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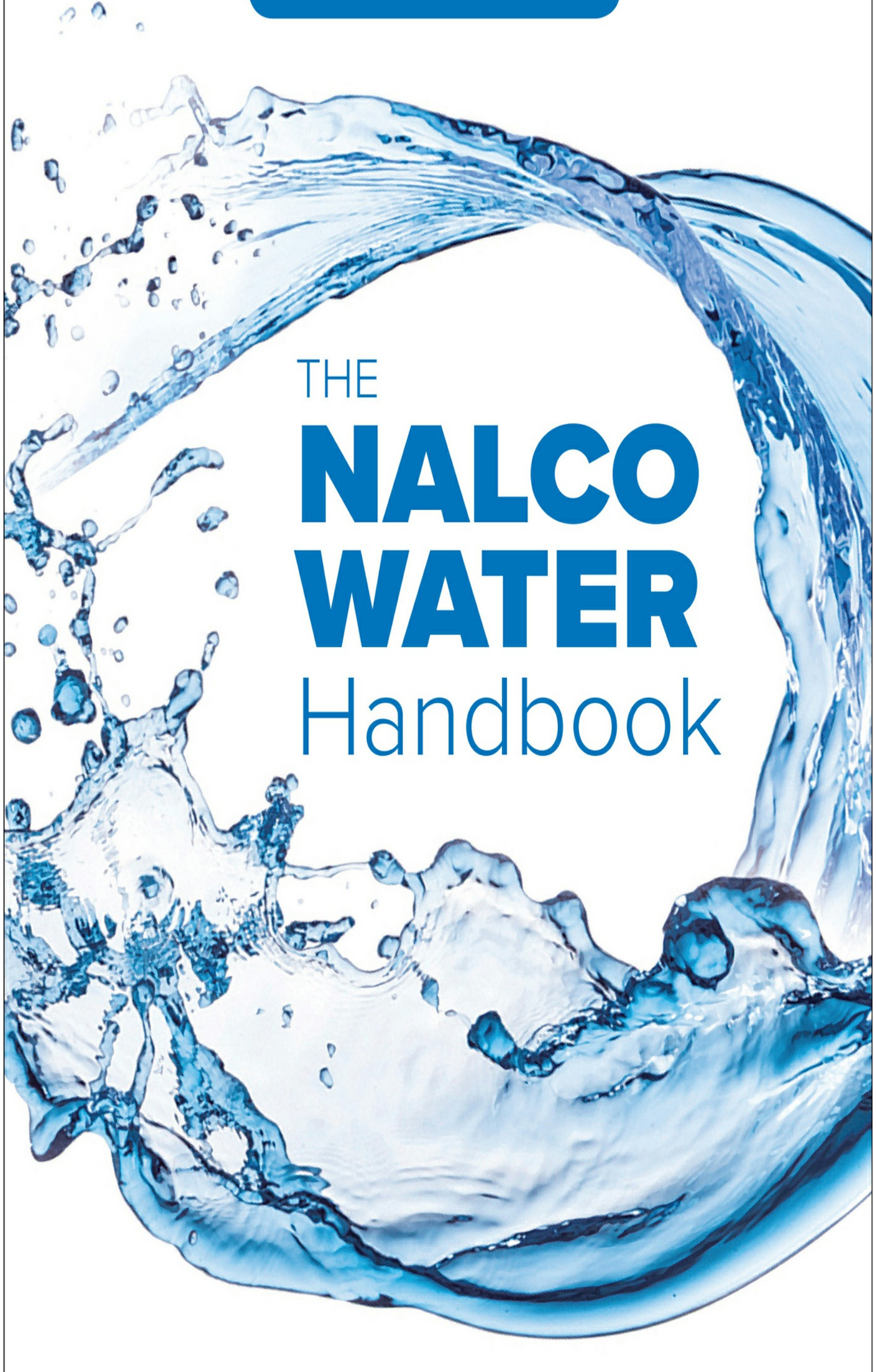

THE NALCO WATER Handbook

Mc Graw Hill Education

NALCO Water
An Ecolab Company

About Nalco Water, an Ecolab Company

Nalco Water, an Ecolab company is the global leader in water, hygiene, and energy technologies and services that protect people and vital resources. Ecolab delivers comprehensive solutions and on-site service to ensure safe food, maintain clean environments, optimize water and energy use, and improve operational efficiencies for customers in the food, healthcare, energy, hospitality, and industrial markets in more than 170 countries around the world.

The Nalco Water Handbook

Nalco Water, an Ecolab Company

Daniel J. Flynn Editor

Fourth Edition

Mc Graw Hill Education

New York Chicago San Francisco
Athens London Madrid
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Foreword

Business and industry are increasingly identifying water scarcity as a business constraint and risk. By the year 2030, the World Economic Forum estimates that the global demand for freshwater will exceed supply by about 40%. The ever-increasing demand for freshwater is causing us to consider the potential outcomes, where water stressors start to inhibit our ability to meet the critical needs of our customers around the world. Yet the risk is not equitable across the globe. Each watershed is different. There are acute shortages in some places and not in others. We also find that universally water is underpriced, and the prices are inverse to the risk.

Our conversation is changing. We are reframing our discussion and vocabulary around water to reflect the challenges, the risk to business, and the true cost of the resource. We are finding ourselves at an inflection point. We have obtained the knowledge and sophistication to make the case for water strategies in our facilities that make good business sense, and enable growth in an environmentally sustainable and socially equitable manner. Implementing water strategies within plants needs to make good economic sense and be accomplished in a manner that allows the business a fundamental license to grow.

Our fourth edition of *The Nalco Water Handbook* opens up the discussion on water scarcity, stressors, and the business case for managing water. The content throughout the book will assist you in maintaining clean heat transfer surfaces as well as addressing water management needs through the lens of reduction, reuse between applications, and recycle. As you read through the book, look for the items that can become actionable in your facility and not just protect your assets, but that can help your water management strategies as well.

Christophe Beck
President, Nalco Water
Executive Vice President, Ecolab

Preface

As Nalco Water approaches its 90th year in business, it seems fitting to release the fourth edition of *The Nalco Water Handbook* at the same time. Our first book, *Water: The Universal Solvent*, was published in 1977 in observance of the company's 50th anniversary. Frank N. Kemmer, editor-in-chief and John McCallion, associate editor of that book, went on to produce the first two editions of *The Nalco Water Handbook* and firmly placed Nalco Water well down the road of knowledge sharing. We at Nalco Water continue to believe this is as important today, as it was when the first book was published.

Water as a resource is becoming increasingly scarce throughout much of the world. In this edition of the book, we have restructured the initial introductory chapters through the lens of water scarcity, stressors, and business risk. In addition, we have added supplementary content around water conservation in various processes where applicable. We have also strengthened the discussions around various industry processes, impurity removal with membrane technology and water safety for building water systems. Finally, we have added additional chapters in the industry section to broaden the scope of the discussion.

We have made liberal use of tables, illustrations, photographs, and line drawings to help place the discussion in context. Hundreds of graphics have been refreshed to assist in clarifying the message they convey. The changes we have made to the content and the presentation should make this book valuable across a wide range of users such as plant operators, engineering departments, process management, maintenance groups, and plant mangers to name a few.

Daniel J. Flynn
Editor

Acknowledgments

When we were evaluating the updating, and refreshing of this text, it became very clear quite early on that we would be asking a good number of people for contributions of time, text, photographs, drawings, illustrations, fact checking, and numerous reviews just to mention a few of the items. As the project progressed, the numbers grew as we cast our net further into the many disciplines and departments throughout Nalco Water. We would like to take this opportunity to acknowledge the participation and efforts of the individuals involved with the fourth edition of *The Nalco Water Handbook*.

The following individuals made significant contributions of writing, reviewing, fact checking, and generally ensuring the content of the book remains best in class for this fourth edition, as well as the previous third edition. It is with great thanks that we acknowledge their efforts. Alex Glass, Amit Gupta, Andrew Cooper, Andrew Hook, Anton Banweg, Barbara Moriarty, Ben Riley, Blaine Krause, Bob Pomeroy, Bonnie Harris, Brad Benz, Brian Jenkins, Carl Rossow, Carolina Diaz-Rodriguez, Carolyn Will, Christine Staples, Chuck Foster, Cindy Ojczyk, Daniel Flynn, Daniel Meier, Debbie Bloom, Dennis Martin, Don Roll, Donald Johnson, Ed Swenson, Emilio Tenuta, Eric Kangas, Eric Myers, Flora Lu, George Peabody, George Totura, Greg Coy, Gregg Galbreath, Heidi Olszewski, Howard Barnes, James Gage, Jane Kucera, Janet Kirkman, Jasbir Gill, Jason Burney, Jason Van't Hul, Jeffrey Oloier, Jim Dillon, Jim Haff, John Sparapany, Jorvic Vital, Ken Fulks, Ken Voytell, Kevin Gehan, Kevin Kaiser, Kirby Lee, Larry Hill, Leroy Swenson, Melissa Callejo, Michael Lesniak, Michael Martin, Mike Backode, Mike Vittum, Mita Chattoraj, Nancy Stan, Patrick Miller, Paul Desch, Paul Williams, Peter Hicks, Peter TenEyck, Ram Nagarajan, Richard Jacobs, Rick Lyons, Rob Henderson, Robert Wetegrove, Ronald Kochik, Ronald Tebbetts, Sam Lordo, Scott McLaughlin, Seth Werlinsky, Sherri Binetti, Steff Vrijhoeven, Steve Andrick, Steven Kramarczyk, Sue Molloy-Vesley, Tammy Lai, Tim Keizer, Tom Lindley, Tracey Guddendorf, Walter Schaefer, and so many others who touched this project in various ways.

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Daniel J. Flynn
Editor

SECTION 1

Introduction

CHAPTER 1

The Business Case for Managing Water

Water—we take it for granted in much of the world. To be sure, it comprises fully three-quarters of the surface of the earth. We build our cities close to it. Vacations are planned to include it. Water's domestic use is critical to our survival. It is fundamental to the portion of our economy that is agrarian in nature. It is important for much of our industrial processes. With so much of the earth covered with water and it being fundamental to our industry, agriculture, and life, humankind has undertaken to utilize water in many different ways to suit our needs and desires.

Despite our reliance on water, there has been no incentive to value it for the precious and limited resource that it is. The world is changing. It is growing, more urban and affluent. These populations are demanding more resource-intensive goods and services. These changing global dynamics are placing increasing pressure on the world's diminishing freshwater supplies. For industry to be sustainable for the long term, mindsets and practices related to water must change.

While a significant portion of our planet is covered with water, most of it is not usable in the form we find it. For human use, we look to break water into two groups, fresh and salt. Human use is centered on freshwater, which comprises only about 2.5% of all the water found on earth. The remaining 97.5% is considered sea or saltwater. Saltwater is not considered suitable for industry, agriculture, or domestic use.

When we look at the freshwater resources on earth, we find that an estimated 68.7% of it is locked in ice sheets and glaciers at our poles, on mountaintops as glaciers and snow pack, and in the ground as permafrost. These resources are considered out of our reach and therefore unusable as they sit. This leaves us a very small 1.2% of the water on earth as usable surface water or groundwater. This fraction of the earth's water resources supports all terrestrial life and powers our industries. This thin 1% sliver of water is our focus in this book (Fig. 1.1).

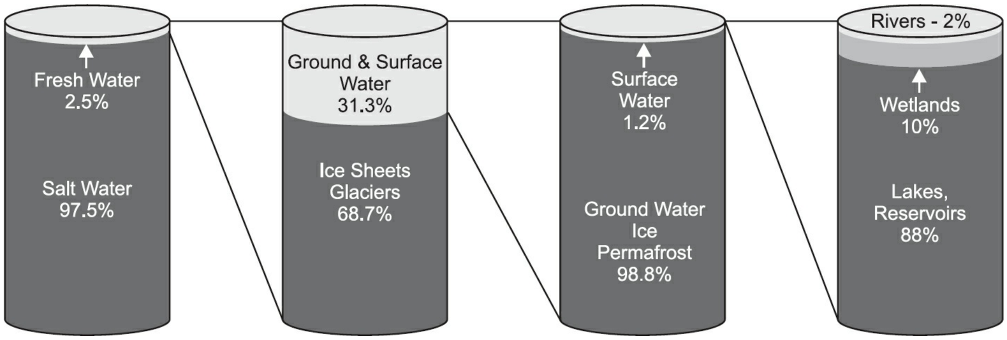


FIGURE 1.1 Breakdown of earth's water resources, illustrating freshwater components by percentage.

Global Trends Affecting Water Supply

The Impact of Climate Change on Glacial Water

Our planet is warming. The effect on weather patterns varies across the world, but the effect on ice packs and glaciers is known: They are melting. This melting does not always result in usable freshwater. Sea icepacks and tidewater glaciers such as those found in the Antarctic break off and melt directly into oceans (Fig. 1.2).

FIGURE 1.2 The Hubbard Glacier in Alaska is a tidewater glacier that terminates in Yakutat Bay in the Gulf of Alaska. (*Courtesy of D.J. Flynn*.)

Mountain or valley glaciers that do not terminate at the ocean are the headwater sources for many of the earth's major rivers. These rivers depend on sufficient snowfall in mountain regions to maintain the glaciers and provide sufficient melt water for yearlong river water flow. As these glaciers retreat, the amount of reserve capacity is decreasing, threatening to turn yearlong rivers into seasonal water sources. Since we rely on these surface waters, the effect of climate change on glaciers creates water stress to downstream consumers (Fig. 1.3).

FIGURE 1.3 The Mendenhall Glacier in Alaska is a valley glacier feeding Mendenhall Lake and Mendenhall River. (*Courtesy of A.C. Van Sistine*.)

Technology has enabled municipalities and industries to access underground reservoirs, or groundwater, which constitutes more than 90% of the total freshwater available for human use. Without sustainable replenishment, groundwater extraction is a short-term solution that adds to the stress on those water sources as well.

Impact of Population Trends on Surface and Groundwater

Global trends, including shifts in population growth, and increasing demand for water, food, and energy are impacting all facets of our world economy. Here are a few emerging macro trends from the United Nations and other organizations worth noting:

- The world's population is predicted to expand to 9.7 billion by 2050.[1]
- By 2025, 90% of population growth will be in developing or emerging markets. Urban populations are expected to rise from 3.9 to 6.4 billion, accounting for 67% of the world's population, with nearly 90% of the increase in Asia and Africa.[2]

- In the next 20 years, there will be three billion more middle-class consumers, increasing demand for goods and services and putting unprecedented pressure on the world’s limited natural resources.[3]
- Increased pollution from municipal and industrial waste and the leaching of fertilizers and pesticides used in agriculture will all contribute to shrinking the world’s potential freshwater for human and industrial needs.

Climate change and population growth are the two main stressors on the global freshwater supply. The agriculture, energy, and manufacturing sectors will all need to challenge their industries to rethink their processes in order to reduce water consumption and remain viable. According to the United Nations World Water Development Report, reconciling different water uses at the surface and groundwater level and improving policy coherence nationally and across borders will be priorities for many years to come.[4]

Sustainability as a Business Driver

The original definition of sustainability from the Brundtland Report reads: involving development that meets the needs of the present without compromising the ability of future generations to meet their own needs. For businesses, this means achieving sustainable, sound growth while minimizing risk and natural resource consumption. Another way to say this is, “doing more with less.”

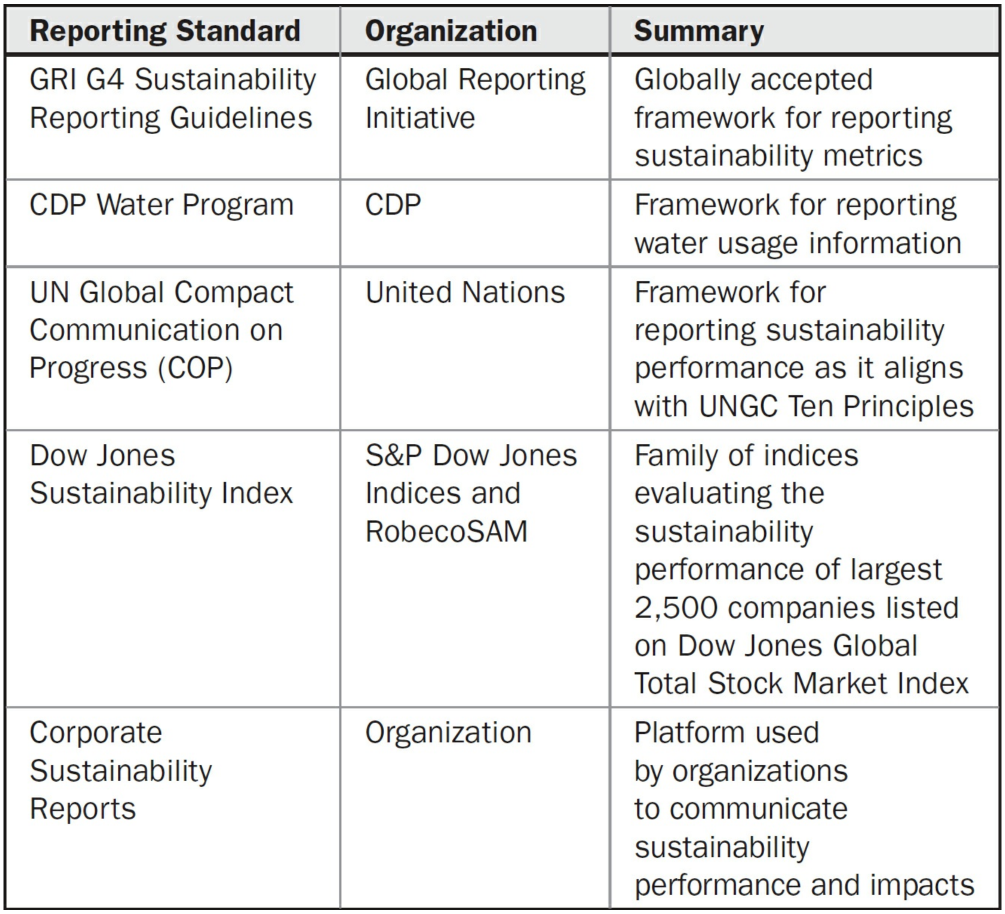
Companies adopting sustainable business practices understand that they are most successful when economic and environmental benefits align. Measuring the link between performance outcomes, environmental impact, and cost savings demonstrates the value of operating sustainably and helps make the business case for water-saving solutions.

Progressive companies are setting more and more aggressive sustainability goals and publicly reporting progress against those goals. These commitments are good for both business and society. For more than a decade, the United Nations (UN) Global Compact-Accenture Strategy have compiled research from leading CEOs around the world and across a diverse set of industries as they are called to take action on their sustainability goals. A UN Global Compact-Accenture Strategy CEO Study of more than 1000 CEOs conducted in

2016 reports that 89% of industry leaders said their commitment to sustainability is translating into real impact in their industries.[5] In this same study, 59% report their company is able to accurately quantify the business value of their sustainability initiatives, up from 38% in 2013. The report further states that business leaders are still looking for additional ways to measure, track, and communicate the impact of sustainability on metrics of business success, and demonstrate their impact on corporate sustainability goals. Growing pressure from consumers, investors, and reporting agencies is starting to mobilize the business world, with increasing urgency and conviction.

Sustainability Reporting and Regulations

In response, a new trend has emerged: increased proactive, voluntary reporting on water and energy use and other sustainability metrics. Table 1.1 includes some of the leading globally recognized reporting standards through which businesses are able to demonstrate their sustainable performance. They are also utilized to hold businesses accountable for reporting on their sustainable performance.



Reporting Standard	Organization	Summary
GRI G4 Sustainability Reporting Guidelines	Global Reporting Initiative	Globally accepted framework for reporting sustainability metrics
CDP Water Program	CDP	Framework for reporting water usage information
UN Global Compact Communication on Progress (COP)	United Nations	Framework for reporting sustainability performance as it aligns with UNGC Ten Principles
Dow Jones Sustainability Index	S&P Dow Jones Indices and RobecoSAM	Family of indices evaluating the sustainability performance of largest 2,500 companies listed on Dow Jones Global Total Stock Market Index
Corporate Sustainability Reports	Organization	Platform used by organizations to communicate sustainability performance and impacts

TABLE 1.1 Globally Recognized Reporting Standards for Sustainability Metrics

Companies committed to public reporting recognize that benefits can include increased share value and investor confidence; increased stakeholder engagement, support and patronage; increased staff motivation, confidence, and productivity; innovation in new products and market development; and increased profitability through cost reductions consequent on consuming fewer resources, creating less waste for disposal, reduced emissions, and better management of cash flow. Many companies are now positioning their business on a platform of sustainable development that visibly proclaims what they stand for and how they are contributing to their own and their customers' sustainability goals.

Companies around the world are also facing increasing regulations in the form of legislation and controls that govern their operations and how they impact the environment and society. For example, where wastewater was an inexpensive output of industry in the past, more stringent regulations are resulting in increasing costs to clean water for discharge back to the environment.

Within the European Union (EU), legislation such as the Integrated Pollution Prevention and Control (IPPC) regulations; the Biocidal Products Directive; and the Registration, Evaluation, Authorization, and restriction of Chemicals regulations (REACH) have demonstrated a strong commitment to control how companies are expected to protect the environment and human health. Availability of data has revolutionized ways in which regulations are applied and monitored. For example, the Toxic Release Inventory (TRI) operated by the U.S. Environmental Protection Agency (EPA) is a public database listing by company, containing the known releases of chemicals to the environment. The European Pollutant Release and Transfer Register (E-PRTR) have now joined the EPA in making pollution and emission data freely available to all citizens. The Pennsylvania Department of Environmental Protection (PADEP) has mapped all the waterways in the U.S. state of Pennsylvania. The PADEP uses the Pennsylvania Single Discharge Waste Load Allocation Program for Toxics and Other Substances (PENTOXSD) water quality analysis application to determine permit limits for toxics and certain other substances. In addition, enforcement agencies in many countries around the world publish data on emissions that affect their specific territories.

Industrialized western countries generally led the way with regulations on waste discharge. Today, emerging countries around the world are following suit and beginning to regulate or enforce laws around waste discharge back to surface waterways. Increased regulation will start to reduce the pollutant load on surface waterways and help ensure that water continues to remain usable downstream from discharge points. This means there will be an increased need for equipment and chemistry to treat waste streams and make water suitable for discharge. Countries like China, India, and many of the countries in Eastern Europe are beginning to strengthen discharge requirements for municipal and industrial processes. China, for example, launched a new environmental protection law (EPL) in 2015 with details on harsh penalties for environmental offenses and provisions for tackling pollution and raising public awareness about offenders.

Making the Business Case for Managing Water

The future of freshwater availability is uncertain. According to the World Economic Forum, global water crises are a threat of highest concern for the next 10 years.[6] As stated earlier, only a very small percentage of the world's freshwater supply is readily accessible for direct human use. Implications for businesses, communities, and individuals are real, and supplies are limited. The following statistics frame this era of freshwater scarcity:

- 36 countries face extremely high levels of baseline water stress, whereby more than 80% of available water is withdrawn annually.[7]
- By 2025, water withdrawals are predicted to increase by 50% in developing countries and 18% in developed countries.[8]
- 47% of the world's population will be living in areas of high water stress by 2030.[9]
- By 2030, global water demand is set to overshoot supply by 40%.[10]

Policymakers and regulators have been reacting to increasing water scarcity by placing restrictions on water use in high-stress areas, as happened in 2015 in the U.S. state of California, where businesses and residents were under a mandate by the governor to reduce water consumption by 25%.

It is uncertain how much control businesses will have in the future over their ability to access the water required for their operations as water demand grows and areas of water stress expand. Limited availability or a compromise in quality can significantly disrupt operations, threaten revenue and investor confidence, curtail growth, and result in stranded assets. Businesses in water stressed areas may also face reputational risks from communities and citizens concerned about unsustainable and inequitable use of water. Businesses stand to lose control of their futures if they do not proactively manage water.

Calculate the Full Value of Water

Very few business leaders know how much water it takes to generate an hour of operation at their business. Water is typically viewed as a readily available commodity associated with an annual water bill, not a resource that is material to operation. Water conservation is low on the list of priorities for many companies because water is underpriced compared to its full value to the business, defined based on real and future risks that water scarcity poses to operations at a local level. The disconnect between the market price for water and a business's inherent water-related risks makes it hard to prioritize water in business decisions.

The first step to making the business case for water management and investment in water solutions involves assessing and monetizing water scarcity and water quality risk over time at the enterprise and facility level. One way to assess water scarcity risk is to consult with water basin maps. The Aqueduct tool by World Resources Institute (WRI) identifies overall water risk around the world through an aggregated measure of selected indicators to reflect long-term conditions (http://www.wri.org/our-work/project/aqueduct).

