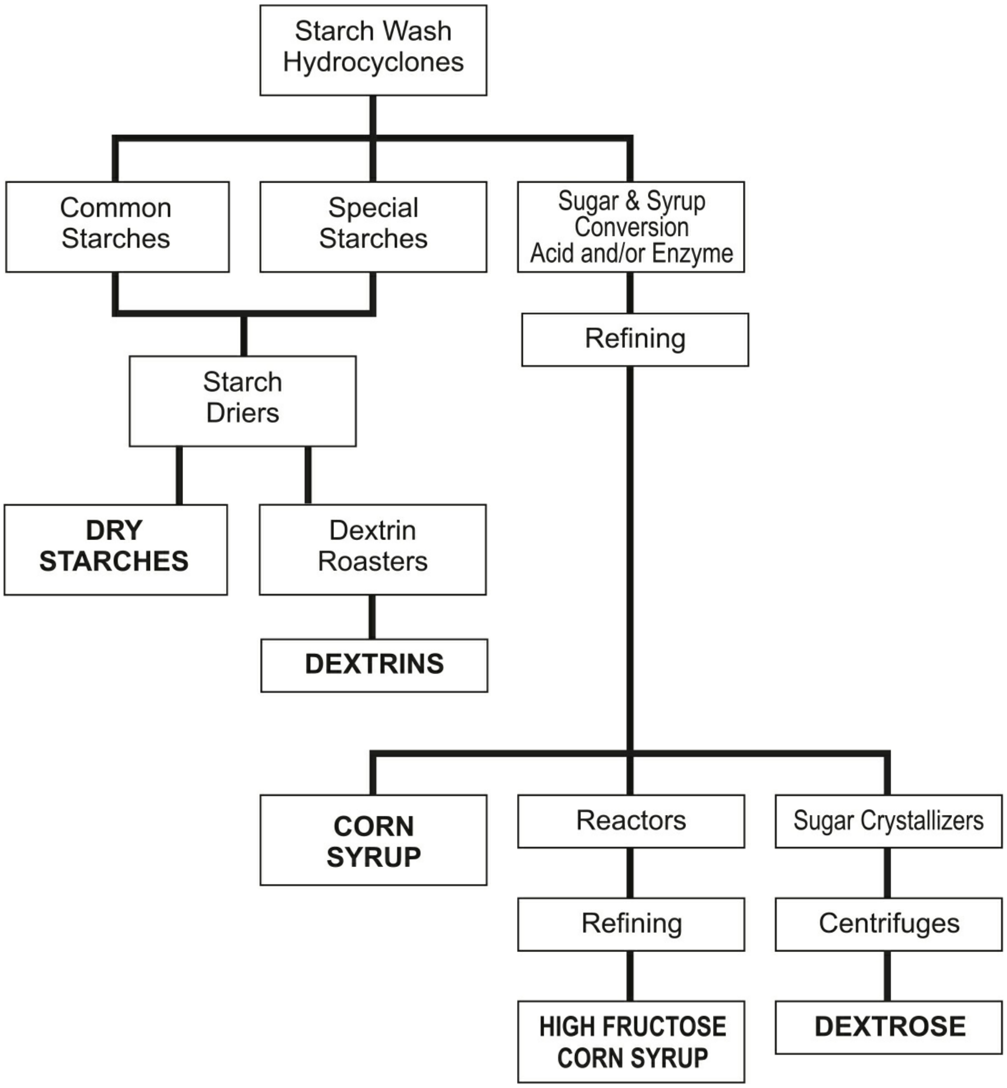


FIGURE 40.9 Starch refining process.

The steam and cooling water systems that provide the necessary heating and cooling requirements are intensive and require chemistries to inhibit corrosion, scale, fouling, and microbiological activity. In addition to the utility systems, other technologies can be applied, including process deposit control, foam control, and fuel additives to treat the end ethanol.

Wheat Processing

Wheat continues to be processed for its starch and gluten components. However, the process is quite different from that of corn milling (Fig. 40.10).

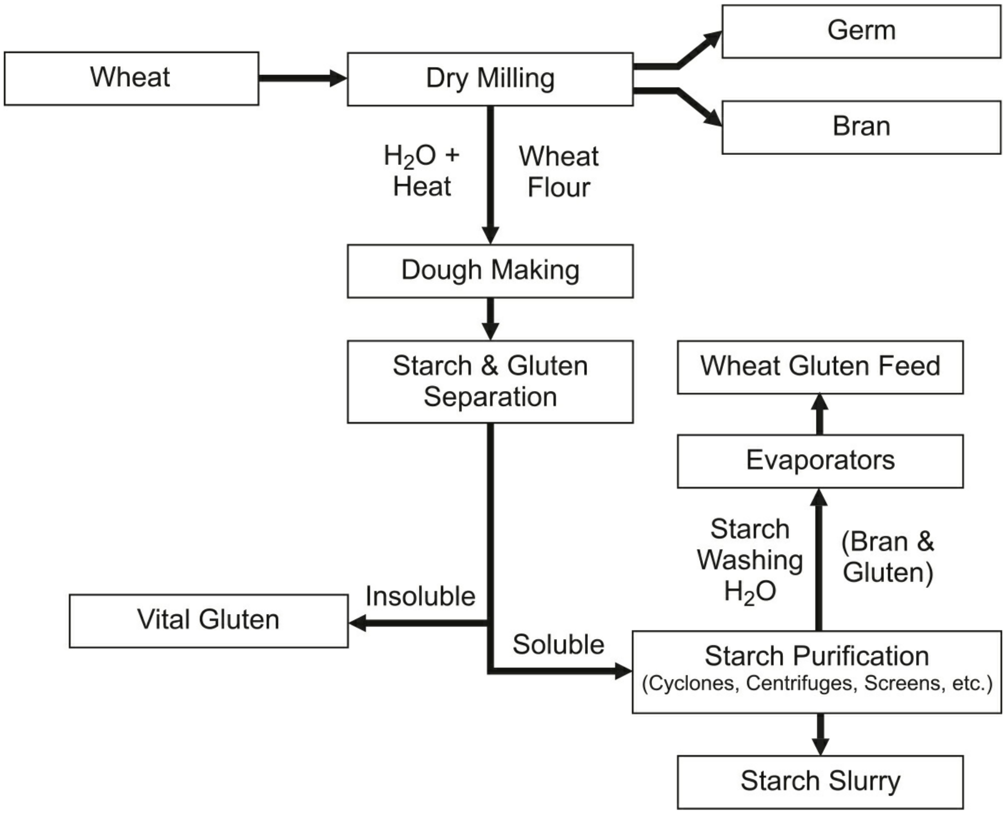


FIGURE 40.10 Wheat processing.

The wheat is first dry milled by grinding and sieving to separate different fractions depending on size, and the bran and germ are thus separated from the wheat flour. Wheat flour is then suspended in water and sheer and heat is applied to create dough. Through this process, the gluten (protein) coagulates. The gluten is separated on a screen, dewatered, and dried. What remains is the starch. Purification is completed by removal of fiber and pentosans in a number of washing steps including hydrocyclones, centrifuges, and screens. The wash water still has high amounts of gluten in it and is recovered through multieffect evaporators. Residual pentosans, if not removed properly or cleaned frequently, can cause major scaling in these unit operations. The concentrated gluten is then dried as a final product.

Water and energy uses are much lower in the production of wheat products versus corn wet milling, as there are not the large amounts of water added to the process. Therefore, the amount of energy needed to drive that water off the end products is much smaller. Cooling towers, boilers, and evaporator systems exist within this process and experience similar problems mentioned earlier, if not properly treated.

Oil Processing

Edible oil processing has a more global reach than any of the other grain processing operations. Oil processing has operations in every corner of the globe. There is a variety of oil processes, depending on the seed being used. The water use is about 50 to 60% less than that of the corn wet milling industry at 10 to 20 gal (38–76 L) per bushel [56 lb (25.4 kg)]. As in most of the processes already discussed, there is a preparation of the crude raw material, before it is made into food products (Fig. 40.11). This preparation consists of milling, drying, and oil extraction. The oil seeds are cleaned and dried and are then passed to cracking rolls to remove hulls. Steam jacketed cookers (called conditioners) are used so that the oil seed can be flaked in the case of soybean, or pressed for partial oil extraction in the case of sunflower and rapeseed (canola). Dry steam is critical in these processes, as it can affect oil seed moisture content and slow drying and overall production. About 10 to 30% of the steam is used here.

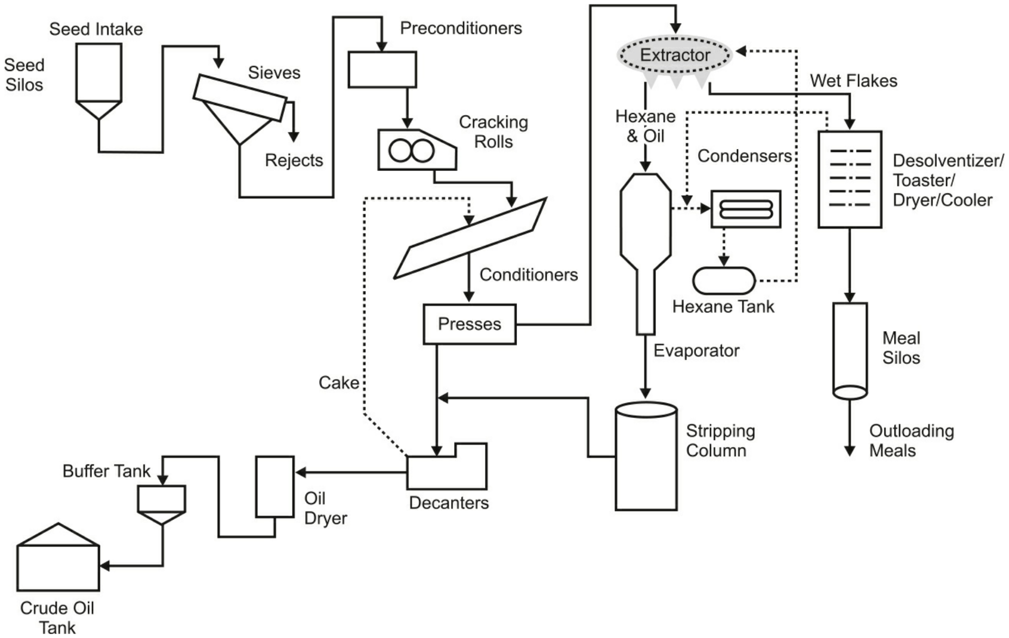


FIGURE 40.11 Oil processing.

The flaked or pressed oil seeds are then passed to hexane extractors. In most cases, percolation extractors are used, where hexane is passed over the bed of flakes. A mixture of oil and hexane percolate down through the bed, and flakes leave containing 35% hexane, 8% water, and 1% oil. The hexane is then stripped from the wet flakes through a desolventizer-toaster. The remaining solid material is made into meal for animal feed. The hexane-oil mixture is passed through flash evaporation, vacuum distillation, and steam stripping to remove the hexane. A critical key performance indicator is the amount of hexane that is recovered. About 1 to 2 gal (3.8–6.9 L) of hexane is lost per ton (tonne) of oil processed. Cooling efficiency is vital to ensure that proper amounts of hexane are recovered. The crude oil is then sent on for further processing. This is can be done on the existing site of the mill, but in many cases, the oil is degummed and sent to an oil refining facility.

The oil refining process is shown in Fig. 40.12. Water degumming removes the gums or lecithin (phosphatides). This step prepares the oil for long-term storage or transport. Caustic refining removes the free fatty acids from the oil. Bleaching is performed using acid activated clays, like bentonite or montmorillonite. Bleaching improves the refined oil flavor and removes trace phosphatides, soaps, metals, and any color. Deodorizing removes additional free fatty acids and odoriferous compounds in the oil. This is accomplished through steam stripping. Therefore, good purity steam is necessary for the process to work efficiently.

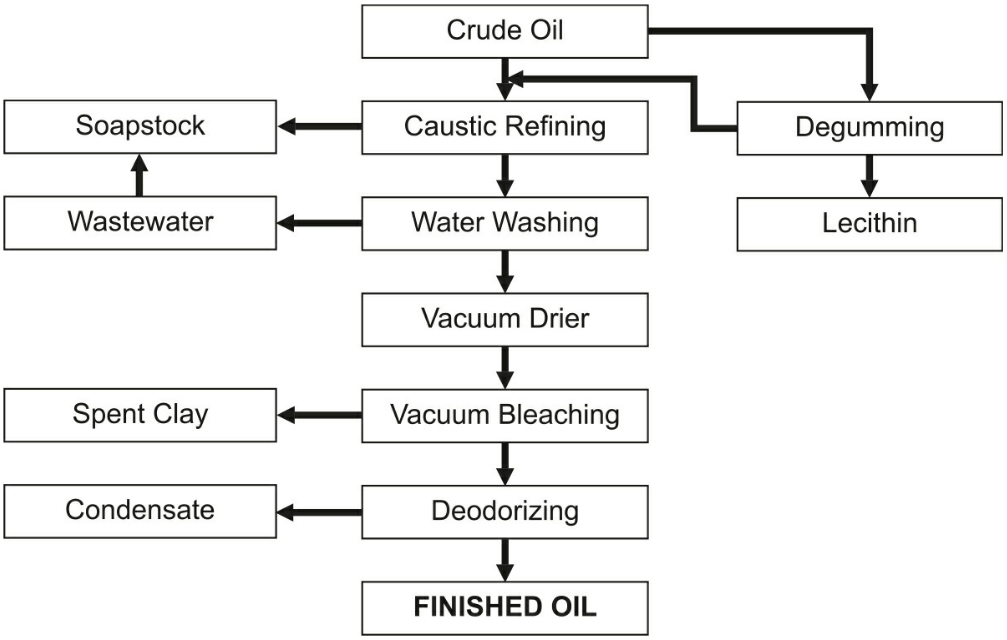


FIGURE 40.12 Oil refining process.

Biofuels

The biofuels industry consists of fuel products created from renewable biological-based products. The two primary fuels are ethanol and biodiesel (fatty acid methyl ester or FAME). Water and energy use in these industries has increased substantially, due to the growth of the global demand for these products (Fig. 40.13). The following sections will focus on the dry grind corn ethanol process, as well as a general description of the biodiesel process.

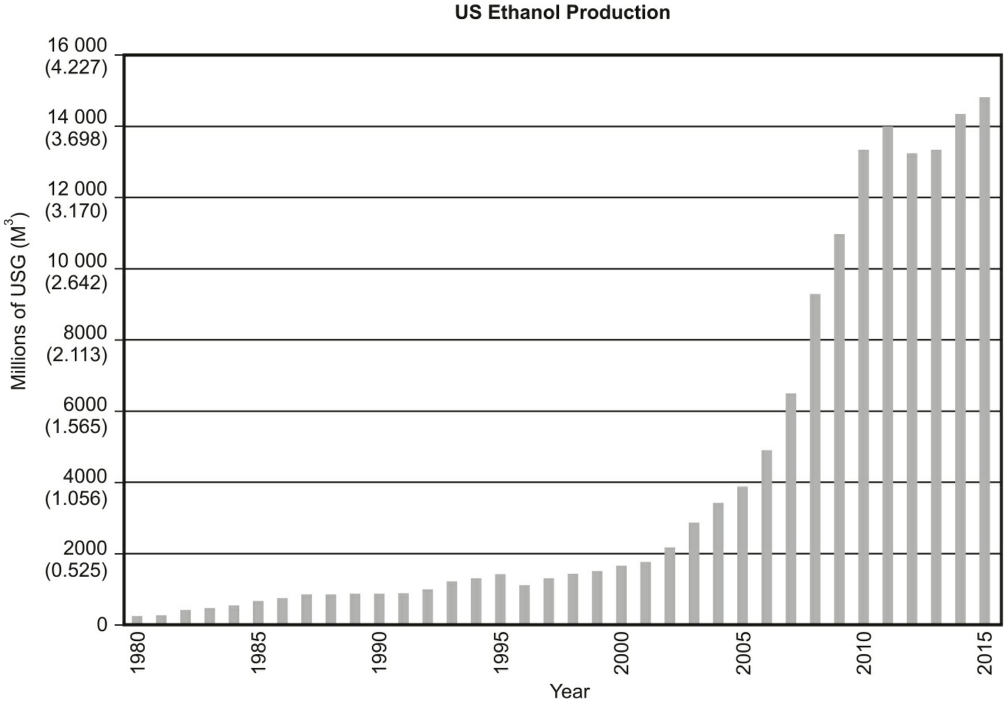


FIGURE 40.13 U.S. ethanol production. (*Adapted from information available from the Renewable Fuels Association www.ethanolrfa.org*.)

Dry Grind Corn for Fuel Ethanol

The other predominant corn processing industry is the dry grind ethanol process (Fig. 40.14). The name, however, is misleading; there is a relatively high level of water used in the cooling of the process. It is only the first grinding step that is dry. Immediately, the ground corn falls into a slurry tank, where various recycled water streams are added, and the temperature is brought to 150 to 170°F (66–77°C). This prepares the corn to enter the jet cooker, via either cook tube (direct steam) or shell tube cooker (indirect steam), depending on design. The corn mash slurry then enters the liquefaction tank, where alpha amylase enzyme is added to begin breaking the starch into polysaccharides in preparation for the next step of the process, saccharification. In most new facilities, saccharification and fermentation have been combined to increase efficiency. As glucoamylase is creating glucose, yeast is consuming it as food and producing ethanol.

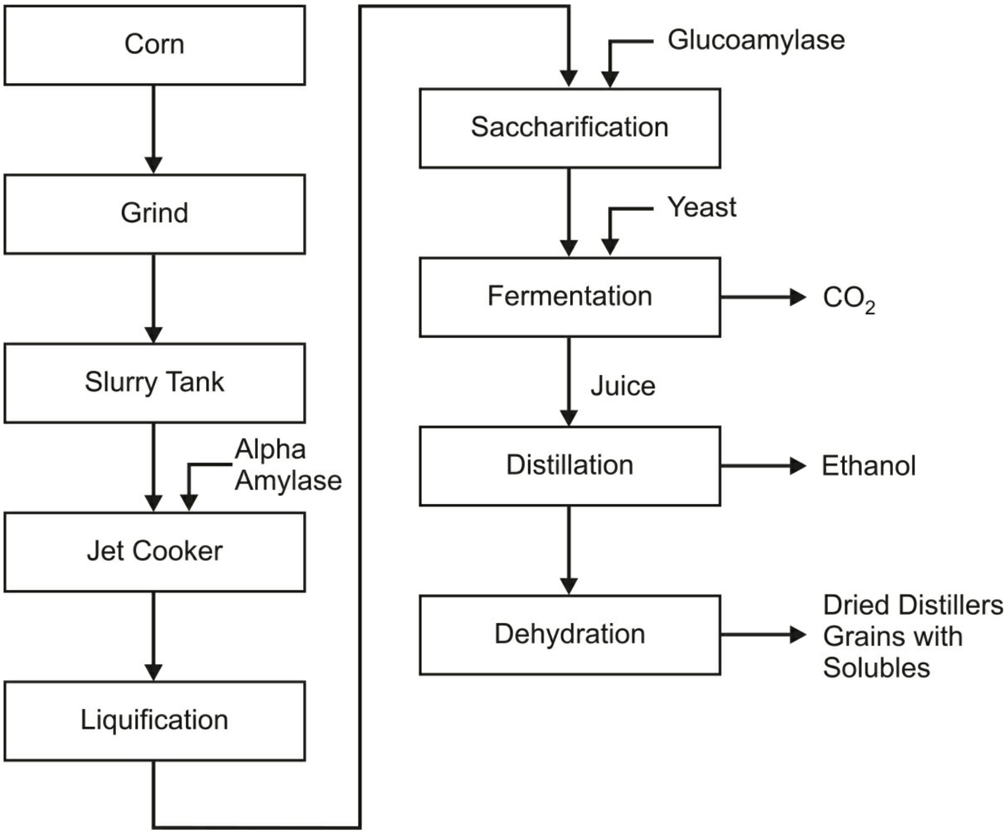


FIGURE 40.14 Dry grind ethanol process.

After 50 to 60 hours, fermentation is complete, and the beer can be taken to distillation to remove ethanol. Distillation only achieves 95% ethanol, commonly referred to as 190 proof. In order to achieve 100% ethanol (200 proof), a drying process is required using molecular sieves. Through the molecular sieves, water is removed by passing the stream over a molecular sieve bed, where a water molecule is small enough to enter the sieve bead, but ethanol molecules are too large and pass by the bead, exiting the molecular sieve bottle as 200 proof ethanol (99–100% ethanol). The ethanol produced in the United States must then be denatured with natural gasoline (a by-product from the natural gas production process) to a 2 to 2.5% level. Then, a pH buffering/corrosion inhibitor product is added.

The “bottoms” of distillation or what is known as whole stillage (12–15% TS) is then sent to a centrifuge. The solids from the centrifuge result as wet cake, which is 30 to 35% total solids (TS) and either goes to a natural gas fired or steam tube dryer to form distillers dry grain (DDG) or can go directly to a feed pile for distillers wet grain (DWG). The liquid from the centrifuge (centrate) is called thin stillage (6–10% TS). Thin stillage has a portion (30–50%) sent back to the beginning of the process, and the remaining is sent to the multieffect evaporators to be concentrated to syrup that is blended with the cake.

This process is water and energy intensive. In 2016, water consumption is about 2.7 gallons of freshwater per gallon of ethanol produced (2.7 L/L). Electrical consumption is about 0.75 kWh/gal (0.20 kWh/L), and energy necessary is about 23 800 Btu/gal (6.63 MJ/L). These ratios are continually being reduced through new technology innovation created by the industry engineering firms and supplier partners. Water in particular has made significant progress, as ratios in 2003 were closer to 6:1. New technology is emerging to drive water use to a 1:1 ratio. As an example, all of the process water from most designs is zero liquid discharge (ZLD). Blowdown from the cooling tower is the only source of blowdown. Cooling tower evaporation can amount for 2.0 to 2.5 gallons of freshwater used per gallon of ethanol produced. Energy has been reduced through heat recycle. As an example, boilers producing steam are generally driven by exhaust from a thermal oxidizer. Boiler feedwater is generally pretreated by RO followed by a water softener. This is reverse from most industrial water processes configurations. It is done to reduce hardness loading on the water softeners in order to reduce the number of regenerations. This leads to far less backwash water and chlorides going to drain. Without a mechanical means for removal of hardness, antiscalants are fed to the front end of the RO units. In addition to the RO pretreatment, heavy focus is placed on additional utility water recycle.

Some biorefineries have been forced to ZLD. Once traditional methods of recycle are exhausted, many mills are forced to look to sophisticated capital solutions. In these designs, incoming plant water, generally from either a well or surface water, is treated by a series of RO units preceded with cold lime softening. These sophisticated pretreatment systems are followed by capital-intensive crystallizers to convert the final water flow to a solid. The ability to minimize this last remaining water flow has tremendous impact on lowering the capital costs of the ZLD systems.

Biodiesel

The biodiesel process (Fig. 40.15) is less complicated and uses less water and energy than the dry grind corn ethanol process. Biodiesel can begin with a variety of oil or fat-based feedstocks, including soybean, corn, corn distillers oil, canola, cottonseed, sunflower, beef tallow, pork lard, palm, or used cooking oil. Depending on the feedstock, the type of triglycerides varies greatly (Fig. 40.16). The type of triglycerides has a direct impact on the production of the end biodiesel and its attributes as a fuel.

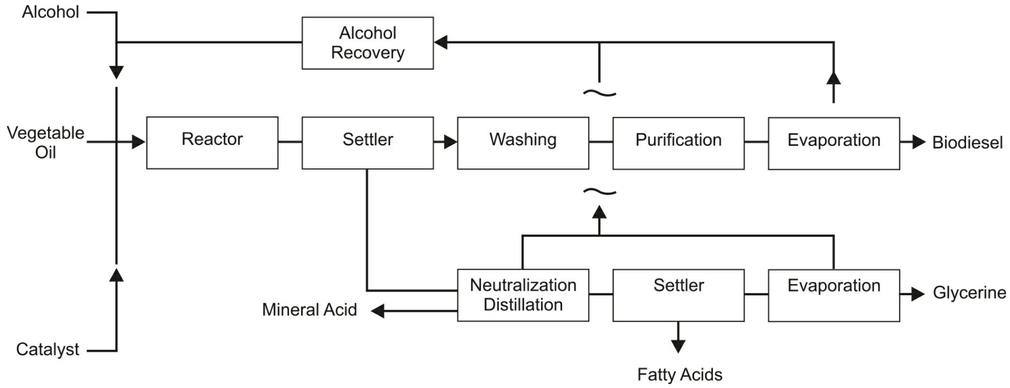


FIGURE 40.15 Biodiesel manufacturing process.

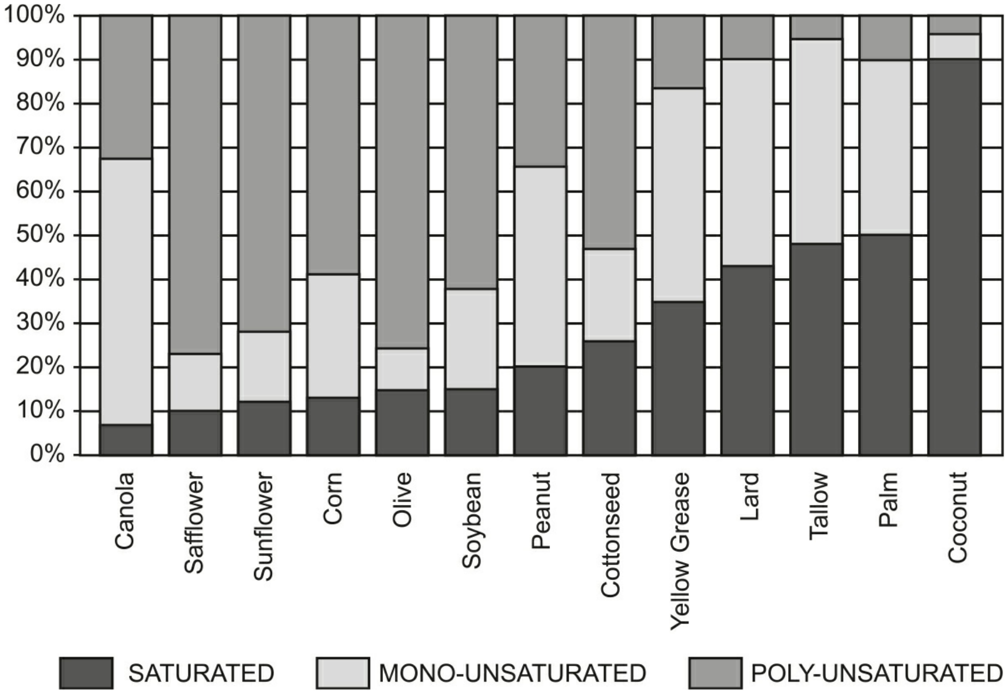


FIGURE 40.16 Triglyceride variance with biodiesel feedstock source.

The process of biodiesel production consists of transesterification, purification, alcohol recovery, and final fuel treatment. The feedstock oil is reacted with an alcohol, usually methanol (due to its lower costs), and sodium hydroxide. FAME, which is the biodiesel product, glycerin, and water are formed. The purification methods vary, but the purpose is to separate the three products as efficiently as possible. The separation process rate can be increased by the addition of settling aids. The glycerin by-product is used in many industrial and consumer products.

The resulting fuel is blended with regular petroleum diesel at various percentages. The final fuel product is referred to as “BX,” with the X representing the percentage of biodiesel in the product. For example, B5 is 5% biodiesel and 95% petroleum diesel. As the percentage of biodiesel increases in the fuel blends, undesirable properties begin to emerge. The properties causing most concern are poor cold flow and stability in the presence of oxygen. Which problem occurs is directly related to the type of triglycerides in the feedstock of the biodiesel. Fuels with a higher amount of saturated triglycerides will be very stable in the presence of oxygen but have poor flow properties in cold temperatures. When higher amounts of unsaturated triglycerides are found, oxygen stability is the predominant issue. To reduce the effects of these problems, fuel additives are added to the end product.

Ethanol from Cellulose

The production of ethanol through the conversion of cellulose is the next major technological breakthrough for the biofuels industry. Major benefits are anticipated with this platform from increased greenhouse gas benefits to significantly higher energy ratios then corn to ethanol, or even sugar cane to ethanol.

Many different processes fall under the term cellulosic ethanol. In general, cellulosic ethanol is the process by which cellulose is extracted from feedstocks like energy crops (switch grass), agricultural residuals (corn cob and stover), or forestry products (hard and soft woods), converted to sugar by enzymes, and fermented to produce ethanol. Extraction will occur in an acidic or basic environment at high temperatures and pressures. This exposes the lignins, hemicellulose, and cellulose to be broken down into xylose and glucose through the application of cellulase enzymes. These sugars then pass into fermentation for ethanol production. The remainder of the process matches that of the corn or sugar ethanol production process. However, the residuals from distillation have no animal feed value.

The production scale use of energy and water to drive these processes is not well understood at the time of printing. However, looking to the corn process as a proxy, wastewater issues will substantially increase. This is due to distillation bottoms not having value as animal feed products as mentioned earlier. Without a higher value, it does not make it economically feasible to dry these products via expensive steam or natural gas. However, opportunity may lie in using them to fuel the boilers. Substantial research is going into how steam and power requirements can come from burning these solid wastes. In addition to the water and energy, several other key issues remain to be solved before economically feasible commercial scale plants will be constructed.