Another publicly available tool, the Water Risk Monetizer (WRM), uses scientific models developed by Trucost, WRI data, and site-specific data from a facility to quantify the impact of water scarcity and quality risk in monetary terms. It calculates a water risk premium by considering the amount of water available at a specific location, the amount of water used by a facility, incoming and outgoing water quality, projected water use over time, additional demands on the supply of water from population and GDP (gross domestic product) forecasts, and the impact of a facility's water use on the watershed. The water risk premium, when added to the local price a business pays for water, quantifies the full value a business should place on water based on real and future risk. The WRM also provides a "revenue at risk" likelihood score by estimating the value of the revenue that could potentially be lost at a facility due to the impact of water scarcity and declining water quality on operations.

Both the water risk premium and potential revenue at risk metrics are financial indicators which companies can use to inform business decisions that address water-related constraints to growth. The WRM tool provides water users with the full value of the water to an operation to help:

- Determine the water risk premium at each facility in an enterprise to understand those facilities most at risk: identify sites where water is most undervalued by calculating a risk-adjusted water price.
- Budget, plan, and develop strategies when considering return on capital expenditure and operating expenditure investments in existing facilities: facilities with the greatest gap between current price and risk-adjusted price should be prioritized.
- Calculate internal rate of return (IRR) for a site-specific water efficiency investment: by using a risk-adjusted water price instead of water costs, a company can calculate the value-based return on

investment to make the case for water-saving solutions.

- Determine preferred locations for expansion projects and manage expansion into high risk areas: assess current and future water-related risks.
- Evaluate the impact on investments when considering expansion in new locations by leveraging a water risk premium in financial models [weighted average cost of capital (WACC) in new construction projects].

Monetized risk can help companies align water use with availability and evaluate new infrastructure investments, procurement strategies, innovation, and product portfolios to make business decisions that are sustainable in the long term (http://waterriskmonetizer.com/about/).

Perform a Total Plant Assessment of Water Use

Plant operators can assess how water is put to work throughout a facility to identify opportunities for water conservation. A total plant assessment should be conducted to help plant operators understand the water intensity and maximize water use reduction (efficiency). It is not uncommon for manufacturing facilities to know how much water comes into the plant and is discharged. Very few, however, know how water is being utilized or lost throughout the operation.

A total plant assessment provides data and insights to help align water intensity improvements throughout an operation with business strategies. It also reveals synergies that are often missed if solutions are focused solely on individual water saving solutions. The most common problems uncovered during total plant assessments include:

- Leaking valves
- Tanks running over
- Valves left open over a weekend or on nonproduction days
- Missed opportunities such as not repurposing clean rinse water into a cooling tower
- Machinery not operating to specification

Undertaking a total plant assessment of water use can also uncover opportunities to improve energy-related outputs. There is a very clear link between maintenance of clean heat exchange surfaces and the amount of fuel required to maintain desired heat transfer, amount of greenhouse and other gases created, and ultimately costs incurred. Likewise, the logic can be applied to many other operations, such as membrane performance and management of heated water. All of these links can be controlled to best contribute to energy and water management of the activity involved, as shown in Fig. 1.4.

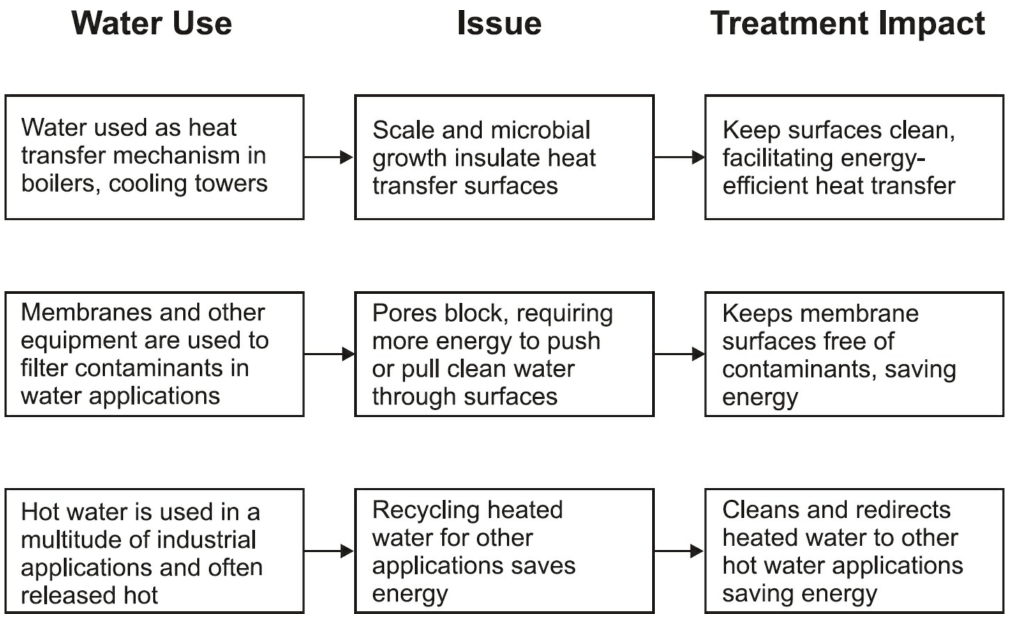


FIGURE 1.4 Water treatment and energy use reduction.

Value and Prioritize

After the opportunities for water conservation have been identified and risks have been monetized, businesses can leverage the data to make the business case for improvements, measure the anticipated impact, and determine return on investment. Decision making under the new normal of increasing freshwater scarcity and declining water quality must prioritize water-saving investments that support growth. Strategic questioning helps to identify a pathway for decision making. Some of these questions include:

- What is the percentage of water used per output as a percentage of the total? This provides a “big picture” analysis to index water use based on output for a particular facility. Whether it is water use per tons of paper or cases of soft drink, knowing how much water is required per product unit will help determine the priorities for water-saving strategies.

- How does water use per output compare to industry norms or industry benchmarks?
- What is the potential for water scarcity at the facility and what potential impact it will have on operations? This is a critical component to the overall assessment because it drives water reduction strategies for operational resiliency while also considering product quality.
- What are other businesses in the industry doing to reduce water consumption?

If water-related risks are not considered in growth strategies or properly managed, the outcome can be reduced revenues, higher operating costs, stranded assets, regulatory fines, and lower investor confidence. All these can restrict access to capital, higher financing rates, or higher insurance premiums.

Water Risk Monetizer Case Studies

The following examples depict industry-specific case studies using industry averages for costs and water risk assessments. Results from the water risk monetizer can guide businesses in their quest to measure, monetize, and manage water scarcity risks to sustain growth.

Business Expansion Projects

Scenario 1: Based largely in Southeast Asia, a company is evaluating a new strategy to increase revenues 17% by 2017. This will require a 32% increase in water use at two existing facilities in India and the addition of one Greenfield facility to come online in 2015. How do the water risk premium, other risk factors (scarcity, reputational, and regulatory), and profitability compare to business as usual?

Scenario 2: A company needs to increase production by 20% to meet demand.

The company is considering two locations in India—Mumbai and Bengaluru—for a new facility to help meet increased production needs. Based on the current water risk premium, which location is preferred? Based on water scarcity risks in 10 years, which location is preferred?

Scenario 3: A company is looking to expand its operations in a new region. A water risk assessment determined that the company is targeting a high-risk water basin for its new facility location. How can the company determine the impact of this location to the company's WACC on this investment?

Existing Facility Water Improvement Projects

Scenario 1: A company is considering investing in technology to improve water use efficiency at its facility in order to reduce regulatory and reputational risk.

What would be the IRR for a facility investment designed to improve water efficiency by 27% using a risk-adjusted price of water (current price plus water risk premium)?

Scenario 2: A company uses the World Wildlife Fund (WWF) Water Risk Filter and WRI Aqueduct tools to assess and determine which existing operating facilities are operating in what are considered water scarce sweet spots. The tools identified three production facilities in a high water stress and scarcity region.

- Which facility should be the highest priority for immediate investments in water stewardship initiatives to reduce its impact on the water basin based on risk-adjusted water bills over a 3-, 5-, and 10-year period?
- What is the water risk premium at each facility and how can that information be used to prioritize investments to reduce water use?

Scenario 3: A company has identified five facilities that require water saving investments and a list of water efficiency improvement projects for these facilities.

Using a water risk premium, what would be the IRR of these improvements and how should they be prioritized?

Scenario 4: A major production change is proposed at a chemical plant that will decrease electricity use by 20% while increasing water use by 15%. The plant is located in a region of China where a carbon tax of $5 per ton is expected in the next two years.

What is the overall net change in utility cost (electricity, carbon tax, and risk-adjusted water costs)? What is the water risk and how does this compare to business as usual?

Understanding the impact—and associated costs—of these risks at the enterprise and site level, as well as the broader implications and consequences of business operations to the surrounding community, enables businesses to make more informed decisions about their water use.

Subsequent chapters of this book will address the use of water in various applications, processes, and industries, and how to manage that water to minimize consumption, lengthen equipment life, maximize intended work, and ensure proper contaminant removal before discharge.

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CHAPTER 2

Water Sources and Stressors

The water cycle (Fig. 2.1), also known as the hydrologic cycle, describes the continuous movement of water on, above, and below the surface of the earth. Water can change states becoming liquid, vapor, or ice at various stages of this cycle. These processes happen rapidly and have occurred over millions of years. The balance of water remains constant over time, but the individual water molecules transform rapidly. The sun drives the water cycle, which has no starting or ending point. The sun heats the water in the oceans, where some of it evaporates as vapor into the air. Ice and snow can sublimate directly into water vapor. Air currents take the vapor into the atmosphere along with water transpired from plants and evaporated from soil. The vapor rises into the atmosphere, where cooler temperatures cause it to condense into clouds. Air currents move clouds around the earth, where clouds collide, grow, and fade out of the sky as precipitation, which falls as rain, snow, hail, fog, and sleet. Snow can accumulate as icecaps and glaciers, which can store frozen water for thousands of years. Snowfall in temperate climates melts in spring and flows overland. Most precipitation falls back into the oceans. That which falls onto land mostly flows over the ground as surface runoff. A large portion enters rivers, which move water toward the oceans. Runoff and groundwater seepage are stored in lakes and reservoirs. A portion of water infiltrates deep into the ground and is stored in aquifers for long periods. Over time, groundwater flows back into the oceans, where the water cycle is renewed.

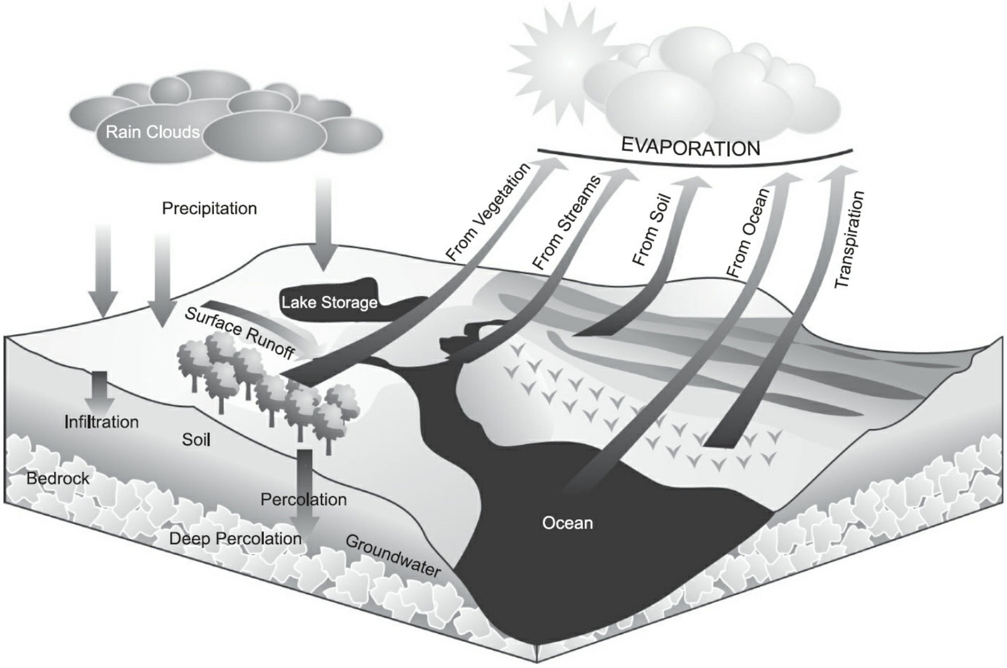


FIGURE 2.1 Illustration of the hydrologic cycle. (*Source: U.S. Geological Survey*.)

Water Sources

Resources of freshwater around the globe are not split evenly. Regionally, North and South America enjoy the most water, while North Africa and the Middle East have the least. When we consider resources by country, the following eight countries have roughly one-half of the renewable freshwater resources of the world: Brazil, Canada, China, Columbia, Indonesia, Peru, Russia, and United States.[1]

Location of renewable freshwater itself is only part of the equation; the balance of the equation is population density. Increasing the population density in an area of the world where renewable freshwater resources are limited creates stress on the water supply. According to the United Nations, a population experiences water stress when the water supply drops below 449 000 gal (1700 m^3) per person per year.[2] At present, roughly 40% of the world's population lives in an area that can be described as under water stress. As noted in the previous chapter, this number is expected to reach more than 47% by the year 2030. Adding to this, areas of the world that possess freshwater less than 264 000 gal (1000 m^3) per person per year are experiencing water scarcity and run the risk of food production strain and economic development difficulties. Absolute water scarcity occurs when water supplies fall below 132 000 gal (500 m^3) per person per year. At levels this low, even basic domestic needs are hard to meet. These problems can be mitigated, if the countries experiencing the issues possess the wealth to undertake and institute newer technologies to reduce, reuse, and recycle water. Water stresses are occurring to both our ground and surface water resources.

Surface water sources include rivers, lakes, and reservoir systems. Groundwater is water stored between layers of rock or in sand beds underground. Groundwater can be removed for use from springs or wells. Cities, industries, and agriculture utilize these sources for drinking water, heating, cooling, process, food, irrigation, transportation, and commerce. This chapter will look at the general characteristics of various sources of surface water and groundwater. Analyses are included to illustrate the differences and similarities of water quality around the world. These analyses are used to determine the type and size of various water treatment schemes and equipment needed to make the water useful for the particular application.

Each continent of the world has significant rivers, lakes, and underground aquifers that provide sources of freshwater. These represent precious resources that enable humans to exist and populate certain areas of the world. In fact, the population density of the world often follows the availability of water resources; water-rich areas can support more people than arid locations. As the world population grows, freshwater resources become ever more important as the need for water also grows.

Surface Water—Rivers

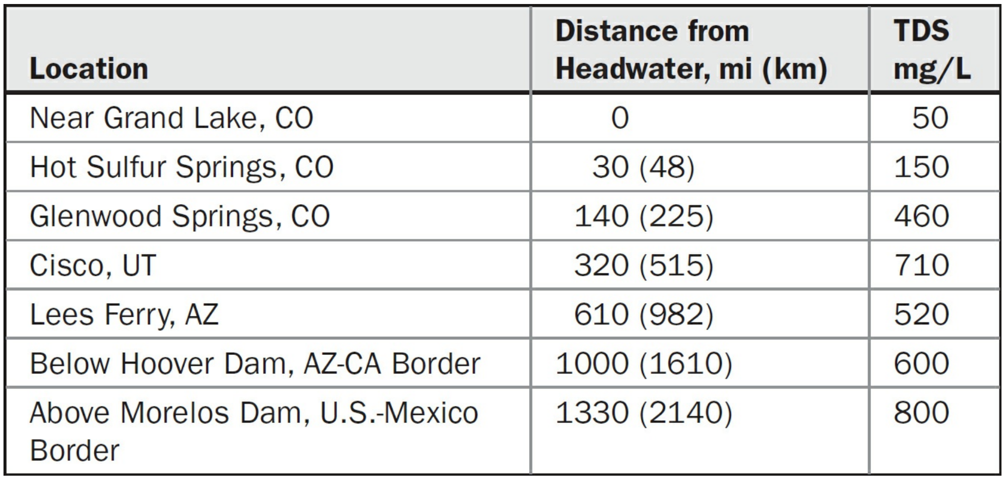
Human civilization and culture developed along major rivers such as the Tigris-Euphrates, Nile, Yellow, and Ganges. Capitols of ancient empires grew and faded as conquerors marched their way across landscapes, down rivers, and overseas. The Tigris-Euphrates Rivers provided much of the water that supported the development of ancient Mesopotamic cultures of Assyria, Babylonia, and Samaria. For millennia, the Nile nurtured ancient Egyptian dynasties with its yearly floodwaters and by allowing transportation and commerce along its length. The Yellow and Yangtze Rivers in China and the Ganges River in India were the hubs of civilizations and of transportation and commerce. Later in history, abundant supplies of water attracted colonists of North America to settle along rivers.

North American Rivers

These are often navigable waterways or important sources of water for domestic use or irrigation. Major examples include the St. Laurence River connecting the Great Lakes to the Atlantic Ocean. It forms the vital link of the St. Lawrence Seaway. The Mississippi River system is another major waterway in North America, especially when combined with its two long tributaries, the Ohio and Missouri Rivers. The Tennessee River is a tributary of the Ohio River and drains much of the southeastern U.S. Combined, the Mississippi, Ohio, Missouri, and Tennessee Rivers drain the majority of Central United States.

In the southwestern portion of the United States, the Rio Grande forms the entire border between Mexico and the state of Texas. It is a long river but has a very small flow, especially compared to the Colorado or Mississippi Rivers. The Colorado River, in the southwestern United States and northwestern Mexico, is a major water source for domestic consumption and irrigation (Fig. 2.2). Aqueducts carry its water to cities like Los Angeles, Phoenix, and Tucson, and a canal carries water to California’s Imperial Valley for crop irrigation. The salinity of the Colorado River (Table 2.1) increases significantly from the headwaters to the outlet in the Gulf of California. In fact, the United States withdraws so much water that the country operates desalination plants to resupply the river before it enters Mexico.

FIGURE 2.2 Erosion caused by the Colorado River has contributed to the creation of the Grand Canyon in the Southwestern United States. (*Photograph by D. Dolde.*)

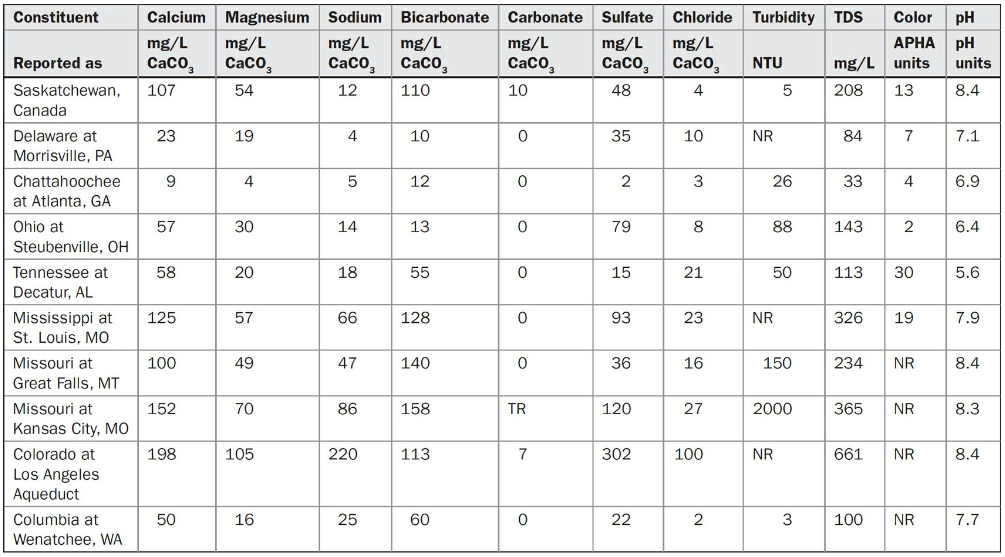


Location	Distance from Headwater, mi (km)	TDS mg/L
Near Grand Lake, CO	0	50
Hot Sulfur Springs, CO	30 (48)	150
Glenwood Springs, CO	140 (225)	460
Cisco, UT	320 (515)	710
Lees Ferry, AZ	610 (982)	520
Below Hoover Dam, AZ-CA Border	1000 (1610)	600
Above Morelos Dam, U.S.-Mexico Border	1330 (2140)	800

Source: USGS Scientific Investigations Report 2006-5315, 2007.

TABLE 2.1 Increase of Total Dissolved Solids (TDS) in the Colorado River from the Origin to the Border between the United States and Mexico, Near Yuma AZ

Table 2.2 shows analyses of several rivers in North America. These rivers contain generally soft to moderately hard water with low total dissolved solids (TDS). The two analyses of the Missouri River show that the dissolved and suspended solids increase from the headwaters in Montana to Kansas City.



Constituent	Calcium	Magnesium	Sodium	Bicarbonate	Carbonate	Sulfate	Chloride	Turbidity	TDS	Color	pH
Reported as	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	NTU	mg/L	APHA units	pH units
Saskatchewan, Canada	107	54	12	110	10	48	4	5	208	13	8.4
Delaware at Morrisville, PA	23	19	4	10	0	35	10	NR	84	7	7.1
Chattahoochee at Atlanta, GA	9	4	5	12	0	2	3	26	33	4	6.9
Ohio at Steubenville, OH	57	30	14	13	0	79	8	88	143	2	6.4
Tennessee at Decatur, AL	58	20	18	55	0	15	21	50	113	30	5.6
Mississippi at St. Louis, MO	125	57	66	128	0	93	23	NR	326	19	7.9
Missouri at Great Falls, MT	100	49	47	140	0	36	16	150	234	NR	8.4
Missouri at Kansas City, MO	152	70	86	158	TR	120	27	2000	365	NR	8.3
Colorado at Los Angeles Aqueduct	198	105	220	113	7	302	100	NR	661	NR	8.4
Columbia at Wenatchee, WA	50	16	25	60	0	22	2	3	100	NR	7.7

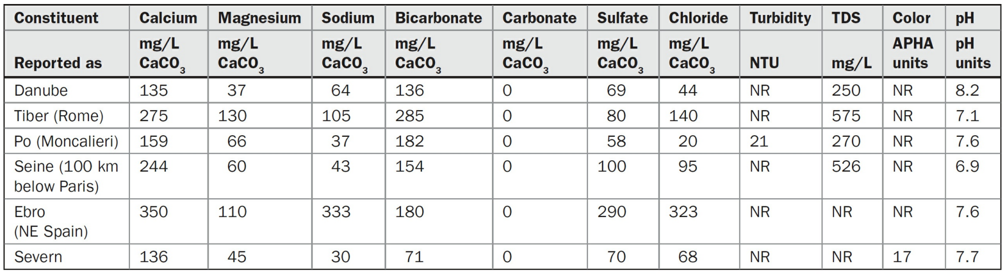
These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)
Source: Nalco Water Analytical Water Analysis.

TABLE 2.2 Analyses of Selected North American Rivers

European Rivers

Western civilization and culture developed along surface waters in Europe. Capital cities developed along rivers and streams, such as Rome along the Tiber River in Italy, becoming centers of commerce and transportation. Rivers became strategic borders between countries and empires. Many of these rivers are major shipping routes for several countries.

Several of the largest reservoirs in the world can be found along the Volga River. It is the largest and most voluminous river in Europe, with the largest watershed area. Many industries are found in the upper regions of the Rhine but most are concentrated along the lower Rhine. The river then turns west and enters the Netherlands, where it combines with other rivers to form one of the most extensive river deltas in Europe. One-fifth of the world's chemical industries are now manufacturing along the Rhine.[3] High levels of chemical pollutants are currently causes of concern for environmentalists in both rivers. Analyses of common inorganic ions in some of these rivers are shown in Table 2.3.



Constituent	Calcium	Magnesium	Sodium	Bicarbonate	Carbonate	Sulfate	Chloride	Turbidity	TDS	Color	pH
Reported as	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	NTU	mg/L	APHA units	pH units
Danube	135	37	64	136	0	69	44	NR	250	NR	8.2
Tiber (Rome)	275	130	105	285	0	80	140	NR	575	NR	7.1
Po (Moncalieri)	159	66	37	182	0	58	20	21	270	NR	7.6
Seine (100 km below Paris)	244	60	43	154	0	100	95	NR	526	NR	6.9
Ebro (NE Spain)	350	110	333	180	0	290	323	NR	NR	NR	7.6
Severn	136	45	30	71	0	70	68	NR	NR	17	7.7

These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

TABLE 2.3 Analyses of Selected European Rivers

Other Great Rivers of the World

The Amazon River system is the greatest on earth, not even counting all of the tributaries (Fig. 2.3). Of these tributaries, 17 are over 1000 mi (1600 km) long, starting in Peru and flowing across Brazil to the Atlantic, where the Amazon is 4 to 6 mi (6–10 km) wide. The Amazon alone produces approximately 20% of all the water that the world's rivers empty into the oceans. Other great rivers are found in Egypt, China, and India.