The Dairy Industry

The dairy industry is an important part of the food industry as a whole due to milk being a single source of the primary dietary elements needed for maintenance of proper health, especially in children and older demographics. The dairy industry is highly regulated due to the fact that milk could be a vehicle for disease transmission and has, in the past, been associated with disease outbreaks of major consequence.

Milk can come from a large variation in animals but for the purposes of this writing we will concentrate on cow's milk. Milk processing is similar for the other types of milk.

The use of water in processing dairy products is very important as it is used for heating, cooling, and cleaning. The effluent water from dairies also has to be treated, either onsite, or at a publicly owned municipal waste treatment facility.

This industry segment consists of fluid milk, cheese, and specialty dairy products. Each will be discussed separately. In addition, there are two important sources of water in the dairy industry that are highly regulated and will be discussed below. These are sweetwater and COW water.

Fluid Milk

Milk that comes directly from the cow, with no further processing is called raw milk and this is the main raw material for the dairy industry, including the fluid milk industry. The raw milk is transported to the dairy by tanker truck. The raw milk needs to be cooled either at the farm or upon transfer from the tanker to the storage silo at the dairy. The temperature for raw milk storage is less than 42°F (5°C). The stored raw milk is typically mixed occasionally to minimize the separation of components such as butter fat. The mixing also helps maintain a constant temperature. Milk contains the following average composition: 87.6% water, 3.6% fat, 4.9% lactose, 3.2% protein (2.6% caseins, 0.6% whey protein), and 0.7% minerals.

The raw milk is processed (Fig. 40.17) to yield pasteurized, standardized fluid milk for distribution to retail outlets and eventual consumption by humans.

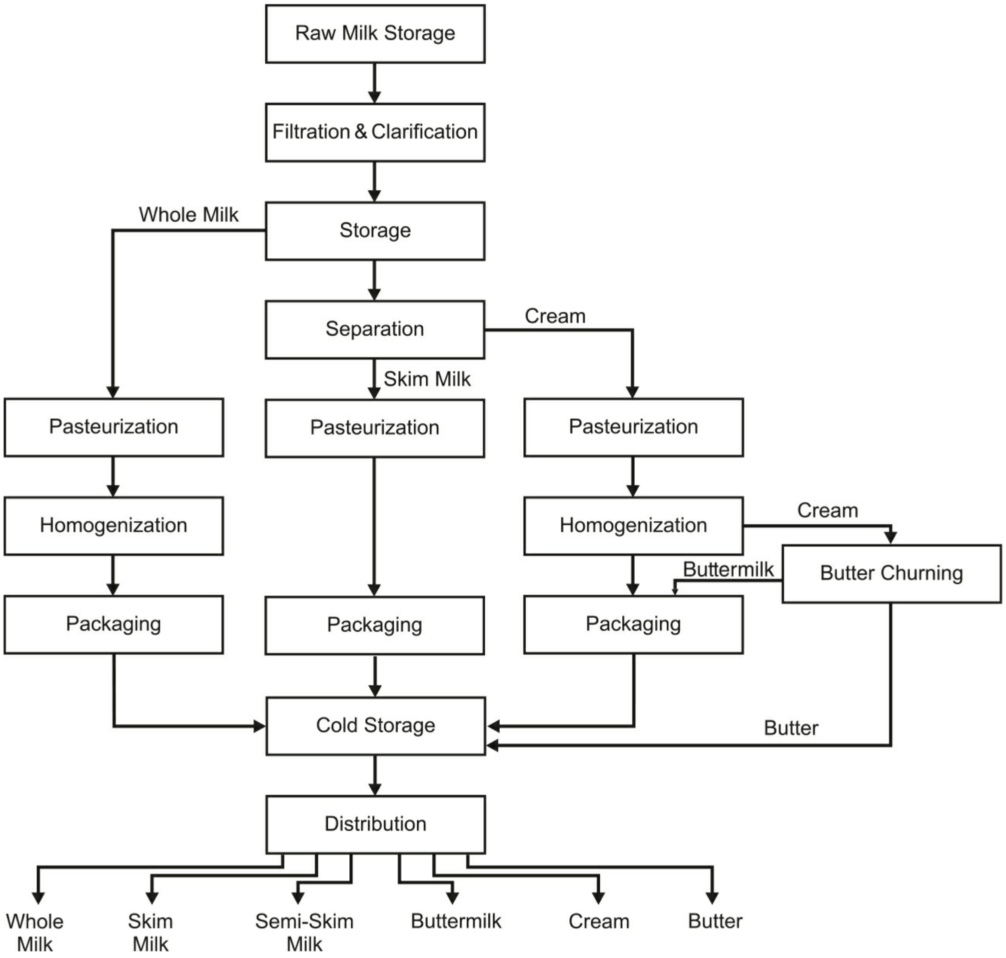


FIGURE 40.17 Typical fluid milk block diagram.

Water is used in several applications in a fluid milk dairy operation including:

- Cooling
    - Once through
    - Closed loop (sweetwater/ice builder)

    - Open recirculating
- Refrigeration
- Heating
    - Steam for hot water
    - Pasteurization
- Cleaning
    - Cleaning in place
    - Cleaning out of place

Cheese

Cheese originated in an effort to extend the shelf life of milk. Fluid milk is the ideal growth medium for microorganisms and is very susceptible to spoilage even when refrigerated. The goal of cheese making is to transform fluid milk into a relatively shelf stable, concentrated, highly nutritious and versatile form of food. The cheese making process includes the steps outlined below. One hundred pounds of milk produces ~9 to 14 pounds of cheese depending on the type.

- Coagulation of proteins
- pH lowering through lactic acid formation
- Removal of some calcium to alter the body and texture
- Lowering the water content through cutting, cooking, and agitating the curd and adding salt,
- And increasing the flavor through aging.

In cheese making dairies, milk is received, concentrated, standardized for fat and protein content, pasteurized, and put into a cheese vat. Cheese “starter” culture is then added to the milk and the milk is agitated. The cheese coagulates and is cut to form curds. The vat is then heated to “cook” the cheese. During this stage of the process, whey is separated from the cheese and is removed in liquid form for further processing, typically to make whey protein powder (Fig. 40.19). The curd is then pressed to form solid cheese which can be further aged or processed into shredded cheese, etc. The cheese making process can be in batches or continuous depending on the equipment employed. Figure 40.18 is the general flow of a dairy cheese plant.

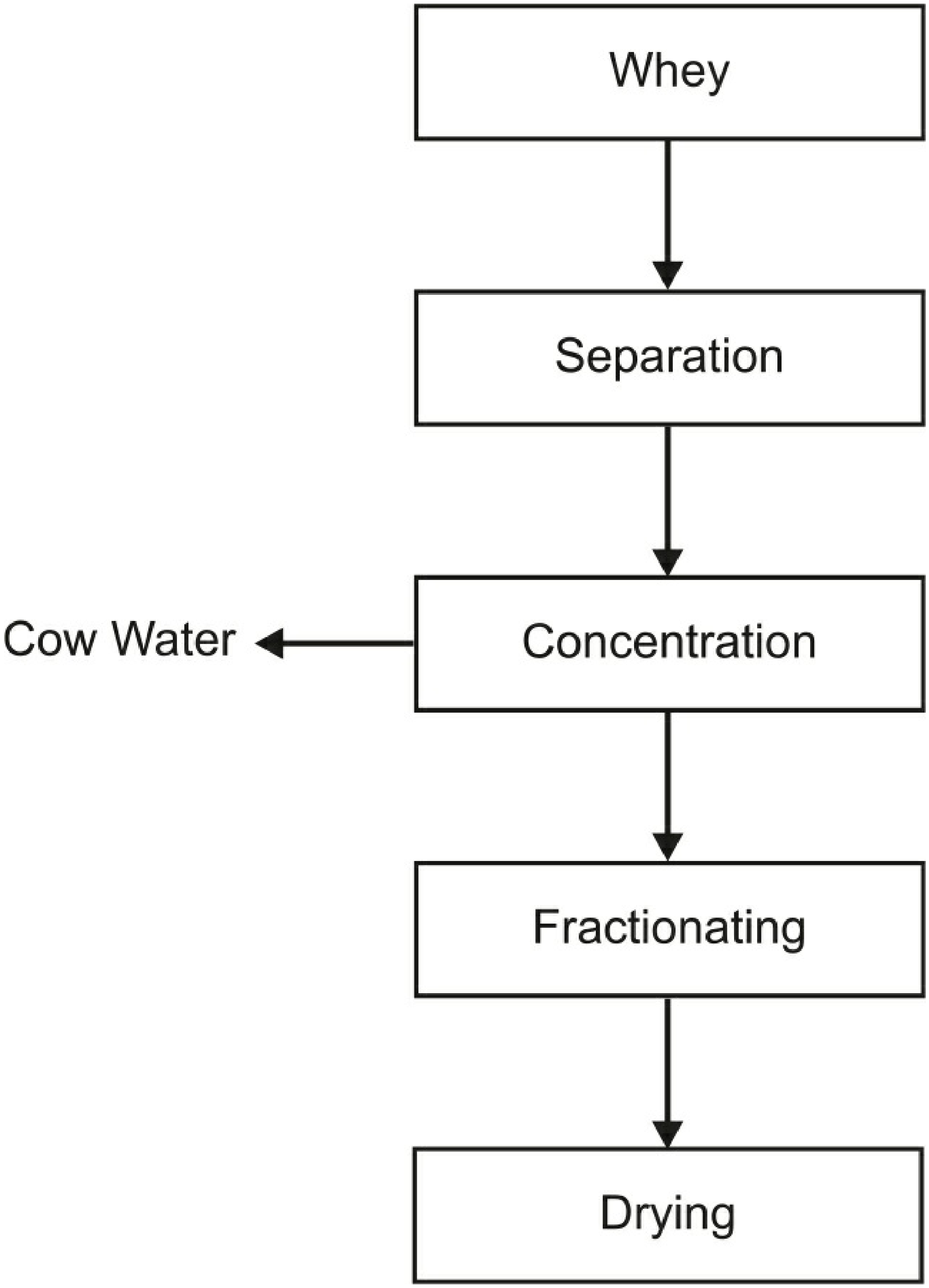


FIGURE 40.19 Flow diagram of whey processing.

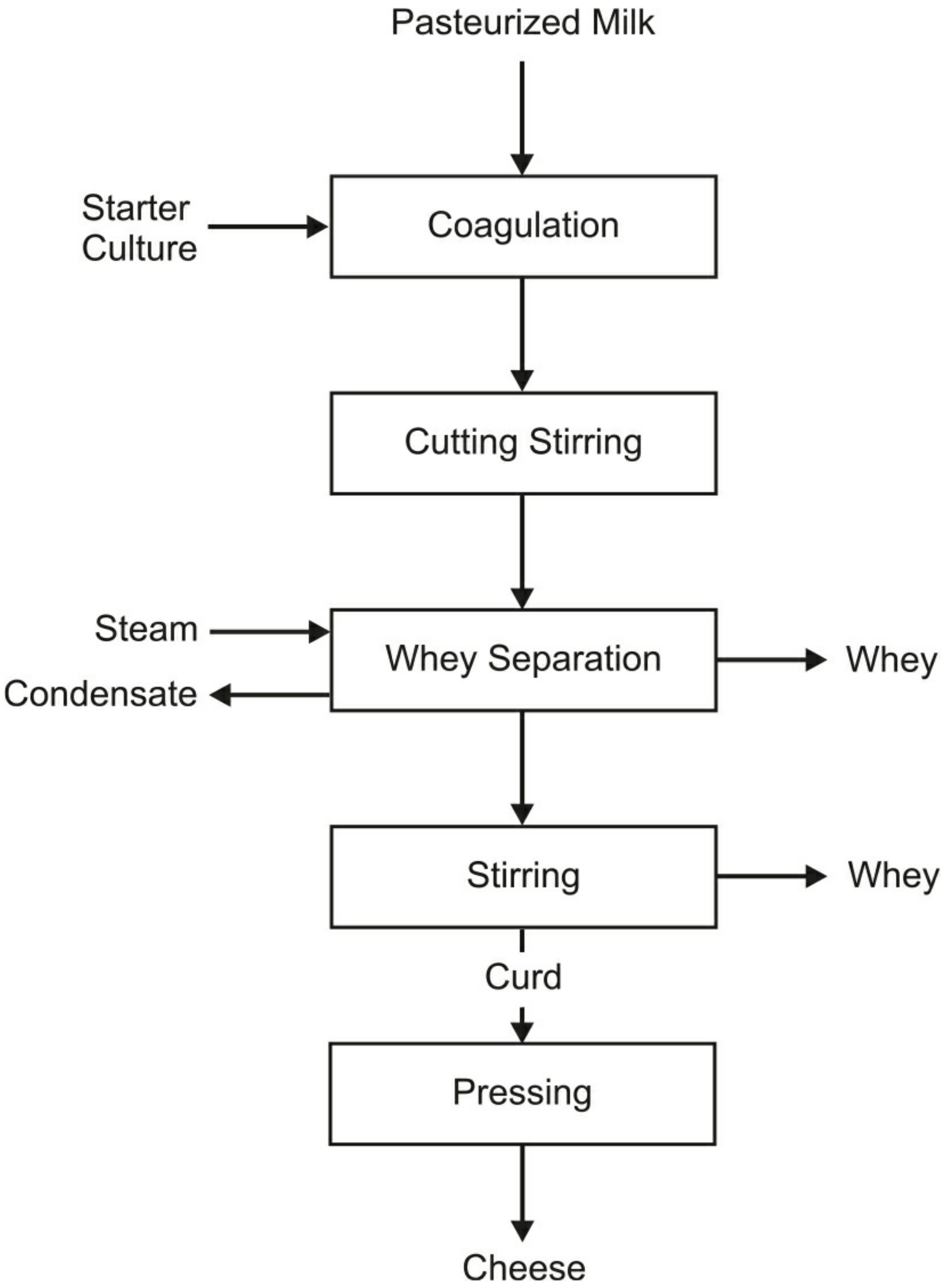


FIGURE 40.18 Dairy cheese plant block diagram.

Water is used in a cheese plant in similar ways; it is used in a fluid milk plant, for cooling, heating through steam, and cleaning. Cheese plants typically have a source of water from the concentrating of milk through evaporation referred to as COW water. COW water can be used in many ways throughout the facility if it meets certain standards set forth by the Grade "A" pasteurized milk ordinance (PMO).

Specialty Dairy—Concentrated Milk, Dry Milk, Yogurt, and Ice Cream

There is standard processing of raw milk that goes into specialty dairy products. These are the separation of the milk from the butter fat, obtaining the correct fat and protein mix and the elimination of pathogens. These steps are typically referred separation, standardization and pasteurization and are all fixtures of these different plants.

Concentrated milk is made by removing water from the milk to obtain a standardized solid content. The removed water is COW water can be reused elsewhere in the facility. Dry milk takes the process further by removing a larger portion of the water to obtain a dry product that can be used as an ingredient or reconstituted with water to make milk. The making of dry milk allows milk to be shipped to areas that do not have milk production available locally (Fig. 40.20).

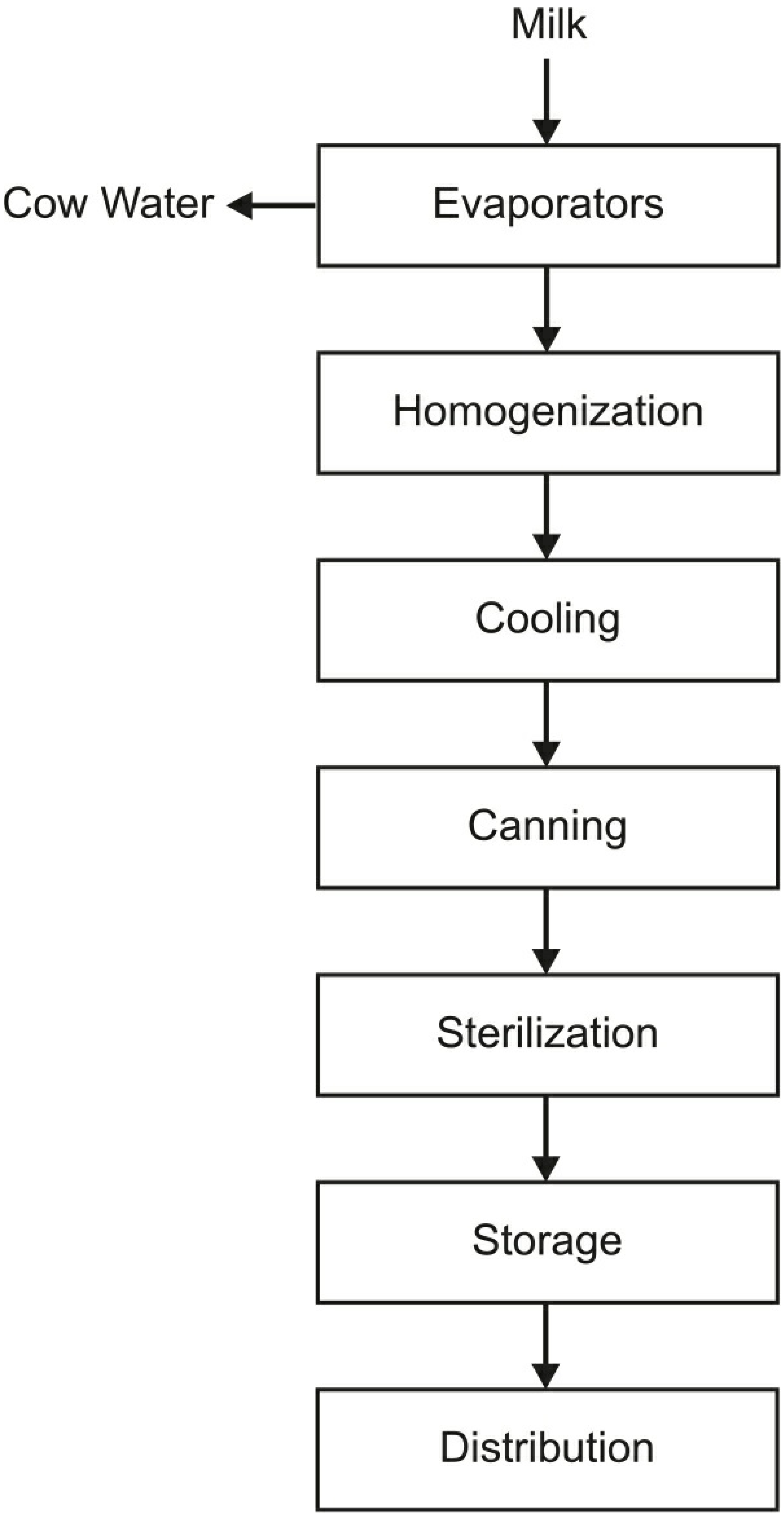

Milk
Cow Water
Evaporators
Homogenization
Cooling
Canning
Sterilization
Storage
Distribution

FIGURE 40.20 Typical condensed milk process diagram.

A dry milk plant typically uses evaporators to concentrate the milk. After the milk is concentrated, it is usually dried in a spray dryer (Fig. 40.21).

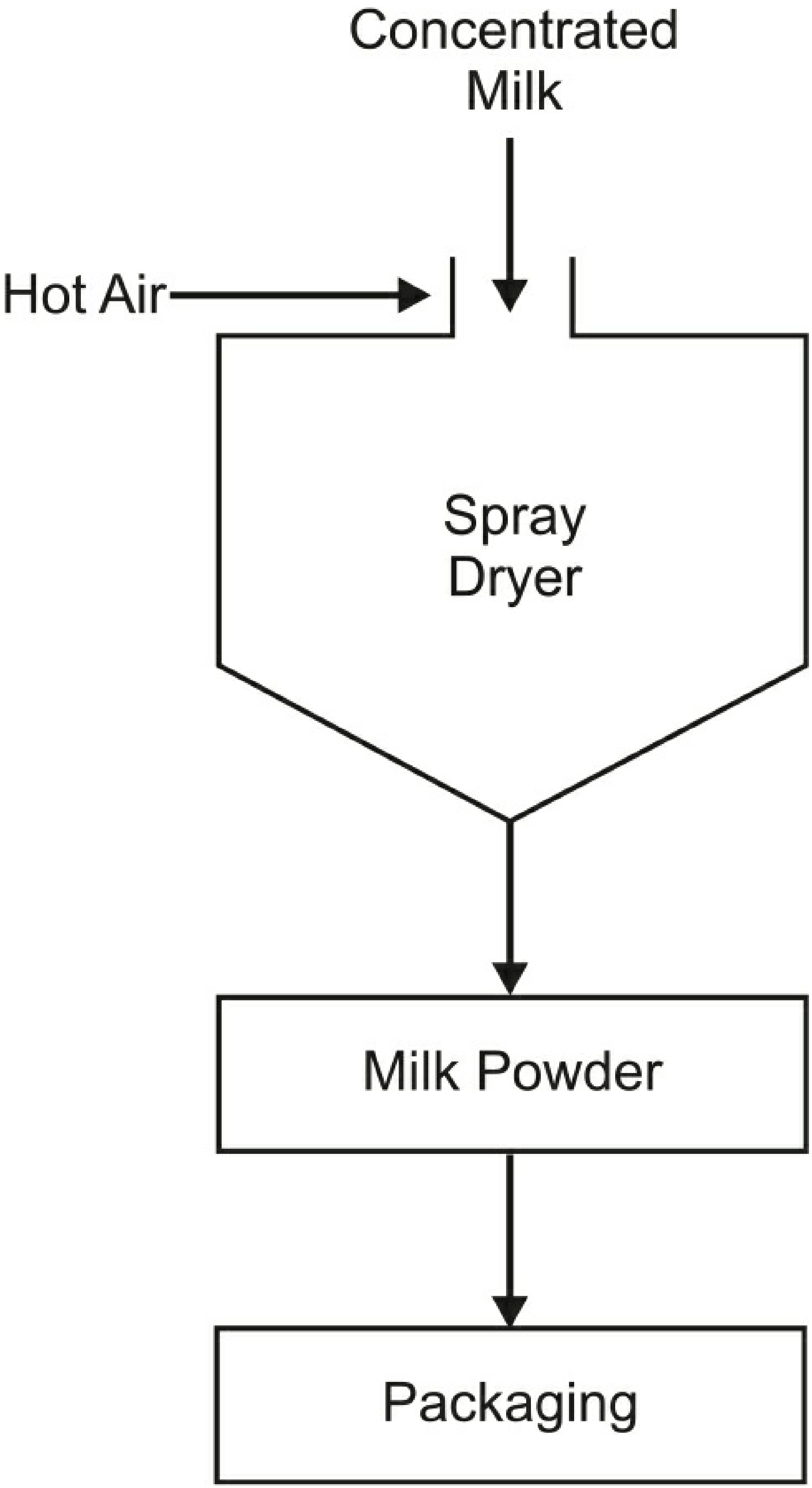

Concentrated Milk
Hot Air
Spray Dryer
Milk Powder
Packaging

FIGURE 40.21 Typical spray dryer.

In a yogurt plant (Fig. 40.22), after pasteurization, separation, standardization, and homogenization, cultures are added to the milk, along with flavorings, to make the final yogurt process. During some of the yogurt making processes, whey is removed from the yogurt mixture which can then be processed by the waste treatment plant. In some, more modern plants, the whey is then stored and processed into whey powder.

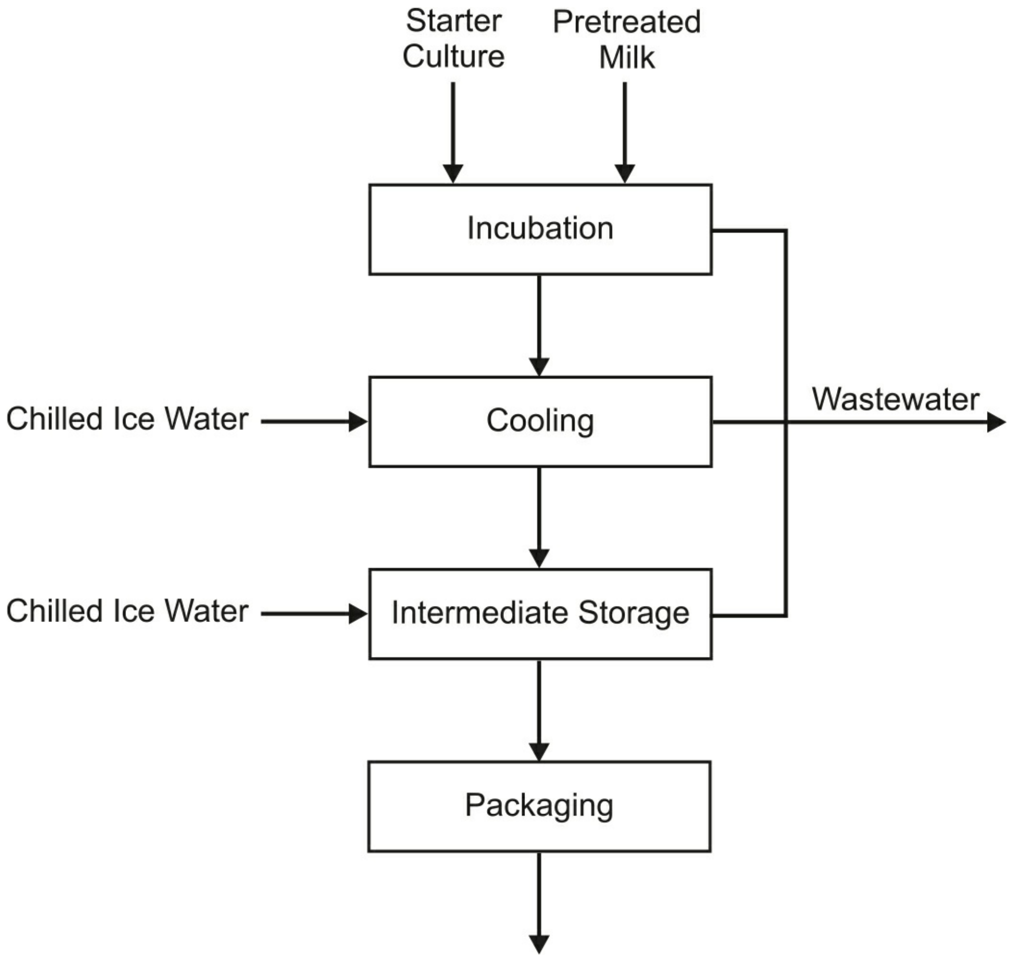


FIGURE 40.22 Yogurt plant block diagram.

In ice cream plants, several different options are available to obtain the correct mixture for the ice cream process. Some plants take in raw milk, pasteurize, separate, standardize, and homogenize to obtain the correct fat content for the final product. In addition, ice cream plants can receive additional milk fat from other dairies as a raw material. In simplistic terms, the correct mixture, with flavorings and additives is then frozen and packaged for distribution. There are several different processes that lead to the final product including making bars, sandwiches, and other novelty items which increase the complexity of the plant.

Dairy Regulations

Dairy plants are some of the most regulated plants in the food industry. The most important document, regulating the dairy process in the United States is the Grade "A" PMO authored by the U.S. Department of Health and Human Services as a public health service as a portion of the U.S. FDA. This document portrays the regulations required from "farm to consumer." This is a comprehensive dictation of all regulations, including provisions for condensed and dry milk products and condensed and dry whey products. In an effort to keep up with additional regulations, this document is updated every two years. As of this writing, the most recent revision is the 2015 revision, which is available at the International Dairy Foods Association website, www.IDFA.org. The Grade "A" PMO includes regulations regarding water treatment, more specifically around the treatment of dairy sweetwater and dairy COW water which are both critical water applications in dairy plants.

Dairy Sweetwater

In milk processing plants, the pasteurization process is a basic operation and the pretreatment step when manufacturing all other dairy type products. The objective of the process is to eliminate pathogenic microorganisms; the plate heat exchanger is most commonly used for pasteurization where the milk is heated to 162°F (72°C) for at least 15 seconds, and then rapidly cooled by coolant of 36°F (2°C). For heating the milk, hot water at 165 to 167°F (74–75°C) is used. This water is heated by steam in a hot water heater. In the regenerative preheating section, the cold untreated milk is pumped into the pasteurizer where this cool incoming milk is preheated with the hot pasteurizer milk. This significantly reduces the temperature of the hot pasteurizer milk to 46 to 48°F (8–9°C). To reach a milk storage temperature of 39°F (4°C), the milk is further cooled by cold water, commonly known as sweetwater. The sweetwater loop is a closed loop as seen in Fig. 40.23.