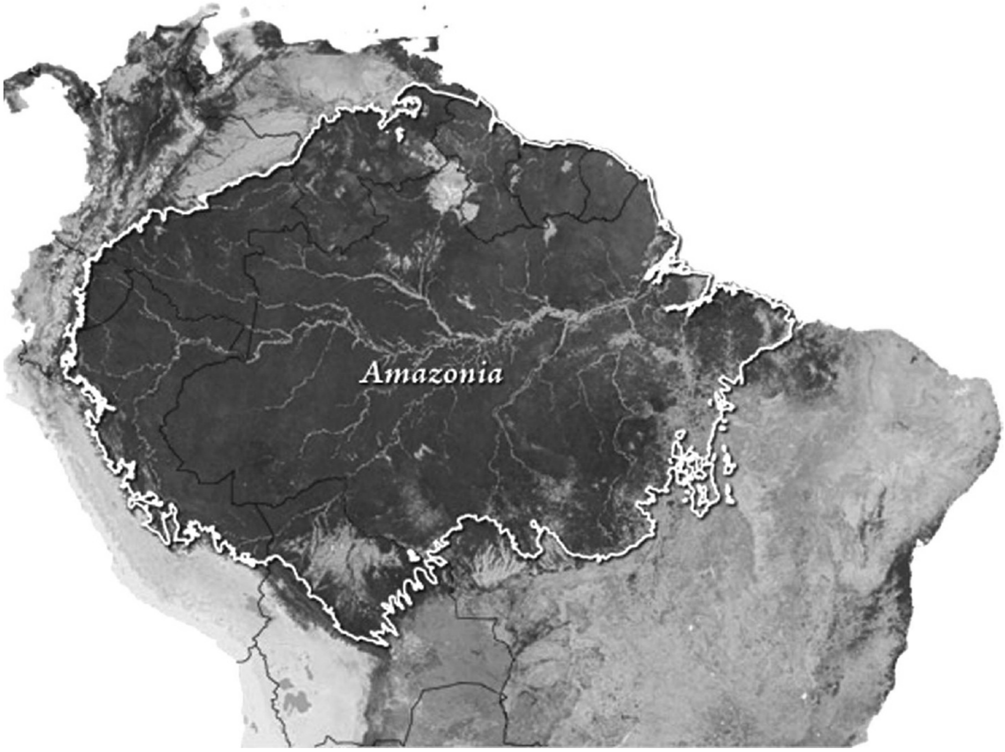


FIGURE 2.3 Amazon drainage basin in South America. (*Courtesy of NASA, Source: http://earthobservatory.nasa.gov/Study/AmazonLAI/.*)

These rivers have characteristics similar to the rivers in North America and Europe. However, rivers originating in equatorial rainforests, like the Amazon and the Orinoco in Venezuela, can be very low in dissolved solids but high in organics, especially near the headwaters (Table 2.4). Some portions of the immense Orinoco basin of Venezuela, a water-rich jungle, were never submerged beneath prehistoric seas and therefore have had no contact with limestone. The dissolution of limestone makes water alkaline. The Orinoco and tributary rivers, like the Coroni, contact chiefly siliceous rock, such as flint, quartz, and sandstone. Decaying vegetation produces humic acid, and in the absence of alkalinity from limestone, the acidity of soils and rivers creates an environment hostile to humans and the kinds of plants and animals we depend on for sustenance. The Coroni River analysis in Table 2.4 illustrates that rivers flowing through drainage basins having dense vegetation and substantial rainfall are generally highly colored. In Venezuela and Brazil, the mineral content of the highly colored Coroni and Amazon Rivers is limited by the nature of the lithosphere and the heavy rainfall, especially the absence of limestone.

Constituent	Calcium	Magnesium	Sodium	Bicarbonate	Carbonate	Sulfate	Chloride	Turbidity	TDS	Color	pH
Reported as	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	NTU	mg/L	APHA units	pH units
Amazon (Brazil)	5	1	13	8	0	5	6	3–4	28	60–70	6.5
Coroni (Venezuela)	2	1	2	3	0	<1	3	30	NR	100	5.8
Nile (Egypt)	68	44	61	112	24	10	25	30	210	NR	8.5
Vaal (South Africa)	104	40	70	102	0	67	45	15	278	2	8.0
Orange (South Africa)	68	26	44	66	0	42	30	10	200	Tr	7.4

These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

TABLE 2.4 Analyses of Other Great Rivers of the World

Surface Water—Lakes

Lakes are a major source of freshwater. The majority of lakes are in the Northern Hemisphere, mostly in the temperate regions. Over half of the world’s lakes are in Canada. The ancient glaciers left an irregular land surface that held water as glaciers melted and this forms the basins of many of the lakes found in Canada. The Great Lakes in North America are usually considered the largest freshwater supply in the world. Lake Baikal in Siberia (Russia) is the largest freshwater lake by volume, containing as much freshwater as the entire Great Lakes system [5700 mi^3 (23 800 km^3)]. Lake Baikal is the deepest lake at about 5371 ft (1637 m) deep, with a surface area of about 12 200 mi^2 (31 500 km^2), compared with 95 000 mi^2 (246 000 km^2) for the five Great Lakes combined. Together, the Great Lakes and Lake Baikal contain 40% of the world’s presently available fresh surface water. North America has countless smaller lakes, holding another 15% of the presently available freshwater of the world. Lake Victoria between Uganda, Kenya, and Tanzania and Lake Tanganyika bordering Tanzania are two of the great lakes of Africa.

North American Lakes

There are many lakes and reservoirs throughout the North American continent. The Great Lakes are a chain of five freshwater lakes located on the border between Canada and the United States (Fig. 2.4). They form the largest group of freshwater lakes on earth. Combined, they contain 5500 mi^3 (23 000 km^3) of freshwater by volume. Of the Great Lakes, Lake Superior is the largest, and the largest lake in the world by surface area [32 000 mi^2 (82 900 km^2)] with a maximum depth of approximately 1300 ft (400 m). It is also “the different lake," with significantly lower dissolved solids content than the other Great Lakes due to differences in geologic formations of the lakebed and the temperature (Table 2.5). Lake Michigan and Lake Huron have the largest area connecting the two lakes and are similar in chemical composition. The concentration of dissolved minerals is uniform, including the upper waters of the St. Lawrence River.

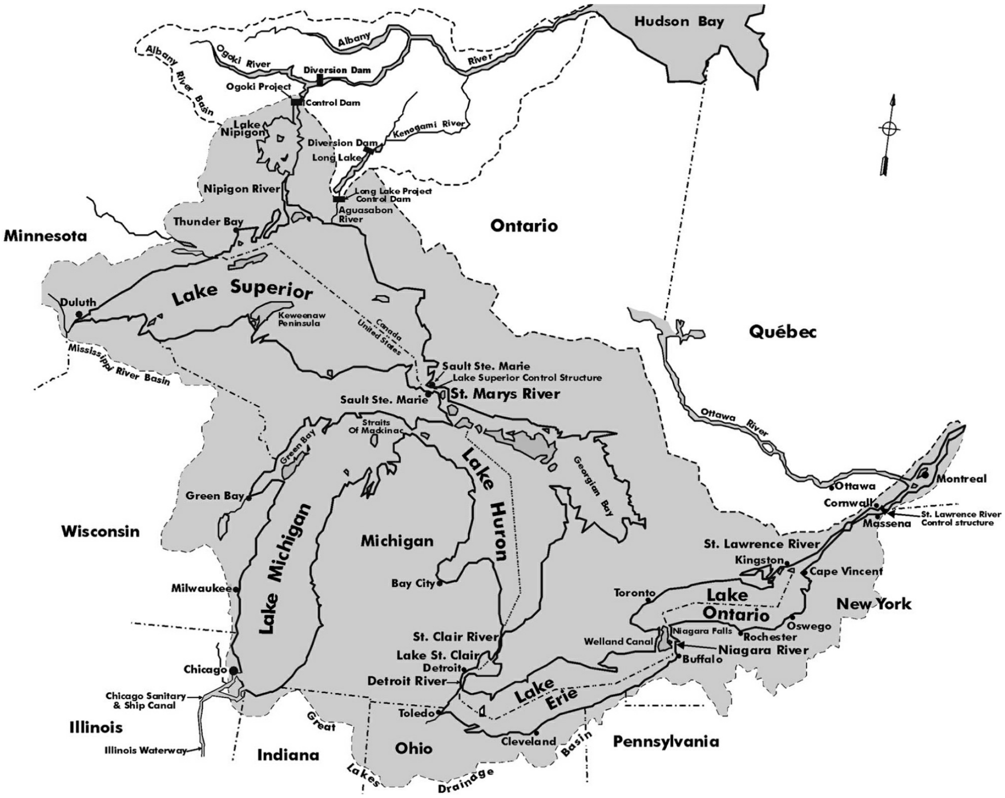


FIGURE 2.4 The Great Lakes and their drainage basin. (*Courtesy of U.S. Army Corps of Engineers, Detroit District.*)

Constituent	Reported as	Lake Superior Duluth, MN	Lake Michigan Chicago, IL	Lake Huron Port Huron, MI	Lake Erie Erie, PA	Lake Ontario Cape Vincent, NY
Calcium	mg/L $CaCO_3$	35	90	90	90	91
Magnesium	mg/L $CaCO_3$	9	45	32	33	31
Sodium	mg/L $CaCO_3$	6	19	90	20	37
Bicarbonate	mg/L $CaCO_3$	42	113	71	91	90
Carbonate	mg/L $CaCO_3$	0	0	0	0	0
Sulfate	mg/L $CaCO_3$	1	18	35	25	25
Chloride	mg/L $CaCO_3$	5	9	37	27	27
Turbidity	NTU	1	12	NR	Tr	NR
TDS	mg/L	54	171	185	172	271
Color	APHA units	1	3	NR	2	NR
pH	pH units	7.4	7.8	8.1	7.5	8.2

Note that lake superior is much lower in TDS than the other lakes. These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)
Source: Nalco Water Analytical Water Analysis.

TABLE 2.5 Water Chemistry of Some of the Great Lakes in North America

Great Lakes of Africa

The African continent has several large lakes, all near the Great Rift Valley in east-central Africa around Tanzania. Generally, Lake Victoria, Lake Tanganyika, Lake Nyasa, Lake Tukana, Lake Albert, and Lake Kivu are considered the main group, although there are several other large lakes in the same area. Lake Victoria and Lake Albert empty into the White Nile, the starting point of the Nile River. Lake Tanganyika and Lake Kivu empty into the Congo River. Lake Victoria is the world's second largest lake in terms of surface area, and Lake Tanganyika is the second largest by volume. Lake Tanganyika is also the world's longest lake, at 410 mi (660 km).

Salt Water Lakes

Some lakes in various parts of the world are saline lakes, some having salt content much higher than the oceans. They are generally remnants of ancient inland seas or were once connected to the oceans, but have been separated by the action of plate tectonics. Examples include the Caspian Sea in central Asia, the Great Salt Lake in the western United States, and the Dead Sea in the Middle East, all of which have no outlet.

The Caspian Sea has the largest surface area of any lake on earth, at 143 200 mi^2 (371 000 km^2) and a volume of 18 800 mi^3 (78 360 km^3). It has no outflow and is fed by many rivers, the largest being the Volga River. It has a maximum depth of 3360 ft (1024 m) and salinity of 1.2%, which is about a third of the salinity of seawater. The northern end of the lake is almost freshwater because of the influx of river water at this end.

The Great Salt Lake in northern Utah in the western United States is the largest saline lake in the western hemisphere. The size of the lake varies significantly because of periodic droughts and its shallow depth. It has variable salinity levels of 5 to 27%, much higher than the oceans of the world. The ratio of ionic components is similar to seawater, even though the ionic concentrations are much higher. The salinity of the water is maintained because of the geology of the Bonneville Salt Flats, where this lake is located, and also, like the Caspian Sea, the lake has no outlet. The lake is a source of salt, produced by solar evaporation ponds on the shore.

The Dead Sea is notable because it is the lowest point on the surface of the earth at about 1380 ft (420 m) below sea level. It is also the deepest hypersaline lake at 1080 ft (330 m). The salinity is approximately 30%, but its composition is very different from the oceans. The ionic content of most oceans and open seas is about 97% sodium chloride. The main ionic salts in the Dead Sea are magnesium chloride 51%, sodium chloride 30%, calcium chloride 14%, and potassium chloride 4%. Another unique feature of highly saline lakes, like the Dead Sea and the Great Salt Lake, is the extreme buoyancy they provide to swimmers; it is nearly impossible to sink in either of these lakes.

Circulation and Seasonal Turnover in Lakes

Lakes can be classified using a variety of characteristics. Looking first at latitude, lakes are broken into three categories:

1. Polar lakes
2. Temperate lakes
3. Tropical lakes

Elevation plays a role in the classification of lakes. The elevation of a lake above sea level can influence its characteristics, such that Alpine lakes can fall into either the temperate lake or the polar lake classification regardless of latitude. Lakes are further classified by the thermal properties of the water and the influence this has on how often the water in the lake mixes from top to bottom.

Temperate Zone Lakes There can be three distinct temperature zones or layers in a lake, particularly in regions where seasonal weather changes occur. These zones are called the epilimnion, metalimnion, and the hypolimnion (Fig. 2.5). The epilimnion is the water layer at the surface of the lake. This water is warmed by the sun, is subject to mixing by wind, and is usually well oxygenated. The surface layer, by virtue of its warm temperature, is the least dense water in the lake. The metalimnion is the middle layer in a lake, where the water temperature goes through a steep drop from warmer temperatures at the top of the metalimnion to cold temperatures at its bottom. The metalimnion is also called the thermocline because of the steep temperature drop in this layer. The hypolimnion is the water at the bottom of the lake. It is the densest and coldest water, generally at 39.2°F (4°C).

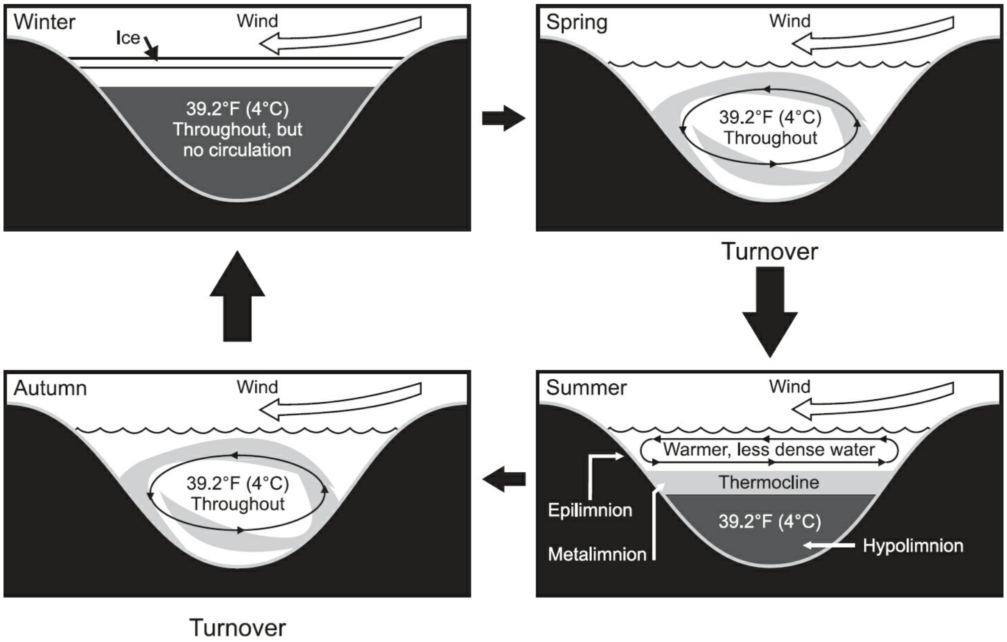


FIGURE 2.5 Temperature zones and seasonal turnover in temperate zone lakes.

Depending on the depth of the lake, surface layer temperature, and season of the year, these layers can be stratified such that mixing of the different layers does not occur. Lakes that have shallow basins [< 25 ft (7.6 m)] tend not to thermally stratify. Vertical circulation in shallow lakes is caused almost exclusively by wind action, since thermal density differences do not exist. Lakes with basins deeper than 25 ft (7.6 m) have the opportunity to thermally stratify into all three zones: the epilimnion, the metalimnion, and the hypolimnion. In these deeper lakes, the bottom layer is at or near the maximum density of water at a temperature of 39.2°F (4°C). In lakes with 25 to 200 ft (7.6–61 m) depth, the bottom temperature can vary slightly. In lakes over 200 ft (61 m) deep, the bottom temperature is at the temperature of maximum density all year round.

Thermal stratification occurs in summer, when the epilimnion of the lake warms and the surface water becomes less dense (Fig. 2.5). The ensuing density gradient prevents mixing of the water in the lake from top to bottom. The water mixes by wind currents in the epilimnion only. As the lake cools in the fall, the temperature of the epilimnion falls, and the water density increases. When the surface temperature reaches 39.2°F (4°C) and the density is the same from top to bottom, mixing can occur. Mixing or turnover of lake water is then a function of temperature and wind. There are other factors such as surface area, depth, topography around the lake, etc. that may inhibit complete mixing of the water. These only come into play once the thermal stratification of a lake is negligible and the lake does not have a density difference to overcome. When a lake turns over, the water may mix thoroughly from top to bottom. This action brings oxygenated water from the surface of the lake to the bottom and nutrient rich water from the bottom of the lake to the top. If the lake bottom is polluted, turnover can bring these contaminants to the surface.

When the lake freezes in winter, the water temperature and density can be the same in all water layers, or the water near the surface can be near 32°F (0°C), where it is less dense than the bottom water at 39.2°F (4°C). In either case, mixing does not occur because wind action is prevented by ice, or the lower density at the surface prevents mixing. In the spring when the ice melts, the water density is again similar from top to bottom and wind-driven mixing can occur. The cycle is repeated as the surface layer warms as spring transitions to summer.

An understanding of these characteristics of lakes is necessary to properly locate water intakes and discharges. It aids in anticipating the changes in water treatment needed to meet changes in composition caused by turnover and wind-induced circulation.

Tropical Zone Lakes Tropical lakes may have irregular mixing of surface and deep water or may be very stagnant. If mixing occurs, it is usually sporadic and occurs over a short time. Climatic conditions favor prolonged stratification of lakes in both the tropics and subtropics. Subtropical lakes may have more opportunity for a single turnover episode, because these areas have slightly more seasonal temperature variation than the tropics. The generally high air temperatures and lack of extreme seasonal fluctuations prevent water temperature and density changes in tropical zone lakes. This is because these lakes are typically warm from top to bottom, and once stratification is established, the density difference reduces opportunity for mixing of the water. In addition, the volume of the epilimnion is very large, and the air temperature would have to be low for a long time to make a significant temperature drop in this large surface layer. Rarely would cooling of the surface provide sufficient driving force for mixing. As a result, the bottom layer of water in many tropical lakes, particularly the deeper lakes, is permanently anoxic.

Groundwater

Underground reservoirs constitute a major source of freshwater. In terms of storage capacity, underground aquifers worldwide contain over 90% of the total freshwater available for human use. Much of this is too deep to be exploited economically, although new technology is increasing drilling capability. There are many different aquifers throughout the world. Figure 2.6 shows various aquifers in the United States. Over 76 billion gal/day (3,330 m^3/s) freshwater is withdrawn from wells for all uses in the U.S. mainland.[4] Approximately one-third of this well water is used by municipalities throughout the United States, and the other two-thirds are used for irrigation and industrial purposes. Over 80% of the municipalities in the United States depend on well water, although less than 30% of the total volume of water treated for municipal use is from this source. Industry draws approximately 14 billion gal/day (613 m^3/s) from wells. The state of California withdraws the freshest groundwater for industrial use, accounting for 14% of the total national groundwater industrial withdrawals.

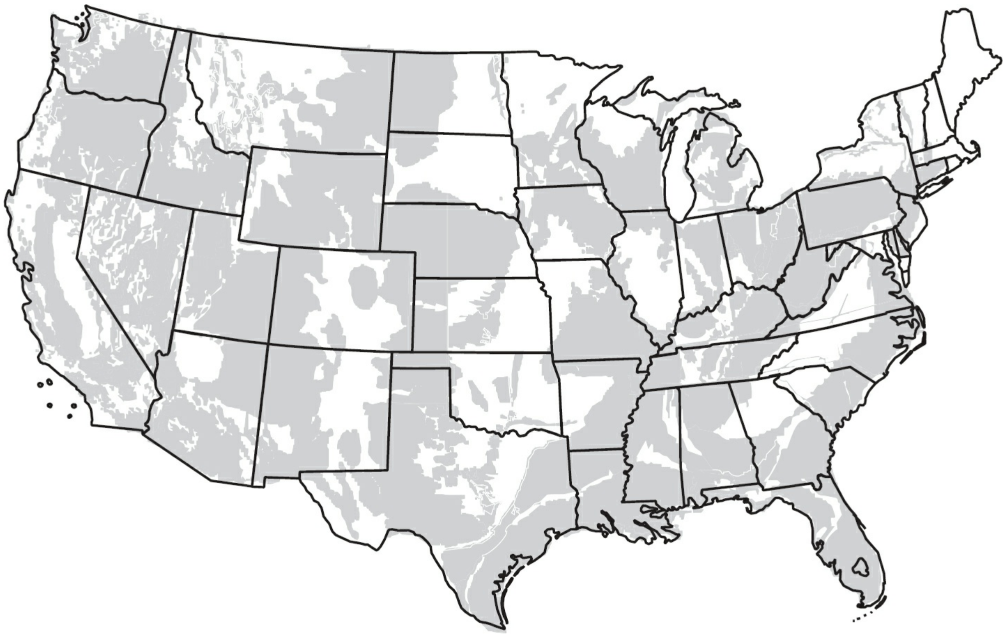


FIGURE 2.6 Illustration of the many different aquifers in the U.S. mainland. (*Courtesy of the U.S. Geological Survey, Source: nationalatlas.gov.*)

Connate Water

The term connate water refers to water that is trapped inside sedimentary rock as the rock formation deposited and solidified. The water is often dense and saline and can change composition over the course of time in a formation.

Connate water is generally released with the production of oil and often called oilfield brine. The brine creates unusual problems for handling and treatment for reuse or disposal. It is usually more concentrated than seawater, sometimes exceeding 100 000 mg/L in total salinity. The high mineral content and the reduction in temperature and pressure as the brine travels upward from great depths cause difficult problems for scale and corrosion control. Several analyses are shown in Table 2.6.

Constituent	Reported as	Sample 1	Sample 2	Sample 3	Sample 4
Calcium	mg/L Ca	8300	2630	1500	630
Magnesium	mg/L Mg	260	690	500	40
Sodium	mg/L Na	56 250	16 800	9150	5640
Bicarbonate	mg/L HCO_3	50	315	1000	500
Sulfate	mg/L SO_4	180	2880	2000	120
Chloride	mg/L Cl	98 300	30 550	17 800	8350
TDS	mg/L	166 650	54 070	32 330	15 420

TABLE 2.6 Four Different Connate Waters Illustrating the High Dissolved Solids, Mostly Sodium and Chloride (*Source: Nalco Water Analytical Water Analysis*.)

Desalination

With all that salt water in the world, one would think desalination plants would be a significant part of the water treatment landscape. Presently, the amount of capacity to generate freshwater by desalination makes up less than 1% of total world freshwater use.[5] Installed desalination capacity on a global basis has continued to rise each year from the late 1960s to present. Cost for desalination continues to remain higher than water use from existing freshwater sources, freshwater reclaim, or freshwater cleanup, but it is coming down. More than 76% of the installed desalination capacity is in the Persian Gulf, Middle East, and North Africa. As these parts of the world are generally considered in a water stressed or water scarce environment, it is no surprise that desalination would be occurring more here than in other parts of the world.

Evaporators

Creating freshwater from seawater using thermal distillation or multi-effect evaporators mimics the earth's natural hydrologic cycle. Pure water is evaporated, captured, and then condensed (Fig. 2.7). The resulting waste stream discharge is of much higher salinity and temperature due to the thermal process of evaporation. These types of plants were used in the early days of desalination and still represent about 40% of installed capacity. They are energy intensive with roughly 60% of the cost to generate freshwater coming from either thermal or electrical energy. As energy costs continue to rise, the costs to produce freshwater also continue to rise in these types of plants.

FIGURE 2.7 Multi-stage flash desalination plant at Jebel Ali G Station, Dubai (*CC BY-SA 3.0, via Wikimedia Commons*.)

Reverse Osmosis

Use of membranes for desalination began in the 1970s. As the cost of membranes continues to come down, the use of reverse osmosis (RO) systems for desalination continues to increase. Virtually all of the brackish water desalination is now accomplished by membrane separation, and a good portion of seawater is now being processed through membranes. These are less energy intensive, with 30 to 40% of the operational cost attributed to electrical energy.[6] RO desalination has the additional benefit of minimal thermal impact on the environment (Fig. 2.8). Several thousand desalination facilities are in operation worldwide, many in the Middle East.