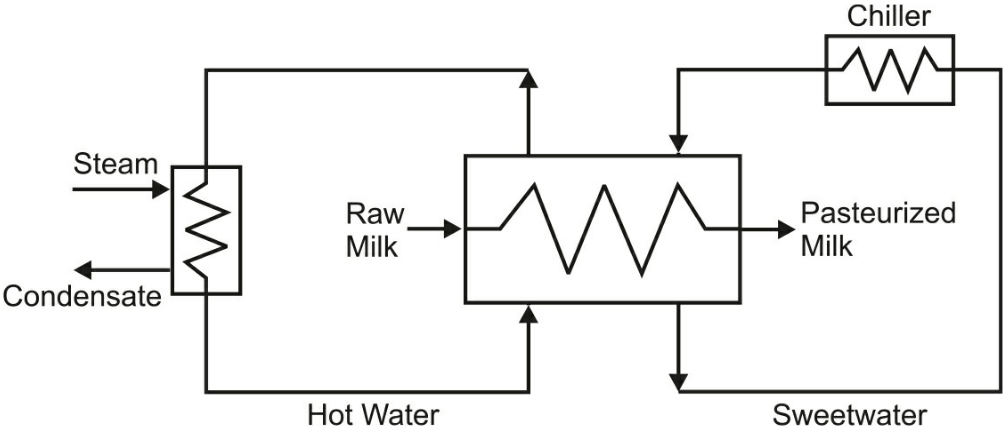


FIGURE 40.23 Typical Sweetwater system.

The sweetwater closed loop varies in system volume, based on the size of the dairy plant, can be constructed of multiple metallurgies, is filled with potable water, and has engineering controls that ensure the pressure on the milk side of the exchanger is higher than the sweetwater to avoid contamination of the milk with sweetwater. Like all closed loop cooling systems, sweetwater systems need to be treated to minimize corrosion and microbiological activity. Left untreated, they will foul and corrode leading to poor heat transfer. Corrosion and fouling negatively impact both production as well as food safety, and can lead to premature equipment failure and unscheduled shutdowns. The chemicals used for corrosion and microbial protection are mandated by the Grade "A" PMO.

Dairy COW Water

In milk processing plants, a large volume of water is generated when the milk is evaporated or concentrated up using either multieffect evaporator or process RO. Since the source of this water is from the milk, it is commonly called COW water. Within milk processing plants, this COW water can be recycled or reused, reducing the demand for freshwater. The dairy industry uses the Grade "A" PMO as a guideline to determine how to recycle or reuse COW water. The PMO has three categories, each of which is dependent on the end use application within a milk processing plant. The three categories are:

1. Category 1—Used for potable water purposes
2. Category 2—Used for limited purposes (such as boiler feedwater used for culinary steam or CIP prerinsing or cleaning solution makeup

water)
3. Category 3—Used for other applications not referenced in the first two categories (such as boiler feedwater not used to production of culinary steam or noncontact cooling water applications)—In this category, the recycled COW water cannot be used in any circumstance where there is potential for incidental contact with milk or milk products

In a dairy plant where COW water is available, this is the single most valuable resource to reduce the use of freshwater in the dairy plant.

Foam Control

Within the food industry, there are many key application points in a variety of food processes where foam is inherently generated. The market segments where foam needs to be effectively controlled via an antifoam program include:

- Vegetable processing
- Ready to eat foods
- Snack foods
- Egg processing
- Potato processing
- Corn wet milling
- Edible oils
- Rendering
- Poultry washing
- Seafood processing

An effective antifoam program allows customers to maintain production throughput and the quality of the end product. With proper control, an antifoam program will help the customer's maintenance budget.

There are many types of antifoams available in the marketplace today. Whether they are silicone-based, water-based, or oil-based products, it is vital in these market segments to ensure the products have the appropriate food approvals.

CHAPTER 41

The Microelectronics Industry

The Microelectronic industry is a subsegment of the electronics industry, and includes, but is not limited to solar cell [photovoltaic (PV)], flat panel display (FPD), disk drive, silicon wafer, and semiconductor manufacturing. These industries are grouped together from a water treatment perspective for the following reasons:

- Similarity of manufacturing processes
- Similarity in use of water
- Similar water preparation processes
- Continued manufacturing innovation that warrants comments on water quality and use

The investment to build and equip a microelectronics fabrication facility (fab) is large; a large semiconductor fab could be a multibillion dollar project. Hence, the cost of production is high, and uptime is a key driver. It is important to remember that, just as there are different semiconductor end products [memory, analog, power, logic, micro-electro-mechanical systems (MEMS)], there are different manufacturing unit operation combinations.

Water is used in a wide number of applications in these industries. The following are some of the major applications, along with information on why the application is unique or critical.

Ultrapure Water

Ultrapure water (UPW) is usually considered the most critical water stream in the fab, since it directly contacts the product during the manufacturing process.

A microelectronics fab uses UPW for a variety of reasons; to dilute process chemistry as it is applied, or to rinse process chemistry from the surface of the product during the manufacturing process. In either case, purity is critical. A UPW train may consist of the multiple unit processes (Fig. 41.1).

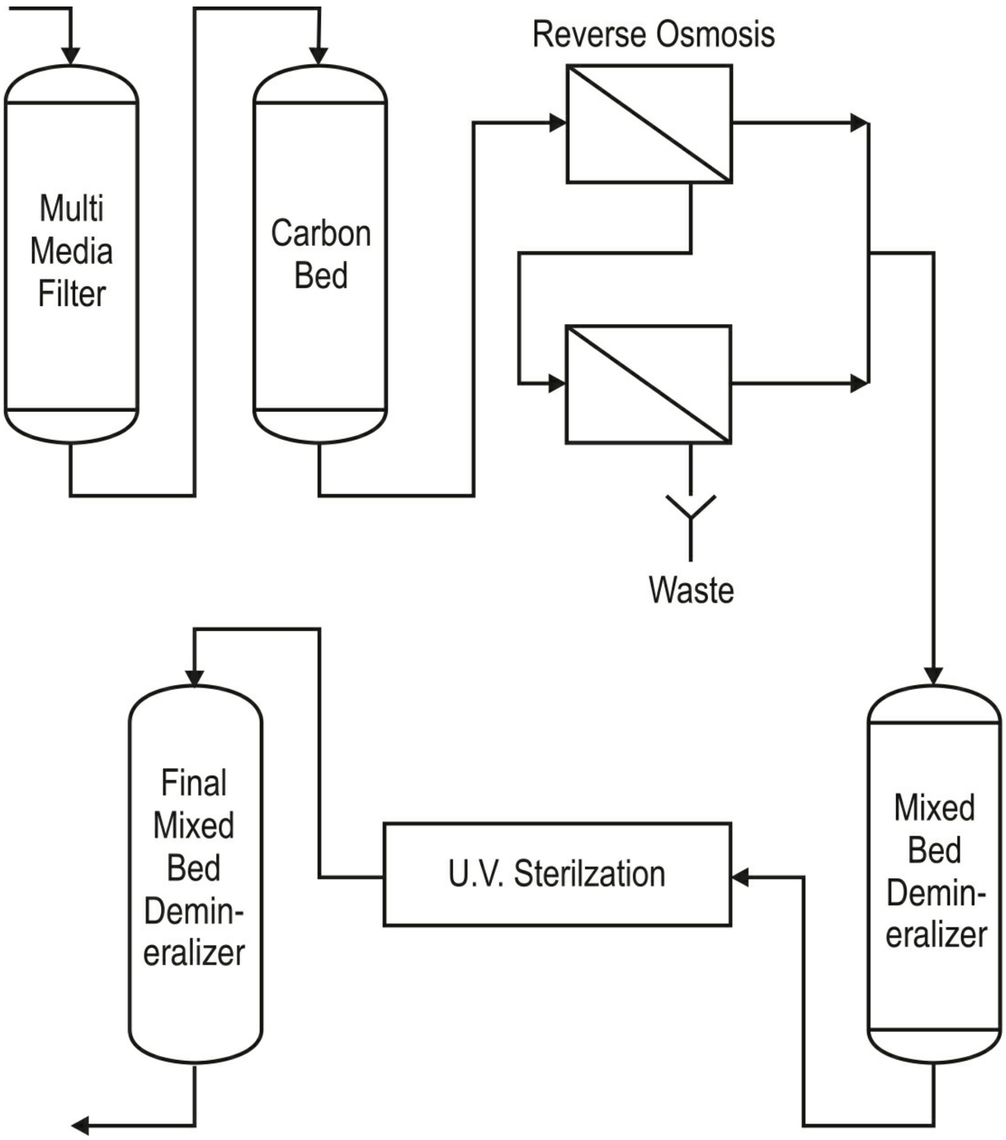


FIGURE 41.1 Typical UPW treatment operations.

Due to the critical nature of this water stream, a sizeable investment is made in its monitoring and control; instrumentation for conductivity, pH, sodium, silica, resistivity, total organic carbon (TOC), and particle counting, are all common instrumentation features on a UPW system. It is also interesting to note that as the industry continues its microminiaturization trend, the demand for higher purity water increases correspondingly.

Typical challenges encountered in these systems include maintaining proper unit operations performance, coping with incoming water quality changes, achieving or exceeding asset life targets, keeping operational costs under control, and adapting to new water quality standards that are the result of an evolving manufacturing process.

In putting together a set of process units to meet high purity standards, the water chemist is faced with selecting equipment that reduces each of the following:

- Soluble matter—minerals, organics, and gases
- Particulate matter—filterable by a 0.22 µm membrane
- Colloidal matter—smaller than 0.22 µm, usually including silica and heavy metal oxides
- Biological matter—microbes, viruses, and metabolites

The unit operations available for meeting the goals of contaminant removal were presented in earlier chapters of this book. At this stage, it is important to recognize that selection of the best treatment processes requires knowledge of how each unit process relates to the others, as well as to the tasks each performs in contaminant reduction. For example, in some cases, a membrane unit [ultrafiltration, reverse osmosis (RO), or electrodialysis] may be best located ahead of an ion exchange unit, to reduce ion loading or to protect the resin from organic fouling. In other cases, the membrane unit may be best located after ion exchange, to eliminate organics that may be present as a result of deteriorating ion exchange resins, or to filter bacterial debris that may slough from the ion exchange beds.

Another factor to consider is the effect of flow rate on water quality. Two contributors to flow-affected quality are the ion exchange units, which should not be kept online at zero or low flows (less than about 20% of rated capacity), and the materials of construction of the storage and distribution system, which may contaminate water at low flow as a result of leaching organics from plastics or corrosion of metallic alloys.

The final UPW configuration depends on local water conditions and economics, growth potential for the fab, desired future flexibility, and other factors. Figure 41.2 illustrates how this process may come together at a plant.

The function of each of the units shown on this flow sheet is described below.

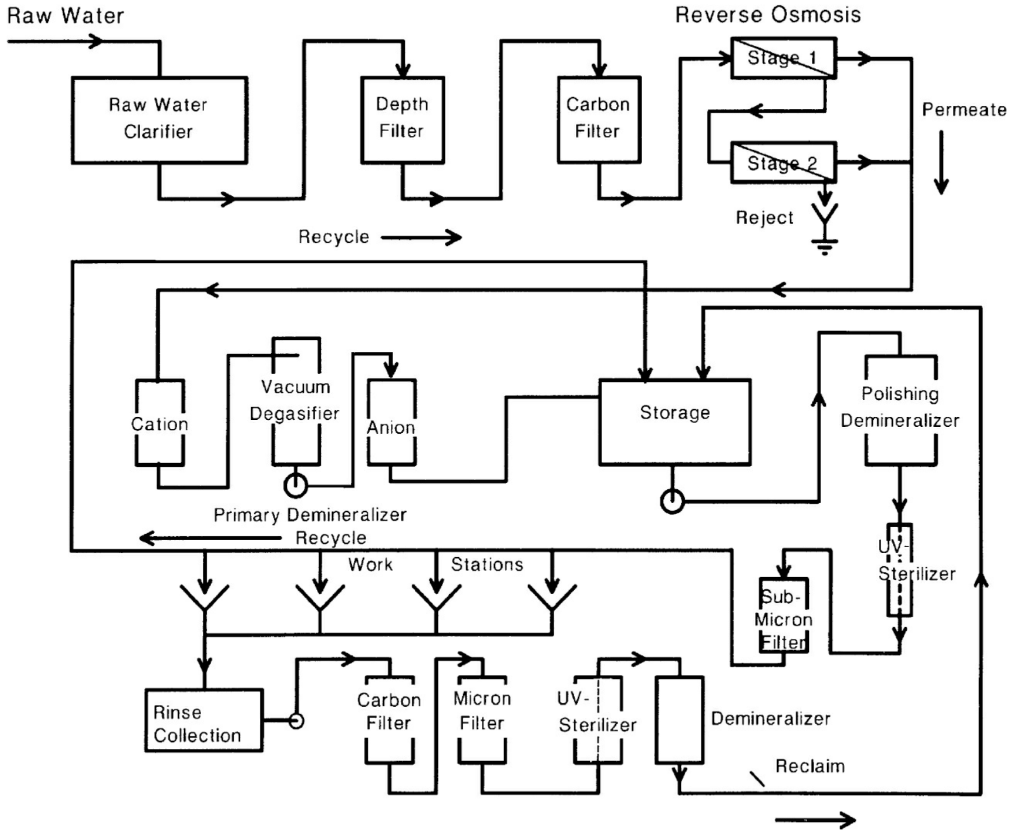


FIGURE 41.2 Schematic of UPW system producing rinse water for microprocessor manufacture. The rinse water after use is generally of such high purity that it can be reclaimed for other uses.

Water clarifier—This is required if the water source is surface water containing suspended solids. Coagulants and flocculants may be applied to the clarifier for the removal of these solids, and chlorine may be applied for disinfection. If the water is hard (usually over 100 mg/L total hardness), the clarifier can be treated with lime for partial softening. The resulting high pH assists in the removal of heavy metals and in disinfection. If the raw water is taken from a municipal distribution system, the clarifier is unnecessary. An ion exchange softener may be utilized in this case to protect the downstream RO unit from fouling. The RO is generally controlled to produce a negative Langelier Saturation Index (LSI) in the reject stream.

Multimedia filter—This unit polishes the clarifier or lime softener effluent and reduces turbidity to below 0.1 NTU. It provides for the removal of many types of microbes; even viruses may be removed if consolidated into a filterable mass by flocculation. A filter is unnecessary if the first unit is an ion exchange softener.

Carbon filter—This filter serves two purposes: it eliminates residual chlorine by direct reduction and thus provides protection for the ion exchange resins downstream, and it adsorbs certain nonpolar organics from the raw water supply. This latter function helps to protect anion exchangers downstream from organic fouling.

Membrane separation—This process may include an RO unit that provides reduction in dissolved ions, reduction in dissolved organic matter, and filtration of colloidal matter, microbes, and microbial debris. The first benefit, reduction in dissolved ions, greatly reduces the ion loading on downstream ion exchange units. The second benefit, reduction in organics, improves the final quality and, at the same time, helps to protect the downstream ion exchangers from organic fouling. The third benefit, filtration of biological materials, protects the downstream equipment from either direct microbial attack or from becoming an incubator of microbial life; it also removes larger colloidal silica fractions. The RO unit may be replaced by a membrane ultrafilter (UF) that has all its advantages, except ion reduction, at a lower cost of operation and with lower loss of reject water.

Primary demineralizer—This is usually a two-bed ion exchanger, especially if the membrane unit contains RO membranes. However, this may be an evaporator, which provides for organic removal, disinfection, and degasification, operating effectively on an influent that has been processed by RO, while providing the additional benefit of reducing dissolved gases.

Storage tank—This unit is provided to allow for continuous recycle of downstream water to minimize leaching and degradation of water quality. A vapor space protection device, nitrogen blanketing, or both must be provided. They are, in fact, process units themselves, designed to protect water quality from degradation by airborne debris, especially microbes, as the storage tank breathes. Ultraviolet (UV) sterilizing lights may be mounted on this storage tank.

Polishing demineralizer—This is usually a mixed bed ion exchanger, but could be a RO unit, and electrode ionization (EDI), or an evaporator. In some plants, the polishing demineralizer is a nonregenerable unit with specially processed, nuclear grade ion exchange resins.

Ultraviolet sterilizer—UV irradiation using a wavelength of 254 nm provides for final nonchemical destruction of any microbes that entered the system after storage and survived the earlier treatment stages. The persistence of microbial contamination through successive physical barriers is an accepted fact to designers and operators of UPW systems. Conventional chemical biocides (e.g., chlorine) are to be avoided, because they represent a source of contamination. UV radiation oxidizes organic matter to produce carbon dioxide, which reduces resistivity. The sterilizer cannot always be used in this location, if the water contains excessive organic contamination at this point.

Submicron filter—This filter removes the residual debris, such as fragments of microbial cells, before the point of final use.

Point of use—There are often disposable mixed bed demineralizer cartridges containing special nuclear grade resin followed by submicron filters at each workstation at the final point of use. Since the excess water used in the rinse operation is often quite pure, it is reclaimed, reprocessed, and returned to the main storage tank. A special UV unit may be installed here for oxidation of organic matter at a wavelength of 185 nm.

Process Cooling Water

Process cooling water (PCW) refers to the loop of chilled water that is circulated to the tools (machines that perform discrete steps in the manufacturing processes). It is important to note that not all tools are water-cooled; some tools simply dissipate heat into the manufacturing area of the fab, where it is absorbed by the fab’s chilled water loop. For those tools that are water-cooled, the PCW loop helps regulate the temperature of that specific manufacturing step, usually by providing dedicated heat removal. PCW loops may be primary or secondary chilled water loops off the main chilled water system.

The number of tools in a fab can be as high as several hundred. These tools represent the bulk of the investment in building a microelectronics fab. The cost of a single tool could be millions of dollars, depending on the manufacturing technology. Likewise, the cost of production is high, and production uptime is critical. In order for a microelectronics fab to remain commercially viable, it may upgrade its manufacturing technology by changing a set of tools. This change often involves disconnection and reconnection to process gases and fluids, process drains, and may involve the PCW loop. A successive tool may connect to the PCW loop, where its predecessor did not.

Despite the PCW loop’s importance, it is often one of the most ignored water streams in the fab. A multitude of metallurgies can be present. These metallurgies are ever changing, as tools are added and removed as the fab upgrades.

Typical challenges encountered in these systems include proactive measurement of system performance and keeping track of system changes.

Cooling Towers and Chillers

The cooling towers in a microelectronics fab are used to cool the chillers, which in turn cool the PCW loops. As with PCW systems, reliability is critical.

The primary issues of corrosion, scale, and microbial fouling have already been covered within this book. Of specific relevance to the microelectronics industry is opportunities and pitfalls regarding water reuse to the cooling tower. The large quantities of water generated by the RO reject system in the UPW train, as well as the various process rinse waters, can be highly attractive opportunities for water reclamation and fresh water reduction. However, as with many opportunities, there are good ways and not-so-good ways of approaching them. Balancing water chemistries, local water and sewer costs, seasonal and process variability and quality, and effective monitoring and control technologies, are just some of the factors to incorporate into a site-appropriate strategy to minimize risk and maximize water reuse. Any water reclamation program involving the cooling tower must keep the heating, ventilation, and air conditioning (HVAC) asset, and the production it supports, at the forefront of its priorities.

Challenges associated with these systems include classic problems of scale, corrosion, and microbial control, with special considerations for water quality variations corresponding to the degree of water reclamation.

Wet Scrubber Systems

Wet scrubbers are used to improve air quality leaving the fab. They accomplish cleaning by mass transfer between the air stream to be cleaned (scrubbed) and a water stream passing through a packed column. These streams are oriented for cross- or countercurrent flow of the air and water streams. Typical contaminants to be removed include ammonia; sulfuric, phosphoric, nitric, hydrofluoric and hydrochloric acid fumes; and various organic solvents.

Normally, wet scrubbers are designed to prevent corrosion; metals are rarely used. However, scale and microbial growth can occur.

Challenges associated with these systems include understanding the nature and composition of the streams being scrubbed, having good analytical data on the chemistry of the water being used in the scrubber, and understanding the variability (quality and quantity) of both air and water streams.

CHAPTER 42

The Building Materials Industry

We see them every day, but seldom do we take the time to really think about where they come from or how they are made, until we decide to fix our leaking roof or renovate our kitchen or bath or, better yet, build a whole new house. We are talking about building materials, those essential components that allow us to build our homes and businesses to be comfortable and effective in what we do on a daily basis.

As our population grows and our societies become more complex, we have a larger need for more and different types of building materials. That need has led to a reduction in our natural resources that in turn has resulted in the development of newer technologies for building. Many different materials are used for residential and commercial buildings. Two of the more common technologies are fiber cement and fiberglass mat. Both of these materials are relatively new on the scale of products used for building in comparison to wood, brick, or metal; however, they have been around for more than 40 years. Fiber cement and fiberglass mat have become fully integrated into our building processes and are used in many different applications in both residential and commercial building.

Fiber Cement

Fiber cement is a process that utilizes pulp, cement, silica, and sand to make durable building materials such as siding products, backerboard, and pipe.

Fiber cement siding provides low maintenance and does not sacrifice the beauty and character of wood. It resists rotting, cracking, and damage from rain and hail. It is noncombustible, with an expected use life of up to 50 years. This siding is available prefinished and may have a 15-year paint warranty.

Fiber cement backerboard, used in potentially moist areas like kitchens and baths, is a moisture and mold resistant substitute for drywall or a backerboard for tile applications. Cement board is a common solution for wet area floors, walls, ceilings, and countertops. Although no system is mold proof, this product delivers the ultimate in mold resistance, passing industry mold tests.

Fiber cement pipes are the product of choice for many below ground storm water drainage applications, providing significant installation and performance benefits over traditional reinforced concrete or steel. The expected service life of over 100 years, the comparative lightweight composition, the construction load capacity, and the availability of longer standard pipe lengths, makes these pipes a product of choice in many applications.

There are two distinct manufacturing methods for fiber cement—Hatschek and Fourdrinier. Each requires different process chemistries to operate effectively (see Fig. 42.1 for a general process overview).

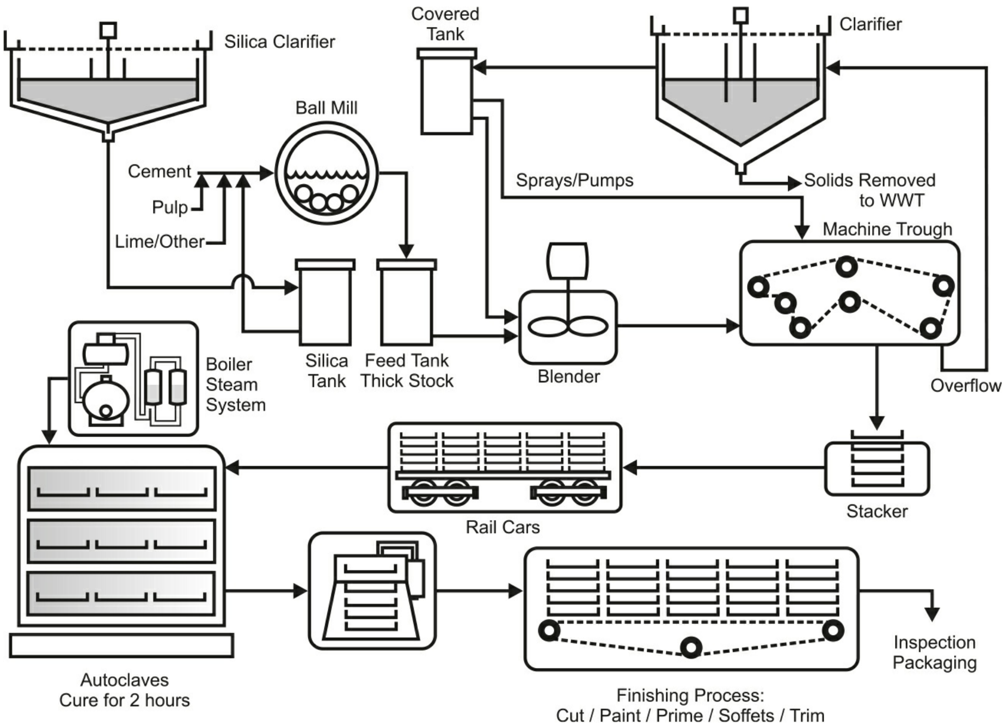


FIGURE 42.1 Fiber cement process overview.

Water is used throughout these processes. Water is the primary solvent used to disperse and carry the pulp, cement, sand, silica, and chemistries that actually make up the finished fiber cement product. This water is drained, collected, and recycled as part of the normal operating process. Chemicals are used throughout this process to enhance product quality, production speed, etc.

Water is also used in the steam boiler operations in these plants. Steam is often used in autoclaves to cure the fiber cement product before further processing to finished goods. These autoclaves are typically operated at 170 psig (1.2 MPag), and product is cured for approximately two hours. In addition to use in the autoclaves, steam may also be used for plant or office heat.

The typical steam boiler plant design will consist of makeup water from the local municipality or local ground or surface water, treated by sodium softeners to remove hardness. This water will then be deaerated to reduce dissolved oxygen. The feedwater will then go to two 200 to 250 psig (1.4–1.7 MPag) boilers of either watertube or firetube design. Steam from these boilers will primarily supply the autoclaves, where it will condense and be collected in a condensate storage tank. This condensate will often be pumped through a plate-and-frame makeup water preheater before sewer discharge. These plants do not typically return condensate to the boilers, as it is most often highly contaminated with by-products from the cured fiber cement.

Problems associated with these boiler water applications are not unlike traditional difficulties experienced in other low-pressure boiler operations. The makeup water must be softened to less than 1 mg/L total hardness to avoid scaling of boiler internals. Because these boiler systems are typically 100% makeup with no condensate return, this is a very critical step. It is common to see poor quality makeup water due to improperly operating softeners. These units should be audited regularly to insure effective operation.

The makeup water must be deaerated to less than 7 µg/L dissolved oxygen to help prevent feedwater and internal boiler corrosion. Typically, a catalyzed sodium bisulfite is added to the deaerator storage to further reduce dissolved oxygen to below critical levels.

To help prevent deposition in the boiler internals, an internal boiler chemical treatment program should be utilized. Any conventional low-pressure boiler program can be used. Regardless of the chosen chemistry, the goal is to prevent deposition of hardness and iron in the boiler while reducing corrosion rates.

A final area of concern in these boiler systems is the makeup preheat exchanger. The condensate from the autoclaves is often pumped through an exchanger to preheat the makeup water thus reducing plant energy consumption. This condensate often contains significant contamination from the fiber cement in the autoclaves. This contamination may cause fouling or scaling on the condensate side of the heat exchanger, leading to reduced heat exchange or even plug gage. To prevent this, a high-temperature polymeric dispersant is often employed. Typically, corrosion is not a problem on these exchangers due to the use of corrosion-resistant construction materials.

Fiberglass Mat

Fiberglass mat refers to a material that is typically used in the roofing industry to make various forms of shingles and roofing barriers. It is also starting to be used as a replacement for paper in the production of drywall sheeting. As one might expect, fiberglass mat is very tightly tied to the building materials market place and specifically the roofing industry. It is made through either a wet-lay or dry-lay nonwoven process that produces a base sheet called mat. In the wet-lay process, the mat is produced using fiberglass chop, binders, dispersants, and surfactant. Mat must meet physical specifications for tensile strength, dispersion, and tear strength.

In the wet-lay process, chemically sized chopped glass fibers of the type, diameter, and length suited to the customer's application are slurried in water and then spread uniformly across a fine mesh belt. This thin layer is impregnated with an appropriate resin binder, dried, cured, and finally wound into rolls. This wet-lay process produces economies of scale, because of its relatively high throughput when compared to dry-lay mat manufacturing processes. It also offers a more consistent and uniform mat than other forming techniques.

Roofing products strengthened with a glass fiber substrate keep their shape during shipping and handling. Once installed, the reinforced shingle provides superior strength and dimensional stability over a wide range of temperatures, without absorbing moisture as organic felt shingles do.

Because it is inorganic, the glass substrate has excellent resistance to rotting and mildew. As a result, the shingle performs better and longer than those made with alternative substrates. They also require less sectant asphalt than organic shingles, as glass mat is an ideal porous reinforcing media.

The major raw materials consist of, glass fiber, sizing, water, resin binders, adhesive enhancers, and specialty chemicals for white water preparation.

The wet-lay process tends to flow as discussed below and shown in Fig. 42.2.

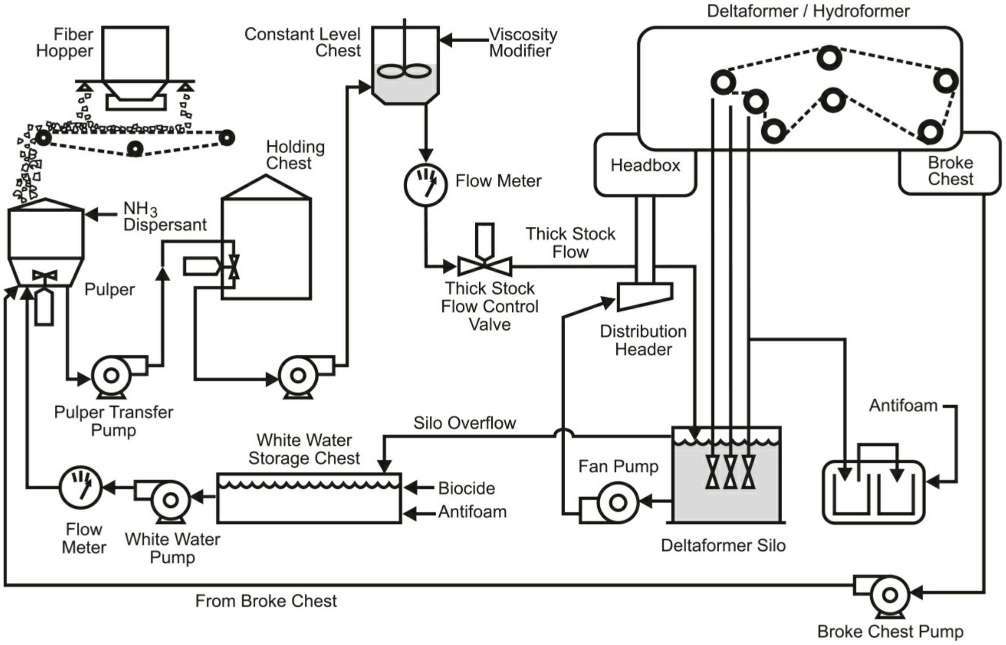


FIGURE 42.2 Fiberglass mat manufacturing.