FIGURE 2.8 Reverse osmosis bank producing freshwater from seawater. (*Courtesy of Water Services of America and Dupont.*)

Recycled Wastewater

Reuse of municipal discharge by industry is no longer a rarity; each instance presents unique problems, but the need for water in arid places has given economic incentive to practical solutions. In the United States, reuse of domestic discharge as barrier water, as described earlier, is the only example where a small flow of treated sewage may eventually return to potable wells. In South Africa, where the total amount of available water is only 20 billion gal/day (876 m^3/s), with 60% being used for irrigation and 40% for all other uses, research has been conducted on direct return of a portion of highly treated discharge to municipal water plant intakes.[7] The city of Windhoek in Namibia has practiced such recycle for over a decade, producing drinking water for nearly 300 000 people.[8] This may become a growing practice as South Africa works to offset a 5% deficit in natural water supplies that began in the year 2000.

Fairfax County in Virginia began recycling wastewater in 1978 into the Occoquan Reservoir, which is the drinking water supply.[9] Municipalities that discharge treated discharge into rivers, upstream of other cities, inadvertently engage in recycling of water. Many other cities and municipal districts directly participate in this growing trend to recycle wastewater. In January 2008, Orange County in California started a new advanced treatment plant to recycle sewage effluent into drinking water. The facility can produce 100 million gal/day (3 m^3/s), enough to meet the needs of nearly 850 000 residents. The treatment plant takes secondary treated sewage, which is disinfected and sent through microfiltration and reverse osmosis. The final step is advanced oxidation by hydrogen peroxide and ultraviolet light. The water is reapplied to the aquifer in two ways. One-third of the water is sent to reinjection wells near the coast to prevent seawater intrusion. The other two-thirds of the water is pumped to two retention basins over permeable soil, where the water percolates into the ground to replenish the aquifer.[10]

Stress on Water Sources

As noted earlier, the United Nations defines water stress as a population with a water supply that drops below 449 000 gal (1700 m^3) per person per year. At present, roughly 40% of the world's population lives in an area that can be described as under water stress. This number is expected to reach more than 47% by the year 2030.

Groundwater Stress

Groundwater over-pumping is resulting in a lowering of water tables in aquifers from which water is drawn. In many parts of the world, water is being removed from the ground faster than it is being replenished by rainfall and snowfall. While the removal rate is a significant portion of the problem, the recharge rate is equally important. As more of our land is converted to urban use, controlled urban runoff is directed to surface waterways, and the natural seepage of water into the ground to replenish groundwater does not occur. Extracted water in these cases is essentially being mined. Wells then need to reach deeper into the ground in order to tap water resources. Many areas of the Middle East, China, India, and North Africa are experiencing significant drops in the water table. Even in parts of Mexico wells have had to be deepened to maintain adequate water flow. The additional cost of deep water wells not only upsets food production costs, but increases domestic and industrial use costs as well. The cost of water is increasing. In some parts of the world, it is increasing to the point of making certain agricultural practices and crop mixes no longer economical.

Groundwater is mined extensively in many areas of the United States, particularly the west and south. In fact, California, Texas, and Florida account for 30% of the groundwater usage in the United States.[11] This removal has resulted in net loss of water, which can reduce the level of water in an aquifer by as much as 100 ft (30 m). Figure 2.9 shows the High Plains Aquifer (also called the Ogallala Aquifer) in the central United States and the changes in water level of this aquifer from predevelopment to 2013.[12] This aquifer, one of the largest in North America, lies under about 175 000 mi^2 (451 000 km^2) of land in portions of eight states. In 2005, the amount of irrigated acreage overlaying the aquifer area totaled about 14%. Water-level declines began around 1950 as substantial groundwater pumping for irrigation began. By 1980, some parts of the aquifer in Texas, Oklahoma, and southwestern Kansas were experiencing a decline of more than 100 feet.[13]

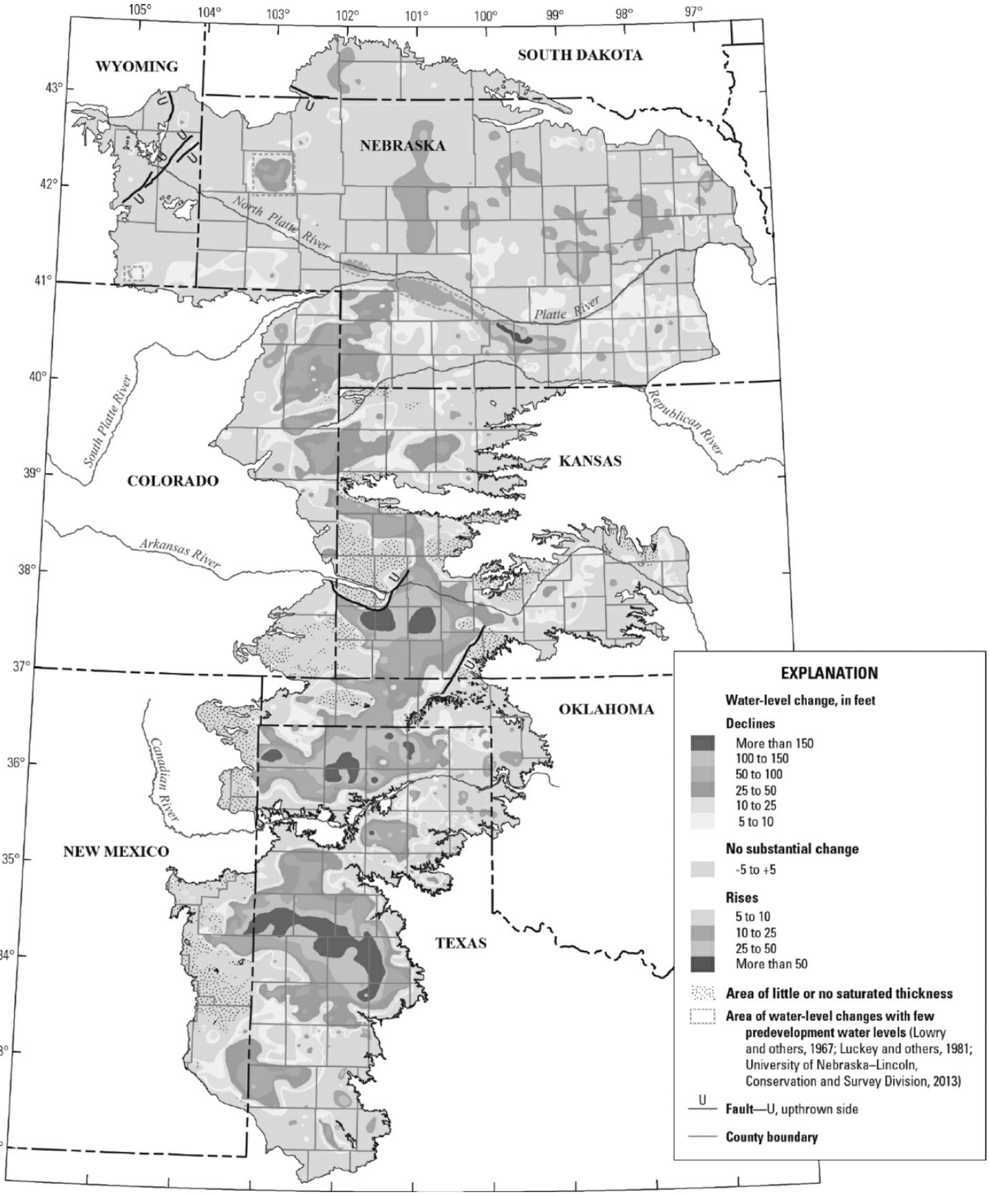


FIGURE 2.9 Area covered by the High Plains Aquifer (Ogallala Aquifer) and changes in water table level predevelopment to 2013. Note that more areas have lost water than gained. (*Courtesy of the U.S. Geological Survey, Source: USGS Scientific Investigations Report 2014-5218*.)

In coastal areas, pressure on the groundwater supply due to increased domestic, agricultural, and industrial use opens up the opportunity for saltwater contamination of freshwater aquifers, turning the water brackish. Should this occur, groundwater in that location can become impaired or even unsuitable for use, depending upon the degree of contamination by saltwater. This situation is a particular problem for island nations in the Pacific and Caribbean, where saltwater intrusion to freshwater wells occurs increasingly further inland.[14]

In other areas, steady reduction of the water table has contributed to land subsidence. Beijing, China, has been experiencing land subsidence since 1935 due to over exploitation of groundwater. While some areas of Beijing have had little impact, eastern Beijing has seen a displacement rate greater than 100 mm/year.[15] In some areas of the United States, such as near Great Neck, New York on Long Island, heavy withdrawal, continuous sea rise and drought conditions drying up streams and lakes have resulted in land subsidence and intrusion of seawater into the aquifer.[16] Caps have been placed on the amount of water that can be pumped to limit further contamination.

Augmentation

Augmentation of a groundwater source by artificial recharge has also been practiced, where a nearby source of surface water has been available for this purpose. The aquifer becomes, in effect, a storage reservoir. The city of Los Angeles reclaims storm water and segregated wastewater of selected quality, by gravity recharge of underground reservoirs using the Los Angeles River.[17] The natural riverbed has been paved with concrete to prevent haphazard loss of collected water to the ground, and a collapsible dam has been constructed at the river's end. Collected waters are spread over the old, natural river delta for percolation through the original gravel riverbed into the underground reservoirs. During a heavy storm, the dam is momentarily and deliberately collapsed to flush out collected solids, then reinflated. This arrangement provides for recovery of most of the storm water in this arid metropolis.

Surface Water Stress

Surface water stress occurs in both quantity and quality of available water. Around the world, several major rivers no longer maintain significant flow at their former deltas. Examples are the Colorado, Ganges, Huang He, Jordan, Nile, and Rio Grande rivers. Competition for water upstream of the delta in the form of hydroelectric dams, crop irrigation, and domestic and industrial use have all taken their tolls on these rivers, and they now regularly run dry before they reach their deltas. By far, the biggest culprit here is water extraction for irrigation. The more water that is removed upstream, the less is available downstream for other consumption.

Agricultural irrigation practices around the world at present only return about 30% of extracted water back to either surface waterways or groundwater; the balance of extracted water is either consumed or lost.[18] While hydroelectric dams do not extract water, they do control the flow of water, exacerbating effects of water extraction downstream of dams. Reduced flow at the delta affects wetlands and water quality, as brackish water pushes further into the delta.

While industrial and domestic water users do return the majority of water back to the environment, the quality of the returned water in many parts of the world is significantly lower than that of the original extraction. This lowering of water quality becomes an issue when discharge back to surface waterways such as lakes and rivers contains industrial pollutants and sewage, which make water unsuitable for human consumption. Up to 12% of the world's population does not have a regular source of clean water for domestic use.[19]

As mentioned, upstream practices affect downstream quantity and quality. As pressure increases on our river systems, we see the effects at the discharge of rivers to either inland bodies of water or estuaries, where rivers reach the seas. Take, for example, the Dead Sea. In the past 70 years, the drainage basin of the Dead Sea has seen increased extraction of water and damming of influent rivers. The influent water volume has reduced by about 85%, and consequently, the Dead Sea has reduced in size. The water level of the Dead Sea has fallen by 20 m, and its surface area has been reduced by about one-third.[20]

The Aral Sea in Central Asia has been also experiencing significant water loss. In the 1950s, the Amu Darya and Syr Darya rivers that fed the Aral Sea were diverted to supply irrigation systems to support a new agrarian project. The water level in the sea began to fall in the 1960s. By the 1980s, indigenous fish species could no longer tolerate increasing salinity of the water, and they began to die. The fishing industry went into complete collapse. At present, the Aral Sea is now only 10% of its former volume, and the remnants are hyper-saline in nature.[21] In this case, it is not that there is not enough water in the Aral Sea basin to support the sea; it is the complete extraction of the water before reaching the sea that is causing the issues.

The Rio Grande River basin that empties into the Gulf of Mexico is another example of upstream over-extraction. The estuary at the delta of the Rio Grande River now only sees about 10 to 15% of historic water flow; the balance of the water is extracted upstream. This severe reduction in flow is resulting in an increased intrusion of seawater into the estuary, resulting in an increase in salinity of the estuary water.[22]

Now that we have taken inventory of the world's freshwater sources, we will drill deeper into the water chemistry or water quality of these various sources. Water quality is not only important for human use, but to every aspect of industry from food producers to oil refineries.

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CHAPTER 3

Water Quality

Water quality of both surface and groundwater can be affected by many things. Natural forces such as rainfall, geological characteristics, and seasonal changes can have significant impact. Human activities, including overuse, pollution, changes in water flow patterns, introduction of non-native species, and dams on rivers can have unintended consequences. These factors can affect how water is treated and the results of water treatment.

Industrial water demands are ever changing, and with these demands come the need to continuously find ways to both improve the quality of water and extend its usefulness in operations. Many of our industries require water of very high purity for their production environment, such as semiconductor manufacturing, certain chemical processes, and pharmaceuticals. Other industries, such as power utilities, require higher purity water for makeup to high-pressure steam generating equipment. These increasing water quality requirements demand increasingly sophisticated equipment and chemistries to ensure the purity of water matches the specification for the industry or application.

In addition to the need for increasing water purity across industries and processes, we are increasingly faced with the need to stretch our use of existing plant waters, by managing the water chemistry before discharge, cascading to other process uses in a plant, or recycle and reuse of waste streams. This multiple use of the same water results in treatment needs to ensure the quality or characteristics of the water are appropriate for the next use.

Natural Factors Affecting Water Quality

The quality of surface waters is affected by rainfall, the geological nature of the watershed, conditions of evaporation, seasonal changes in stream flow, and location. The effect of rainfall on lakes and rivers obviously depends on the size of the body of water. For example, the headwaters of most rivers are more greatly affected by rainfall and other inputs when compared with points downstream, because the volume of river water flow is much greater downstream (greater dilution).

A key factor involved in increases in mineral content of water is the dissolution of mineral bearing rock. Calcium bearing rock is the most prominent of those readily soluble in water and is contained in limestone ($CaCO_3$), which is an alkaline compound. $CaCO_3$ comes from shells and skeletons of aquatic organisms in the bottom of prehistoric seas. The dissolution of minerals, as well as entrainment of soil as suspended solids in the catchment area, can affect the composition of lakes and rivers.

Well water composition is related to the chemistry of the geologic formations through which the water passes. Thus, waters from wells drilled into different strata have different characteristics. Underground water usually moves very slowly. Its flow is measured in feet per year (meters per year) compared with surface streams, where velocity is in the feet per second (meters per second) range. Because of this slow movement, the composition of any given well is usually quite constant. Although shallow wells may vary seasonally in temperature, most wells are constant in temperature, usually in the range of 50 to 60°F (10–15.6°C). Since the water often passes through miles of porous rock formation, well water is generally clear, if the well has been properly constructed to keep fine sand from entering the casing (Fig. 3.1).

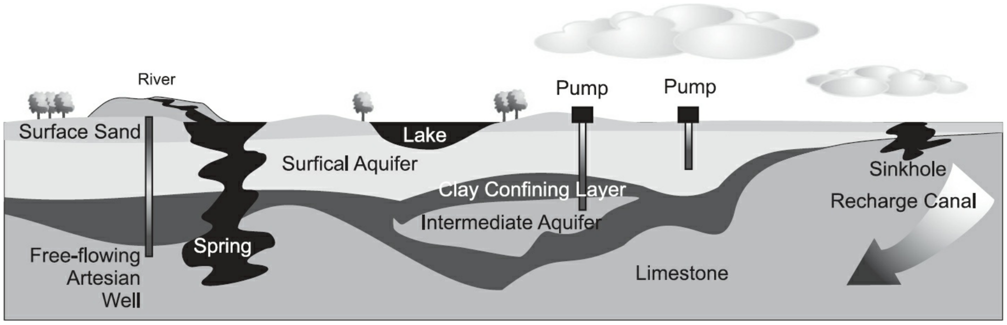
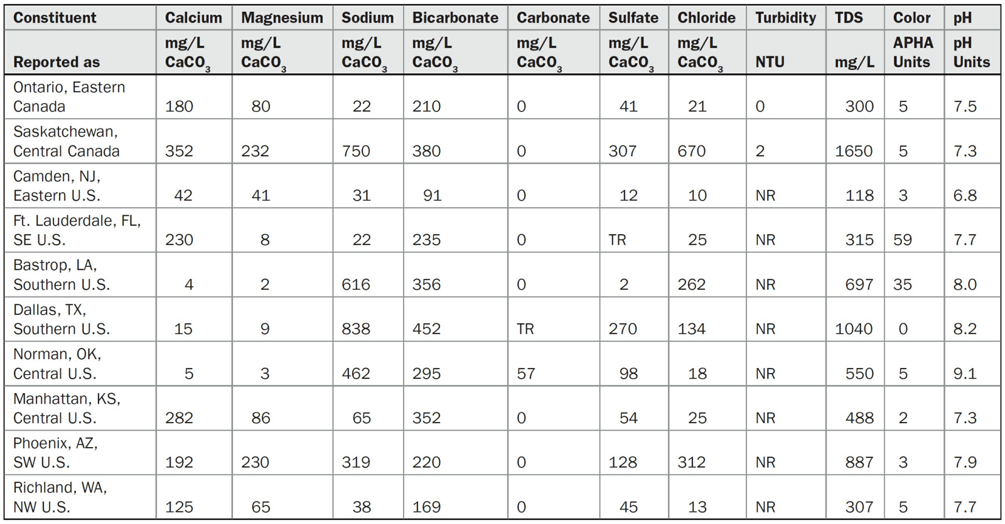


FIGURE 3.1 An aquifer system illustrating wells at various depths into the water table.

Rainwater filtering through the ground picks up nutrients and minerals, depending on the composition of the soil and rock strata. From flowing streams and rivers, water may diffuse into underground aquifers when the surrounding water table is low; or water may feed into the river from these aquifers when the water table is high. This too influences chemical composition, particularly iron and manganese in certain streams. See Chap. 5 for more information on this process and the differences between surface and groundwater.

Some aquifers are so large that they may cover several states in total area, and wells drilled into that particular aquifer produce water of similar composition. For that reason, with good geological information, it is possible to generalize about the composition of well waters in different parts of the world. Selected analyses of North American wells are shown in Table 3.1. Most of the waters have calcium, magnesium, and alkalinity typical of wells in limestone-based formations. Some, like the well in Dallas, TX, may have passed through strata that are rich in sodium carbonate, chloride, and sulfate rather than calcium carbonate.



Constituent	Calcium	Magnesium	Sodium	Bicarbonate	Carbonate	Sulfate	Chloride	Turbidity	TDS	Color	pH
Reported as	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	NTU	mg/L	APHA Units	pH Units
Ontario, Eastern Canada	180	80	22	210	0	41	21	0	300	5	7.5
Saskatchewan, Central Canada	352	232	750	380	0	307	670	2	1650	5	7.3
Camden, NJ, Eastern U.S.	42	41	31	91	0	12	10	NR	118	3	6.8
Ft. Lauderdale, FL, SE U.S.	230	8	22	235	0	TR	25	NR	315	59	7.7
Bastrop, LA, Southern U.S.	4	2	616	356	0	2	262	NR	697	35	8.0
Dallas, TX, Southern U.S.	15	9	838	452	TR	270	134	NR	1040	0	8.2
Norman, OK, Central U.S.	5	3	462	295	57	98	18	NR	550	5	9.1
Manhattan, KS, Central U.S.	282	86	65	352	0	54	25	NR	488	2	7.3
Phoenix, AZ, SW U.S.	192	230	319	220	0	128	312	NR	887	3	7.9
Richland, WA, NW U.S.	125	65	38	169	0	45	13	NR	307	5	7.7

Note the variation from very soft water to hard water. These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)
Source: Nalco Water Analytical Water Analysis.

TABLE 3.1 Analyses of Various Well Waters in North America

Often, the well waters of Mexico are high in silica, like well waters of the southwestern United States. Well waters of central Europe are like those of the U.S. Midwest and are as variable in quality based on location, the nature of the geologic formations, and depth. An analysis of an industrial well outside Vienna is shown in Table 3.2. A well-water analysis from a refinery on the Adriatic coast of Croatia is unusual in its low sulfate and chloride level, and a low ratio of magnesium to calcium. It is obvious from these and other analyses in this chapter that accurate prediction of a water analysis is not possible, and throughout the world, each source is unique.

Constituent	Calcium	Magnesium	Sodium	Bicarbonate	Carbonate	Sulfate	Chloride	Turbidity	TDS	Color	pH
Reported as	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	NTU	mg/L	APHA Units	pH Units
Vienna, Austria	160	120	6	220	0	40	26	Tr	NR	NR	7.7
Rijeka, Croatia	136	27	39	180	0	10	12	Tr	NR	NR	7.5
Canary Islands	50	135	760	144	6	48	251	NR	NR	NR	8.4
Tarragona, Spain	557	672	1891	181	0	181	0	NR	NR	NR	7.9

These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

TABLE 3.2 Analyses of Selected Wells in Other Countries

Seasonal Changes That Affect Water Quality

The sudden dilution of a river by heavy rainfall can change the water quality significantly. This change can be a disruptive factor in a water pretreatment application that prepares water for either industrial or domestic use, such as clarification or lime softening. The location of a river water intake should be carefully chosen with this problem in mind. In the operation of a treatment plant, it is common practice to adjust the chemical dosages according to effluent water quality. However, when the water supply is so variable, it is necessary to base changes in chemical treatment on raw water characteristics, rather than on finished water quality. This imposes a hardship on treatment plant operators, requiring constant attention to analysis and control.

Seasonal temperature change is another characteristic of surface water that complicates treatment, particularly affecting the coagulation process and softening reactions in the winter. Low temperatures create problems with air binding of filters due to the increased solubility of gases and higher water viscosity. Air binding causes pressure drop through the filter beds to increase releasing gas and disrupting flow.

Seasonal water temperature change can cause problems in cooling water systems. The heat exchange equipment is usually designed for the least favorable condition, which is the higher summer temperature of surface waters. In winter, when the water temperature is low, the flow through heat exchangers must often be restricted to prevent overcooling. Lower water velocity may allow fouling in heat transfer equipment, which can lead to corrosion and lost heat transfer capacity. Generally, the lost heat transfer capacity cannot be recovered with higher flow rate when higher cooling rates are needed.

Impact of Dams on River Water Quality

When a river is dammed, the water quality may be considerably different from that of the flowing stream. The impoundment behind the dam takes on the characteristics of a lake. In deep impoundments, it is common to find stratification, with oxygen depletion in the bottom stagnant zone. Significant levels of iron and manganese can develop in the bottom water, even though the surface remains free of these metals. Concentration gradients are sometimes found in impounded lakes, indicated by an increase in conductivity with depth. For example, Lake Mead, the impoundment of the Colorado River above Hoover Dam on the Nevada-Arizona border, has a conductivity of 900 μS/cm at the surface. Conductivity begins to increase at a depth of 50 ft (15 m), reaching 1150 μS/cm at 300 ft (91 m). At the bottom, about 460 ft (140 m), the conductivity abruptly increases to almost 1500 μS/cm.

In the impoundment of major rivers, such as the Columbia, the Colorado, and those in the Tennessee Valley system, the mineral content of the lakes behind the dams is similar to that in the river, as would be expected. On the other hand, natural or artificial impoundment of streams in smaller watershed areas of abundant rainfall produces water supplies of very low mineral content. This accounts for the excellent quality of such municipal waters as Greenville, South Carolina, New York City, and Boston, as shown in Table 3.3.

Constituent	Reported as	Greenville, SC	New York, NY (Catskill Mt.)	Boston, MA
Calcium	mg/L $CaCO_3$	3	12	10
Magnesium	mg/L $CaCO_3$	2	7	3
Sodium	mg/L $CaCO_3$	4	4	1
Bicarbonate	mg/L $CaCO_3$	6	8	5
Carbonate	mg/L $CaCO_3$	0	0	0
Sulfate	mg/L $CaCO_3$	2	11	6
Chloride	mg/L $CaCO_3$	1	4	3
Turbidity	NTU	NR	2	1
TDS	mg/L	17	34	33
Color	APHA units	6	1	7
pH	pH units	6.2	6.9	6.3

Source: Nalco Water Analytical Water Analysis.

TABLE 3.3 Analyses of Reservoirs or Lakes Where Water Quality Is Impacted Mainly by Rainfall

Water Quality When River Meets Ocean

Rivers generally flow into oceans through either an estuary or a delta. An estuary is typically a wide mouth of a river open to the ocean. A delta is formed by the deposition of river sediment into another body of water, such as the ocean. Many of the major rivers of the world finally reach the ocean through deltas, which may have some of the characteristics of an estuary. In many instances, the flow of these rivers is so great that the dilution of the ocean can be measured for miles (kilometers) out to sea.

Power utilities in coastal areas often use brackish water for once-through cooling water. Some industrial plants have used the brackish waters of tidal basins for cooling tower makeup, since the water is low enough in dissolved solids to be concentrated by evaporation without severe scaling problems. The use of brackish water for this purpose permits installation of much smaller pipelines than would be needed if once-through cooling were practiced. One example is a chemical plant on the island of Trinidad, which is able to use water from the bay side of the island as cooling tower makeup. This water is diluted enough by the immense flow of the Orinoco River so that its salinity is lower than typical ocean water, permitting it to concentrate by evaporation without causing scale problems.

The quality of water in estuaries where rivers meet the sea is unpredictable, depending on river flow, tidal conditions, the size of the basin or bay, and the presence or absence of land formations that restrict flow to the sea. In large basins, such as Albemarle Sound in North Carolina on the U.S. east coast, the water, although saline, is of relatively uniform composition because of mixing of the shallow water by wind; but in smaller bays, the quality can change with the tides and the flow of the river. It is one of the miracles of nature that aquatic life adapts to these changes and flourishes in such tidal areas.

Tides influence surface water quality in that they slow, or actually reverse, normal river flow. This is particularly pronounced during periods of low rainfall. The change in water quality between high and low tide sometimes justifies installation of raw water supply reservoirs to receive water at low tide, when the river flows unimpeded and quality is at its best. Plants so equipped stop pumping at high tide, when saline bay waters move upstream into the river channel. An example of the effect of tides and seasonal runoff is given in Table 3.4, showing the enormous variations in the Delaware River near Wilmington, Delaware.

Date	Maximum	Minimum	Mean
October 16	6880	2660	4420
November 26	2460	420	1370
December 27	240	100	145
January 17	2700	100	1470
February 24	560	100	235
March 21	3240	200	1450
April 23	1240	220	289
May 24	4220	920	NR
June 22	3900	200	1110
July 20	6380	860	2930
August 19	8920	1900	5030
September 20	8300	3500	5630

Source: USGS Water Supply Paper 2151, 1970.

TABLE 3.4 Conductivity (μS/cm) of Delaware River Near Wilmington, DE from October 1969 to September 1970 Showing Daily Variations Due to Tidal Flow

Out at sea, where surface waters have become part of the circulation system, the composition of the ocean water is remarkably uniform. There are, of course, local changes in salinity, as mentioned earlier, caused by upwelling of subsurface waters into the ocean, the flow of mighty rivers into the sea, or the melting of glaciers and the polar ice caps. Even though it is not usable by land animals, seawater is a valuable source of water for industry and is widely used for cooling.

Pollution

Pollutants from domestic water discharge, industry, and agriculture can degrade surface water systems and seep through the ground causing contamination of aquifers. Reinjection of water to replenish aquifers can affect water quality and pollute groundwater, if the injected water is not of sufficient quality. Industrial discharges may lower pH and alkalinity or increase organic and biological contamination. Municipal water may show an increase in dissolved solids of 50 to 100 mg/L through human use. Pollution is a major concern for lakes and rivers around the globe. In many lakes, this consists of runoff from farms during rainstorms in which the major pollutant is fertilizer. Lakes in industrial areas can receive various chemical pollutants. Cities around larger lakes may actually dump raw sewage into lakes, when rainfall is heavy and the waste treatment systems become overloaded. As a result, there are wide varieties of pollutants that affect water quality.

The temperature of industrial cooling water discharge can be considered pollution. A large once-through cooling system can cause local temperature changes in a river or small lake. The added heat from plant processes, compounds the natural rise of the summer water temperature, sometimes producing an effluent warm enough to create an unhealthy condition for aquatic life. The higher temperature discharge can add to the oxygen demand and may have a pronounced influence on the oxygen content of the river water.

When pollutants are biodegradable, bacterial activity in surface water increases with pollution load, tending to reduce the dissolved oxygen level in the stream, but there are offsetting factors. The principal one is the presence of algae, which produce oxygen by photosynthesis in daylight often causing oxygen supersaturation on bright sunny days, followed by a concentration decrease at night as photosynthesis stops. This diurnal cycle affects not only dissolved oxygen, but also carbon dioxide, and thus pH. This can have a strong influence on the coagulation of a water supply in municipal and industrial water treatment plants.

Effects of Acidic Rainfall

The term "acid rain" commonly describes the deposition of acidic components in rain, snow, fog, dew, or dry particles. Distilled water, which contains no carbon dioxide, has a neutral pH of 7. Liquids with a pH less than 7 are acidic, and those with a pH greater than 7 are alkaline. Clean or unpolluted rain is slightly acidic with a pH of about 5.5. This is due to natural carbon dioxide in the air reacting with water to form carbonic acid.

Since the industrial revolution, emissions of sulfur dioxide and nitrogen oxides to the atmosphere have increased. They are discharged from utility stations, ore smelters, and internal combustion engines, including diesel locomotives, automobiles, and trucks. In general, the major contributor of nitrogen oxides is transportation, and the major contributor of sulfur oxides is the electric utility industry. The sulfur and nitrogen oxides react with water to form sulfurous, sulfuric, and nitric acids. These gases acidify the rain, sometimes to a pH of 2.4, downwind from industrial areas. The pH profile over the United States is shown in Fig. 3.2. Industrial acid rain is not only a problem in the United States but also a substantial problem in China, Eastern Europe, Russia, and areas downwind of populated areas. Acid rain has become more widespread with industrial and population growth. Figure 3.3 illustrates areas in Western Europe that are susceptible to low pH rainfall.

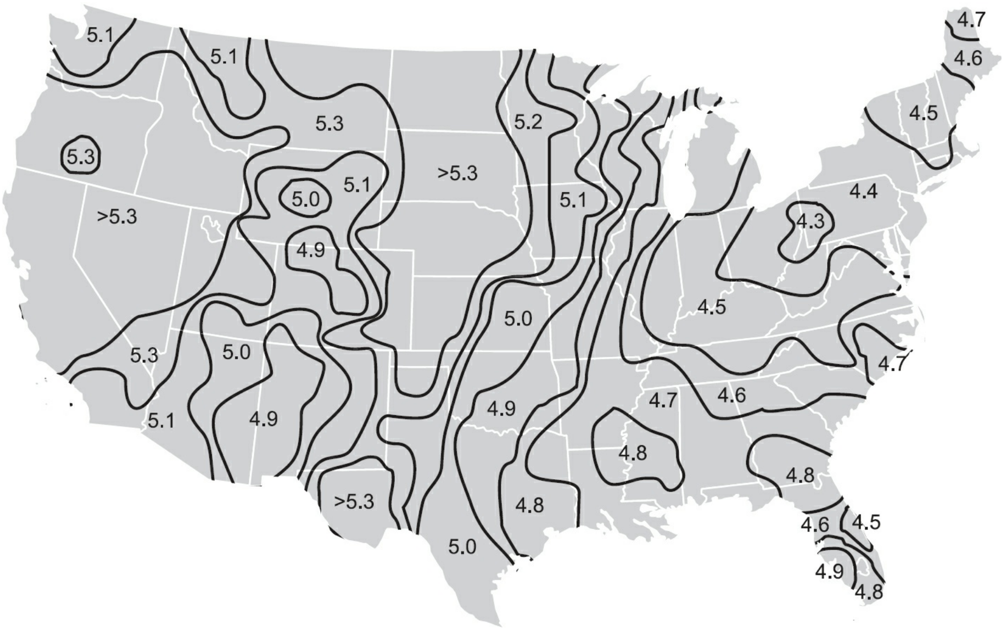


FIGURE 3.2 The pH of rainfall across the United States in 1997, showing the lower pH in the east due to acidic gases and prevailing winds. (*Compiled from information available through the National*

Atmospheric Deposition Program of the Illinois State Water Survey.)

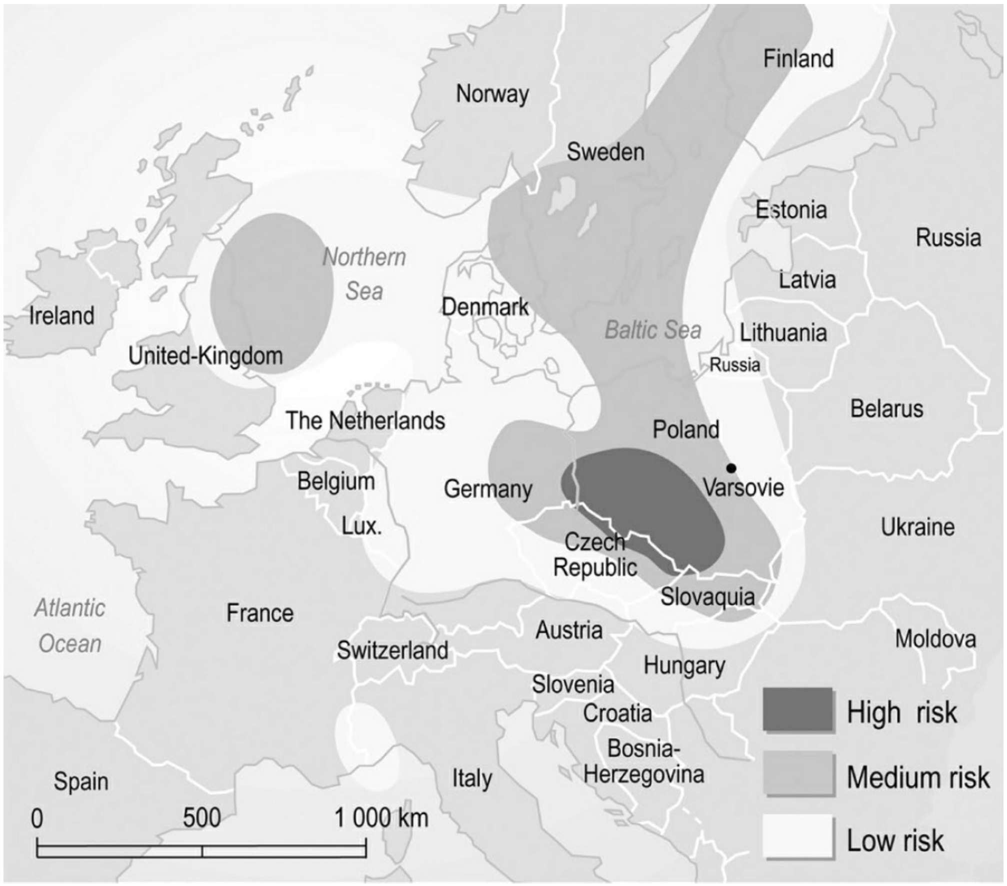


FIGURE 3.3 Areas across Western Europe susceptible to acidic rainfall. (*Source: Ed. Hatier, Paris, 1993, Cartographer: Philippe Rekacewicz, UNEP/GRID-Arendal, http://maps.grida.no/go/graphic/acid_rain_in_europe*.)

If the lakes and reservoirs receiving this rainfall are already low in natural alkalinity, acidic lake water may result. This condition can lead to a sterile aquatic environment, unless the acidity is neutralized by application of lime, soda ash, or other alkaline material. In general, the lakes and reservoirs affected by acid rain are contained in basins with granite bedrock. These waters have little alkalinity, as shown earlier in Table 3.3, and can be quite corrosive even without the added input of acid rain.

Effects of Landfill Leachate

The disposal of both domestic (municipal) and industrial wastes as solids and packaged liquids in landfill areas is a common practice. In industrialized countries, the enormity of the risk this has created for groundwater contamination can be a major environmental issue, if the landfill is not properly constructed.

In the United States, the Environmental Protection Agency (EPA) is identifying hundreds of major sites that must be cleared, decontaminated, and restored to a nonhazardous status. Many of these sites owe their hazardous nature to the presence of toxic chemicals, usually leaking from damaged or partially drained shipping containers. Water-soluble materials are usually carried into the soil by storm water. In some cases, soil bacteria may digest organic chemicals. In the aerobic zone, the by-product is mostly carbon dioxide. However, if the leachate reaches the anaerobic zone, the by-products are ammonia, carbon dioxide, methane, and residual refractory organic materials.

In many cases, soil adsorbs some toxic substances like polychlorinated biphenyls (PCB) and pesticides until saturated, and then these materials continue downward until they reach and contaminate the water table. The soil must then be decontaminated.

Effects of Acidic Mine Drainage

When mines are abandoned, they often fill with water. The oxidation or bacterial decomposition of metal sulfides from the surrounding rock or tailings can produce very acidic water, which can carry high concentrations of metals, most commonly iron, copper, and zinc. Other metals, including nickel, lead, arsenic, aluminum, and manganese, can also contaminate mine drainage. Because of the low pH and metal ion content, this water can be very toxic to environmental organisms. Contaminated mine water can seep through the ground and increase metal ion concentrations in local areas. When contaminated mine water flows out of the mine, it can pollute rivers and lakes. The low pH and metal ion content can cause fish kills or destroy microbes and plants.

Impact of Water and Process Treatment

An attitude of conservation is taking hold across industries and water managers need to approach total plant water assessments with a framework that incorporates reduce-reuse-recycle objectives. A total site and system approach is essential to manage cost and improve environmental performance. Correct application of water and process treatment programs, including a combination of chemistry, monitoring and control services, and equipment, can make a major contribution to sustainable development of industrial and other operations. Proper water treatment can reduce demand for natural resources, deliver improvements to system efficiency, and improve a company's financial performance, while providing many environmental benefits:

- Cleaner water to use and air to breathe
- Increased energy efficiency, reducing fuel use and emissions of greenhouse gases
- Improved water recycling, leaving more freshwater for other uses
- Reduction in solid wastes and liquid emissions
- Improved environmental performance
- Sustainable development of site operations

Boiler Water

Boiler water treatment is essential in maintaining energy efficiency and integrity of steam and heat generating systems. Poor management of heat exchange surfaces and water use can have major effects on system performance, fuel demand, gas and water emissions, asset life, and all associated costs. This in turn affects environmental performance and ultimately sustainable development of the plant operation.

Boiler operation is a high-intensity use of energy and a key opportunity for environmental gains. By preventing corrosion, assets are protected and asset life extended, reducing replacement frequency and the consequent demand for more nonrenewable resources to replace it. Scale prevention and water management can give substantial environmental benefits through reducing fuel use and greenhouse gas emissions. This offers consequential economic benefits.

Improvement of boiler water treatment practices can offer significant benefits. Steam systems with an effective treatment program can operate 1 to 3% more efficiently than one with an ineffective treatment program. Although higher operating efficiency is one benefit, an effective program extends equipment life, improves system performance, and reduces risk of operating problems. All of this reduces resource use, emissions, and costs.

The impact of boiler tube scale and deposits can include:

- Loss of energy efficiency = more fuel = increased greenhouse gas emissions
- Risk of tube failure from overheating or corrosion
- Reduced steam purity
- Reduced steam system reliability

The approach to securing better environmental performance and increased cost savings includes identification and prioritization of opportunities for energy savings. Projects can be sorted according to areas where treatment programs and services can have the greatest positive impact. A combination of environmental and economic improvements can then make a significant contribution to sustainable development.

A summary of the linkage between boiler water treatment and sustainable development is shown in Fig. 3.4.

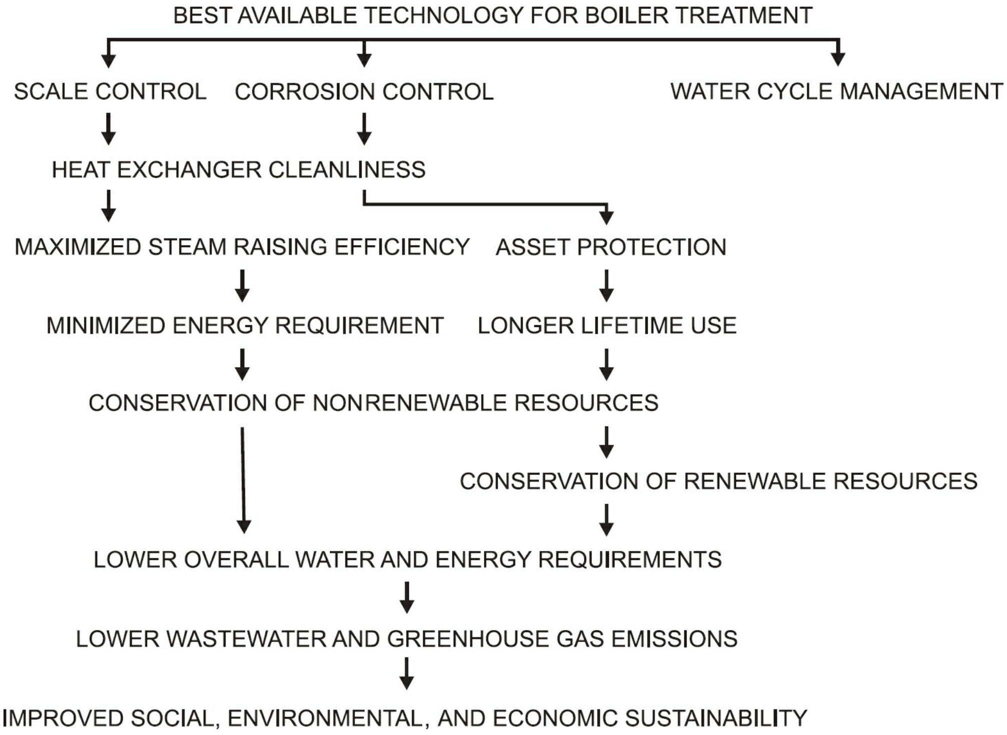


FIGURE 3.4 Linkage between boiler water treatment and sustainable development.

Cooling Water

Treatment of cooling water affects environmental protection and contributes to sustainable development. Programs target control of scale, corrosion, and microbiology, while improving water and energy management. This assures system cleanliness, minimizes water and energy use, controls emissions to air and surface waters, and maximizes asset life.

This in turn protects the local community and the environment through minimized resource demand and emission generation. Programs also support the plants own commitments to sustainable development, increasingly building stakeholder confidence (employee satisfaction, investor interest, and community respect).

In systems that rely upon heat transfer into cooling waters, impaired heat transfer can affect overall efficiency of the system and the processes or production linked to it. Proper application, control, and monitoring of a water treatment program can provide the correct level of ongoing protection and maintain system performance at required levels. Where necessary, the use of best practices in cleaning and system maintenance can assure cost-effective operations.

Failure to keep heat exchanger surfaces clean and free of scale deposits and corrosion can lead to significant reductions in heat transfer and cooling efficiency. In condenser systems, this has an immediate primary impact upon energy use and indirectly upon fuel use and greenhouse gas emissions. Secondary impacts can include reduced production capacity or even shutdown, equipment malfunction, and poor finished product quality. Clearly, any loss of efficiency can prejudice sustainability.

Biofouling or scale can insulate the heat transfer surface and prevent efficient cooling performance, and this is usually caused by inadequate treatment on either the water or process side. This can be prevented by proper treatment, control, and monitoring of the cooling system, and it can be remedied by "best practice" cleaning and treatment. Other factors can impair heat transfer into the cooling water and can be remedied with maintenance, cleaning, and treatment.

Correct treatment of cooling water maximizes asset life and minimizes economic and environmental impacts of replacement; minimizes fuel use and greenhouse gas emissions through scale and corrosion control; protects the population from potential illness through the effects of infection by *Legionella* bacteria; conserves both renewable and nonrenewable resources; and controls costs. This matrix shows the complex relationship between water treatment and some of the ultimate impacts upon sustainable development (Fig. 3.5).

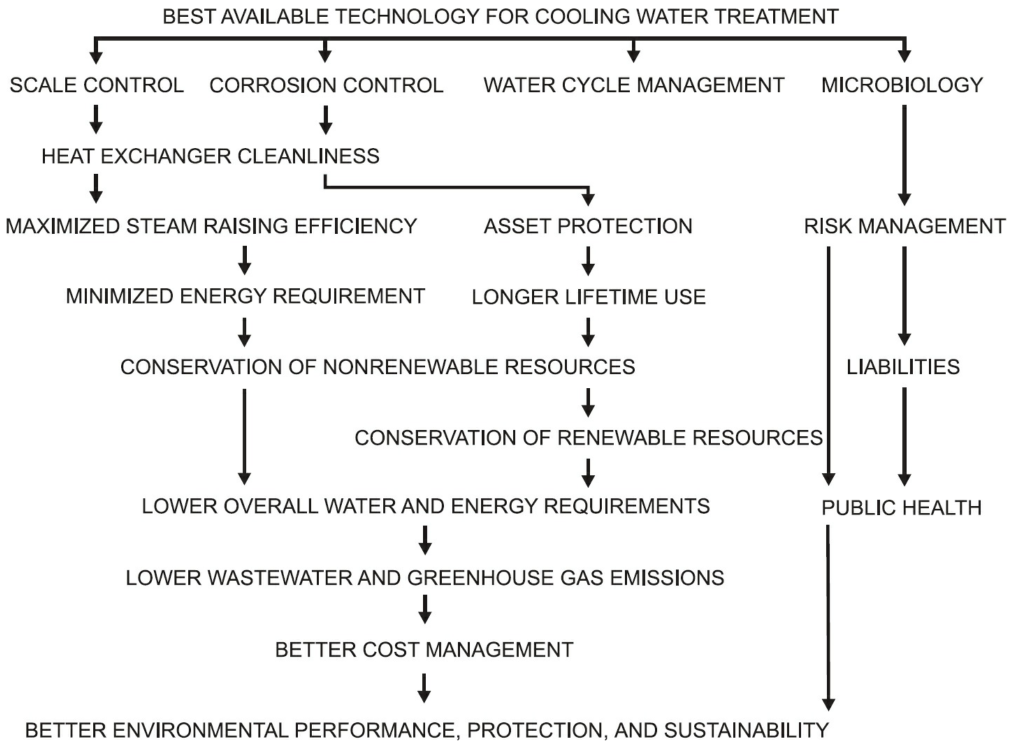


FIGURE 3.5 Linkage between condenser cooling water treatment and sustainable development.

Wastewater

With wastewater treatment, correct program delivery has a direct impact upon environmental performance and sustainability. It is important to understand plant activities that affect environmental performance; where the treatment program can affect these; what impact this has upon resource management, standards compliance, and cost management; and how this flows through to protection of the environment, better environmental performance, and sustainable development. The linkage between all these factors is shown in Fig. 3.6.

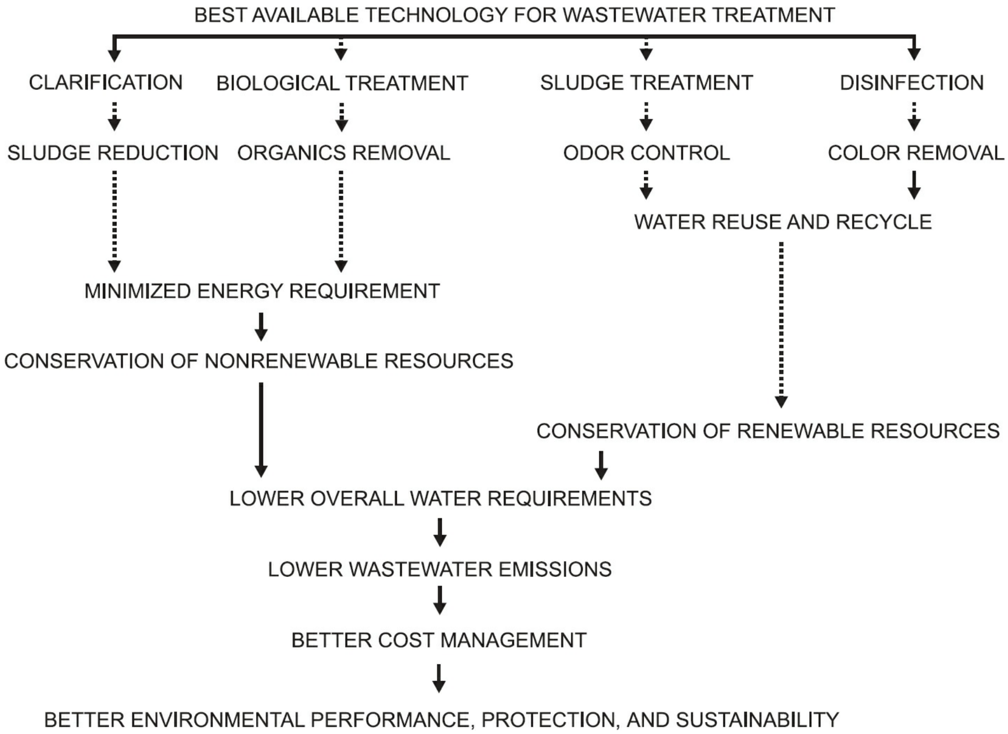


FIGURE 3.6 Linkage between wastewater treatment and sustainable development.

Focus on Total System Performance

Market-leading programs can represent a significant contribution to improving environmental performance of production units, through lower resource use, reduction in emissions, and innovative management of cost. This contributes to sustainable operation and development of processes by lowering demand for nonrenewable resources and reducing global warming potential through lowering greenhouse gas emissions. Improvements in profitability and environmental performance are a constant focus for plants.

Careful management of heated water resources affects both water resource use and energy costs and associated fuel use and gas emissions. This type of analysis can be very helpful in quantifying cost avoidance and savings opportunities, and justifying the investment in operational improvement projects.