The major components of a typical fiberglass mat machine are:

- Head box
- Forming wire
- Vacuum forming box
- Broke chest
- Machine silo or DELTAFORMER^{TM}
- Collection chest
- Clarified chest
- Water storage chest

The fiber feed system automatically feeds a specified quantity of fibers to the pulper that blends the fibers, water, and chemicals with agitation to disperse bundles of fibers into filaments in the thickstock slurry. The machine/holding chest acts as a surge tank and buffer between the batches from the pulper and allows for continuous thickstock flow. The constant level chest provides a constant head to the flow control valve to give a steady flow through the valve and pipe.

Head box—The head box is a large flow control chamber that feeds the stock to the forming wire. Sufficient agitation is maintained by means of baffles. This agitation ensures the proper mixture to prevent flocculation of the fibers. The agitation spreads the fiber slurry evenly to the full width of the wet-lay machine to provide delivery of stock to the forming wire.

Forming wire—The forming wire is a polyester fabric of various weave patterns used for fiber deposition and to carry formed fiberglass mat. The goal is to form a continuous and uniform web of fibers. To accomplish this, the white water slurry is controlled to lay fiber out on the former wire.

Vacuum forming box—The vacuum-forming box removes excess water in the sheet before binder saturation. A binder solution is added to the fiber web to essentially "glue" the fibers together. After the binder is added, the water is removed via vacuum, and the sheet is sent through a drying and curing process to complete the chemical reactions to bond the fibers.

Broke chest—The broke chest collects the wet trim, full-sheet dumps, water, and fibers from the wire until they can be pumped back to the front of the process.

Machine silo or DELTAFORMER™—The machine silo returns white water from the formation zone, deaerates the water to reduce foam, and supplies a constant head of water to the fan pump.

Collection chest—The collection chest collects white water from the vacuum separators and the white water silo to be used to supply the filter system.

Clarified chest—The clarified chest holds water returned from the filter screen until it is pumped to the high-pressure showers.

Water storage chest—The water storage chest water is sent to the pulper to make up white water batches.

Water is a key element in the production of wet-lay fiberglass mat. Water is the primary carrier of the fibers that make up the mat. Mat thickstock, as it is called, is a combination of water with chopped up and sized glass fibers and proprietary specialty chemicals, including viscosity modifiers, dispersants, antifoams, and biocides. This mixture is often referred to as white water due the white color of the slurry. The quality of water, including its pH, temperature, and total hardness, is critical in attaining the expected product results. Through monitoring and controlling these variables and the applied chemistries, the fiberglass mat manufacturer can modify the type, quality, and speed of production.

CHAPTER 43

The Automotive Industry

The automotive industry segment is composed of a variety of automotive manufacturing operations, including parts manufacturing, body manufacturing, and vehicle assembly. Within these different manufacturing processes, four basic operations are found in the production of most of these products:

1. Casting (foundry operation)
2. Machining
3. Stamping and fabricating
4. Final assembly

Some plants may perform just one of the above operations, while others carry out the entire process from casting through assembly at a single integrated plant. Figure 43.1 shows the flow of material for the total operation of an automotive plant. Although water consumption is relatively modest in each of these operations, water quality is important, and aqueous wastes are quite concentrated.

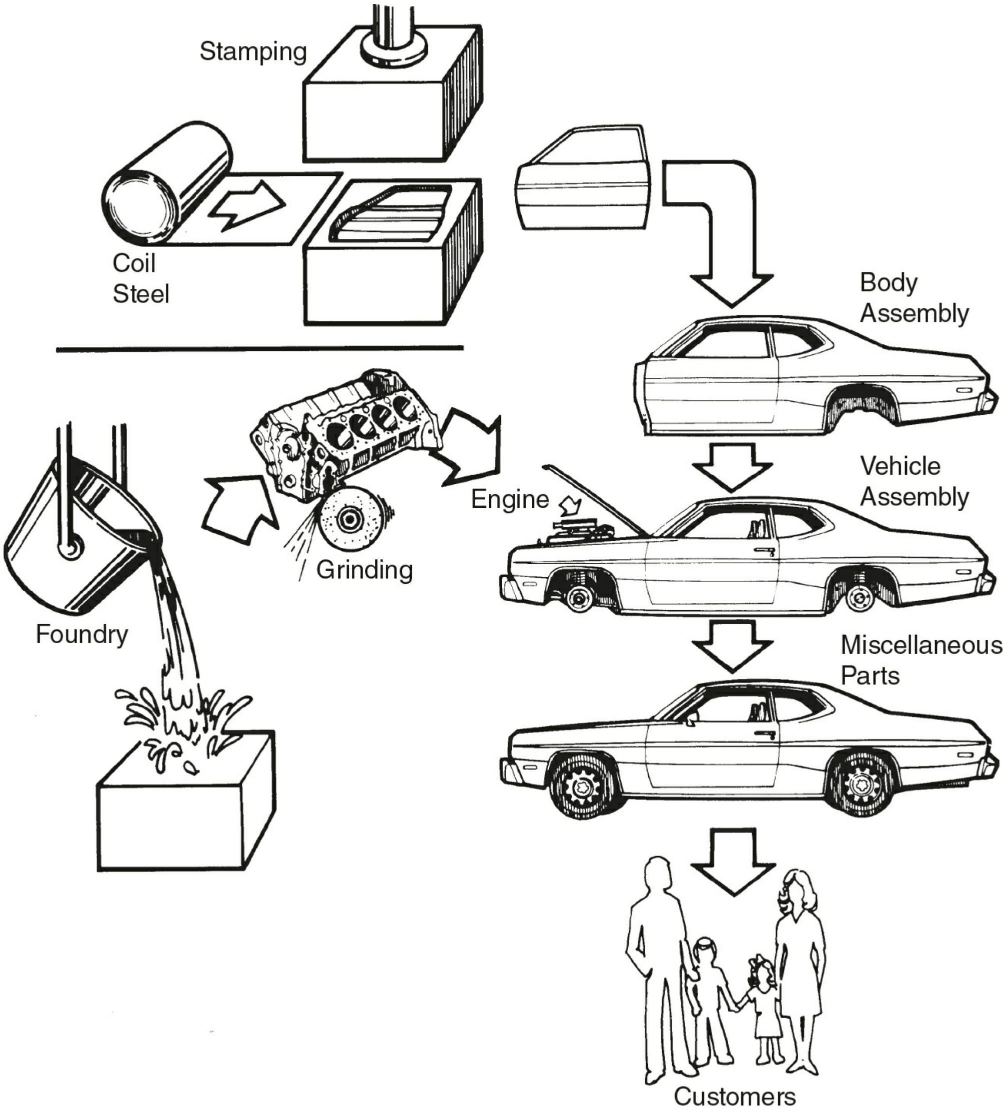


FIGURE 43.1 Basic automotive manufacturing.

Foundry Operations

In the foundry, parts such as crankshafts, engine blocks, and transmissions are cast. In a typical iron foundry, pig iron is purchased from a steel mill and melted in a furnace called a cupola, similar in design to a blast furnace. The iron is mixed in the furnace with a charge of coke and a flux or slag-forming material, which may be limestone or fluorspar. Air is blown into the furnace at the tuyeres, as in the blast furnace, and the combustion of the coke melts the charge, with molten iron draining to the bottom and slag floating to the top.

The gases leaving the cupola are combustion products, predominantly carbon dioxide (CO_2) with perhaps a small amount of carbon monoxide (CO) plus a small amount of sulfur dioxide (SO_2), if the coke was made from sulfur-bearing coal. When the charge is dumped into the burden, there is some breakup of the relatively weaker coke lumps, and there is an initial surge of coke fines into the exit combustion gases. There usually is iron oxide broken loose from the bars of pig iron, so the discharge from the cupola is high in suspended solids (SS).

To avoid creating an air pollution problem, the foundry may install a baghouse for dry collection of the dust or a wet scrubber. If the latter is installed, this becomes the principal use of water in the foundry operation. A typical foundry operation is shown in Fig. 43.2.

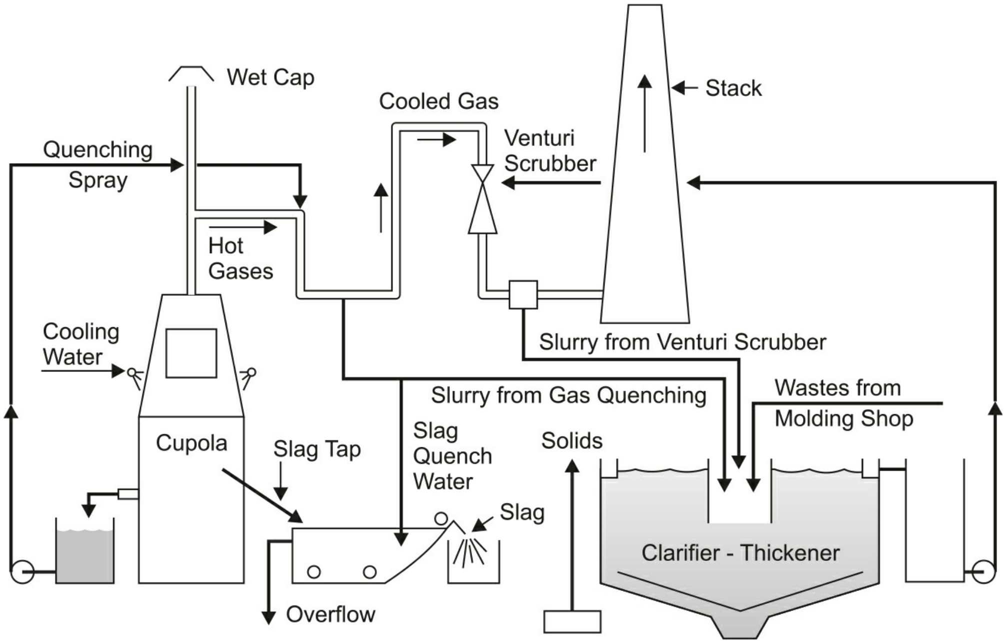


FIGURE 43.2 Water circuit in a gray iron foundry with wet scrubber.

Because the products of combustion are acidic, the pH of the scrubber water is generally quite low. Figure 43.3 shows a pH chart taken from a recorder sampling scrubber water. The effect of opening and closing the charging door is to dilute the stack gases, which is apparent on the strip chart.

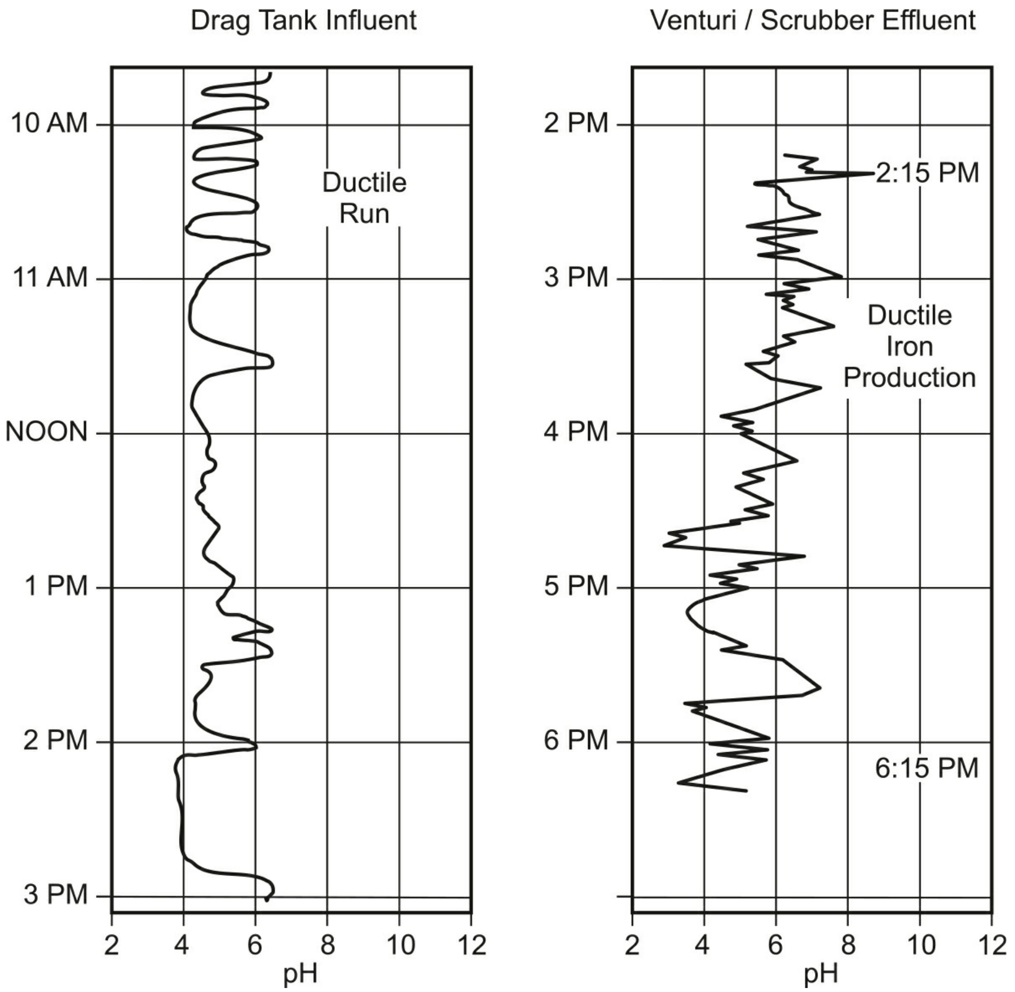


FIGURE 43.3 Strip charts showing pH variations in Venturi scrubber effluent.

A second use of water in the foundry is for cooling the cupola shell. This is usually done by direct spraying of the steel shell with water through a circumferential pipe at the top of the cupola. This water may be collected at the bottom of the cupola, pumped over a cooling tower, and returned to the top of the cupola. Most foundries adjust pH and add a corrosion inhibitor to protect the cupola shell.

A third use for water is in the granulation of slag tapped from the cupola. The molten slag collects in the granulation tank, and the slag grains are removed by flights up a ramp and discarded into a tote box.

Most foundries encounter dust problems in the preparation of sand molds and the breakup of the sand from the finished casting, where the material is crushed for return to the molding room. A variety of chemicals may be mixed with the sand to produce the green mold, which must be cured before molten metal is poured into it. Phenolic compounds are sometimes used in preparing the mold, so phenol may be present in the foundry wastewater, both from this source and from the coke charged to the cupola. Oils may also be used in the preparation of the mold, and these volatilize during the baking of the mold and must be collected by a wet scrubber. Depending on the operations, there may be individual wet scrubbers at the cupola, the sand mold, and the shakeout room, or wastewater from these areas may be combined before treatment.

Table 43.1 shows the analysis of a foundry wastewater related to the installation illustrated in Fig. 43.2. The oil content was quite high, but there was no evidence of free oil in the sample. This is a common occurrence, where the bulk of SS consist of carbon and iron oxide, as in foundry operations.

Constituent	mg/L
TDS	770
SS	1900
Extractables (oils and grease)	290
Phenols*	1.5
pH	7.6

---

*Present in the coke and core binders

TABLE 43.1 Analysis of a Typical Foundry Wastewater

After the treatment of this particular wastewater, the oil content was reduced to less than 50 mg/L, SS to about 56 mg/L, and phenol to 0.5 mg/L. The collected solids were vacuum filtered for disposal, and the oil content of the dry cake was about 15%.

There is often some fluoride present in the wastewater, which may be introduced by volatilization into the cupola stack gas, or may be dissolved from the slag in the granulation tank. Since most foundries discharge into a city sewer, the amount of fluoride is not usually so high as to require special treatment.

There is evaporation of the scrubber water, leading to concentration, so that chemical treatment is usually required for control of scale and corrosion in the recirculating system, and special alloys are often required for the circuits of a multiple-circuit washer, where the pH may become very low.

Machining

Rough cast parts are sent to power train plants to be machined and assembled. Figure 43.4 shows the typical operations in a plant that machines parts for and assembles car engines. Major operations include machining, cleaning, engine testing (hydrotest), and waste treatment.

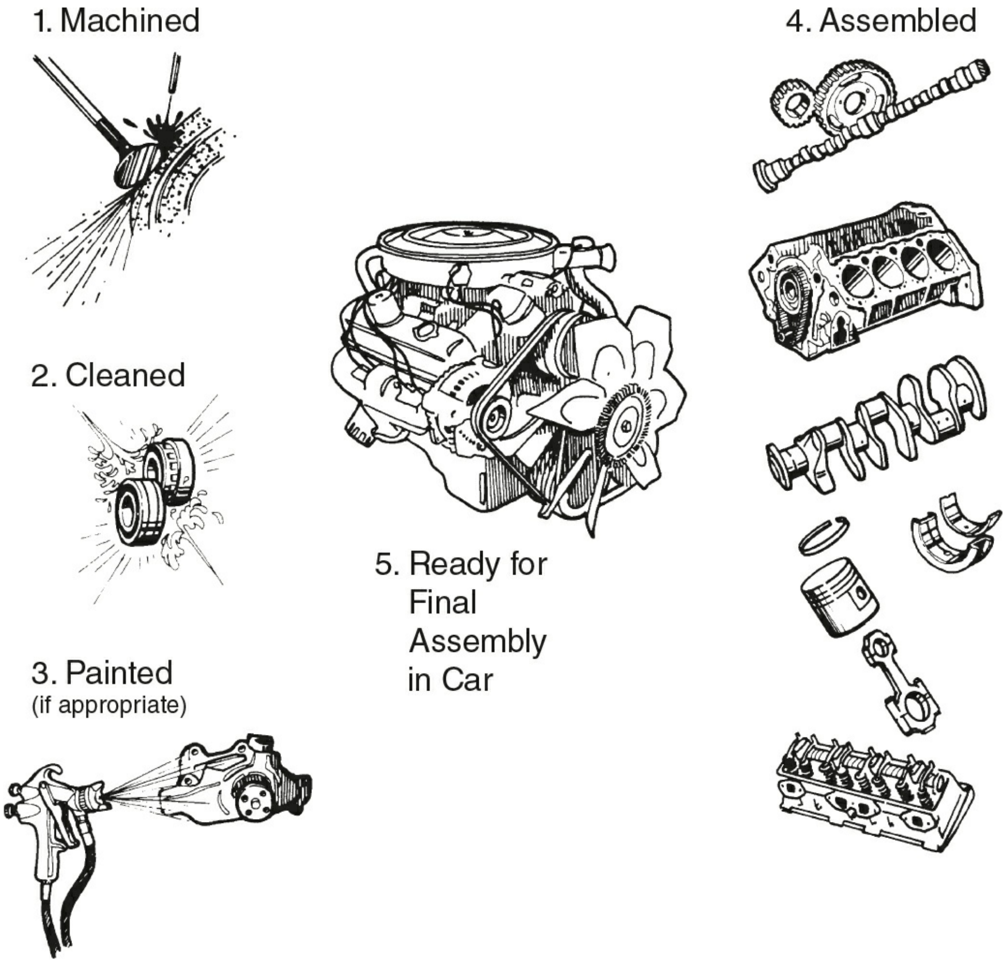


FIGURE 43.4 Typical operations in an engine plant.

Rather than a single assembly line for the machining operation, a series of small lines is set up for each part and department. Each department performs its own particular machining operations on the subassemblies, and each of these may require a specific type of machine coolant, varying from water-based material to heavy sulfur oil. These coolants provide lubricity and cooling to the metal and tool used for shaping. Many of these oils contain emulsifiers that readily create oil–water emulsions when mixed with water.

Some coolants are soluble synthetic and semi synthetic oils. The synthetic coolants contain no oil, while the semi synthetics contain some oil but less than soluble oil coolants. These have some advantages over soluble oils in the machining process.

Soluble oil coolants are usually maintained at 5 to 15% oil concentration and stored in central sumps. The oil is recirculated through screens or filters to the machine tool and back to the sump. At the machine, the soluble oil absorbs heat and picks up metal fines and hydraulic oil from leaks. Plants will normally dump part of the coolant system periodically, because the emulsion is no longer stable or the coolant is contaminated with bacterial growth. It is good practice to add biocide to control bacterial activity, but even this cannot extend coolant life indefinitely.

City water is used to make up the coolants. If high hardness levels are found in the makeup water, soft water is sometimes advantageous, because calcium ions tend to destabilize the emulsions, especially if the coolant concentrates. Removing the calcium and magnesium extends the stability of the soluble oils.

Parts Cleaning

Another major operation in the machinery plant is cleaning. The parts must be cleaned before and after machining to remove dirt, rust preventive, and coolant. Chemical cleaners are used, usually alkaline and nonionic surfactants. The cleaner usage is substantial, since the cleaners are continually depleted and fresh chemicals are needed to maintain the strength necessary for effective performance.

In the machine shop, blowdown from the parts cleaners may represent a significant portion of the flow to the waste treatment plant. Because a primary function of the cleaner is to remove coolant, blowdown usually contains high levels of oils and synthetic oils. These wastes are emulsions stabilized by the surfactants in the coolant and in the cleaners. Other flows to the waste plant include soluble oils, other cleaners such as floor cleaners, cooling water from a variety of sources (such as air conditioning systems), boiler blowdown, hydraulic oil leaks and spills, and other process waters.

Changing from soluble oil to synthetic coolant has caused problems in the waste treatment plant, when acid and alum were being used for emulsion breaking. Organic emulsion breakers have proved more effective in removing oil from the effluent under a wide variety of coolant selections. However, reduction in soluble biochemical oxygen demand (BOD) by alum or organic emulsion breakers is usually very limited. BOD loadings to the waste plant may actually increase, since synthetics usually have higher BOD than soluble oils.

Another factor that can have an impact on the quality of the waste treatment plant effluent is process cleaner usage. Excessive cleaner usage, especially of certain strong nonionic cleaners, can increase dosages in the waste treatment plant or even make the waste virtually untreatable. The volume and type of cleaner should be balanced against the impact on both the cost and quality of the waste treatment plant operation.

Table 43.2 shows a typical analysis of untreated effluent from a machining plant. The effluent is an oil-in-water emulsion. This analysis does not include free or floating oils.

Constituent	mg/L
Hexane extractables	4000
P alkalinity (as $CaCO_3$)	424
Total alkalinity (as $CaCO_3$)	708
SS	300
Total iron (as Fe)	4
TDS	1500
pH	10.4
Calcium hardness (as $CaCO_3$)	20
Total hardness (as $CaCO_3$)	26
Total phosphate (as PO_4)	3

TABLE 43.2 Raw Waste from Machining Operations

Utilities

Machining plants use cooling water for air conditioning, powerhouse diesel generators, air compressors, hydraulic oil coolers, and furnace cooling if the plant is involved in heat treatments such as annealing.

Each plant, depending on what it manufactures, may have its own unique uses for cooling water. For example, engine plants typically hydrotest the assembled engine on a dynamometer before shipment. A typical test system is shown in Fig. 43.5. On the tube side or closed side, the heat exchanger takes the place of a radiator. Soluble oil products are used on the closed side, if the engine is going to be drained before shipment. These products lay down a film that prevents flash corrosion. If the engine is not going to be drained, either soluble oil or conventional corrosion inhibitors can be used, depending on the manufacturer's restrictions.

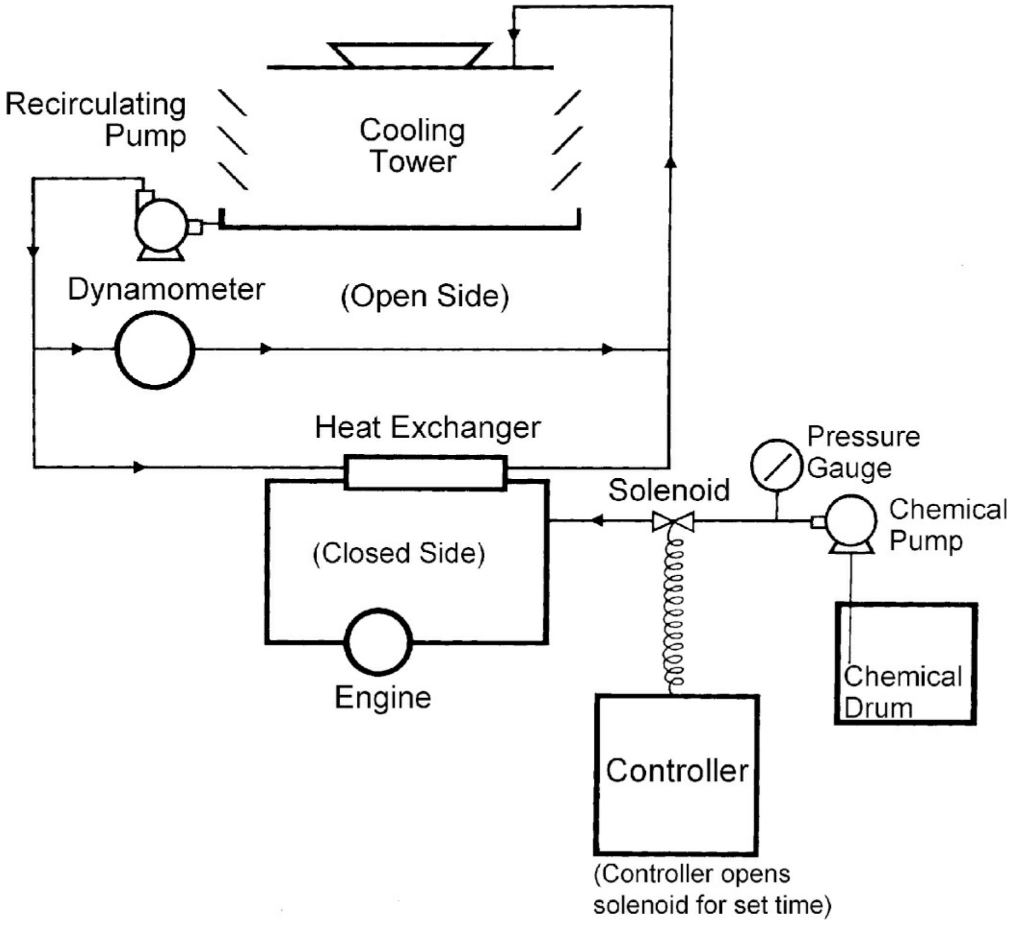


FIGURE 43.5 Cooling water circuit for hydrotesting finished engines.

A typical boiler plant generates steam primarily for heating various cleaner and bonderizing baths, but the winter heat load is also significant. Therefore, summer steam demand is light. If the plant has a forging operation, steam may be used to drive the hammers (Fig. 43.6). Sodium softening, reverse osmosis, and demineralization are the most common methods of pretreating boiler makeup water.

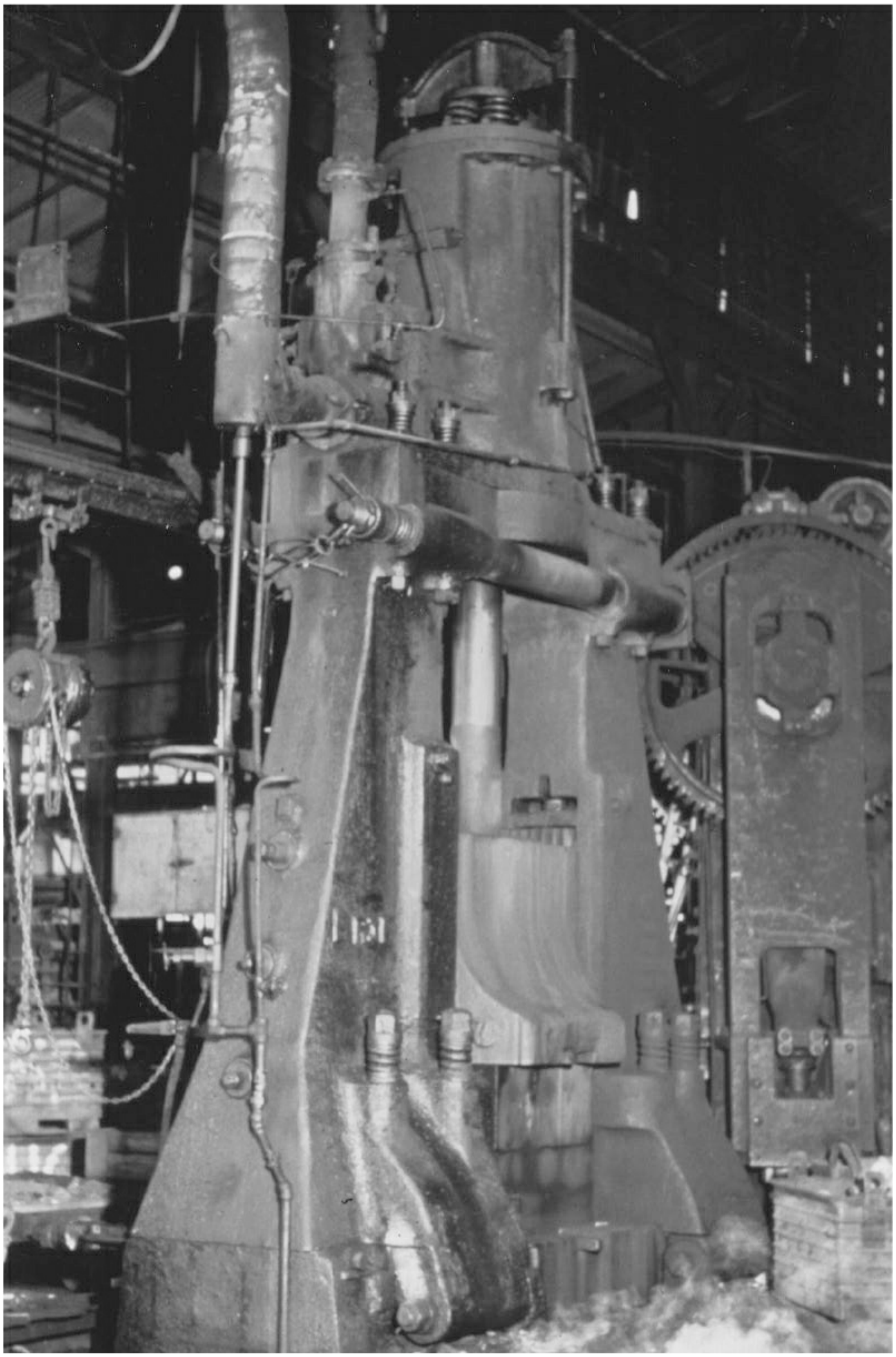


FIGURE 43.6 Large steam-operated forging hammer. The dies and sow block have been removed for routine maintenance. (*Courtesy of Forging Industry Association*.)

Paint Spray Booths

Some machinery plants (such as engine plants) have small spray booths, where primer is sprayed on parts. These small booths experience the same maintenance problems as larger ones, such as those used to paint car bodies, and they require chemical treatment. They are not as important to production, so they are frequently poorly maintained.

Since spray booths are so widely used throughout the automotive and machinery industries, a description is given here to illustrate the type of water technology required for successful operation. Goals of the water treatment program are:

- Keep the water circuit free of deposits.
- Make the paint overspray collected in the water nonsticky and readily removable from the water.
- Minimize deposits to prevent obstructing flow of paint-laden air from the booth.
- Minimize contaminants in the air discharged to the outside so it will not create an air pollution problem.
- Minimize booth maintenance.

Figure 43.7 illustrates a typical paint spray unit for small parts, such as would be found in the machinery plants. The conveyor carrying the parts to be painted passes in front of the wet well, and the operator sprays paint on the parts as they pass by, with the excess or overspray being collected on the film of water flowing down the wet wall. The water must be chemically conditioned so that the pigment and the excess vehicle and solvent are killed and do not form a sticky mass that would be difficult to remove from the pan. Water is continually withdrawn and recirculated to the spray header, which provides scrubbing of the ventilating air discharge before water drains back down the wet wall.

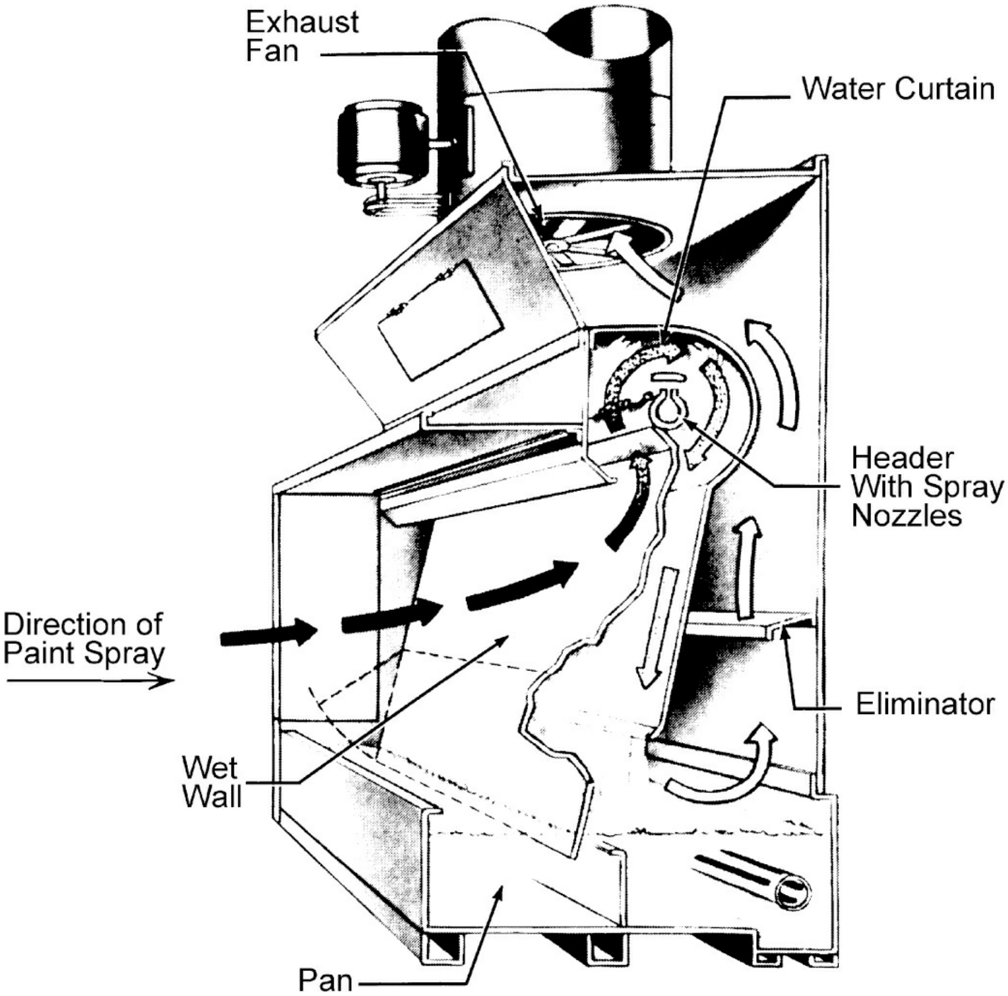


FIGURE 43.7 Small parts paint spray booth.

The large paint spray booths used in the automobile assembly shops are illustrated in Figs. 43.8 and 43.9. Robots and operators work inside these booths, applying paint to the car body. The floor of these units is grating supported above a water basin, and falling paint deposits on the water, while other paint particles are carried by the air flow into the water curtain either on the wet walls or into the wall cavity, or back section, where additional sprays scrub the flow of air.

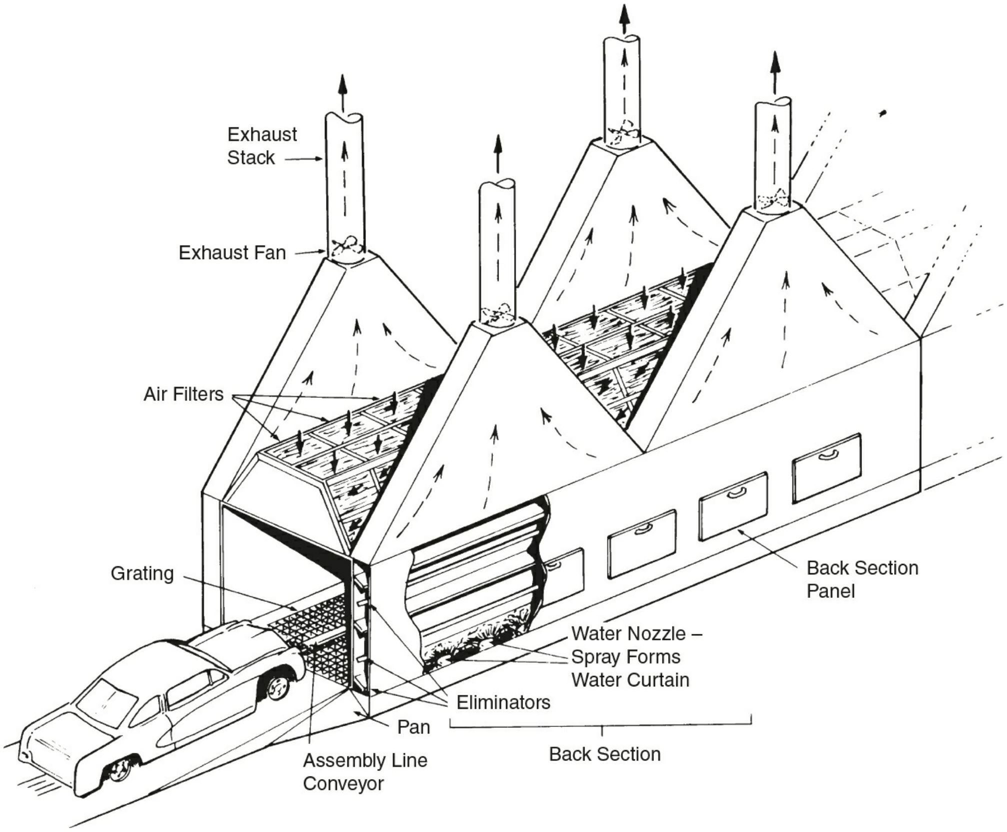


FIGURE 43.8 Automobile paint spray booth.

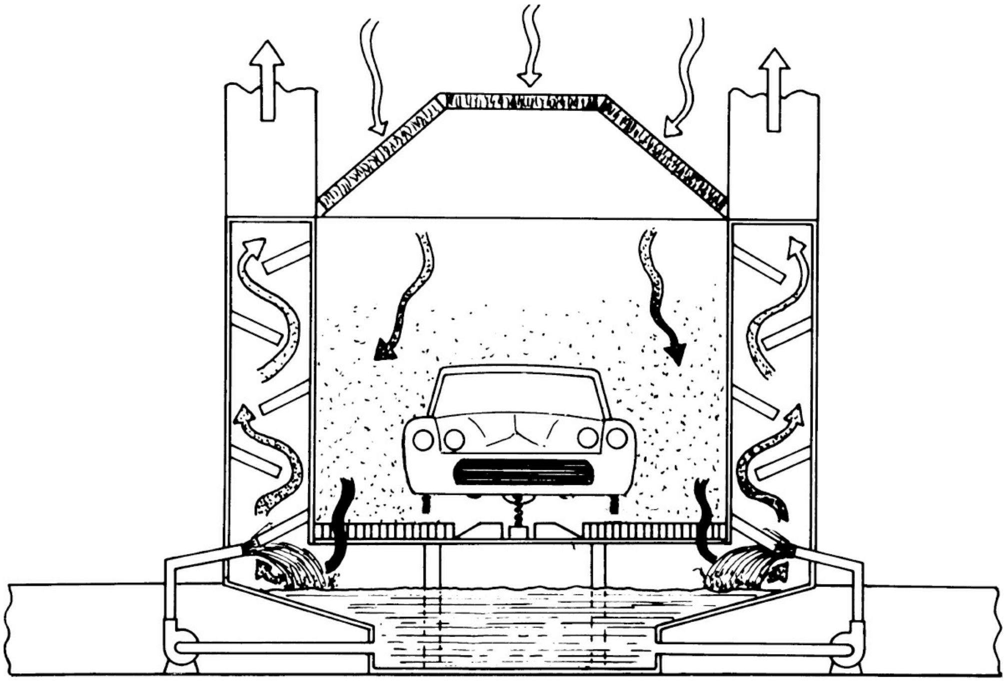


FIGURE 43.9 Cross section of automobile paint spray booth.

Detackifying Paint

Properly treated water will collect the pigment and organic components of the paint and condition these so that they are not tacky, producing a sludge that can be readily handled without sticking to the scrapers or flights used for removal. The material that carries up into the back section is scrubbed out and killed by properly designed and treated water wash, so that deposits do not form in this relatively constricted wall cavity. If the scrubber is not performing properly, particles penetrate the water curtain, build deposits in the back sections, and go out the stack as particulate emissions. In addition to the air pollution problem, extensive maintenance is required to remove the deposits in the back sections, on the eliminators, on the fan blades, and in the basin below the grating to keep the booth operating, so that it provides safety to the operator and a clean discharge to the outside air.

Paint spray booths are in some respects like an air washer, in that the spray water may evaporate and cause concentration of dissolved solids, or water may be condensed from the air, resulting in dilution of the spray water. This means that a check on total dissolved solids (TDS), pH, and alkalinity is required periodically to keep the system under good control.

Recirculation volumes on booths of this type are high, about 10 000 gpm (2270 m^3/h) for a typical body spray booth and 500 to 1000 gpm (114–227 m^3/h) for a parts spray booth. The basin is usually dumped once or twice per year. The actual makeup water requirements are difficult to estimate, because they depend on the evaporation rate and the frequency of dumping, which are unique for each installation.

Stamping

In preparation for stamping, the first step is to loosen mill scale from the metal surface by passing the strip steel through a flex roller (Fig. 43.10). This flex roller bends and flexes the steel through a series of rollers. Wash oil is brushed on during the flexing operation to remove the mill scale and dirt.

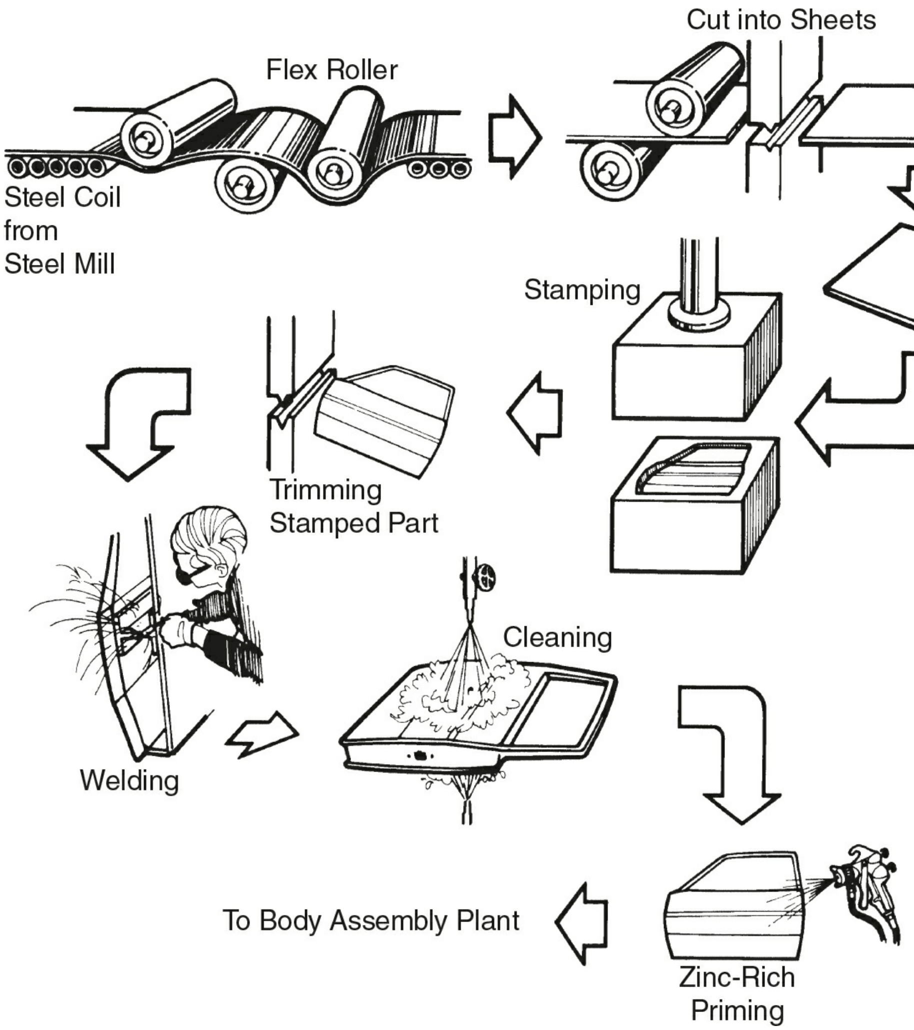


FIGURE 43.10 Fabricating and stamping.

The flexed steel is cut to size and then stamped to the desired shape by large hydraulic presses. Drawing oil is sprayed on the dies to aid in stamping.

The stamped part is further cut and trimmed to the precise size, and the drawing oil, cutting oil, and dirt are removed in a parts washer, creating an oily wastewater. The part may then be welded or primed, depending on the manufacturing requirements. The assembled part is then ready for shipment to the assembly plant. Finished products from stamping and fabrication plants include doors, floor pans, trunks, hoods, and fenders.

The flows from stamping and fabrication are usually quite low [50 000 gpd (189 m^3/d)] and consist of oily wastes from the parts washers, cooling water blowdown, and blowdown from the spray booths. The wastewater contains 100 to 500 mg/L oil and can be effectively treated with oil–water emulsion breakers. Occasionally, wash oil, hydraulic oil, and drawing oil are sent to the waste plant, but most plants try to segregate these relatively clean oils from the wastewater for recovery or sale.

Plating Wastes

Where plating of parts is a major operation, waste treatment plants are designed to remove heavy metals. Traditional treatments of reduction and pH adjustment to remove the metal as its hydroxide are commonly used. A typical heavy metal removal plant is shown in Fig. 43.11. Destruction of cyanide may also be required.

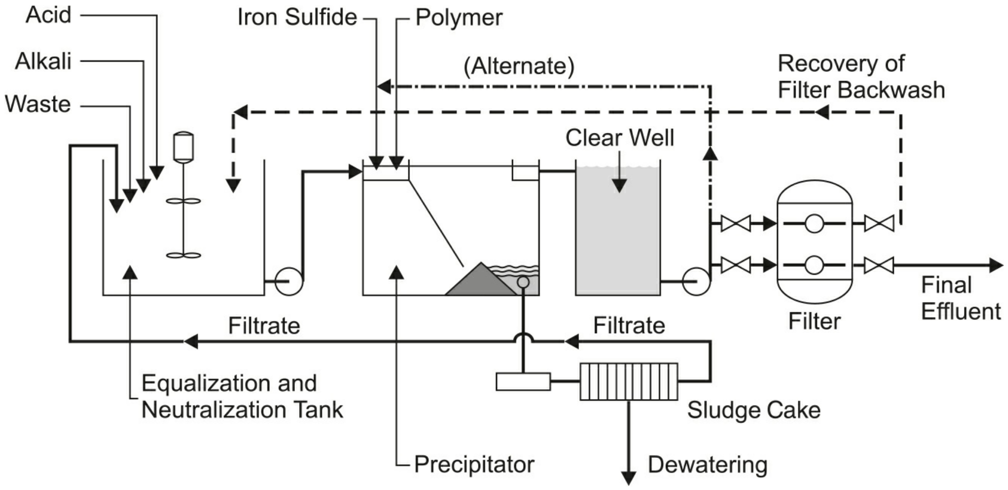


FIGURE 43.11 Heavy metals precipitation in a metal finishing shop using sulfide precipitation.

Economics may justify heavy metal recovery, most frequently by an ion exchange operation. Nickel is easily reclaimed from rinse tanks following nickel plating on acid regenerated cation resin, with the nickel-rich regenerant returned to the plating tank. Chromium is also recoverable, but not in a form useful in the plating operation.

Plating is as much an art as a science. Parts to be plated require careful cleaning and rinsing, often with soft water to avoid spotting. The plating baths are precisely controlled and may require demineralized water makeup. A typical plating line is shown in Fig. 43.12.

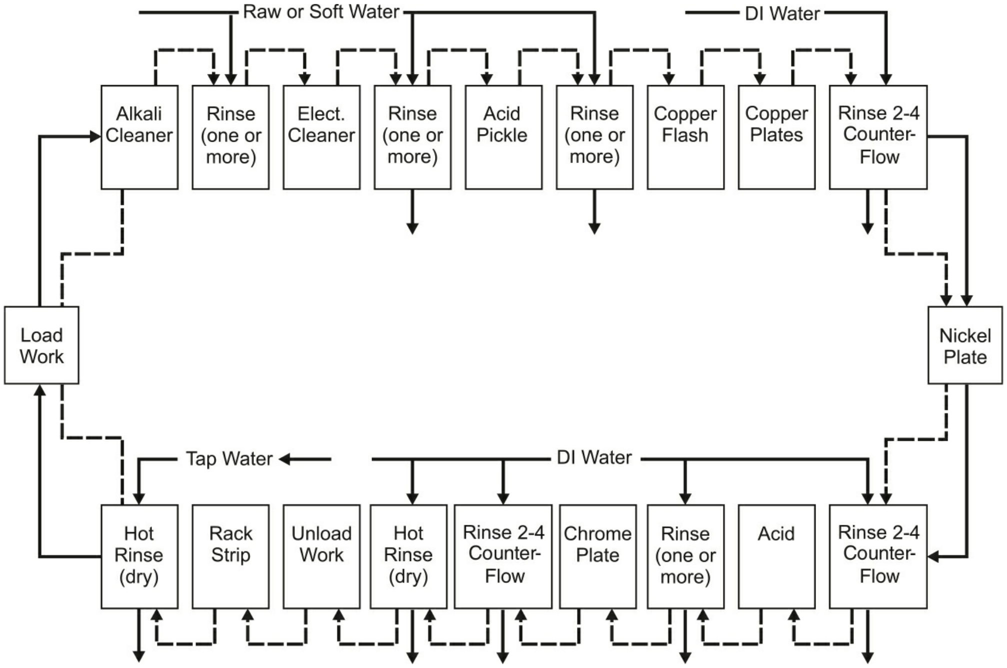


FIGURE 43.12 Flow sheet for a chrome plating line, including cleaning step and three stages of metal deposition.

Painting is increasingly important in the metal fabrication plants, as the efforts to stop body corrosion increase. Zinc-rich primers are sprayed on the interiors of doors, fenders, and other areas that are enclosed after assembly to improve corrosion protection. This operation is performed in the same type of spray booth described earlier.

Utilities, such as steam and cooling water, are much the same in stamping and fabrication as described for the machining operation.

Assembly Plants

Figure 43.13 shows a typical flow diagram for an assembly plant. These plants receive all of the parts and subassemblies produced in supplier plants and assemble them into a finished car. Major operations include welding, bonderizing, painting, and assembly.

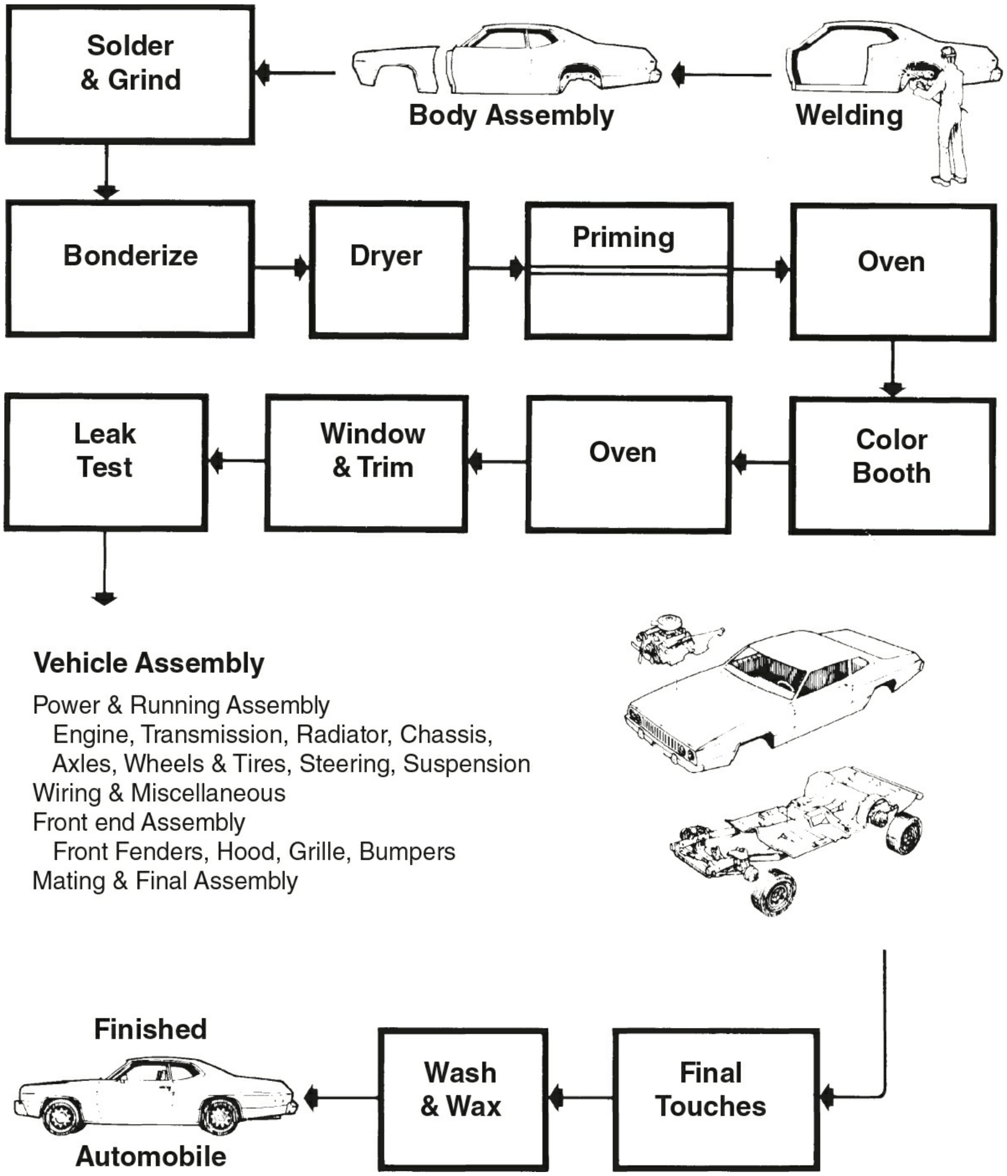


FIGURE 43.13 Process flow in an automobile assembly plant.

In the assembly plant, the sheet metal is welded to the frame and floor pan to construct the shell of the car. During the welding operation, the welder tips are cooled by recirculating water. The most common problem in this closed cooling system is fouling, which plugs the tips with corrosion products. If the water flow is reduced by plugging, the tips will overheat or even melt, causing a shutdown of the assembly line. Filtration and chemical treatment with conventional corrosion inhibitors minimize this corrosion and plugging.

In the bonderizing step, a metal phosphate layer, such as zinc phosphate, is applied to the metal surfaces to provide corrosion protection and a surface for the paint finish. Figure 43.14 shows a typical phosphatizing operation consisting of cleaning, rinsing, phosphating, rinsing, and sealing. After bonderizing, many plants use a process called electrodeposition to electrostatically deposit a primer coat of paint on the metal surface, by dipping the electrically charged metal into a vat of water-based paint. The oppositely charged paint particles are attracted evenly to the metal surface (Fig. 43.15). Makeup to this system is demineralized water, so that the bath conductivity can be controlled.

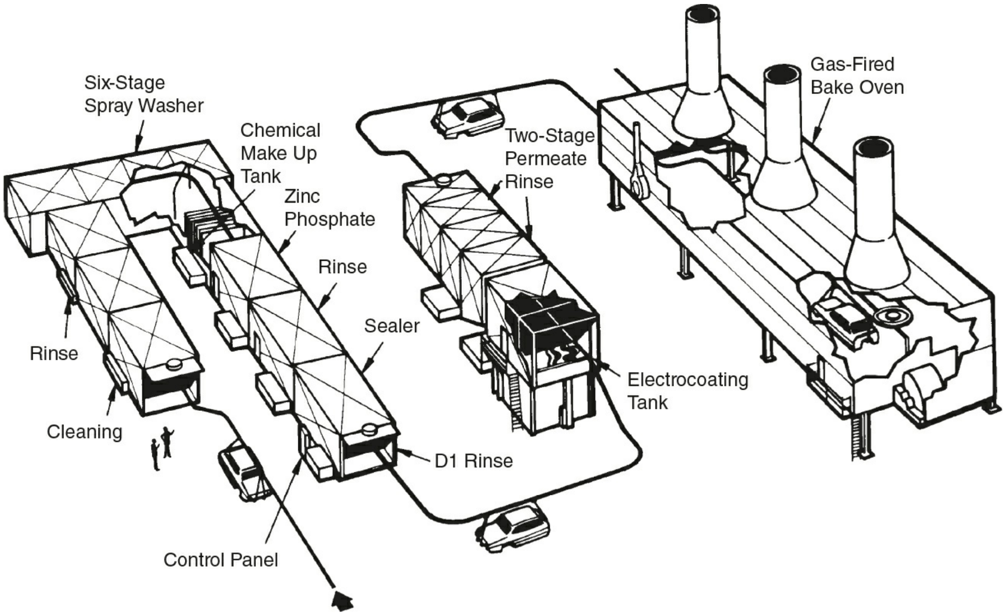


FIGURE 43.14 Phosphating and electrocoating lines.