Innovation in renewable materials for transportation is creating new alternatives to fossil fuels; however, many of the new manufacturing processes involved require large amounts of water. Precise management and treatment of water used insures that gains made through renewable fuel availability are not prejudiced by a greater demand for other resources. By managing the whole lifecycle, environmental and economic gains can be realized with the greatest benefits for society.

As a whole, proper application, monitoring, and control of water and process treatment programs can offer a wide range of benefits, and many of these are beyond the realm of traditional thinking. Figure 3.7 shows the impact of reduction in demand for fresh (makeup) water on sustainable development.

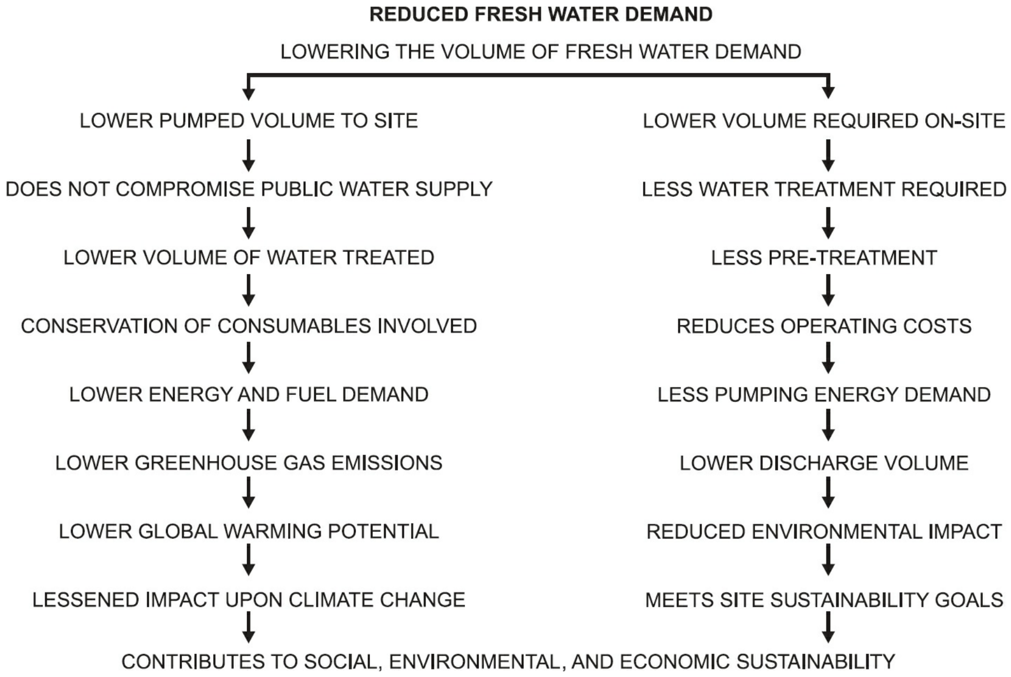


FIGURE 3.7 Impact of reduction in demand for fresh (makeup) water on sustainable development.

Proper water treatment, therefore, can be a significant source of economic value for industry—driving energy efficiency, waste reduction, improved material utilization, and other environmental and financial benefits in addition to water savings. A clear focus on proper water treatment allows full gains to be made by reducing, reusing, and recycling precious water resources.

SECTION 2

Basic Water Chemistry

CHAPTER 4

Water Chemistry

Chemistry involves the study and the interactions of atoms and molecules that make up all matter. Three aspects of matter considered to be of primary importance are the properties, composition, and transformation or reactions of matter. The physical properties of matter distinguish different substances. Water and alcohol are different substances due to different melting points, boiling points, and density. The second aspect is the composition of matter. This refers to the compounds, molecules, and atoms present in a substance and the relative ratios of those components. The last aspect is the transformation of matter from one substance to another. Simple examples are the combination of hydrogen and oxygen to make water or the transformation of iron ore into iron metal. The transformation of matter from one substance to another involves the exchange of energy, which may be given up, as in the case of burning fuel, or may be added, as in the case of generating steam from water.

At a higher level, the water chemist studies the nature and variable properties of water, and the effect of those properties on the application and use of water. Water is not a pure substance but a solution that can include many dissolved substances. Does the water source contain impurities that can lead to scaling? How does water chemistry affect corrosion of system metals? Can these impurities be easily removed by ion exchange, filtration, chemical reaction, etc., making the water more useful for industry or municipal use? This chapter will explore aspects of chemistry, from the basics to some key properties and interactions, which are necessary for a working knowledge of water chemistry.

Atoms, Molecules, Ions, and Compounds

The atom is defined as the smallest unit of matter retaining the characteristics of an element; a molecule is the smallest unit of matter retaining the properties of a compound. A variety of combinations and states exist:

- Atoms can form ions and combine into molecules.
- Molecules may be as simple as the association of two hydrogen atoms to form molecular hydrogen, or as complex as the combination of amino acids that make up deoxyribonucleic acid (DNA).
- Ions can be an atom or molecule, which has lost or gained one or more electrons, making it positively or negatively charged.
- A positively charged ion has fewer electrons than protons and is called a cation.
- A negatively charged ion has more electrons than protons and is called an anion.
- Molecules containing a number of different atoms or ions are called compounds.

Atoms and Molecules

The study of matter begins with the atom, the smallest particle characterizing a chemical element. The atom consists of an electron cloud surrounding a dense nucleus of protons and neutrons (Fig. 4.1). Protons have a positive charge, and neutrons are without charge. The positive charge of the nucleus is balanced by the negative charge of the electrons in the cloud around the nucleus. Chemical reactions between atoms or molecules involve only these electrons. The physicist is concerned with activity within the nucleus. The chemist is concerned with the properties and reactions of the atoms. For practical purposes, the mass of the atom must be considered the mass of the nucleus, since the electron is less than 0.02% of the mass of the proton.

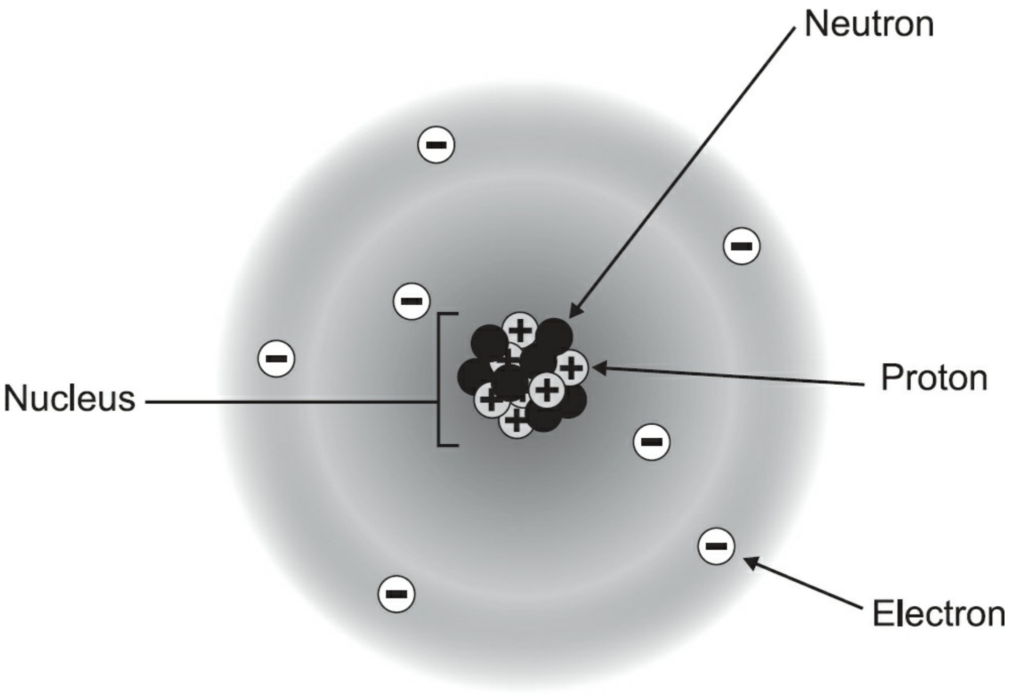


FIGURE 4.1 Illustration of the electron cloud model of an atom.

Atoms are identified by name, atomic number, and atomic mass. The atomic number in an atom of neutral charge is the number of electrons in orbit around the nucleus, which is also the number of protons in the nucleus. The atomic mass of the atom is the sum of the protons and neutrons in the nucleus. The names and symbols are of historic interest and consist of both ancient and recent history. The symbol for lead (Pb) is from the Latin plumbum, from which is derived the word plumber, whereas fermium (Fm), atomic number 100, is named for Enrico Fermi. The general properties of elements can be grouped into a table that illustrates the repetition, or periodicity, of physical properties. This table is called the periodic chart of the elements (Fig. 4.2).

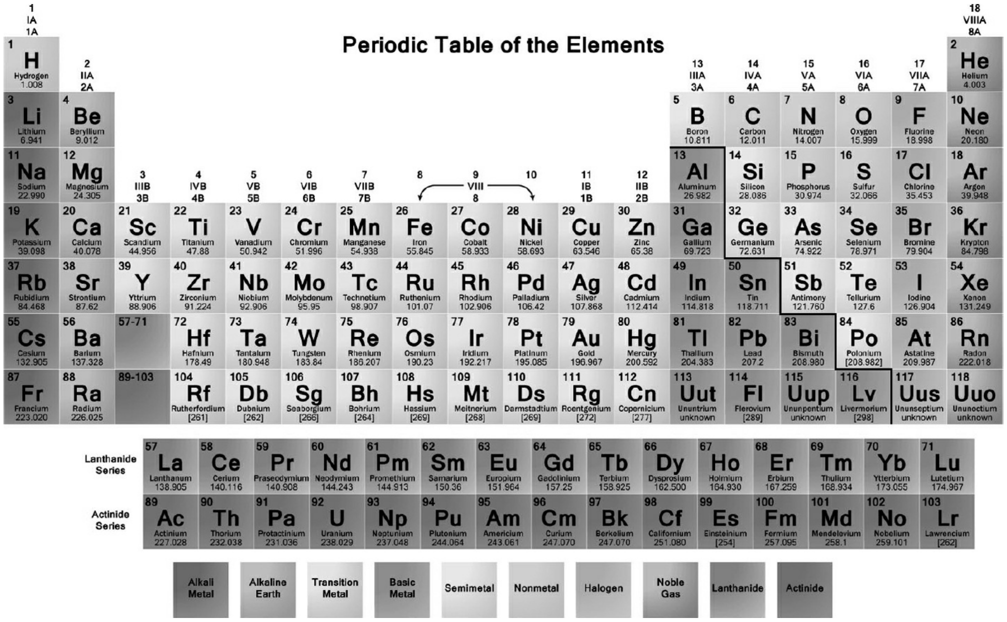


FIGURE 4.2 Periodic table of the elements.

Bonding in Compounds

Molecules are combinations of elements or atoms bonded together to form the basic building blocks of compounds. Molecules contain at least two different atoms bonded together strongly enough to be a stable combination. Three types of bonding mechanisms may hold molecules together:

1. Ionic bonding (Fig. 4.3)

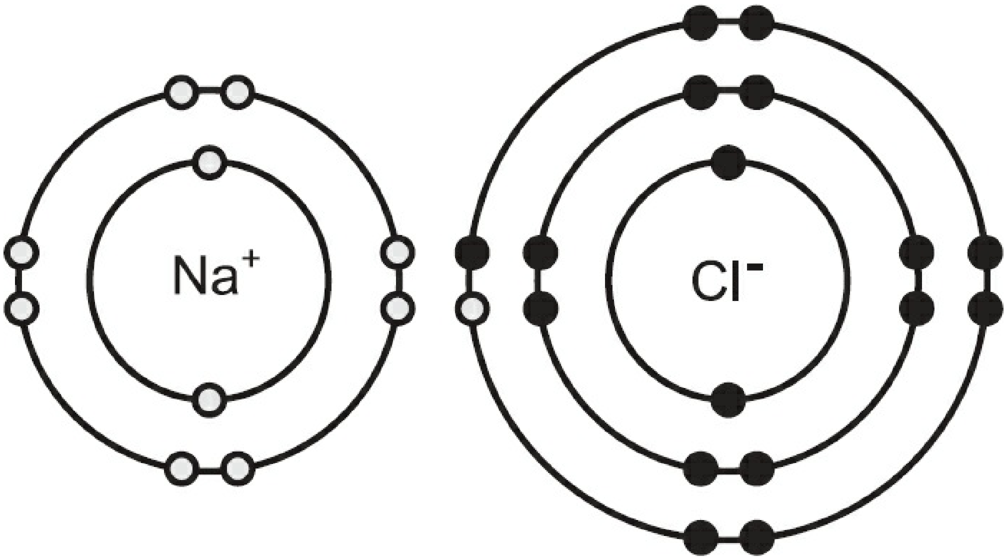


FIGURE 4.3 An ionic bond in sodium chloride is created when a sodium atom transfers an electron to a

chlorine atom creating positive and negative ions held together by the force of the electrostatic attraction. (Note: The Bohr electron model is use for simplicity, although it is not an actuate model of electron orbital structure.)

2. Covalent bonding (Fig. 4.4)

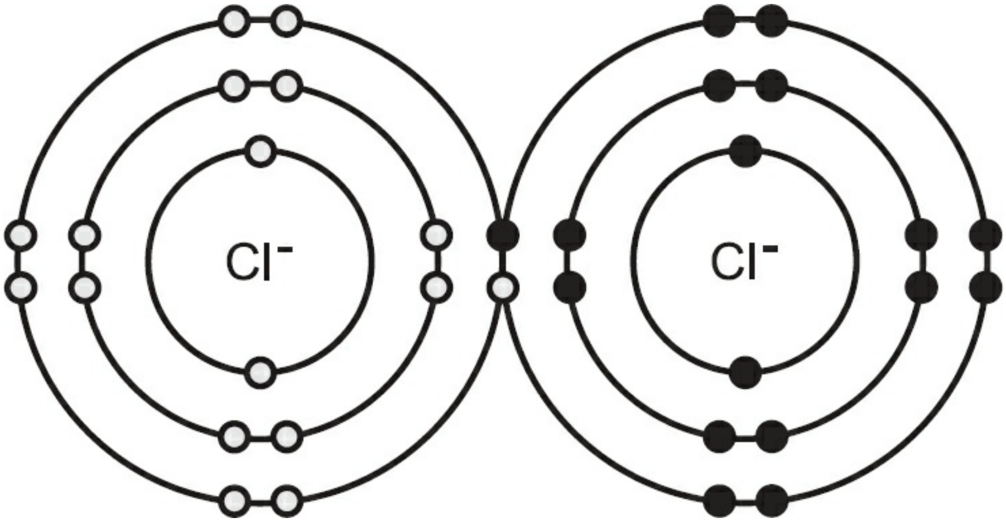


FIGURE 4.4 A simple example of covalent bonding illustrated by the diatomic molecule, chlorine, where the shared pair of electrons is attracted to the nucleus of both atoms. The electrons are all equal, even though they are represented by different shades of gray.

3. Coordinate covalent bonding (Fig. 4.5)

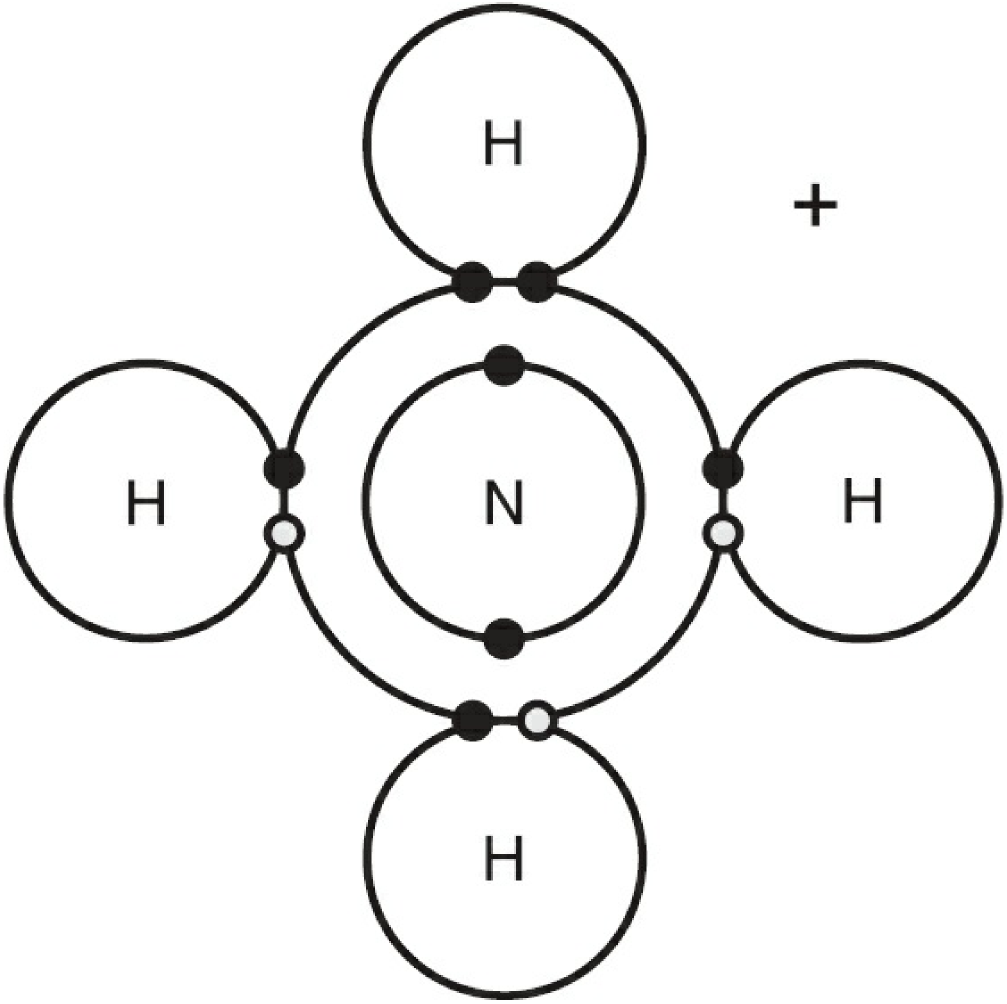


FIGURE 4.5 A coordinate covalent bond is a type of covalent bond where one atom donates both of the shared electrons to one bond, as illustrated in the ammonium ion. The two dark dots in the upper bond represent electrons donated by the nitrogen atom.

An ionic bond is formed between two oppositely charged ions. It typically forms between metal and non-metal ions through electrostatic attraction. Sodium chloride is an example of a metal and non-metal ionic bond. The metal (sodium) donates one electron, forming a positively charged cation. The electron enters the nonmetal (chloride), forming a negatively charged anion. Both cation and anion have stable electronic configurations. The attraction between the oppositely charged ions causes them to come together and form a bond. In general, ionic bonding occurs only if the overall energy change for the reaction is favorable. This is when the bonded atoms have a lower energy than the free ones.

The second type of bonding mechanism is the covalent bond. It is characterized by the sharing of pairs of electrons between atoms or molecules. The hydrogen molecule is an example of shared electrons via covalent bonding. Covalency is greatest between atoms that are similar, like the carbon-carbon bond in organic compounds. The most common type of covalent bond is the single bond, which is the sharing of only one pair of electrons. More than one electron pair is called a multiple bond. Double bonds are simply sharing two pairs of electrons. Triple bonds are sharing three pairs of electrons. Higher bonds exist for transition metals.

The third mechanism of bonding is actually an artificial one, in which both electrons come from the same atom. This type of bonding is called coordinate covalent bonding and is useful to describe coordination compounds. An example is the calcium cation with a +2 charge. In water, calcium coordinates with six water molecules and covalently shares six pairs of electrons.

Since the mass of atoms and molecules are relative and because the units themselves are very small, the chemist uses units called moles. A mole is an arbitrary unit given in grams. The number of grams in a mole of a given substance is determined by adding the atomic mass of the constituents. An example is calcium carbonate ($CaCO_3$), a compound very familiar to water chemists, having a molecular weight of 100 g/mol (grams per mole). This is also called the gram-molecular weight. The number of molecules in a mole of any substance is defined by Avogadro's number ($6.02 \cdot 10^{23}$/mol).

The Water Molecule

The proper study of water begins with the water molecule. The formula for water is H_2O, which by itself tells us only its composition and molecular weight. The water molecule is formed by the reaction between molecules of hydrogen and oxygen, as shown in Fig. 4.6. Water exists in liquid and solid states in addition to being found in the atmosphere as vapor.

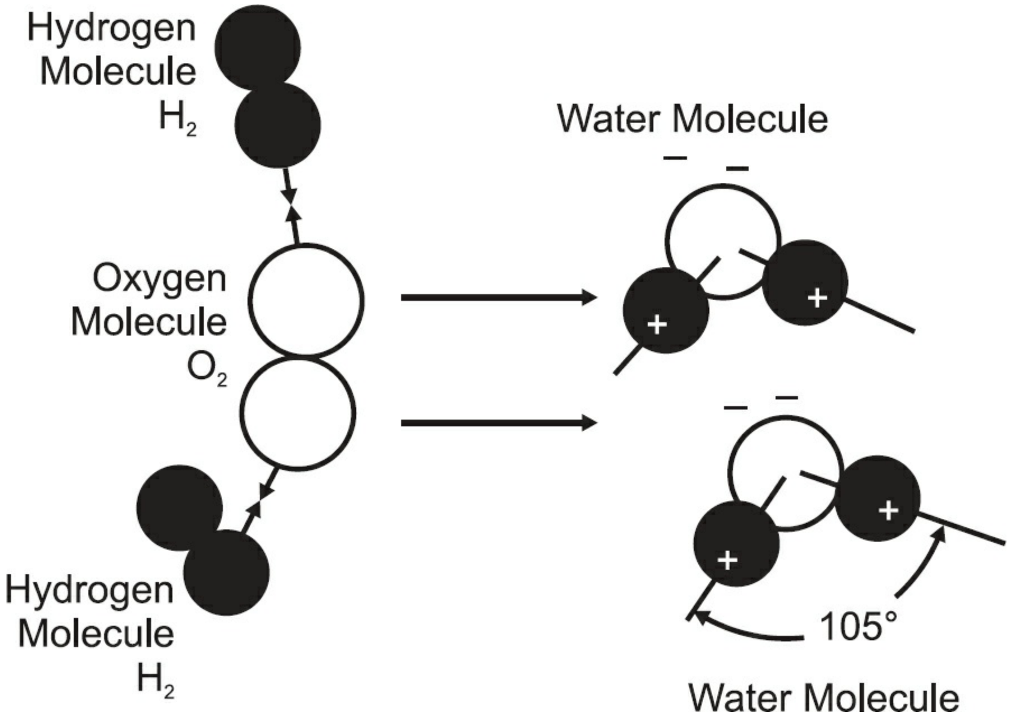


FIGURE 4.6 Reaction between hydrogen and oxygen molecules to form water molecules. The polar nature of the molecule is illustrated by the positive charges on the hydrogen ions and the negative charge on the oxygen ions.

Water's unique molecular arrangement (Fig. 4.6) shows two hydrogen atoms located 105° apart and adjacent to the oxygen atom. The molecule is asymmetric with partial positive charges on the hydrogen atoms and partial negative charges on the oxygen atom. This causes the water molecule to be dipolar (opposite charges at opposite ends of the molecule). Many substances dissolve in water because of this polarity. Water in nature is rarely pure and can dissolve many inorganic and organic compounds. However, many compounds are insoluble in water, such as oils.

Solubility of Matter in Water

Water molecules surround charged particles and pull them into solution. Using sodium chloride (NaCl) as an example, water molecules work their way into the crystal lattice and between the individual ions. They surround the alternating sodium and chloride ions and slowly dissolve the salt (Fig. 4.7). The negative oxygen side of the water molecule surrounds the sodium ion, and the positive side of the molecule (hydrogen side) surrounds the chloride ion. The liberated ions are held in solution by this hydrating action and prevented from recombining. Oil, for example, does not dissolve in water because there is no net electrical charge across the molecule, making it a nonpolar molecule.

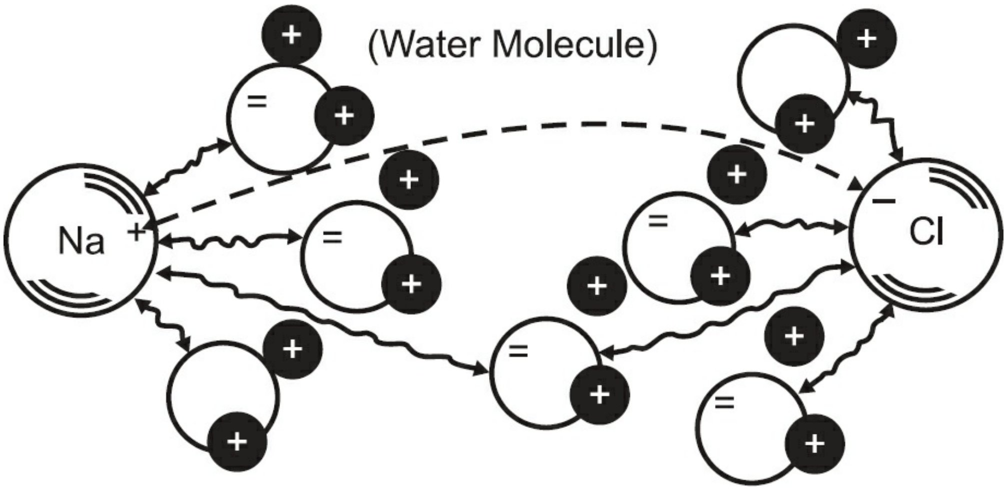


FIGURE 4.7 Dissolution and solvation of sodium chloride by dipolar water molecules.

Hydrogen Bonding

The dipolar nature of the water molecule causes aggregation of water molecules. The hydrogen end of the molecule attracts the oxygen side of an adjacent molecule, linking them by an attractive force called hydrogen bonding (Fig. 4.8). In this manner, one water molecule is hydrogen bonded to four adjacent water molecules.

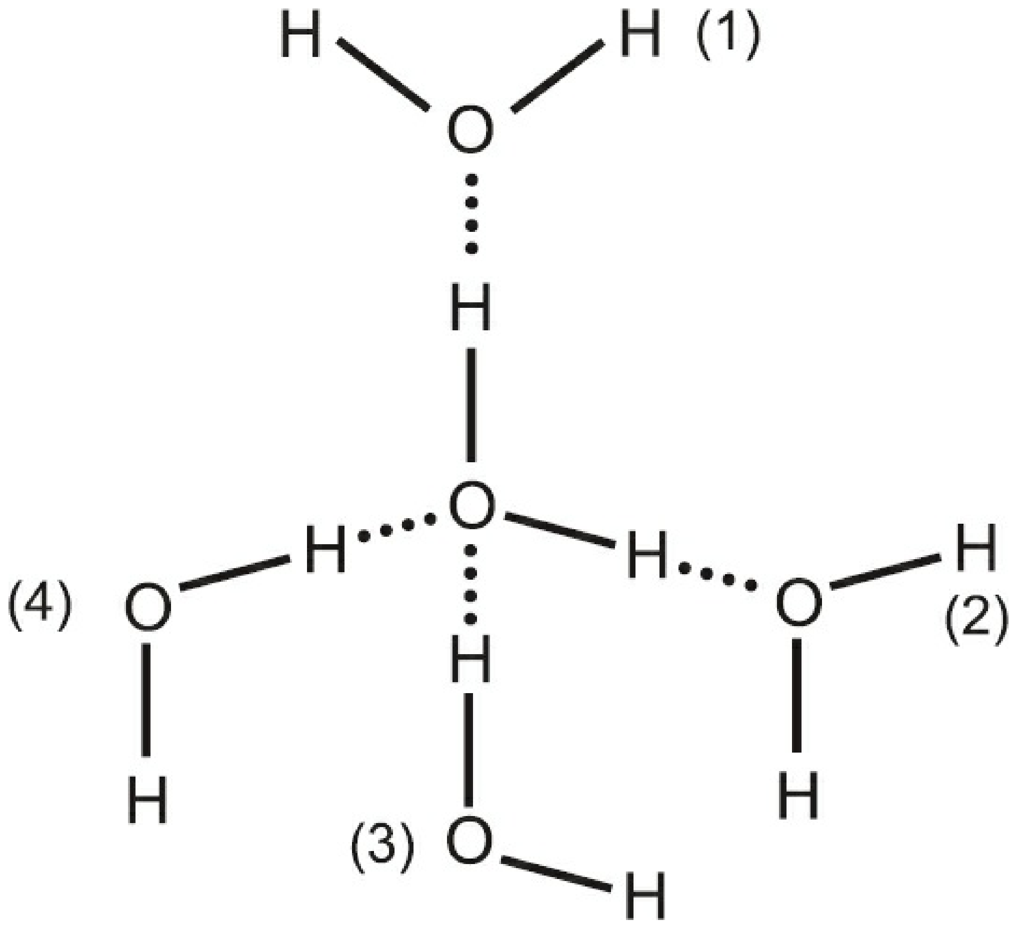


FIGURE 4.8 The dashed lines illustrate hydrogen bonding between water molecules. The hydrogen bond is much weaker than bonds between oxygen and hydrogen in the water molecule, but still strong enough to affect properties of water.

One of the consequences of hydrogen bonding is that molecules of water cannot leave the surface of a body of water as readily as they could without this intermolecular attraction. The energy required to break the hydrogen bond and liberate a molecule of water to form vapor is greater than for other similar chemical compounds. This leads to three important properties of water for industrial use:

1. The energy content of water vapor (steam) is high, making it a great heating source.
2. Water absorbs or releases more heat (higher heat capacity) for each incremental change in temperature than many substances, making it an effective heat transfer medium.
3. Water releases more heat upon freezing than many other compounds.

The freezing of water is unusual compared to other liquids. Most compounds become denser when frozen (solid) than in liquid form. Hydrogen bonding produces a crystal arrangement that causes ice to expand beyond its original liquid volume, so that its density is less than that of the liquid. As a result, ice floats on liquid water. If this was not the case, lakes would freeze from the bottom up, and life as we know it could not exist.

Because of the unusual structure of the water molecule, it is present in the natural environment in all three states of matter: solid as ice, liquid as water, and gas as vapor. It is the only chemical compound having this unusual character. Table 4.1 compares the boiling point and other heat-related properties of water with similar molecules, such as hydrogen sulfide (H_2S), and with other compounds that are liquid at room temperature.

Substance	Specific Heat, Btu/[lb·°F] (kJ/[kg·°C])	Freezing Point, °F (°C)	Boiling Point, °F (°C)	Latent Heat of Evaporation, Btu/lb (kJ/kg)
Water	1.0 (4.18)	32 (0)	212 (100)	970 (2255)
Hydrogen Sulfide	0.24 (1.02)	–122 (–86)	–77 (–61)	237 (552)
Methanol	0.60 (2.51)	–144 (–98)	151 (66)	473 (1099)
Ethanol	0.65 (2.72)	–174 (–114)	172 (78)	364 (846)
Benzene	0.43 (1.80)	42 (6)	176 (80)	168 (391)

TABLE 4.1 Comparison of Physical Properties of Water to Similar Compounds

Other Properties of Water

In addition to its unusual heat properties, water has physical properties quite different from other liquids. Its high surface tension is easily demonstrated by the experiment of floating a needle on the surface of water in a glass (Fig. 4.9). High surface tension, due to hydrogen bonding, causes water to rise in a capillary tube (Fig. 4.10). This capillarity is partly responsible for the system of circulation developed by living plants through their roots and tissue systems.

FIGURE 4.9 A steel needle, with a density about seven times that of water, can be made to float because of the high surface tension of water.

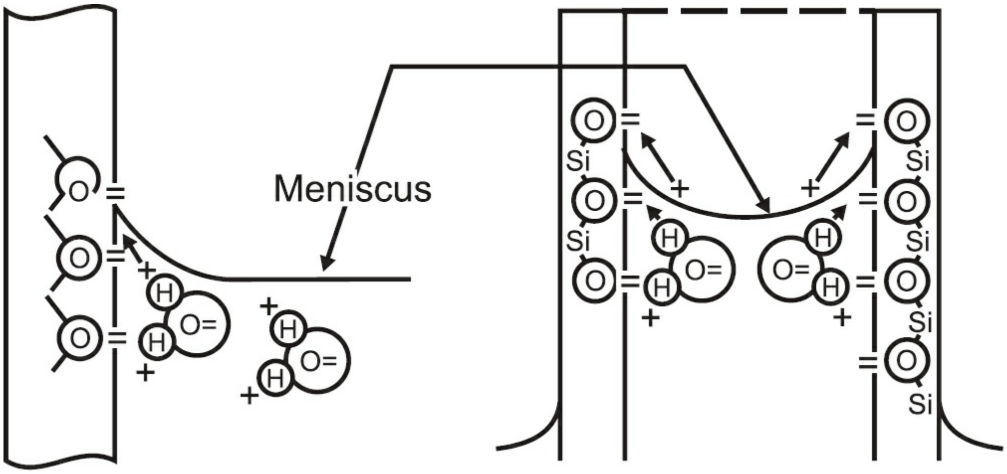


FIGURE 4.10 A meniscus forms (left) when hydrogen atoms reach upward to wet oxide surfaces of the glass tube at the water line. The drawing at the right shows how hydrogen bonding of water to a thin glass tube causes water in the tube to rise above the level of the surrounding water.

Pure, distilled water ionizes so very slightly, producing only 10^{-7} moles of hydrogen and 10^{-7} moles of hydroxyl ions per liter, that it is an insulator. Pure water does not conduct electrical current. As salts or other ionizing materials dissolve in water, electrical conductivity develops. The dissolved minerals in natural waters vary from place to place, and the conductivity is a measure of the dissolved solids (Fig. 4.11). For most public water supplies, the conversion factor is 1.55 µS/cm per mg/L of total dissolved solids. This conversion factor must be established for each situation and for other types of water, like wastewater and boiler water.

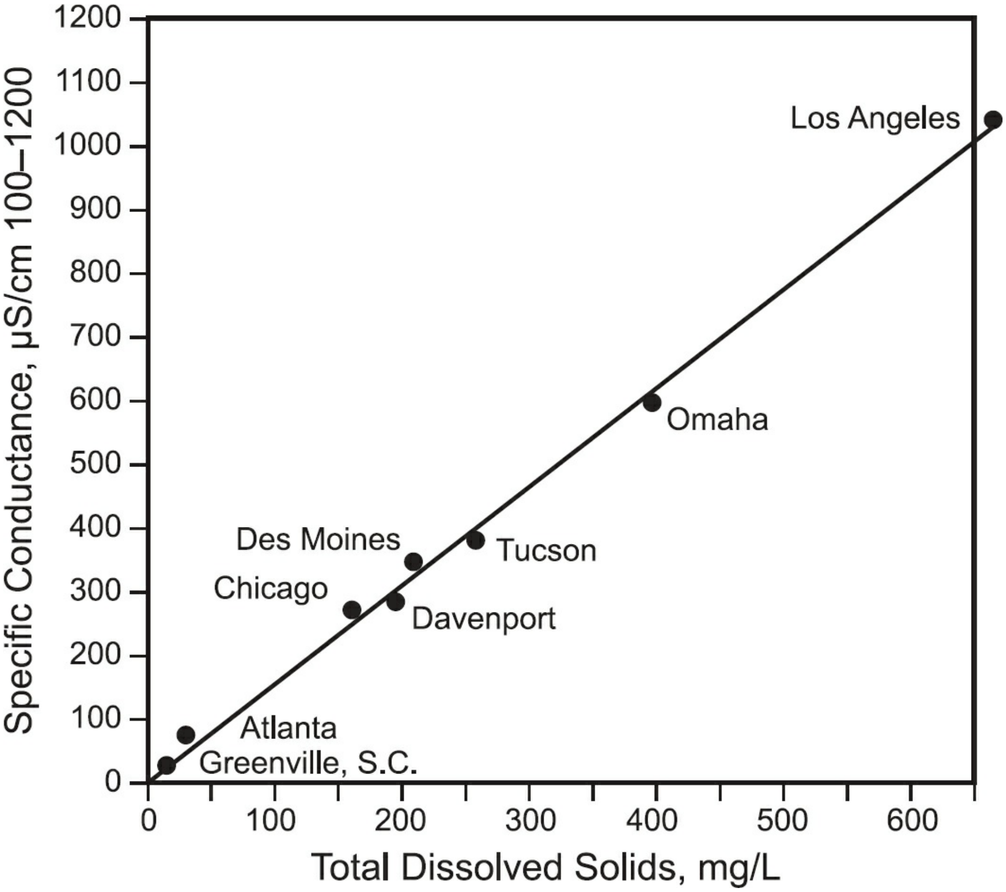


FIGURE 4.11 Dissolved solids content of water can be estimated from its specific conductance.

Another important phenomenon occurring in water solutions related to dissolved matter (solutes) rather than to the water (solvent) is osmotic pressure. If a membrane separates two aqueous solutions, water passes from the more dilute into the more concentrated solution. This important process controls the performance of all living cells. It explains the effectiveness of food preservation by salting. The salt creates a strong solution, disrupting cells of organisms that might cause food spoilage. Water inside their body leaves in an attempt to dilute the external salt solution. In specially designed membrane cells, the osmotic flow of water across the membrane can be reversed by applying a sufficiently high pressure to the more concentrated solution. This process of reverse osmosis is used for desalination of water.

Finally, viscosity is another property of water affecting its treatment and use. It is a measure of internal friction, the friction of one layer of molecules moving across another. As water temperature rises, this internal friction decreases. Because of the temperature effect, dissolved salts and gases can diffuse more rapidly through warmer water, chemical treatment is hastened, and the physical processes of sedimentation and degasification proceed faster. The effect of temperature on viscosity and surface tension (described earlier) is shown in Fig. 4.12.

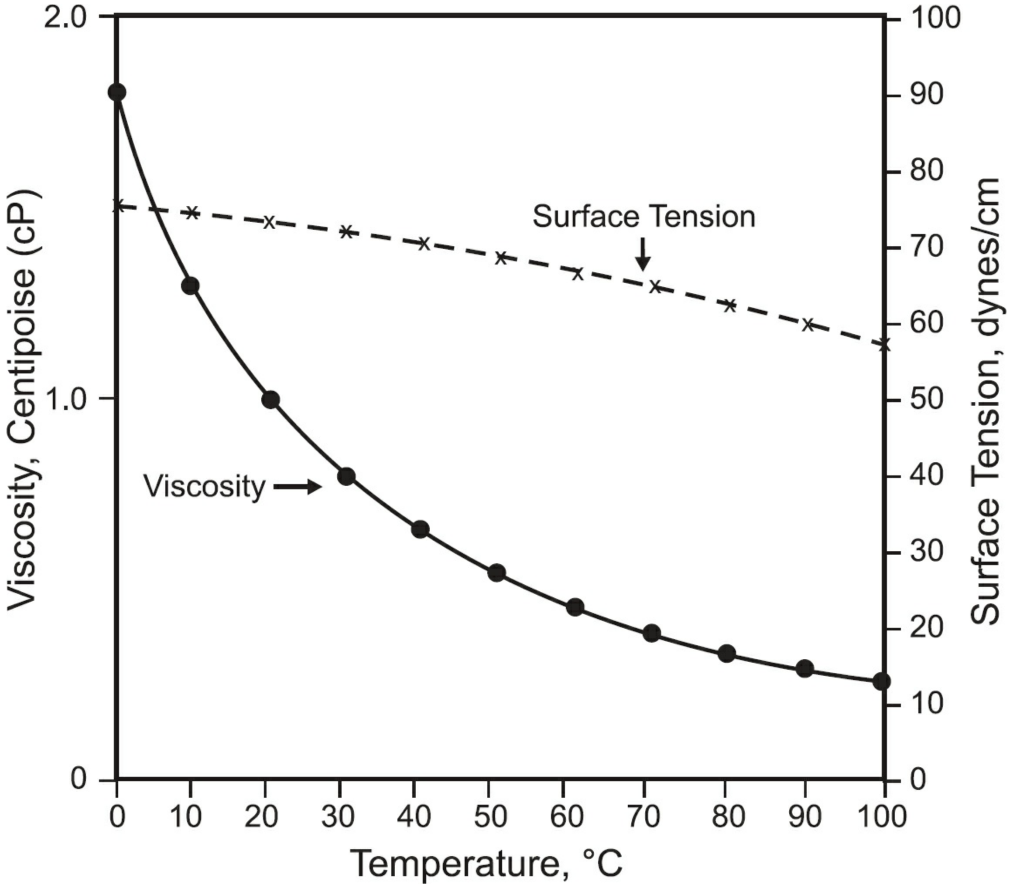


FIGURE 4.12 Surface tension and viscosity both decrease as water is heated.

Basics of Water Chemistry

The unique properties of water make it an ideal medium for industrial use, particularly for heat transfer applications. However, the solvent properties can create problems, like scale formation and corrosion. The ability to support life adds the opportunity for biological growth in some industrial water systems. An understanding of water chemistry is essential to combat these problems.

Impurities in Water

Practically speaking, no chemical is pure, whether naturally occurring or artificial. The impurity level in freshwater is measured in milligrams per liter (mg/L), with 10 000 mg/L equaling 1%. A sample of good lake water having total dissolved solids of 150 mg/L has an impurity level of only 0.015%. Sometimes, parts per million (ppm) is used in place of mg/L to measure impurities in water. Since a liter of distilled water weighs 1000 g or 1 000 000 mg, it is apparent that 1 mg/L of an impurity represents 1 ppm. However, a liter of seawater weighs about 1032 g, and 1 mg of impurity in seawater is less than 1 ppm. Because the density of different waters and water solutions, like brines, can vary, the use of mg/L is more precise than ppm. This book will use mg/L, the preferred notation.

Anything in water that is not H_2O is a contaminant or impurity. The principal job of the water chemist is to define these impurities, set specifications for acceptable levels of each impurity based on the intended use of the water after treatment, and devise economical treatment methods to reach the quality limits that have been set. It is important to recognize that the terms impurity, contamination, and pollution are subjective qualities of water. In this book, a contaminant is considered a pollutant when its presence and concentration are harmful either to aquatic life, or to public health if the water is for potable purposes. Dissolved impurities in water are broadly classified as inorganic salts (dissolved from minerals in the geologic formations in contact with the water source) and organic matter (related to aquatic life and vegetative cover of the watershed). In most freshwaters, dissolved matter is largely inorganic.

Electrolytes

When water dissolves a mineral, ions of the mineral separate or dissociate in the solution to form cations and anions. Generally, an increase in water temperature causes an increase in the solubility of most salts, like sodium chloride (NaCl) or potassium sulfate (K_2SO_4). Important and notable exceptions are calcium carbonate ($CaCO_3$), calcium sulfate, anhydrite ($CaSO_4$), magnesium carbonate ($MgCO_3$), and magnesium hydroxide [$Mg(OH)_2$], all of which become less soluble as temperature increases (Fig. 4.13).

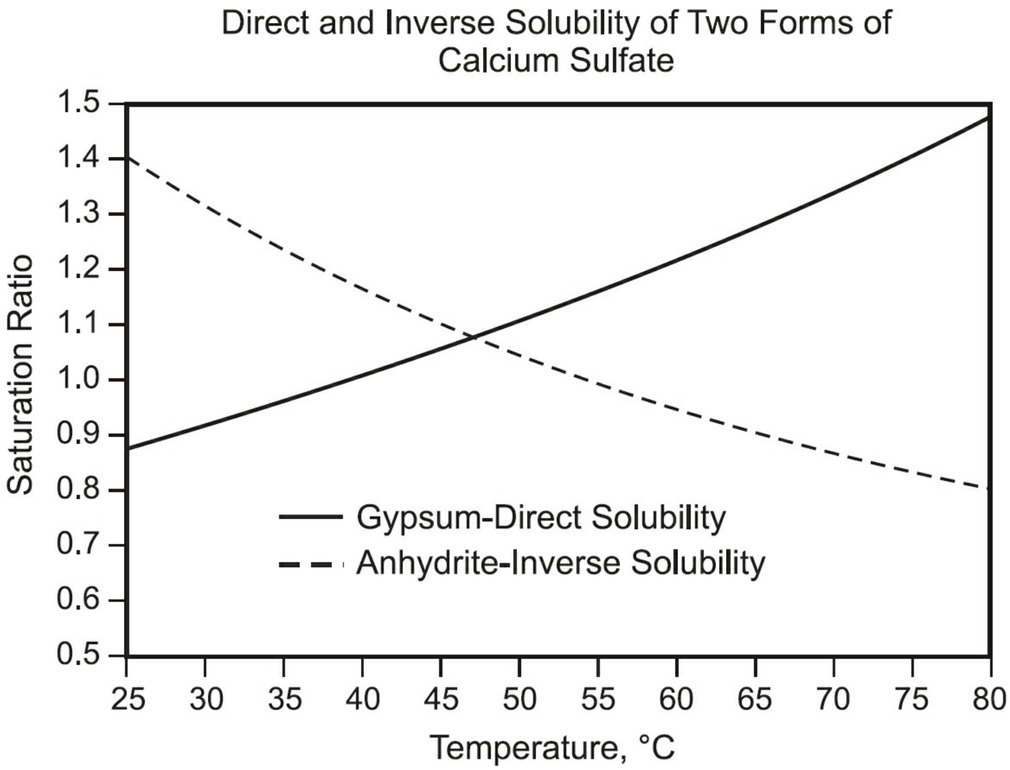


FIGURE 4.13 Solubility of some minerals increases with temperature (direct solubility) while other minerals have decreasing solubility with increasing temperature (inverse solubility).

A simple demonstration of ionization is an experiment in which an electric light is connected to a circuit with two separated electrodes inserted in a beaker of water (Fig. 4.14). In pure water, the lamp does not light when the switch is on, because pure water is an insulator not a conductor. Salt is added to the water in small increments, and gradually the light brightens. The light intensity is proportional to the amount of salt added. Current begins to flow only after sodium and chloride ions from the salt are present to transport electrons through the solution. If crystals of sugar are added to the water instead of salt, nothing happens; salt is an electrolyte, and sugar is not. Sugar is a polar organic compound that does not dissociate into ions when it dissolves.

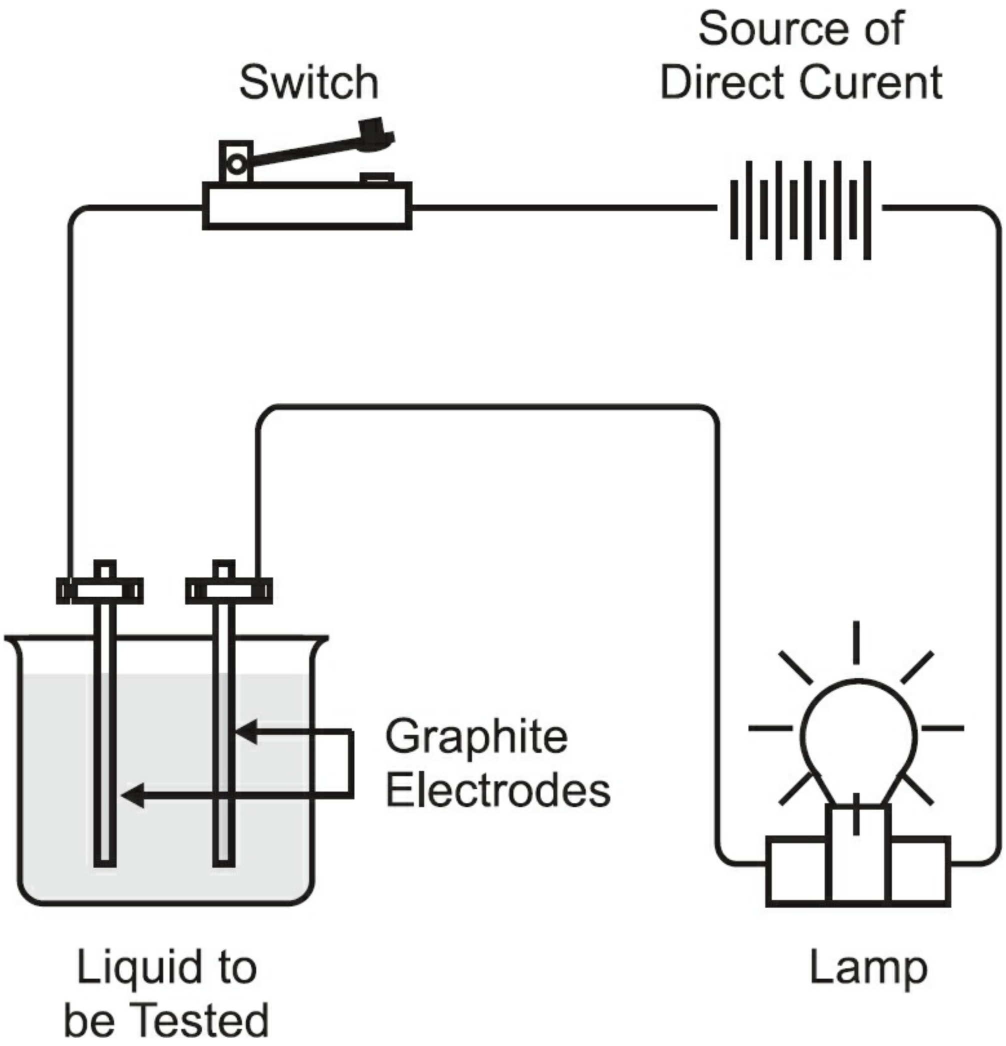


FIGURE 4.14 Pure water is nonconductive, but addition of an ionizing salt allows current to pass.