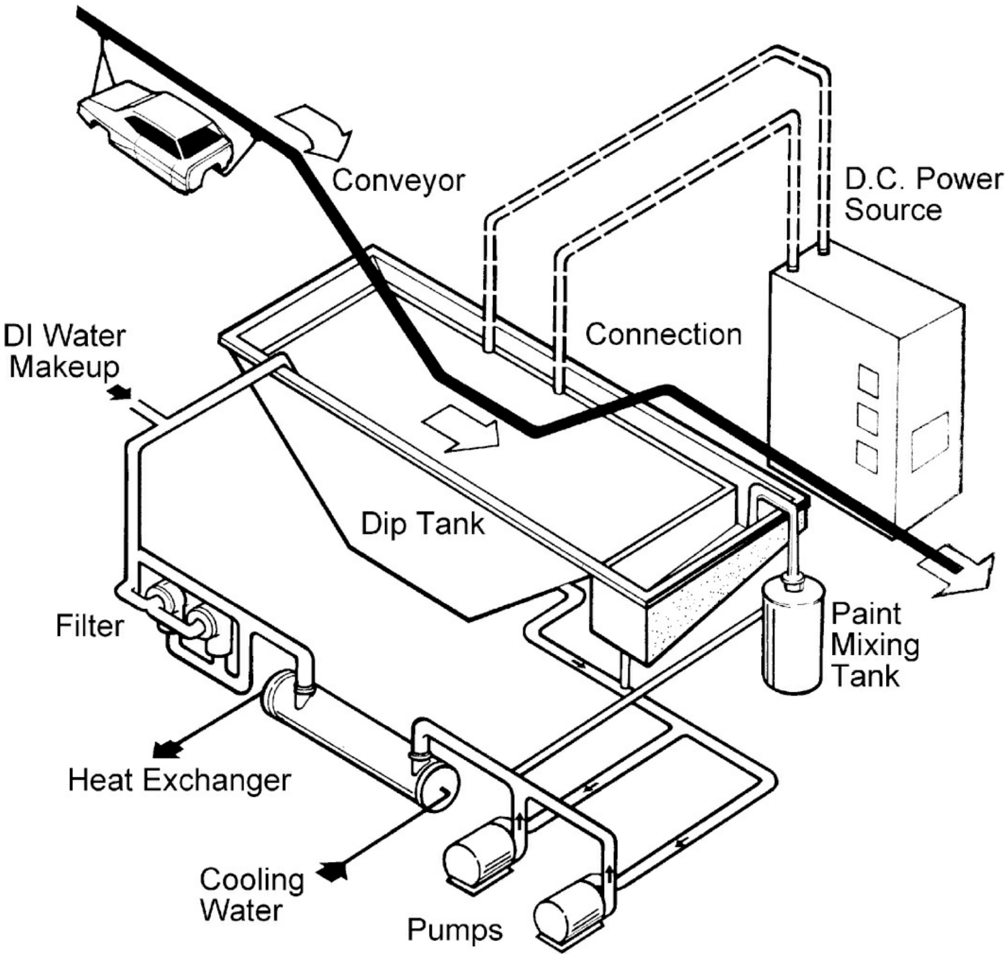


FIGURE 43.15 Electrocoating process for automobile bodies.

In this process, the bath tends to heat up. The paint is cooled below 90°F (32°C) through a heat exchanger by either a chiller or an open recirculating cooling tower system. After the electrostatic dip, the painted car is baked in an oven to set the finish. The exhaust gases from the oven pass through heat exchangers to recover heat by warming the oven makeup air. These exchangers foul with paint residue and require frequent cleaning.

Periodically, concentrated rinse water from electrostatic coating is discharged to the waste treatment plant. These discharges can upset the waste plant by introducing waste that is difficult to treat. If the pH of the electrocoat paint is increased above 6.0, large sticky deposits form and plug the lines and pumps. If the pH of the electrocoat paint is reduced below 3.5, a tar-like substance will form and plug the lines and pumps.

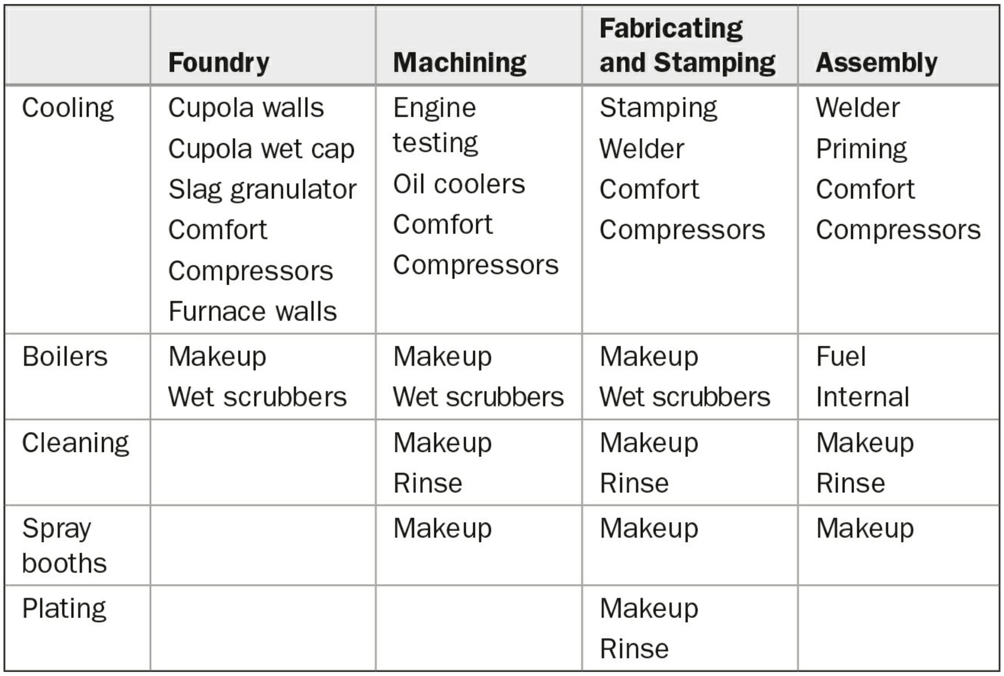
Most vehicle assembly plants have the type of wet spray booths described earlier.

There are two specific miscellaneous water uses in the assembly plant:

1. The assembled car is passed through a spray to test for leaks. Fluorescent dye is put in the water so a black light will clearly reveal leaks. Wetting agents are also added to make the test more severe and to prevent water spots.
2. The final process is a typical car wash operation. Various soaps are added to help clean the car.

Wastes from assembly plants are usually quite similar. Typical contaminants are oil, BOD, SS, zinc, nickel, phosphate, and sometimes paint sludge. Coagulants and oil-in-water emulsion breakers work well on these waters. Water comes from spray booths, stripping tanks, phosphatizing, wet sanding, car wash, cooling water, leak test, and various parts washers. Typical flows range from 500 000 to 1 000 000 gpd (1890–3790 m^3/d).

Table 43.3 summarizes water uses in the major automotive manufacturing steps.



	Foundry	Machining	Fabricating and Stamping	Assembly
Cooling	Cupola walls Cupola wet cap Slag granulator Comfort Compressors Furnace walls	Engine testing Oil coolers Comfort Compressors	Stamping Welder Comfort Compressors	Welder Priming Comfort Compressors
Boilers	Makeup Wet scrubbers	Makeup Wet scrubbers	Makeup Wet scrubbers	Fuel Internal
Cleaning		Makeup Rinse	Makeup Rinse	Makeup Rinse
Spray booths		Makeup	Makeup	Makeup
Plating			Makeup Rinse	

TABLE 43.3 Summary of Water Uses

CHAPTER 44

The Municipal Sector

Communities differ widely in character and size, but all have common concerns of finding, treating, and distributing water for industrial, commercial, and residential use. Residential uses include washing, transporting wastes, drinking, food preparation, watering lawns and gardens, heating and cooling, and fire protection. According to the U.S. Environmental Protection Agency (EPA), there are 156 000 public drinking water systems in the United States. Although the common purpose is water treatment, systems vary widely. Groundwater systems are more prevalent than surface water, but more people drink water from surface water systems.

Because water is so basic to life, public interest in governing water quality has been strong. This has created a demand for modern treatment plants, trained operators, and careful inspection of chemical treatment and water quality. Consumption of water per capita ranges from approximately 100 gpd (0.38 m^3/day) in very small municipalities to about 200 gpd (0.76 m^3/day) in larger systems having greater industrial and commercial demand. Water use primarily depends on availability of water resources, climatic and seasonal variations, and cost of finished water. Where water is scarce, it is used only for essential purposes. Where cost is a prominent factor, it primarily restricts nonessential uses of water such as lawn watering, since essential uses are served regardless of cost.

EPA broadly categorizes water users and volumes used in the United States as follows:

1. Domestic
2. Power plants
3. Agriculture
4. Industrial and mining

Domestic—Water is used for residential, commercial, industrial, and public uses such as street cleaning, firefighting, municipal parks, and public swimming pools. This includes both publicly supplied sources (water delivered by a public or private system) and self-supplied sources (water withdrawn directly from surface or groundwater, such as from privately owned wells). Fifteen percent of American households are self-supplied, while more than 240 million people depend on public supply systems. Withdrawals for public supply systems total more than 43 billion gpd (163 million m^3/day). Historically, nearly 60% of public supply is delivered to households. Self-supplied water to households totals nearly 4 billion gpd (15 million m^3/day).

Power plants—Water is used during production of energy from fossil fuel, nuclear, or geothermal sources. Most water withdrawn for power plants is used for cooling purposes; power plants use 136 billion gpd (515 million m^3/day) of freshwater.

Agriculture—Water is used to irrigate farm crops and for livestock, dairies, feedlots, fish farms, and other farm needs. Agricultural irrigation accounts for more than 142 billion gpd (538 million m^3/day) of freshwater.

Industrial and mining—Water is used for cooling in factories and washing and rinsing in manufacturing processes. Some major water use industries include mining, steel, paper, chemicals, and associated products. Industrial facilities withdraw more than 20 billion gpd (76 million m^3/day) of freshwater.

Disinfection

Water has been treated before use for thousands of years by a variety of processes. Methods of water treatment are illustrated in early Greek and Sanskrit writings and include descriptions of filtering through charcoal, straining, and boiling. As early as 1500 B.C., Egyptians used alum (aluminum sulfate) to clarify water. During the 18th century, filtration was established to remove particles from water, and by the next century, sand filtration was employed in Europe. It was not until the 19th century that it was evident many serious epidemics was associated with contaminated water. In the early 20th century, discoveries centered on disinfectants such as chlorine and ozone that could destroy pathogenic (disease causing) organisms. At that time, chlorine was used in the United States and ozone predominantly in Europe.

NSF International, founded in 1944 as the National Sanitation Foundation, is known for the development of standards, product testing, and certification services in the areas of public health, safety, and protection of the environment. According to NSF, the majority of public utilities in the United States uses some form of disinfection to protect against pathogens in drinking water supplies. In the 21st century, the most common disinfection techniques are: chlorine, ozone, ultraviolet (UV) light, chloramines, and chlorine dioxide. Scientific research has found that by-products (called disinfection by-products or DBP) can form when some of these disinfectants react with natural organic matter (NOM) such as decaying vegetation. DBP also form when certain compounds such as bromide are present in source water.

Although studies are being conducted to determine potential health effects of DBP consumed by humans over long periods, EPA has already set monitoring requirements and maximum contaminant levels (MCL) for some of the more common by-products, including trihalomethanes (THM), haloacetic acids (HAA), bromate, and chlorite.

Chlorination By-Products

During the 1970s, scientists discovered a possible origin of DBP from disinfectant reaction with organic matter. Subsequently, research ensued to study health effects and develop measures to prevent formation of these products during the disinfection process. Formation of DBP generally takes place by chlorine reacting with organic substances, such as humic and fulvic acids, generically called total organic carbon (TOC) or NOM. These materials enter water during decomposition of plant matter. Literature provides little information on the complex chemical structures of humic and fulvic acids, and the mechanism of DBP formation remains unclear. Because of the extensive number of substances that make up NOM, research is difficult.

Formation of THM and HAA is temperature and pH dependent. Under conditions with extended reaction time, transitory DBP may become disinfection end products. At elevated temperatures, reaction rates are faster, and greater chlorine dosages are required for adequate disinfection, thereby producing halogen by-products. A delicate balance is required to optimally treat drinking water.

When pH values are high, more hypochlorite ions are formed, causing effectiveness of chlorine disinfection to decrease. At higher pH values, more THM are formed, whereas more HAA are formed when pH values are lower.

Chlorine

Chlorine (Cl_2), in the form of hypochlorous acid (HOCl), is one of the most widely used forms of disinfection for drinking water in the United States today. Chlorine is effective at deactivating many forms of pathogenic bacteria and viruses. Chlorine gas is yellow-green in color and added to water to form hypochlorous acid. The gas itself can be pressurized and cooled to a liquid, so that it can be shipped and stored. Sodium hypochlorite (NaOCl), formed from chlorine and sodium hydroxide, is also used to disinfect public water supplies but does not have the added hazardous chemical storage constraints of chlorine gas.

Chlorine is less effective at treating other microorganisms such as parasites. Because parasites or cysts such as *Cryptosporidium* and *Giardia* have a protective outer shell, chemical disinfectants such as chlorine do not penetrate and deactivate these microorganisms well.

Chlorine reactions are temperature and pH dependent. Chlorine works best in water with a low pH and a high temperature. Free residual chlorine (FRC) is the disinfectant that has not combined with chemicals, microorganisms, and plant material found in the water. Chlorine dosage must be adequate to meet chlorine demand and provide a measurable residual at the end of the water distribution system.

Chlorine has been found to react with NOM in source water to form DBP. THM include chloroform, bromoform, bromodichloromethane, and dibromochloromethane. The EPA has regulated the maximum annual average of total trihalomethanes (TTHM) detected in local water supplies to less than 80 µg/L. Haloacetic acids include five acids (HAA5): monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid. Currently, EPA has regulated the maximum annual average of HAA5 to less than 60 µg/L.

Ozonation

Ozone (O_3) has been used for many years at bottled water production facilities and public water treatment facilities, particularly in Europe, for disinfection. This type of disinfection super oxygenates water, which kills many forms of bacteria and parasites. Ozone does not leave a disinfection residual in the water; therefore, most water utilities combine the use of ozone with another disinfectant such as chlorine to help maintain microbiological quality of water throughout the distribution system.

If bromide ion (Br^-) is present in source water and ozone is used for disinfection, a chemical known as bromate (BrO_3^-) can form. EPA has determined that bromate may pose a health risk, and utilities using ozone must monitor for bromate and maintain a maximum annual average of less than 10 µg/L.

Chloramines

Chloramines are becoming more prevalent as disinfectants in drinking water systems. Chloramines, a combination of chlorine and ammonia, have been widely and successfully used as a drinking water disinfectant since the 1930s. Generally, chloramines are used to maintain chlorine residuals in large distribution systems because of longer stability relative to chlorine alone. EPA estimates that more than half of U.S. large water systems currently use chloramines. Major U.S. cities, including Denver, Boston, Indianapolis, St. Louis, Portland, and Minneapolis, use chloramines.

Because of concerns about DBP, some communities have switched from chlorine to chloramines for disinfection. Chloramines do not react as readily with organic matter, thereby reducing potential DBP formation.

Chlorine Dioxide

Chlorine dioxide (ClO_2) can be used for disinfection purposes. DBP may also form when utilizing chlorine dioxide for disinfection. EPA currently requires utilities using chlorine dioxide to monitor the water for chlorite (ClO_2^-).

Fluoridation

In 2000, the U.S. Centers for Disease Control and Prevention (CDC) estimated that 66% of residents using community water systems (162 million people) had access to fluoridated tap water. Since 1945, North American water systems have added fluoride, a naturally occurring element, to water supplies to help prevent tooth decay. According to the American Water Works Association (AWWA), since that time child cavity rates have been reduced by 20 to 40%, where fluoridation has been implemented. Fluoridation of drinking water is endorsed by the American Dental Association, the American Medical

Association, and the U.S. Public Health Service. CDC proclaimed fluoridation to be one of the top ten greatest public health achievements of the past century.

U.S. Regulatory History

Federal regulations pertaining to water treatment began in 1914 when the U.S. Public Health Service set standards on the bacteriological quality of water. The standards were revised in 1925, 1946, and 1962. The 1962 standards regulated 28 substances and were the most robust standards until the Safe Drinking Water Act (SDWA) of 1975, when EPA was mandated to institute a new system of quality regulations. Interim primary (enforceable) standards became effective in July 1977. This law was significantly amended in 1986 and 1996.

Proposed in 1994, the SDWA Amendments of 1996 required EPA to comply with the regulatory timeline it set forth in its initial Disinfectant and Disinfectant By-product Rule (DDBPR) and Interim Enhanced Surface Water Treatment Rule (IESWTR). Amendments to the SDWA in 1996 require EPA to develop rules to balance risks between microbial pathogens and DBP to increase defense against microbial contaminants, especially *Cryptosporidium*, while simultaneously reducing potential health risks of DBP. The Stage 1 DDBPR and IESWTR, announced in late 1998, are the first of a set of rules under the 1996 SDWA Amendments. Stage 1 of DDBPR established the following course of action:

- Establishes a goal of completely removing the top four THM from U.S. water supplies
- Reduced acceptable level of TTHM by 20%
- Introduced a new group of DBP, HAA5, for regulation
- Requires water suppliers to reduce levels of TOC, which react with disinfectants to make DBP
- Requires levels of disinfectants in water after disinfection to be reduced

Stage 2 of DDBPR was released in January 2006. Stage 2 focuses on public health protection by limiting exposure to DBP, specifically TTHM and the

HAA5. Exposure is limited by removing TOC from finished water based on raw water TOC and alkalinity levels (see Table 44.1).

Source Water TOC (mg/L)	**Source Water Alkalinity (mg/L as $CaCO_3$)**		
	0–60	60–120	>120
2–4	35%	25%	15%
4–8	45%	35%	25%
>8	50%	40%	30%

TABLE 44.1 Required Removal of TOC by Enhanced Coagulation and Enhanced Softening for Systems Using Conventional Treatment

The EPA establishes MCL for those contaminants known to cause, or suspected of causing, health problems. MCL defines the highest concentration allowed in public water supplies.

Water may be safe to drink but have an undesirable taste, odor, or color. Some water may stain clothes and fixtures, corrode plumbing, or form a scale and film. Secondary maximum contaminant levels (SMCL) are often recommended by EPA for these aesthetic water quality factors. SMCL are useful guidelines for evaluating suitability of water for drinking, bathing, clothes washing, cooking, and other domestic uses.

For a current list of MCL and SMCL, the reader is directed to the EPA web site.

In some cases, requirements of the SDWA necessitate a change to a more acceptable water source. Implementation of the SDWA Act has resulted in consolidation of many small water suppliers into larger regional systems to take advantage of economy of scale.

Cryptosporidium and *Giardia*

Cryptosporidiosis is a diarrhea disease caused by microscopic protozoan or single-celled parasites, which live in the intestines of animals and humans. Both the disease and the parasite are commonly known as “Crypto.” *Cryptosporidium* was first discovered as a cause of human disease in 1976 but was rarely reported in humans until 1982.

A hard outer shell protects the parasite and allows its inactive (dormant) form or oocyst to survive outside the body for long periods. The hard outer shell also makes it very resistant to chlorine disinfection.

While this parasite can be transmitted in several different ways, water is a common method of transmission, and *Cryptosporidium* is one of the most frequent causes of waterborne disease (drinking water and recreational water) among humans in the United States. Conventional treatment techniques including filtration and adequate chlorine contact time are most appropriate to inactivate the oocyst.

Groundwater usually has good microbiological quality, because it passes through various geologic layers in the ground, which function as a natural filter. Afterwards, water still requires disinfection because groundwater, especially shallow groundwater, can be contaminated by sewage or wastewater.

Untreated surface water can infect humans with *Cryptosporidium*, as the origin is from animal waste that enters municipal drinking water intakes. Oocysts are present in most surface waters in the United States, and concentrations are exacerbated during heavy rains because of runoff of animal wastes from land and overloaded wastewater treatment facilities.

In 1987, 13 000 people in Carrollton, GA became ill with cryptosporidiosis. In 1993 in Milwaukee, WI, 400 000 people fell ill from using drinking water that was contaminated by *Cryptosporidium* cysts. These outbreaks directed attention to waterborne diseases and the need for more stringent drinking water standards.

Cryptosporidium is chlorine resistant due to its hard outer shell, and therefore, multiple methods are required to protect public water supplies. Watershed protection, filtration, and disinfection are all used in combination to protect drinking water. Additionally, UV light and ozone are capable of inactivating the parasite, the latter with adequate contact time. The EPA standard requires 99% removal of *Cryptosporidium* for public drinking water systems.

Other pathogenic microorganisms that can be found in drinking water are *Escherichia coli*, caliciviruses, *Helicobacter* bacteria, *Mycobacteria*, and *Giardia lamblia*. In the future, more pathogenic microorganisms will likely emerge and spread through water because of increased agricultural activities, population growth, migration, and climate change. Pathogenic microorganisms can also emerge because they develop resistance to disinfectants.

Giardiasis is a diarrhea illness caused by a single cell microscopic parasite, *Giardia intestinalis* (also known as *Giardia lamblia*). Once an animal or person has been infected with *Giardia intestinalis*, the parasite lives in the intestine and is passed in the stool. Because an outer shell protects the parasite, it can survive outside the body and in the environment for long periods.

Since the late 20th century, *Giardia* infection has become recognized as one of the most common causes of waterborne disease (found in both drinking and recreational water) in humans throughout the United States.

The *Giardia* parasite lives in the intestine of infected humans or animals. Millions of parasites can be released in a bowel movement from an infected human or animal. *Giardia* is found in soil, food, water, or surfaces that have been contaminated with feces from infected humans or animals.

Tests used to specifically identify *Giardia and Cryptosporidium are* often expensive, difficult, and usually require large volumes of water to be pumped through a filter.

The primary disinfectant used in the United States is chlorine. In order to be effective and inactivate oocysts and *Giardia*, adequate contact time is required. Contact time depends on the temperature and pH of water. Chlorine works best in water with low pH and high temperature. Concentration and contact time required to inactivate *Giardia* using chlorine is approximated by Eq. (44.1).

$$\mathrm{CT} = 0.2828(\mathrm{pH}^{2.69})(\mathrm{FRC}^{0.15})(0.933^{(T-5)})(L) \tag{44.1}$$

where CT = contact time in, min
pH = pH of water
FRC = free residual chlorine, mg/L $\mathrm{Cl_2}$
T = temperature, °C
L = log removal

The CT concept was developed specifically for surface water, assuming that water treatment focuses on inactivating both *Giardia* and viruses. CT required to provide 3-log inactivation of *Giardia* is at least enough to provide the required 4-log inactivation of viruses; therefore, EPA just set the standard for *Giardia*.

An example of the discussion above would be the determination of the CT required for a 3-log inactivation at a chlorine residual at 1 mg/L and a water pH. of 8.0 with a 10°C temperature. Substituting the variables into the equation we can determine that 161 minutes of contact time is required.

$$\begin{aligned} CT &= 0.2828(8^{2.69})(1.0^{0.15})(0.933^{(10-5)})(3) \\ CT &= 161\,\text{min} \end{aligned} \tag{44.2}$$

Raw Water Characteristics

Raw water characteristics vary widely, the major differences being between surface and groundwater, hard and soft water, and river water compared to reservoir water. These differences present varying needs for algae control, turbidity removal, softening, water stabilization, and disinfection.

Generally, water supplies within a defined geologic region are similar. There has been a trend to use surface water because of its availability, and it minimizes risks of earth subsidence due to uncontrolled groundwater withdrawal. Raw water with a constant low turbidity has more treatment options than one of high or variable turbidity. The presence of color in many low alkalinity waters requires special treatment considerations.

Corrosion and Scale

Corrosion in distribution system pipes occurs through electrochemical action and is the reversion of refined metals back to their natural state. The electrochemical cell consists of an anode (site of oxidation) and a cathode (site of reduction). Electrolytic solution (water) connects the anode and cathode. Metal enters solution at the anode, while the cathode attracts electrical current and collects atomic hydrogen. Proper corrosion control methods disrupt one or more of the corrosion cell reactions to reduce the extent of metal release.

To control corrosion in drinking water distribution systems, chemical treatment recommendations and dosage requirements must consider an overall system approach. All waters are corrosive to some degree. Chemical characteristics of water and metallurgy of materials it contacts determine how aggressive the water is. Raw water supplies and treatment schemes vary considerably, resulting in waters with aggressiveness from mild conditions causing negligible attack, to antagonistic conditions causing rapid deterioration. Factors affecting corrosiveness of potable water in distribution systems are dissolved gases, temperature, bacteria, pH, and dissolved ions.

Raw water sources vary with respect to dissolved gases. Some groundwater contains carbon dioxide (CO_2), which converts to carbonic acid (H_2CO_3) and produces pH less than 6. Other groundwater contains hydrogen sulfide (H_2S) that reacts with carbon steel and causes pitting from deposition of ferrous sulfide (FeS). Dissolved oxygen in both surface and groundwater sources is a major influence, since carbon steel corrosion is directly proportional to the oxygen content of water. While chlorine is a chemical used for biological control, excessive chlorination can increase the corrosion rate of steel.

Lead occurs in drinking water from two sources: lead in raw water supplies and corrosion of plumbing materials in the water distribution system (corrosion by-products). Most lead contamination is from corrosion by-products. Lead in drinking water results primarily from corrosion of materials located throughout the distribution system containing lead and copper, and from lead and copper plumbing materials used to plumb public and privately owned structures connected to the distribution system. The amount of lead in drinking water attributable to corrosion by-products depends on a number of factors, including the amount and age of lead and copper bearing materials susceptible to corrosion, how long the water is in contact with the lead-containing surfaces, and how corrosive the water in the system is toward these materials.

Potential sources of lead corrosion by-products found in drinking water can include: water service mains (rarely), lead goosenecks or pigtails, lead service lines and interior household pipes, lead solders and fluxes used to connect copper pipes, and alloys containing lead, including some faucets made of brass or bronze.

Most public water systems serve at least some buildings with lead solder or lead service lines. EPA estimates that there are about 10 million lead service lines/connections. About 20% of all public water systems have some lead service lines/connections within the distribution system.

The amount of lead in drinking water depends heavily on the corrosiveness of the water. All water is corrosive to metal plumbing materials to some degree, even water termed noncorrosive or water treated to make it less corrosive. Corrosiveness of water to lead is influenced by water quality parameters such as pH, total alkalinity, dissolved inorganic carbonate, calcium, and hardness. Galvanic corrosion of lead into water also occurs with lead-soldered copper pipes, due to differences in the electrochemical potential of the two metals. Grounding of household electrical systems to plumbing may exacerbate corrosion.

Corrosion Control

Based on work completed at New England water plants in the late 1930s, Calgon Corporation obtained a patent in 1943 for the use of sodium hexametaphosphate (SHMP) as a corrosion inhibitor. Polyphosphate combines with calcium in water to form a protective film on the metal pipe surface. Low levels of polyphosphate are fed to the finished bulk water supply that carries the chemical to the metal surface. As the action of flowing water sloughs off the established protective molecular film, it is replaced immediately. Therefore, sufficient polyphosphate must be fed to form a molecular film throughout the distribution system. The main function of the polyphosphate is to treat the metal surface and not the water itself; thus, a residual must be maintained at the end of the distribution system.

The use of "bimetallic" (sodium-zinc) glassy polyphosphate began in the 1950s. Addition of zinc enhanced performance of polyphosphate by increasing the rate at which the protective film is formed on the metal surface. It proved to be a more tenacious protective film than that provided by polyphosphate alone, particularly in low-flow or dead-end areas of the distribution system.

In 1970, zinc orthophosphate was used for corrosion control in a southern California potable water system. Orthophosphate is an anodic inhibitor, while zinc polarizes the cathode. This treatment is particularly effective in low alkaline, low hardness waters. It is also used in stifling the release of asbestos fibers into water flowing through asbestos-cement pipe. Zinc is the critical component in this treatment and can be obtained with zinc polyphosphate as well. However, care must be taken when hardness and alkalinity increase, because calcium orthophosphate can precipitate. In this case, the inhibitor is not available to protect the metal surface, and both corrosion and scale can occur.

With passage of the Lead and Copper Rule in 1991, many systems failed obtaining compliance with first draw samples of less than 15 μg/L of lead in 90% of samples. Use of orthophosphate can reduce lead solubility; however, lead is only one of the many different alloys in the distribution and household systems. Orthophosphate has been successful in bringing systems into compliance for lead, but it promotes steel pitting and has no efficacy for scale control or iron and manganese stabilization. Orthophosphate is being used as a corrosion inhibitor in such cities as the District of Colombia, Chicago, Richmond, New York City, and Detroit. Although available in several forms, orthophosphate can be added as phosphoric acid. A better alternative is either zinc orthophosphate or a poly/orthophosphate blend.

Blends of polyphosphate and orthophosphate are used increasingly for treating systems for corrosion control. Orthophosphate is an anodic inhibitor, while polyphosphate is a cathodic inhibitor. The product forms a protective molecular film and provides the added benefit of scale control, due to the polyphosphate portion of the product.

Sodium silicates are good for protecting iron and steel and particularly effective in hot water systems. Silicates require some initial corrosion to occur to form a protective film on the metal surface. It is self-limiting since the film stops developing when the corrosion products are no longer available. This film forms over clean or corroded surfaces. Usually, pH of the system is maintained in the range of 8 to 9.5. With high hardness waters, the higher the pH increases, the higher the potential for calcium carbonate scale. Since silicates cannot prevent scale, they should be used in soft water areas. In addition, with higher pH, there is the concern of chlorine effectiveness and TTHM formation.

Controlling corrosion is a complex process requiring water treatment system operators to be aware of all the issues of regulations, water quality, and water treatment scheme that affect performance of the selected program. Economic and aesthetic benefits are easily measured in lower maintenance and pumping costs, as well as fewer customer complaints. Meeting regulatory requirements at the tap allows treatment systems to lower the frequency and number of samples collected. This results in lower analytical costs as well as gaining consumer confidence, by never needing to notify them of being out of compliance.

Scale Control

Scale formation causes severe problems in potable water distribution systems. If untreated, raw water sources with high hardness levels can deposit calcium carbonate ($CaCO_3$) or calcium sulfate ($CaSO_4$) scale throughout the distribution system. In addition, accelerated corrosion can occur under the deposit, or the scale can provide a safe harbor for biological activity, which is sheltered from the disinfectant being used.

The result of scale formation is reduction in pipe diameter and increased pumping cost. Scale forms at the interface of the bulk water and distribution pipe. This solid/liquid interface is the site for crystal growth. At the interface, pH of water is higher than bulk water pH, because the oxygen–reduction reaction produces hydroxyl ions. Calcium carbonate solubility decreases with increased pH. In the homeowners hot water system, calcium carbonate scale forms due to increased water temperature, which decreases $CaCO_3$ solubility. Once solubility of the reaction product has been exceeded, scale deposition can occur.

There are several methods used to control scale in potable water systems: pH depression, softening via ion exchange or precipitation with lime and soda ash, as well as chemical treatment.

Modifying pH creates safety issues of handling strong mineral acids, and depending on the acid chosen, calcium sulfate or calcium phosphate scale can develop, magnifying scale problems. In addition, if not closely monitored, corrosive conditions can cause additional concerns, and one problem is just traded for another.

Total or partial softening to remove hardness is a more common practice to control scale formation. Softeners replace calcium and magnesium ions with sodium ions. This requires large quantities of salt (NaCl) to regenerate the resin when it has become exhausted. There is a high cost for the original equipment and the operating cost of handling concentrated spent brine from the regeneration process. Typically, large volumes of water are not processed through ion exchange equipment, since it reduces hardness to an extremely low level. Usually, the plant softens part of the water and blends it back with untreated water before sending it to the consumer.

Often, chemical precipitation with lime and soda ash (cold lime softening) is used to remove hardness and alkalinity. This treatment usually requires an extra step to add CO_2 after softening for recarbonation to reduce pH. Often times, the treatment process has two steps for solids removal: one for turbidity and one for precipitated hardness. This approach is effective but expensive. Handling dry lime and soda ash and monitoring chemistry to achieve the proper dosage to obtain desired hardness is labor intensive.

The simplest solution to control scale in potable water systems is to use polyphosphate as a “threshold treatment.” The use of polyphosphate for scale control was developed by Calgon Corporation in conjunction with the U.S. Bureau of Mines in 1918 to prevent scale build-up in boilers. The technology was transferred to the municipal potable water treatment market in 1938, when SHMP was applied for scale control.

Polyphosphate controls scale by threshold treatment. This means that polyphosphate is used in substoichiometric quantities to control precipitation of scale. It uses a mechanism that retards nuclei formation as well as crystal growth. In raw water, calcium (Ca^+) and bicarbonate (HCO_3^-) are oppositely charged ions that are attracted and tend to form ion pairs. As they gather to create clusters, the polyphosphate molecule upsets equilibrium of the sub nuclei ion clusters, causing the ions to go back into solution. The polyphosphate molecule is available to upset this equilibrium on many groups of calcium carbonate clusters. Should clusters reach a subcrystallite or calcium carbonate stage, the polyphosphate molecule is attracted to the growth and inhibits further growth. With excessive calcium carbonate ions or low polyphosphate concentration, calcium carbonate crystals become deformed because of polyphosphate adsorption on the crystallite surface. Deformed crystals cannot grow and attach to surfaces, and are easily dispersed by flowing water.

Polyphosphate is manufactured by dehydrating orthophosphate in a furnace to form a linear chain structure. When adding it to water, it reverts to orthophosphate over time. For scale control, only polyphosphate protects the system. It has been found that both polyphosphate and zinc polyphosphate are effective scale control treatment schemes.

Since polyphosphate adheres to calcium carbonate surfaces, systems with high concentrations of scale build-up can use the dissolving and dispersing abilities of polyphosphate to eventually clean deposits from the system. Care should be taken when initiating treatment to prevent shocking the system and causing deposits to break away from pipe and accumulate in elbows and tees. Polyphosphate is used before mechanical cleaning to soften deposits in the system, so that the pigging operation is more effective. In addition, polyphosphates are used to keep filter media clean in softening plants by applying it to the influent water.

Typical Treatment Schemes

The type of treatment practiced at a given municipality depends largely on raw water characteristics. Wherever possible, water resources are acquired and maintained to require a minimum amount of treatment, thereby reducing the capital and operating costs to the municipality. Table 44.2 shows common impurities found in raw water supplies and examples of general types of treatment that can be employed. Which treatment is optimum depends on local conditions and the level of impurity.

	Surface Water						Groundwater			Surface or Groundwater				
Treatment	**Turbidity**	**Taste/ Odors**	**Hardness**	**Color**	**Fe/ Mn**	**Algae**	**Hardness**	**Fe/ Mn**	**H_2S**	**Bacteria/ Virus**	**Metals**	**Organics**	**Corrosion**	**Scale**
Aeration		X			X			X	X					
Filtration only	X			X	X	X		X						
Ion exchange			X		X		X	X						
Lime softening	X	X	X	X	X	X	X	X						
Clarification/ filtration	X	X		X	X	X		X						
RO		X	X	X			X				X	X		X
Oxidation		X		X	X	X		X	X	X	X	X		
Chlorination		X		X	X	X		X	X	X	X	X		
Adsorption		X		X								X		
Phosphates													X	X
Zinc phosphates													X	

TABLE 44.2 Typical Water Impurities and Common Treatment Methods

A simple summary of various processes used for treating municipal water is shown in Fig. 44.1. By far, the largest number of municipalities simply uses the scheme shown by flow path 1, with water taken from a well, sterilized by chlorination, and pumped directly to the distribution system. Most systems like this are small and often operate with only part-time surveillance. Each state is responsible for reviewing the quality of water, both chemically and bacteriologically. In some cases, when this scheme is used, a chemical such as polyphosphate may be applied for final stabilization to minimize either scale or corrosion.

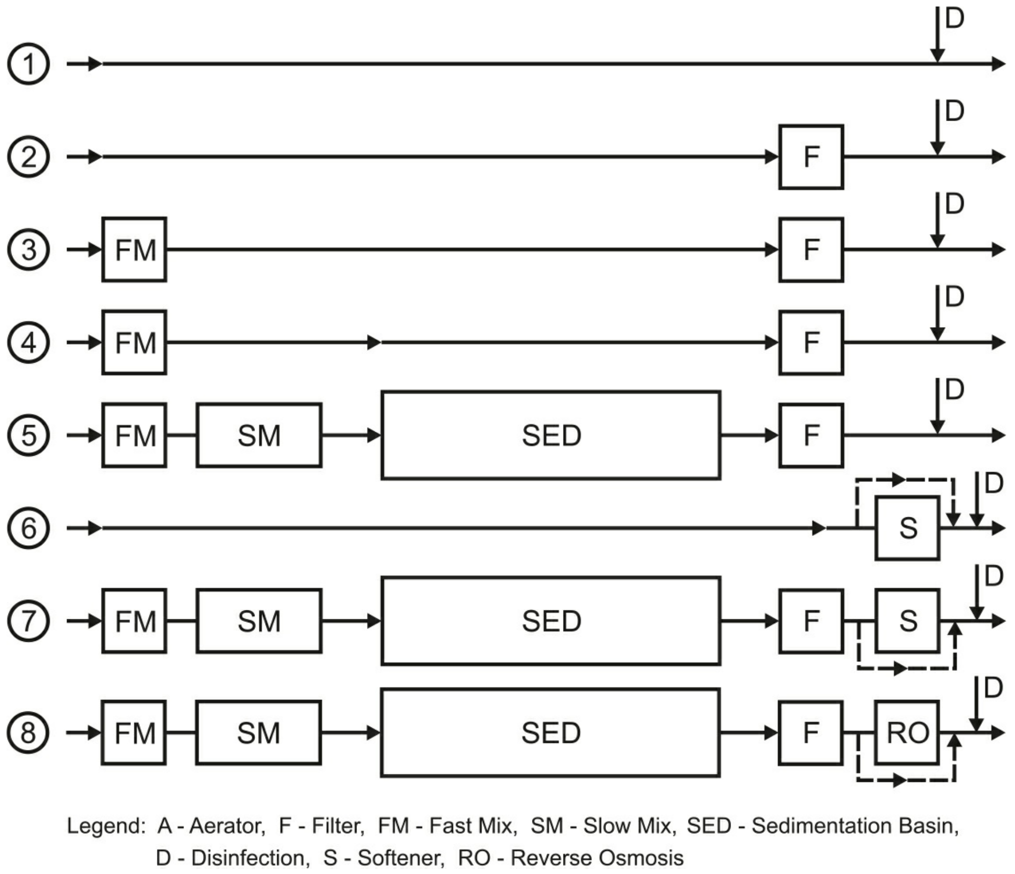


FIGURE 44.1 Simplified schematic of municipal water treatment flow sheets.

Often, low turbidity water should be clarified by direct filtration processes rather than by conventional coagulation and flocculation processes. This may significantly reduce the amount of sludge produced while maintaining water quality. Many plants with low raw water turbidity practicing conventional processes, apply chemical solids that far exceed the amount of suspended solids present in the raw water to be clarified. A more detailed explanation of coagulation and flocculation can be found in Chap. 6.

The second flow path shows only addition of a filtering system. In some old plants, the slow sand filter is still used for this purpose, but the rapid sand filter is now more commonly used. Because the sand filter is limited in its ability to handle suspended solids, this system is usually applied only to impounded waters of excellent quality, where post-chlorination can assure safe potable water. The filter may be installed to clarify shallow well water, where suspended iron may be an occasional problem. There are risks in this kind of system, because the filter does no more than removing suspended solids, which is seldom the only problem with a raw water supply.

The third flow path shows addition of an aerator before the filter for removal of tastes and odors and for oxidation of iron. Usually, this is followed by lime for pH increase to about 8 to 8.5 and a flocculant, since iron precipitate is usually colloidal.

In modern practice, the minimum equipment is usually considered that shown by flow path 4, and it is usually confined to impounded waters where there are consistently low suspended solids, depending on seasonal presence of algae and where final disinfection can assure safe finished water.

In handling surface waters that contain significant suspended solids, the fast mix devices of flow path 4 are followed by a slow mix flocculator and a sedimentation basin in flow path 5, providing detention for settling most flocculated solids, so that load on the filter is measurably reduced. Detention can also provide for disinfection of raw water, with chlorine being added with or ahead of coagulation chemicals to relieve the final chlorine demand. The prechlorination step may improve flocculation by destroying some organic contaminants. This keeps settled solids from becoming septic and rising to the surface as gas forms.

In some cases, where water is already clear, the major problem may be caused by calcium and magnesium. In flow path 6, water is softened through ion exchange softeners. Some water is by-passed, so that the effluent can have hardness controlled at 100 to 150 mg/L as $CaCO_3$. Often, the cost of municipal softening is more than covered by savings to individual homeowners in areas where water is so hard that most homes would use individual softening units. A side benefit is reduced discharge of regenerant brine by the more efficient municipal plant.

Flow path 7 includes not only clarification of surface water but also final softening. In this scheme, the sedimentation tank may provide for lime softening as well as clarification, to reduce load on the ion exchange softening unit.

Finally, in flow path 8, the water plant includes tertiary treatment with reverse osmosis (RO) to produce exceptional quality water.

There are various other combinations of individual treatment processes incorporated into an overall treatment scheme, but the principles are generally little different from those illustrated.

Case History—Lake Bluff, IL

The Central Lake County Joint Action Water Agency (CLCJAWA) is a wholesale provider of drinking water for several communities in central Lake County, Illinois. The 1991 plant is composed of four identical treatment trains, has a total capacity of 50 mgd (131 m^3/min), and serves a population of approximately 200 000 (see Fig. 44.2).

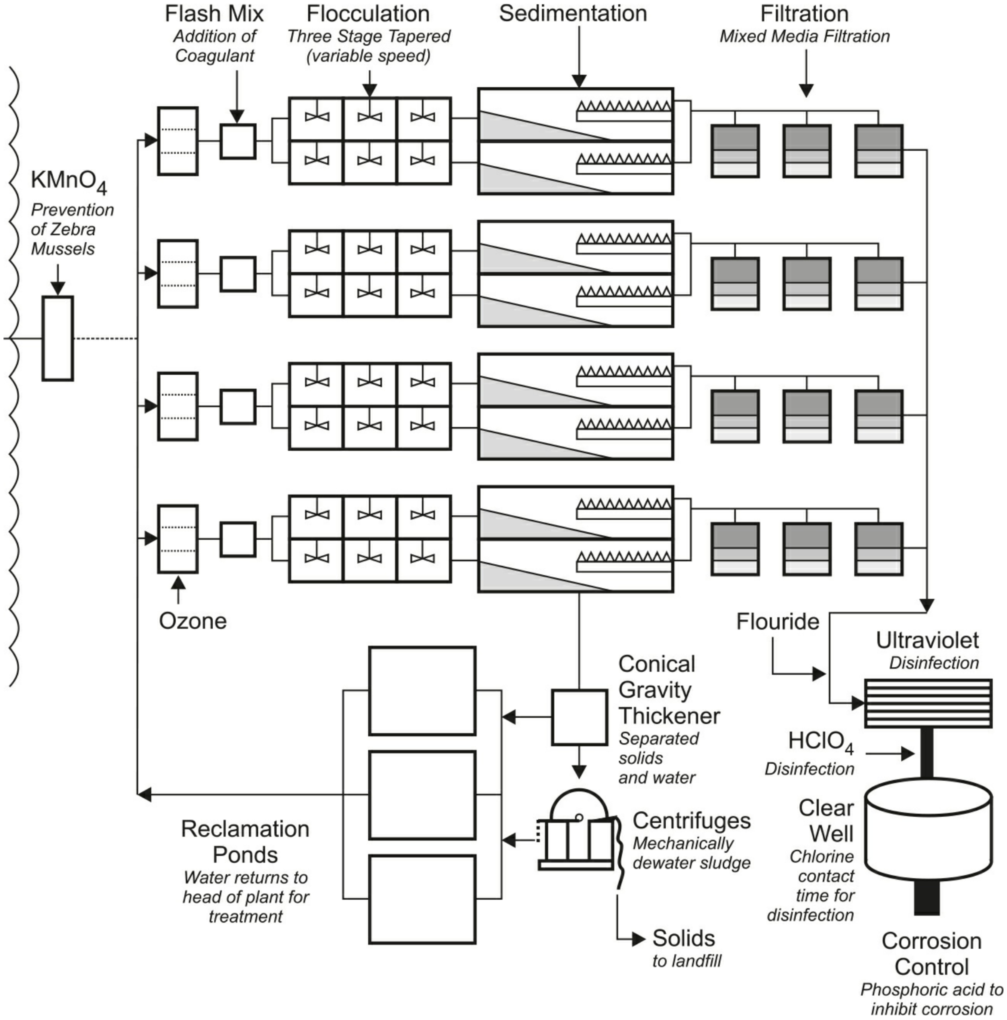


FIGURE 44.2 Lake County Illinois, plant schematic.

Treatment Process

CLCJAWA draws water from Lake Michigan. Potassium permanganate ($KMnO_4$) is added seasonally to inhibit mussel growth on the water plant intake and pipe. In the treatment plant, ozone is applied in ozone contactors for predisinfection, taste and odor minimization, and to enhance coagulation performance. Following ozone, coagulant is added in rapid mix basins. Water then flows through three consecutive flocculation basins, each basin mixed more gently than the previous to enhance floc size. Flocculated water then flows into settling basins equipped with inclined plate settlers. Here, floc falls a short distance to the inclined plate and rolls down the plate to the basin floor. Accumulated floc or sludge is removed twice daily using a chain and flight device to move solids to the sump of a telescopic valve. When lowered below the water surface, water pressure from the basin forces solids up and over the valve weir. Solids then flow to a processing facility equipped with gravity thickeners and centrifuges. Settled water flows upward through the bottom of perforated troughs that convey the water to filters. Once in the filters, water flows downward through 4 ft (1.2 m) of biologically active granular activated carbon, 1 ft (0.3 m) of sand, and either 1 ft (0.3 m) of gravel or a sintered plastic cap. Effluent from individual filters is collected, treated with fluoride, and conveyed to UV disinfection reactors. This process is followed by chlorination with sodium hypochlorite (NaOCl) and storage in two consecutive clearwells for a State mandated minimum of one hour before delivery. Phosphoric acid (H_3PO_4) is added at the head of the transmission system to control lead corrosion in resident's homes.

Treatment Chemicals

Potassium permanganate is added at an average dose of 0.2 mg/L. Ozone is produced on site using ambient filtered and dried air; average ozone dose is 0.8 mg/L. Average polyaluminum hydroxychlorsulfate coagulant dose is 7.1 mg/L, with historic maximum dose of 23.5 mg/L. UV light is dosed at 15 mJ/cm^2. Sodium hypochlorite dose averages 1.4 mg/L. This dose is lowered slightly in winter to maintain constant chlorine residual at the tap of approximately 0.5 mg/L. Average finished water free and total chlorine residual is 0.79 and 0.93 mg/L, respectively. Both fluoride and phosphoric acid are dosed to maintain constant residuals of 1.0 mg/L as F^- and 0.35 mg/L as PO_4^{-3}, respectively.

Typical Operations

Potassium permanganate is added when Lake Michigan water is above 50^{o}F (10°C) or from May through October to discourage mussel attachment. Divers inspect the intake periodically to assure the practice is working as anticipated. Ozone is dosed to maintain a target residual of approximately 0.04 mg/L in the final contact basin. Adjustments to dose are dependent on water quality and flow rate through the plant. Besides raw water turbidity, coagulant dose is adjusted primarily based on filter effluent turbidity and by monitoring the time it takes for a filter to ripen following backwash.

Filters are backwashed when they reach a final head loss of 8 ft (2.4 m). Filter runs last from 40 hours in summer up to 300 hours in winter. The Supervisory Control and Data System (SCADA) automatically diverts filter flow from service when turbidity exceeds 0.10 NTU. Filter backwash consists of a 3-minute air scour and low wash, 5-minute-high wash, and 12-minute final low wash. Plant flow is adjusted to maintain water levels in three 3.5 million gallon (13 000 m^3) standpipes. Table 44.3 shows typical raw and treated water quality.

	Temperature	Turbidity	pH	Alkalinity	Hardness	Conductivity	TOC	Coliform Bacteria
Water	°F (°C)	NTU		mg/L $CaCO_3$		µS/cm	mg/L	MPN/100 mL*
Raw	50 (10)	8.2	8.32	106	128	296	2.1	192
Finished	NA	0.04	7.81	104	124	304	1.7	0

*Most probable number per 100 mL

TABLE 44.3 Average Water Quality for Lake Bluff, IL Water Treatment Plant

Membrane Filtration in Drinking Water Systems

Membrane filtration in drinking water applications can employ microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), or RO (see Fig. 44.3). According to the American Membrane Technology Association (AMTA), low-pressure MF and UF have emerged as viable options for addressing current and future drinking water regulations related to treatment of surface water, groundwater under the influence of surface water, and water reuse applications for microbial and turbidity removal. Both MF and UF have been shown to exceed removal efficiencies identified in the EPA Surface Water Treatment Rule and related rules, such as *Cryptosporidium* oocyst, *Giardia* cyst, and turbidity. Membrane filtration is becoming popular for conventional plant retrofits, replacing sand media for enhanced water quality and capacity increase. Membranes have shown success removing TOC, reducing potential for TTHM formation.

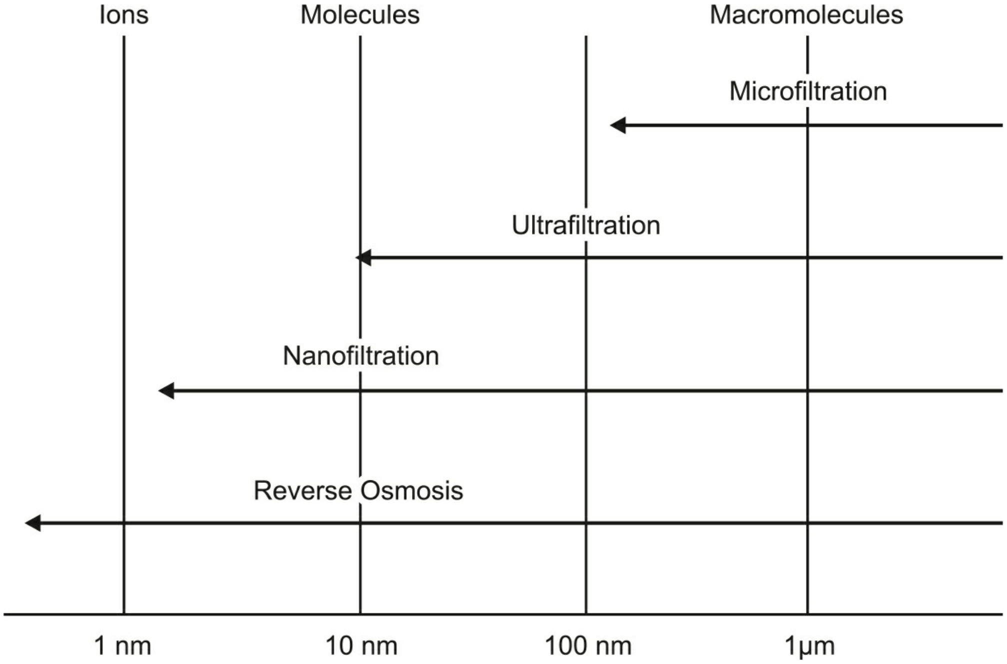


FIGURE 44.3 MF, UF, NF, and RO pore size comparison.

MF and UF membrane systems typically use hollow fibers that can be operated in the outside-in or inside-out direction of flow. The typical operational transmembrane pressure (TMP) of 5 to 35 psi (34–241 kPa) or vacuum [3–12 psi (21–83 kPa)] for outside-in membranes only) is the driving force across the membrane. TMP is the difference obtained when subtracting the filtrate pressure from the feed pressure. Typical flux (rate of finished water permeate per unit membrane surface area) at 68°F (20°C) for MF and UF ranges between 15 and 35 gallons per square foot per day (gfd) [2–4 $m^3/(d \cdot m^2)$].

Disinfection is recommended after membrane filtration as a secondary pathogen control barrier, and for distribution system protection. Automated periodic backwashing and chemical washing processes are used to maintain the rate of membrane fouling within acceptable limits.

Chemical cleaning is employed once a maximum TMP differential has been reached. Some systems utilize air/liquid backwash. Typical cleaning agents include acids, caustic, surfactants, enzymes, and certain oxidants, depending upon membrane material and foulants encountered. Chemicals used for cleaning and the method used in the cleaning process must be acceptable to the membrane manufacturer.

NF and RO are used to remove salts from seawater or brackish water. NF and RO membranes do not work according to the principle of pores but rather separation takes place by diffusion through the membrane. Pressure that is required to perform NF and RO is much higher than pressure required for MF and UF, while produced volume is much lower (higher reject flow). NF is a lower pressure RO and is referred to as “membrane softening.” NF has been successfully used to treat hardness, high color, and high organic content feedwater. Compared to RO membranes, the NF membrane has lower monovalent ion rejection properties, making it more suitable to treat waters with low salinity, thereby reducing post-treatment requirements. The NF membrane works as an absolute barrier for cysts and most viruses. NF plants typically operate at 85 to 95% recovery. Brackish water RO plants typically transfer 70 to 85% of source water into permeate, and seawater RO recovery rates range from 40 to 60%. Further discussion of RO can be found in Chap. 8.

Membrane filtration has several benefits over conventional drinking water treatment techniques:

- Acceptable treatment possible at low water temperatures
- Simpler pathogen removal
- Low energy costs
- Process easily expanded as units are delivered in skids

To make drinking water from brackish water or seawater, a combination of UF followed by RO can be very cost-effective. UF cartridges used as pretreatment can significantly extend the useful life of RO elements. When treating brackish water with relatively low total dissolved solids (TDS), UF can be used both as pretreatment to a RO system and to produce permeate for blending with RO product water.

Sludge Production

In the water treatment process, by-product solids (sludge) produced by removal of contaminants from raw water become a disposal problem. To minimize costs of sludge handling, the volume of sludge produced should be reduced as much as practicable.

Reduction in the weight of solids removed from raw water is impossible of course, if quality goals are to be achieved. Any weight reduction then must come from reduction in chemicals added for coagulation and flocculation.

In addition to weight reduction, the type of sludge produced should be controlled if possible, to produce a minimum volume and to yield a compact sludge that is easy to dewater and dispose of. In general, this may be accomplished by reduction or elimination of inorganic salts that tend to produce light, fluffy sludge, not readily dewatered. To reduce sludge volume and improve sludge compactness, it is possible to partially or completely replace the metal salt by organic polymers, or replace the metal salt with newer generation hydrolyzed metal salt coagulants.

In the 1980s, new generations of inorganic metal salts called (PACl) and aluminum chlorohydrates (ACHs) emerged in the United States. ACH is a highly concentrated solution of polyaluminum hydroxychloride. ACH is characterized by having the highest aluminum concentration (23% Al_2O_3) of any commercially available aluminum-based solution. The basicity of ACH at 83% is also the highest available for any polyaluminum-based solution. Basicity refers to the degree of acid neutralization and represents a measure of the ACH aluminum polymerization. PACl are concentrated solutions of lower aluminum concentrations (5–18%) and lower basicity as compared to ACH.

The highly polymerized aluminum species in ACH have much higher cationic charges than aluminum in standard salts such as alum or aluminum chloride and even other polyaluminum products. Therefore, ACH can offer both a higher level of performance and lower overall dosages. The high degree of acid neutralization (basicity) means that the effect on pH when applying ACH is negligible. ACH effectively coagulates over a broader pH range (as high as 9.5) versus traditional metal salts and lower basicity PACl.

ACH is generally employed as the primary coagulant in potable water and industrial water treatment plants, replacing need for other coagulants such as alum, and in many cases eliminating or at least greatly reducing need for pH adjustment chemicals. ACH is often employed in an environment where pH of the receiving stream is higher than 7.5. As with other metal salts, ACH and PACl dosages may be reduced with use of organic polymers.

Sludge from precipitation softening processes usually cannot be reduced significantly in weight, since they are primarily a result of dissolved hardness precipitation rather than addition of unnecessary chemicals. Where softening is achieved by ion exchange, it is possible to reclaim salt from spent regeneration solutions, while producing solid waste consisting of calcium and magnesium salts. Recycled salt brine can then be used for subsequent regenerations.

Once water treatment chemistry has been investigated to determine the optimum process producing the least amount of by-product sludge, consideration then focuses on the type of disposal process needed to handle solids. Where applicable, potential use of by-product material by a local industry should be considered. This may include such diverse activities as brick manufacturing, wallboard production, and agriculture. The alkali value of lime sludge may be valuable to neutralize acidic wastes, such as pickle liquor in a steel mill. Finding practical uses for sludge not only reduces sludge handling cost, but also eliminates need for landfill of solid material. Many states regulate disposal of aluminum sludge in public landfills.

Disposal of sludge by retention in sludge lagoons appears, at first, to be the obvious solution to a sludge disposal problem. Unfortunately, this often is simply a delaying process. Ultimately, sludge must again be handled, if the lagoon must be reclaimed. Lagoons may provide interim storage for a dewatering system, which continuously withdraws sludge from the lagoon at a controlled rate, optimizing design of the dewatering device. This also provides a means to completely flush sedimentation basins in older plants not equipped for continuous sludge withdrawal. Where land is readily available, sludge lagoons may provide an economical method of sludge drying, providing lagoon depth is not excessive and climatic conditions are favorable.

Sand drying beds have proved acceptable for dewatering water plant sludges. In warmer climates, they may be used year-round; in cold climates, sand beds are usually used in summer to dewater sludge accumulated throughout the year. Coupled with high molecular weight flocculants, sand beds provide a practical, inexpensive method of sludge dewatering. Sand drying beds require little attention by operators and consume very little energy. Sludge harvesting methods should be considered in designing the beds, so that mechanical equipment can be used.

Dewatering by centrifugation has gained popularity because of the compact nature of the equipment, and its ability to be operated with relatively little operator attention. Special attention must be given to details of equipment design to minimize internal abrasion by grit, which leads to costly maintenance. This equipment is able to handle wide variations in feed solids without significant upsets in production. Supplemental polymers required for inorganic sludge dewatering must comply with Treatment Techniques for Acrylamide and Epichlorhydrin. Products must contain less than 0.05%

residual acrylamide monomer, if centrate is reused in the drinking water process.

The plate-and-frame filter press has been successfully adapted to dewatering municipal water plant sludge. To properly assess this process, both capital and operational costs must be compared to alternative methods. In some cases, very high doses of filler such as diatomaceous earth, lime, or fly ash have been required to produce an acceptable cake. Early designs required considerable labor per unit of dry cake production, but newer designs have improved upon this.

The belt press includes several varieties of designs of screens or cloths on a conveyor device to reduce sludge volume. Often, solids are discharged as paste. In some cases, additional stages use press rolls to squeeze out more water and produce a more concentrated cake for disposal.

Filter backwash water, containing relatively little solids, requires separate treatment. In many cases, it is possible to simply pump backwash water directly to the head of the plant without upsetting the normal clarification process. However, consideration of the proliferation and concentration of *Cryptosporidium* and *Giardia* must be weighed, when water is reused in the treatment process. To facilitate this, it is desirable to add a polymer coagulant directly to the recycle stream during the time the backwash waste is being returned. This agglomerates the solids and prevents them from upsetting the clarification process. Backwash flow rate is often so high that direct return to the sedimentation basin may create a momentary overload. High flow rates can be controlled by an intermediate equalizing basin. Where sedimentation basins are not employed, use of decant tanks to concentrate the sludge, followed by sand bed dewatering, should prove adequate.

Municipal Sewage Treatment

While municipal sewage treatment is a well-established practice, it is an area of water treatment experiencing revolutionary changes because of increasingly stringent effluent quality limitations, and the potential value of treated effluent as a source of water for industry, agriculture, and municipalities. Until a few generations ago, plants were designed to remove 30 to 40% of undesirable impurities before discharge into the receiving body of water. There were no real limits on effluent quality as long as the discharge was chlorinated and met bacterial count standards. Municipal sewage plant operators had only minimal training, but fortunately, many of them were able to learn from experience and became knowledgeable in plant operations. With growing sophistication of modern plants designed to meet stringent goals, training programs in sewage plant operation have become available to supplement on-the-job training for upgrading personnel.

In the late 19th century, fewer than 30 cities had sewage treatment facilities. Today, more than 16 000 municipal wastewater treatment plants operate in the United States, ranging in size from several hundred mgd to less than 1 mgd (< 158 m^3/h). Roughly 1000 of these facilities operate with a total influent flow greater than 5 mgd (789 m^3/h). According to the EPA, 75% of U.S. wastewater is treated in regional collection and treatment systems.

Overview

Sewage treatment refers to the processing of primarily domestic sewage produced by typical community and household activities. In rural areas, characteristics of raw sewage tend to adhere to this definition. As cities become larger and more industrialized, waste volume and characteristics of one particular industry may affect sewage composition. In addition, sewage may be from combined or separate sanitary sewer systems.

With combined systems, storm water drains into sewer lines to become part of the total flow to the sewage treatment plant. Such uncontrolled surges in flow can be very disruptive to the process of sewage treatment, severely limiting the plant's ability to remove pollutants. Future practice aims toward segregating storm water flow in sewer systems from those used to collect sanitary waste. This will materially reduce and control flow entering the treatment plant, thereby increasing ability to maintain adequate treatment. Storm water retention basins are being built in many cities to even out severe surges caused by storm water, allowing a more reasonable chance of processing the extra volume.

The flow of sewage to be treated may approximate the flow of municipal water supplied to the same community, being in the range of about 100 gpd (0.38 m^3/day) per capita in rural areas to 150 gpd (0.57 m^3/day) per capita in urban areas with industrial users. However, there may be differences between municipal water and sewage flows that could be substantial. Such differences may be caused by evaporation losses in industrial plants (over cooling towers or as noncondensed steam), storm water or groundwater influx, and local industries that may have their own water sources but discharge into municipal sewers. Sewage is always warmer than the water source, and shows an increase in salinity over potable water of about 50 to 75 mg/L. The most common contaminant additions to filtered municipal water as it is converted to sewage are:

- Suspended solids, typically about 200 mg/L, of which about two-thirds is organic and two-thirds is settleable
- Dissolved organic matter, typically about 150 mg/L as biochemical oxygen demand (BOD)
- Nutrients, typically 10 to 30 mg/L phosphate and 10 to 30 mg/L ammonia

Standards being established for pretreatment of industrial wastes for discharge into municipal sewers are helping to reduce harmful contaminants found at lower concentrations, such as heavy metals and cyanides from plating operations, oil and grease from metalworking and food-processing plants, and toxic materials [e.g., polychlorinated biphenyls (PCB), pesticides, and solvents] as specified by the EPA.

Because sewage flow patterns are directly related to residential water use, there are wide variations in inflow during the day, the week, and even the season. Figure 44.4 indicates the degree of variation throughout the day caused by typical residential use patterns. During the week, flows vary because of other factors, such as the traditional Monday washday. Seasonal variations also affect separate sanitary sewers owing to the impact of storm water caused by damaged sewer pipe (infiltration) and sump pump operation. While combined sewer systems are mostly influenced by sudden downpours (inflow), separate systems are affected over a broader period because of the slower drainage of water from saturated soil. After a considerable dry spell, soil acts as a sponge, reducing the impact of short infrequent showers.

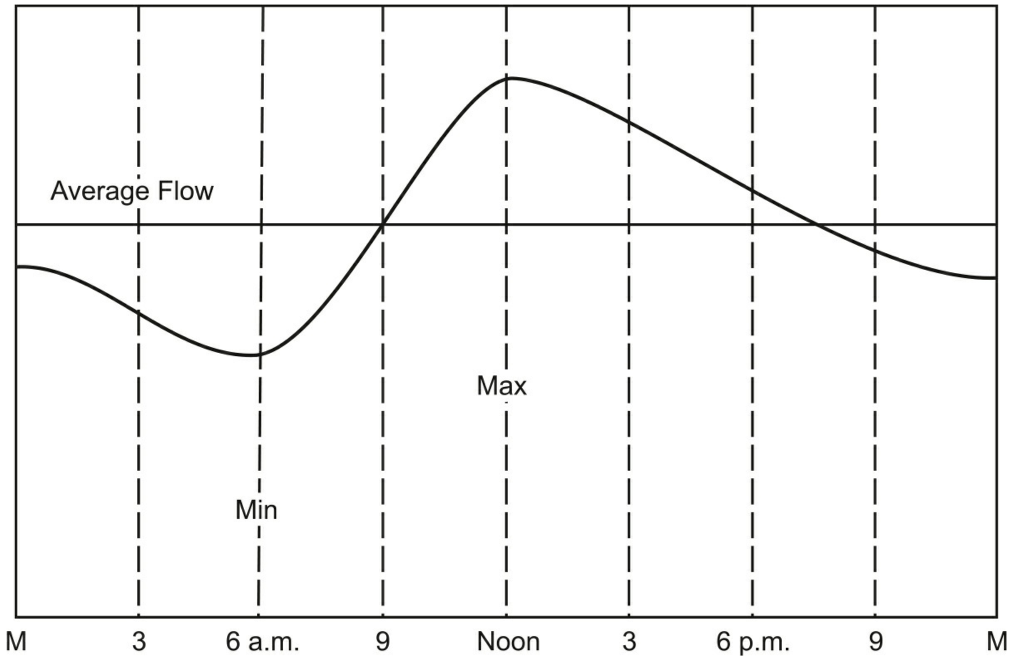


FIGURE 44.4 Typical diurnal variation in sewage flow.

Wastewater Treatment Methods

Wastewater treatment practices vary in the type of equipment used and in treatment sequences. Most plants fall into a few basic categories, as shown by the simplified flow sheets in Fig. 44.5. While these flow sheets show basic unit operations that make up the total process, they do not include supplemental treatments such as ammonia stripping or selective ion exchange. These additional processes develop from individual plant needs related to sewage characteristics and flow and effluent limitations to be met. Since the Clean Water Act requires all plants to practice secondary treatment, only those treatment schemes that include secondary treatment are shown. Stabilization ponds, which provide treatment for smaller municipalities, are omitted. Here, wastewater is contained in a pond for long periods during which useful bacteria and algae consume undesirable pollutants. Refer to Chaps. 22 to 24 for a detailed discussion on primary, secondary, and tertiary treatment.

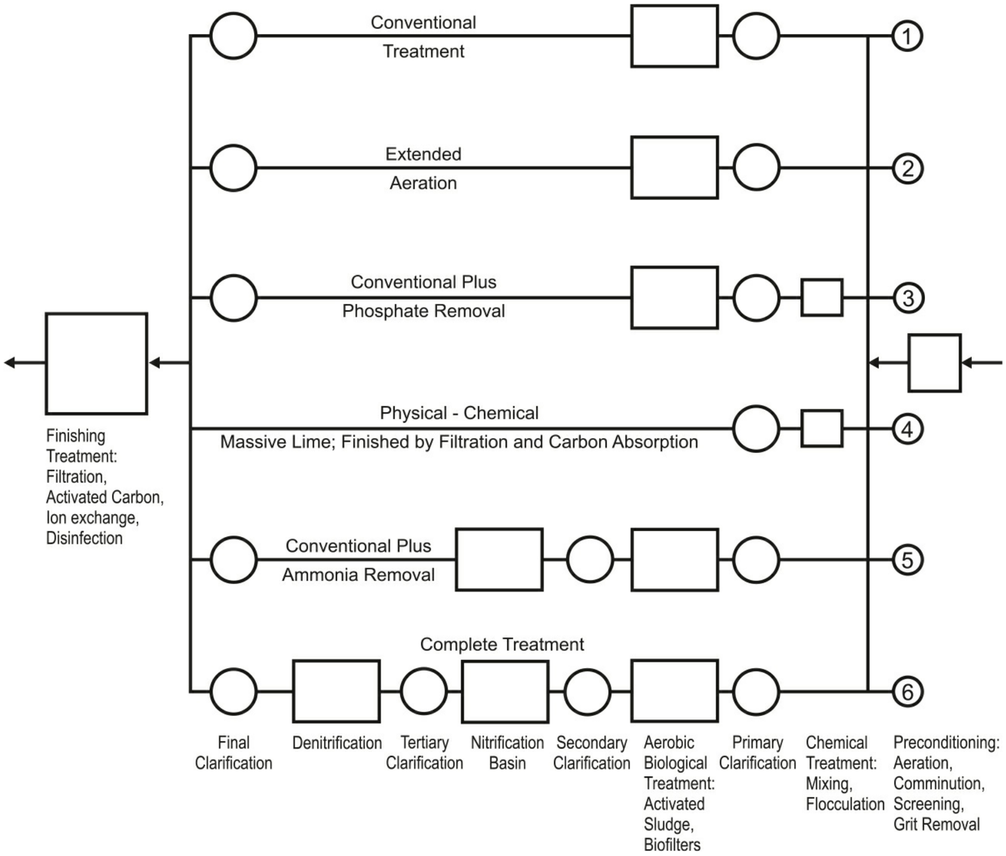


FIGURE 44.5 Typical processes available for municipal sewage treatment.

Disinfection

Wastewater discharged into a receiving body still contains microorganisms and pathogens that can produce disease and therefore requires disinfection. While disinfection may take various forms, chlorine application to a detention basin providing at least 15 minutes reaction time has usually been used for this purpose. In many cases, dechlorination may follow to remove trace amounts of residual chlorine that might be toxic to stream organisms. Due to hazards associated with chlorine gas, it is used less frequently then in the past. Because of concern for the production of chlorinated organics, which might also be toxic, other methods of disinfection are gaining popularity. Ozone and UV light are other disinfection techniques. Ozone, while expensive, does not leave a residual that requires further removal and is very effective at destroying viruses and bacteria. UV light also does not require further treatment for removal of residuals.

Lagoons

Since the 19th century and even earlier, wastewater lagoons or ponds have been used as a process for wastewater treatment. In the 1920s, artificial ponds were designed and constructed to receive and stabilize wastewater. By 1950, ponds had become recognized as an economical wastewater treatment method for small municipalities and industries. As of 1980, approximately 7000 waste stabilization lagoons were in use in the United States. By the 21st century, over 30% of all secondary wastewater treatment facilities in the United States with flows less than 1 mgd (< 158 m^3/h) include some type of pond system. However, ponds can be used for larger cities, primarily in stable climates, for wastewater treatment as well. Some of the largest pond systems in the United States are in Northern California, serving such cities as Sunnyvale, Modesto, Napa, and Stockton.

A wastewater lagoon or pond is an engineered system designed to allow water, algae, bacteria, and oxygen to interact biologically and physically. There are several types of lagoons.

Waste stabilization ponds (WSP) are also known by the name of oxidation ponds or lagoons and decompose carbon biologically in up to three stages in series, depending on organic strength of input waste, and effluent quality objectives. Generally, WSP consist of an anaerobic pond following primary or secondary facultative ponds. If further pathogen reduction is necessary, maturation ponds are introduced to provide tertiary treatment. In WSP, bacteria and algae stabilize and reduce pathogens to convert organic content of the effluent to more stable forms. These ponds are useful in treating a variety of wastewater, from sewage to complex industrial waters. They can function well in a wide range of weather conditions and can be used either alone or integrated with other treatment processes. WSP are regarded as the method of first choice for treatment of wastewater in many parts of the world, because of design, construction, and operation simplicity, cost-effectiveness, low maintenance and energy requirements, easy upgrading, and high efficiency.

Advanced integrated wastewater pond systems (AIWPS) are feasible for application in the developing world. AIWPS designs incorporate a minimum of four low-cost ponds or earthwork reactors in series. These are advanced facultative ponds (AFP), secondary facultative ponds or algal high rate ponds (HRP), algae settling ponds (ASP), and maturation ponds. Sludge management and removal in AIWPS is minimal since sludge remains in place and biologically degrades over decades. Methane fermentation and biological assimilation transform carbon. Conversion of waste organic solids to methane, nitrogen gas, and carbon dioxide via methane fermentation, and assimilation of organic and inorganic carbon to algal biomass via photosynthesis provide the basis for primary, secondary, and tertiary treatment in AIWPS.

Water Reuse

Water reuse is becoming more prevalent in municipalities in the United States. Reuse offers a source of water that is dependable, locally controlled, generally beneficial to the environment, not affected by climatic changes, and applicable for nonpotable applications such as irrigation; toilet and urinal flushing; industrial processing; power plant cooling; wetland habitat creation, restoration, and maintenance; and groundwater recharge. Additionally, water reuse allows communities to become less dependent on finite groundwater and surface water sources. Indirect and direct potable reuse (IPR and DPR) plants are being considered in many municipalities throughout the United States. In some cases, reuse is potentially more cost-effective than seawater as a source water because of the cost of desalination.

Water reuse facilities use a variety of treatment processes to treat influent water. Generally speaking, the four stages of treatment are primary, secondary, tertiary or advanced, and disinfection. The number of treatment steps vary based on the end use for the water. The majority of recycled water is disinfected using technologies mentioned previously.

Nonpotable recycled water is distributed in a separate pipeline system to customers. Cross-connection tests ensure that nonpotable recycled water pipelines are not connected to the drinking water system.

According to the WateReuse Association, several states consider reclaimed water viable as an alternative water source, and have developed regulations with specific water quality requirements or treatment processes for a variety of reuse applications. Other states lack specific guidelines and regulations. In 2004, EPA developed a comprehensive technical document entitled Guidelines for Water Reuse, specifically as a technical resource for those states without regulations on reuse of municipal wastewater.

Denver Water Recycling Plant

Denver is a good example of a city that practices wastewater recycling and reuse for nonpotable applications. Existing wastewater plant capacity is 30 mgd (4700 m^3/h), and it is expandable to 45 mgd (7100 m^3/h). The distribution system includes over 50 miles (80 km) of pipe with two major pump stations and dedicated storage facilities. At completion, the project will supply about 17 mgd (2700 m^3/h) of treated wastewater to irrigation and industrial customers.

Wastewater Treatment Process Source water for the recycling plant comes from Metro [Denver] Wastewater's treatment plant. Figure 44.6 shows how wastewater is treated before release. Denver Water gets its share of water after the water has been fully clarified.

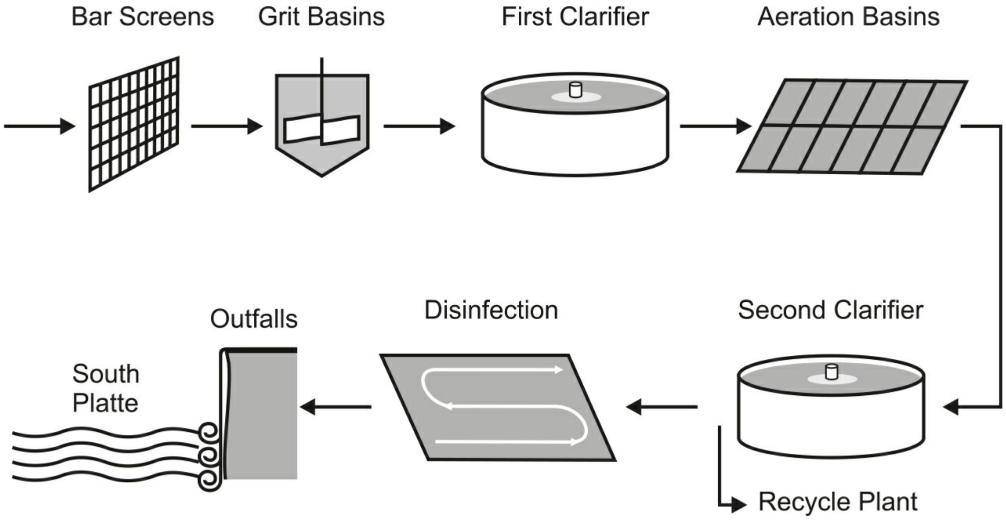


FIGURE 44.6 Metro (Denver Colorado) wastewater treatment process.

Wastewater from the sewer system enters the plant, where it is filtered through bar screens and grit basins, which remove large objects. During the first clarification process, solid waste settles to the bottom. Water is exposed to aerobic microorganisms in secondary treatment that digest the remaining organic waste. The secondary clarifier removes most of the suspended solids. At this point, part of the treated water is pumped to Denver Water's recycling plant. The rest of the water is chlorinated and dechlorinated. Finally, the cleansed wastewater enters the South Platte River.

Denver Water Treatment Process The process that Denver Water uses to create recycled water is very similar to the process for creating potable water. The primary differences are the source of the water and a pretreatment (biological filter aeration) that wastewater goes through to remove ammonia not present in the normal mountain water source. Figure 44.7 shows the four main steps in preparing water for use after the special aeration. Recycled water contains somewhat higher salt and mineral content as well as other introduced elements that make it not safe to drink but acceptable for nonpotable applications.

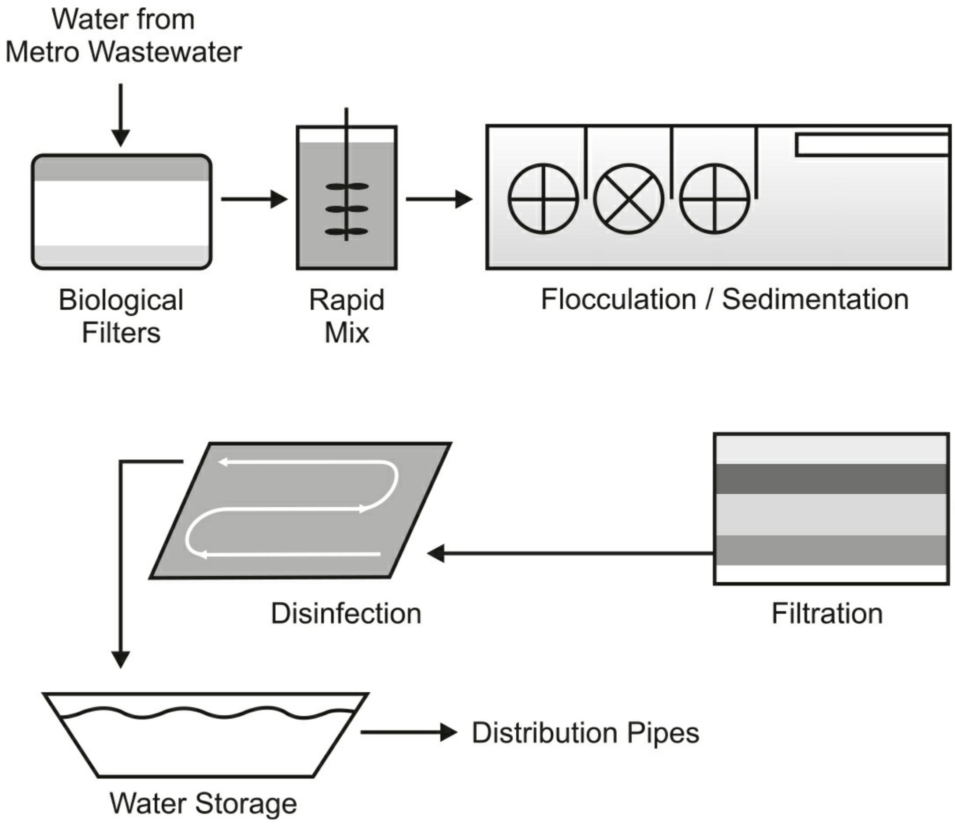


FIGURE 44.7 Denver Colorado water recycle water treatment process.

Source water enters the plant and is rapidly mixed with coagulants that can capture floating sediment. The water is flocculated, which creates turbulence and increases contact of sediment and coagulant. This allows particles to grow bigger and heavier. Within the sedimentation basin, clumps of sediment settle. Water then passes through anthracite filter beds, trapping remaining sediment. Once fully filtered, water passes into contact basins for disinfection. Finally, water is stored in a reservoir, where it is ready for industrial and large irrigation customers.

Membrane Bioreactors

Membrane bioreactors (MBR) combine activated sludge treatment with a membrane separation process. The membrane component uses low-pressure

MF or UF membranes, thereby eliminating need for clarification and tertiary filtration. Membranes are typically immersed in the aeration tank. MBR systems are differentiated in that they effectively overcome limitations associated with poor settling of solids in conventional activated sludge processes. MBR can operate higher mixed liquor suspended solids (MLSS), often in the range of 8 to 12 g/L compared to conventional systems operated in the range of 2 to 3 g/L, as the latter are limited by sludge settling. Elevated biomass concentration in MBR allows for very effective removal of both soluble and particulate biodegradable materials at higher loading rates. Thus, increased sludge retention time (SRT), usually exceeding 15 days, allows for complete nitrification regardless of ambient temperature.

In municipal wastewater applications, MBR processes are capable of producing effluent of high enough quality to be discharged to coastal, surface, or brackish waterways or to be reclaimed for urban irrigation. MBR processes typically produce water of a quality that can be used as NF or RO feed water in reuse or aquifer storage designs. Other advantages of MBR over conventional processes include small footprint, easy retrofit, and upgrade of old wastewater treatment plants. MBR are used for municipal and industrial wastewater treatment with plant sizes up to 15 mgd (2400 m^3/h).

Solid Waste Treatment

In treatment of municipal wastewater, some contaminants are actually consumed, but a significant portion simply is converted to solid wastes (biosolids). When biosolids are removed from water, they become by-product sludge, which requires disposal. The disposal of residual process solids is addressed in the Resource Conservation and Recovery Act (RCRA), which requires environmentally sensible disposal and reuse of biosolids, if possible. Over 50% of municipal biosolids in the United States are used as soil conditioners or fertilizers, and the remaining biosolids are incinerated or landfilled.

The first step in disposal of biosolids is to stabilize the sludge to eliminate odors and pathogenic organisms, as well as reduction in volatile material. Most plants use aerobic or anaerobic digesters to accomplish this. Following stabilization, sludge is concentrated and dewatered before final disposal. New processes are being continually investigated to use waste sludge. It has been used for years as a lawn and agricultural soil supplement. Sludge also finds use as fuel and as raw material for conversion to activated carbon.

Sludge is often concentrated before dewatering to permit more efficient utilization of final dewatering equipment. This is particularly true in the case of waste activated sludge, which may contain only 0.5 to 1.5% solids. Position of the sludge concentrator varies, though when used to concentrate waste activated sludge, it is generally ahead of the digester to provide a concentrated feed. In some cases, this is the final sludge processing step before landfill of digested sludge, where higher moisture does not represent significant haulage costs. Equipment used may vary greatly from plant to plant. Figure 44.8 shows a large sewage treatment plant with multiple sludge handling systems.

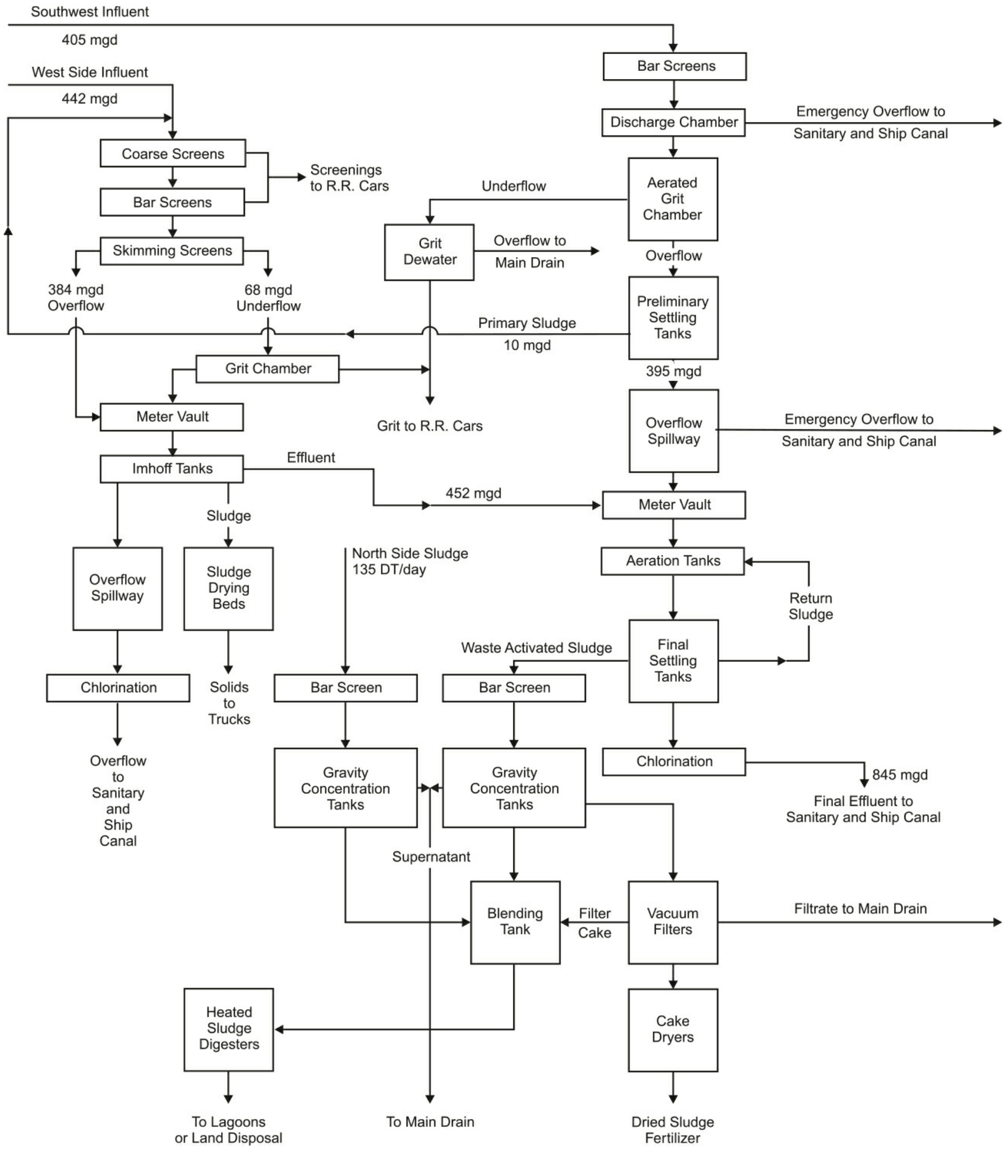


FIGURE 44.8 Large, complex sewage treatment plant with multiple sludge handling systems.

Many cities use incinerators to dispose of sludge generated from sewage. Additionally, many cities are considering use of biogas from anaerobic digesters as free fuel to generate electricity and power. Sometimes, sludge is combined with municipal solid waste (garbage) for incineration. Because of energy considerations, emphasis is being placed on power generation in newer units.

Dewatering

Sludge dewatering is normally the final liquid/solids separation step in a wastewater treatment process. The dewatering method is often dictated by the nature of solids being dewatered, final method of sludge disposal, and specific local conditions. The goal is to produce a dewatered sludge cake of such density, solids content, and strength to meet subsequent sludge disposal requirements. For example, maximum water needs to be extracted from sludge if it is going to be incinerated to minimize use of auxiliary fuel. Low cake moisture (high solids concentration) can be required to pass cake drainage tests for landfills and minimize hauling costs. Sludge may not need to be dewatered to such a high extent when cake is used for a land reclamation program.

Chemical conditioning is a term that denotes sludge that has been treated to decrease specific resistance and increase porosity. Chemical conditioning may include any combination of polymer addition, mixing energy, and at times dilution water. The process is designed to produce a porous, three-dimensional sludge matrix, which releases water readily during the dewatering operation. Optimum chemical conditioning increases particle size of solids, releases surface-adhering water, and decreases sludge compressibility.

The majority of municipal anaerobically digested biosolids require a cationic polymer of some form due to the natural anionic charge of biosolids.

Refer to Chap. 26 for a detailed discussion of sludge thickening and dewatering.

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