High concentrations of impurities are known to lower the freezing point of water. For example, 1 mol/L of a nonelectrolyte such as sugar or alcohol dissolved in water lowers the freezing point by 3.35°F (1.86°C). However, 1 mol/L of sodium chloride lowers the freezing point by almost twice the value found for sugar and alcohol, and 1 mol/L of sodium sulfate produces almost three times this temperature depression. This is due to the production of multiple ions in solution from the salts, compared to only one dissolved molecule from sugar or alcohol. Each molecule of sodium chloride produces two ions, and one molecule of sodium sulfate (Na_2SO_4) produces three ions.

Elements in specific groups of the periodic chart become either cations or anions, depending on the group of elements (Fig. 4.2). Some of the elements that form cations in aqueous solution belong to the following groups:

- Alkali metals (lithium, sodium, potassium, etc.)
- Alkaline earth metals (magnesium, calcium, strontium, etc.)
- Some transition metals (iron, manganese, zinc, etc.)

Some of the elements that form anions in aqueous solution belong to the following groups:

- Halogens (fluorine, chlorine, bromine, etc.)
- Other nonmetals (oxygen, sulfur, selenium, etc.)

Electromotive Series

In their elemental form, alkali metals and alkaline earth metals can displace hydrogen from aqueous solutions. Sodium and potassium are so active that they react with water itself to liberate hydrogen:

$$2\mathrm{Na} + 2\mathrm{H_2O} \rightarrow \mathrm{H_2}\uparrow + 2\mathrm{NaOH} \tag{4.1}$$

Magnesium does not react with cold water, but it does react with acid, which releases hydrogen in a solution:

$$\mathrm{Mg} + 2\mathrm{HCl} \rightarrow \mathrm{H_2}\uparrow + \mathrm{MgCl_2} \tag{4.2}$$

Cations can be classified according to their reactivity in an order known as the electromotive series, shown in Table 4.2. Not only will the more reactive metals displace hydrogen from solution, but they even displace metals below them in the series. For example, if a strip of iron metal is placed in a solution of copper sulfate, copper ions deposit on the iron strip as copper metal, as the iron dissolves into solution by the following reaction:

Element	Half-Cell Reactions	Standard Electrode Potential (V)
Potassium (K)	$K^+ + e^- \rightarrow K$	–2.93
Calcium (Ca)	$Ca^{+2} + 2e^- \rightarrow Ca$	–2.87
Sodium (Na)	$Na^+ + e^- \rightarrow Na$	–2.71
Magnesium (Mg)	$Mg^{+2} + 2e^- \rightarrow Mg$	–2.36
Aluminum (Al)	$Al^{+3} + 3e^- \rightarrow Al$	–1.66
Zinc (Zn)	$Zn^{+2} + 2e^- \rightarrow Zn$	–0.76
Iron (Fe)	$Fe^{+2} + 2e^- \rightarrow Fe$	–0.44
Nickel (Ni)	$Ni^{+2} + 2e^- \rightarrow Ni$	–0.25
Tin (Sn)	$Sn^{+2} + 2e^- \rightarrow Sn$	–0.14
Lead (Pb)	$Pb^{+2} + 2e^- \rightarrow Pb$	–0.13
Hydrogen (H)	$2H^+ + 2e^- \rightarrow H_2$	0.0
Copper (Cu)	$Cu^{+2} + 2e^- \rightarrow Cu$	0.34
Mercury (Hg)	$Hg^{+2} + 2e^- \rightarrow Hg$	0.79
Silver (Ag)	$Ag^+ + e^- \rightarrow Ag$	0.80
Gold (Au)	$Au^{+3} + 3e^- \rightarrow Au$	1.50

TABLE 4.2 Electromotive Series of Elements That Form Cations in Solution. The Voltage Is that Developed by an Electrode of the Element Immersed in a Molal Solution (1 Mole of Ion/kg of Water)

$$Fe^\circ + CuSO_4 \rightarrow Cu^\circ + FeSO_4 \tag{4.3}$$

In comparing reactions (4.1) and (4.2), to produce one molecule of hydrogen requires two atoms of sodium but only one atom of magnesium, because sodium has a charge of +1, while the magnesium ion has a charge of +2. This provides one basis for the concept of equivalent weight. The equivalent weight of a cation is that weight which replaces 1.0 g of hydrogen from aqueous solution. Another way to determine equivalent weight is the molecular weight of a substance divided by its valence. Thus, the equivalent weight of sodium is equal to its molecular weight, and the equivalent weight of magnesium is half its molecular weight. Table 4.3 shows the molecular weights and equivalent weights for common compounds encountered in water treatment.

Common Name	Formula	Molecular Weight (g/mol)	Equivalent Weight (g/eq)
Table salt	NaCl	58.5	58.5
Caustic soda	NaOH	40	40
Salt cake	Na_2SO_4	142	71
Soda ash	Na_2CO_3	106	53
Limestone	$CaCO_3$	100	50
Quicklime	CaO	56	28
Slaked lime	$Ca(OH)_2$	74	37
Gypsum	$CaSO_4 \cdot 2H_2O$	172	86
Muriatic acid	HCl	36.5	36.5
Sulfuric acid	H_2SO_4	98	49
Aqua ammonia	NH_4OH	35	35

TABLE 4.3 Molecular Weights and Equivalent Weights of Common Water Treatment Compounds

Colloidal Systems

Some types of matter can be dispersed in water even though not truly soluble. Dispersion is accomplished by breaking down the material into extremely small particles, slightly larger than ions and molecules. Particles of this size, suspended in liquid, are called colloids.

The surface of almost all matter (glass, steel, plastic, etc.) has a residue of electric charges. This can lead to the development of high surface voltage, as demonstrated on a small scale by the discharge of a spark of static electricity on a cold dry day and on a large scale by lightning. As particles become smaller, the ratio of surface charge to mass increases exponentially. Assume that a cube of sand measuring 1.0 mm on each side is reduced to colloidal cubes of 100 nm (1 nm = 10^{-6} mm) on each side; this would produce 10^{12} colloidal particles with a total surface 10 000 times larger than the original grain with a correspondingly larger surface charge. It is this high surface charge that causes colloidal particles to repel one another, thus maintaining stability of the dispersion.

Solubility of Gases in Water

Like minerals, gases are soluble in water. Henry's law states that the amount of gas dissolved in water at a given temperature is directly proportional to the partial pressure of the gas above the water surface. Yet, each gas has its own solubility limit in water, just like any mineral. The atmosphere is approximately 20% oxygen and 80% nitrogen. At one atmosphere pressure [14.7 psia (101.35 kPaa)], the partial pressure of oxygen is 2.94 psia (20.27 kPaa), and the partial pressure of nitrogen is 11.76 psia (81.08 kPaa). At these partial pressures and standard temperature, the approximate concentration of oxygen in water is about 10 mg/L, while nitrogen is about 15 mg/L. Even though the partial pressure of nitrogen is four times higher than oxygen, less than twice as much goes into solution. If the total gas pressure at the water surface doubles, so would the concentration of oxygen and nitrogen in the water solution. Unlike most mineral salts, which become more soluble at higher temperatures, gases decrease in solubility as temperature rises.

Some gases react with water when in solution. For example, carbon dioxide (CO_2) reacts to form carbonic acid (H_2CO_3), which ionizes to produce hydrogen (H^+) and bicarbonate (HCO_3^-) ions [Eq. (4.4)]. Other ionizing gases include sulfur dioxide, hydrogen sulfide, and hydrocyanic acid, which form weak acids when dissolved in water.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{4.4}$$

On the other end of the scale is ammonia, which dissolves and ionizes to form a weak base:

$$NH_3 + H_2O \leftrightarrow NH_4OH \leftrightarrow NH_4^+ + OH^- \tag{4.5}$$

These are both equilibrium reactions, meaning that addition of more gas to the water produces more acidic conditions in Eq. (4.4) and more basic conditions in Eq. (4.5). On the other hand, addition of acid would drive Eq. (4.4) to the left. Similarly, addition of base in Eq. (4.5) would drive that reaction to the left.

Organic Compounds and Solubility in Water

Organic matter is a broad category that includes both natural and synthetic molecules containing carbon, usually hydrogen, and often other atoms like oxygen. All living matter is made up of organic molecules, and a wide variety of synthetic chemicals are organic. Organics can be extremely soluble in water (as is the case with alcohol and sugar) or may be quite insoluble (as are most plastics).

Most organics are unwanted contaminants in water. They can foul water systems, be food for bacteria that also cause fouling, or have harmful effects on aquatic life. Even at concentrations less than 1 mg/L, certain organic compounds may cause serious physiological effects. Modern technology makes it possible to analyze toxic organic materials such as pesticides at the µg/L level (1 µg of contaminant per liter of water). To put this in perspective, analyzing 1 µg/L is comparable to seeing a bottle cap on the earth's equator from an orbiting satellite.

There are an astounding variety of organic compounds in water, resulting from both nature and human activity. Many organic compounds in water are naturally occurring, like tannin and lignin from decaying wood. Tannin and lignin are generally present as colloidal suspensions in water. A water analysis does not show all of the individual organic molecules in a water sample, because of the great variety of compounds that may be present. Generally, an analyst looks for specific compounds, like polychlorinated biphenyls (PCB) or adsorbable organic halogen (AOX) using a special analytical method for each type of compound.

A variety of nonspecific tests are used to give a measure of the organic content of water. Examples of these methods include biochemical oxygen demand (BOD), total organic carbon (TOC), and color. Interpretation can be difficult, because these analyses cannot easily convert to a concentration of typical organics. In addition, these analyses may not follow the same pattern of increase or decrease over time in a given water. Figure 4.15 shows the diversity of change in color, TOC, and BOD in the Hackensack River in New Jersey, United States.

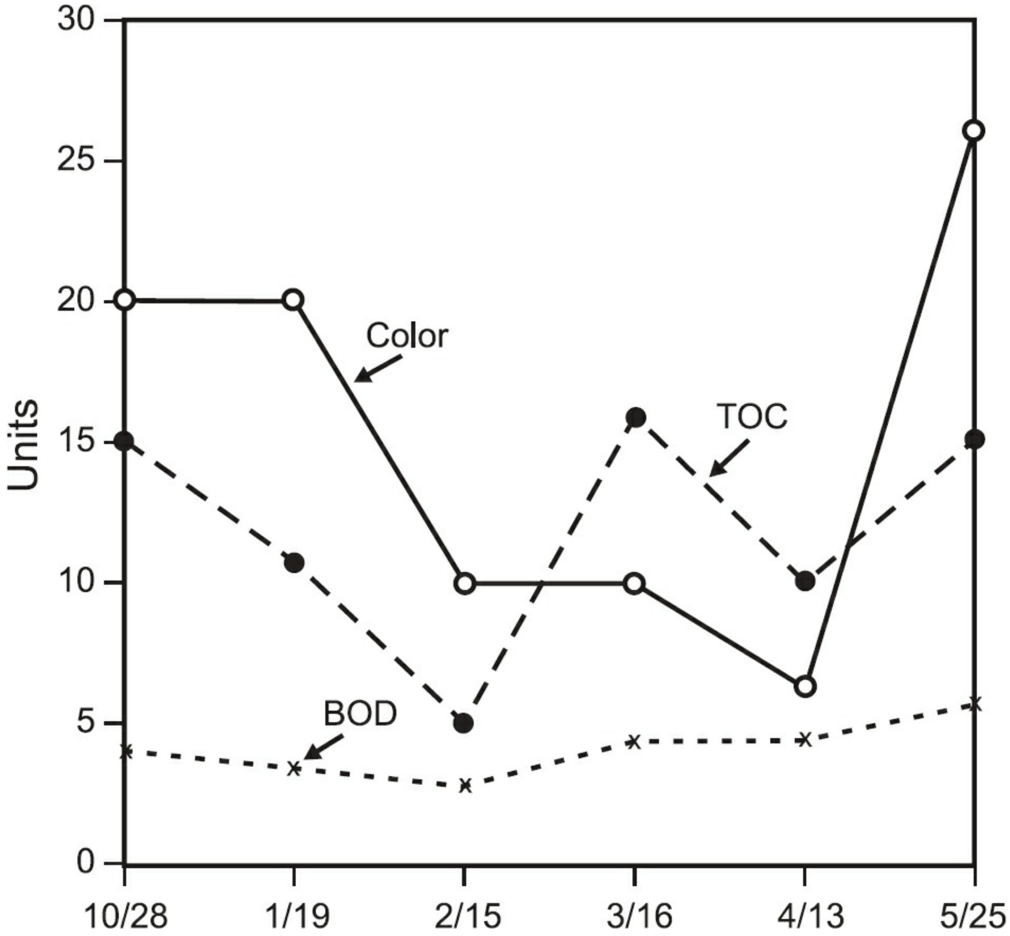


FIGURE 4.15 Variation of color, TOC, and BOD in the Hackensack River in New Jersey, United States.

Solubility Product Constants

There are a few rules-of-thumb to use in determining the solubility of any chemical compound in water:

- The salts of sodium, potassium, and ammonium are highly soluble.
- Mineral acids (H_2SO_4, HCl, etc.) are soluble.
- Most halides (Cl, Br, I, etc.) are soluble, except for fluoride.
- Certain heavy metal cations (Pb and Ag) form insoluble halides.
- Most carbonates, hydroxides, and phosphates are only slightly soluble, with the exception of those associated with Na^+, K^+, and NH_4^+.

According to the solubility product concept, the concentration of cations multiplied by the concentration of anions gives a product, which is a constant at a given temperature. For calcium carbonate, a simple example, this expression would be:

$$K_s = [\mathrm{Ca}^{+2}][\mathrm{CO}_3^{-2}] \tag{4.6}$$

The ions in square brackets indicate the concentration of either calcium or carbonate in mol/L. The solubility product is expressed in $\mathrm{mol}^2/\mathrm{L}^2$. In a reaction where more than a single cation and anion are formed, the expression is more involved, as with magnesium hydroxide:

$$\mathrm{Mg(OH)}_2 \leftrightarrow \mathrm{Mg}^{+2} + 2\mathrm{OH}^- \tag{4.7}$$

$$K_s = [\mathrm{Mg}^{+2}][\mathrm{OH}^-]^2 \tag{4.8}$$

The units of K_s for magnesium hydroxide are $\mathrm{mol}^3/\mathrm{L}^3$.

In the case of $\mathrm{CaCO_3}$, this mathematical expression is the equation for a hyperbola (Fig. 4.16). The solubility of calcium carbonate is determined by the calcium and carbonate concentrations at any given point on the curve. The introduction of extra carbonate ions reduces the calcium concentration, at a given temperature, since the solubility product is constant. The solubility product makes it possible to calculate the residual solubility of a chemical after chemical treatment to remove a mineral from water by precipitation.

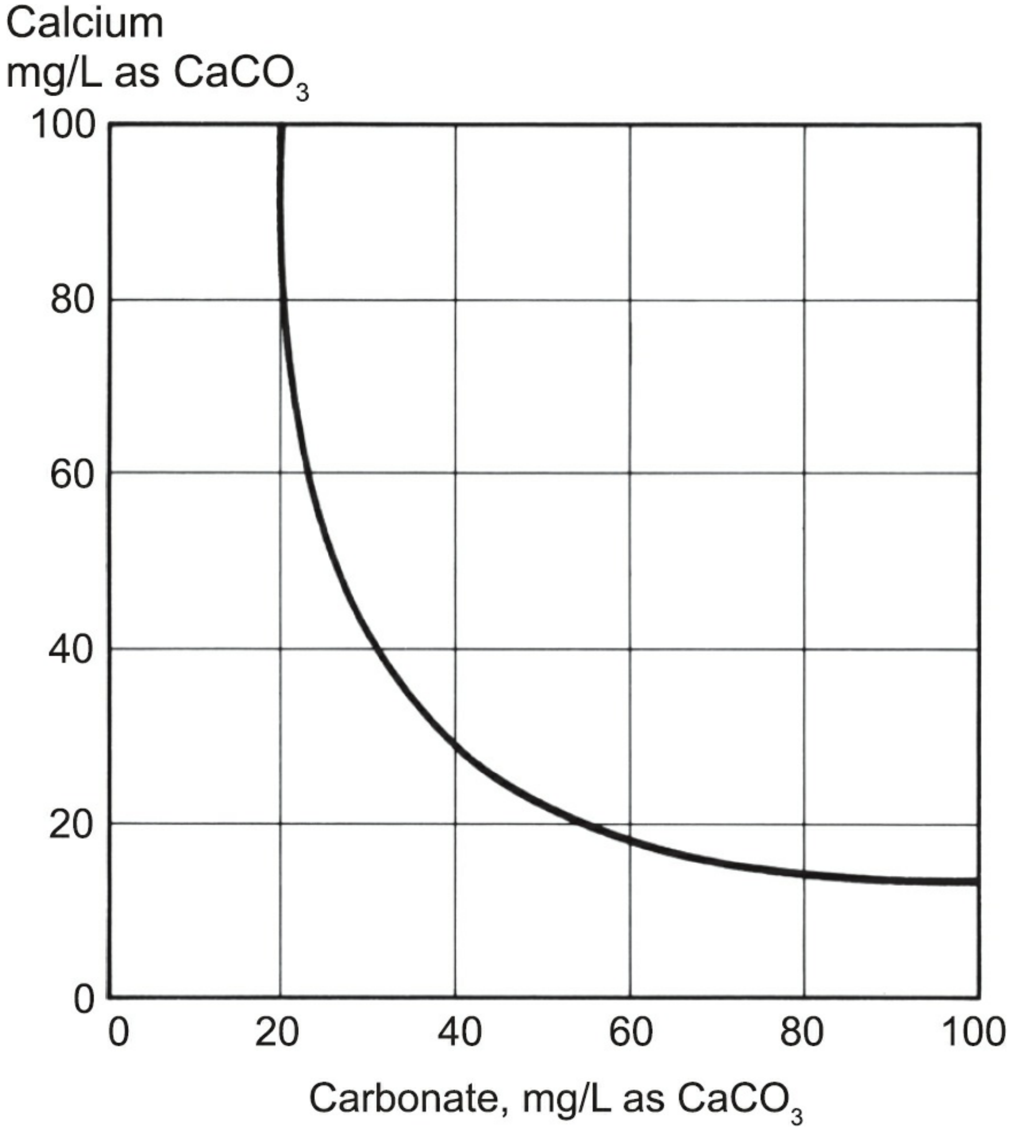


FIGURE 4.16 Curve showing the balance of calcium ions versus carbonate ions in saturated $CaCO_3$ solutions forms hyperbola.

Foreign Ion Effect

Ions in solution can associate themselves with one another. For example, calcium may be present in water as Ca^{+2}, or it may exist as $CaHCO_3^+$ or $CaOH^+$. Magnesium may be present in a variety of ionic forms, for example, Mg^{+2} and $MgHCO_3^+$. The formation of ion pairs and other types of complexes in solution can significantly affect the solubility of minerals like calcium carbonate.

Because of the great variety of ions in most water systems, a pure precipitate, such as $CaCO_3$, rarely forms. The inclusion of foreign ions in the precipitate and the formation of a variety of ion pairs in the solution, in effect, increase the solubility of $CaCO_3$. Even if pure $CaCO_3$ precipitates, it may form two kinds of crystals, calcite (the more stable) and aragonite, which have different solubility. Therefore, the solubility product is of limited value in predicting actual treatment results. More detail on this will be given later in this chapter, in the discussion of calcium carbonate solubility.

Other Effects on Solubility

Another factor affecting solubility is the presence of organic matter dissolved in water. It is well known that the residual calcium from lime softening of sewage at ambient temperature is 2 to 3 times the calcium solubility in freshwater. This increased calcium solubility presumably is due to organic complexes. If the same sewage is heated over about 150°F (66°C), the reactions with lime are about the same as obtained with freshwater. Inexplicably, the same effect is not observed with magnesium precipitation.

One example of complex effects on precipitation is found in the coagulation of water with alum [$Al_2(SO_4)_3 \cdot 18H_2O$], where the following reaction would be expected:

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2SO_4 \tag{4.9}$$

However, analysis of the precipitated floc shows the presence of sulfate in the solids, indicating that some SO_4^{-2} anions replaced OH^- anions in the lattice of the precipitate. This affects the solubility of aluminum hydroxide.

A final factor affecting solubility of these slightly soluble compounds is the ionic strength of the aqueous solution. The higher the concentration of ions in solution, the more soluble is the precipitate. This means that $CaSO_4$, for example, is more soluble in seawater, containing about 30 000 mg/L NaCl, and in oilfield brines, containing up to 150 000 mg/L NaCl, than in freshwater containing 100 mg/L dissolved solids. The solubility increase with ionic strength is shown in Fig. 4.17. The solubility product then, is seen to be a useful concept when used qualitatively, or developed empirically for a specific system, but of limited value when taken directly from a handbook.

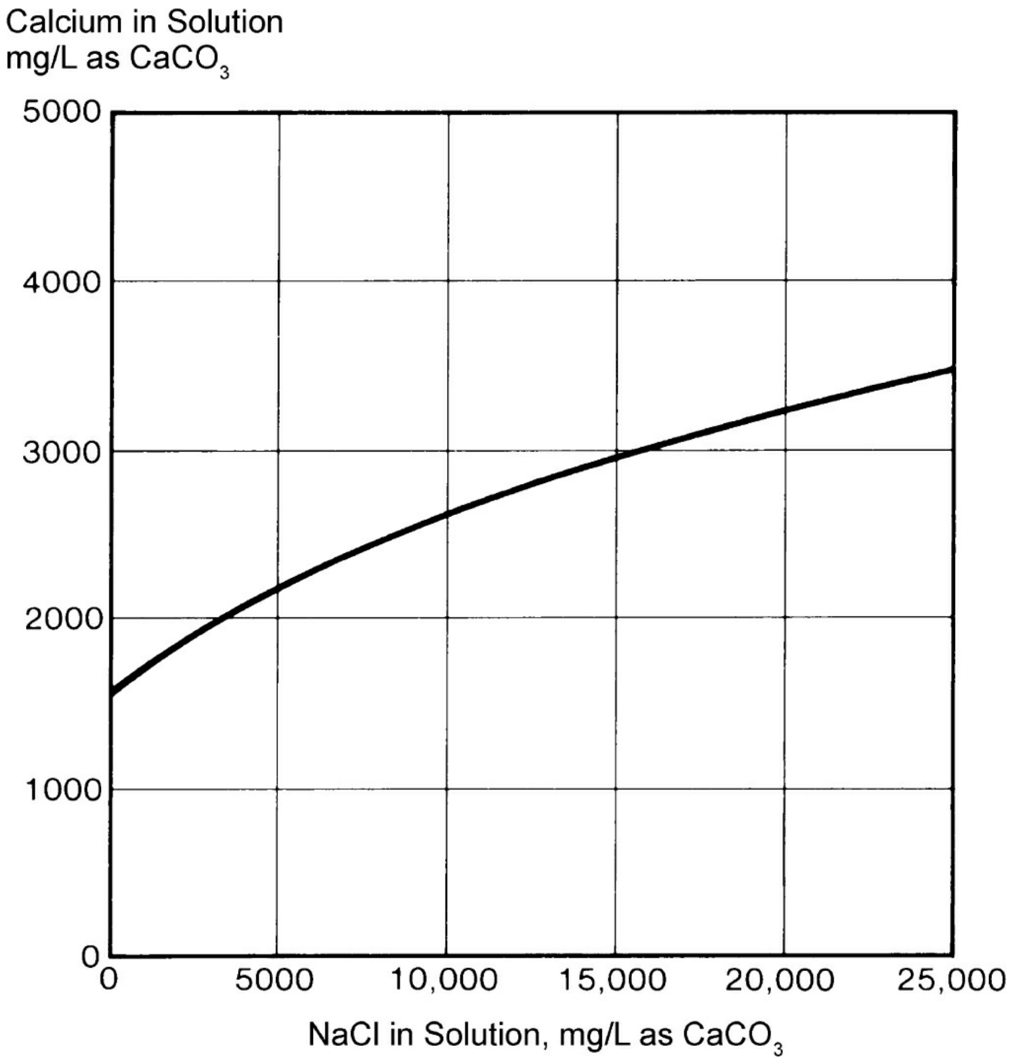


FIGURE 4.17 Calcium sulfate (gypsum) solubility increases with increasing sodium chloride concentration.

Equilibrium

Another concept closely related to the solubility product is the equilibrium constant, also called the dissociation constant. Some reactions go to completion, using all of the reactants, assuming they are in the proper proportion. Not all chemical reactions go to completion, because the products of the reaction exert a restraining effect on the reactants.

An example of a reaction that goes to completion, sometimes explosively, is shown in Eq. (4.10). The arrow shows this reaction going in only one direction.

$$2H_2 + O_2 \rightarrow 2H_2O \tag{4.10}$$

An example of an equilibrium reaction is the precipitation of calcium carbonate, in Eq. (4.11). In this reaction, the precipitation of calcium carbonate is balanced by the dissolution of calcium carbonate, as illustrated by the arrow pointing in both directions. At equilibrium, the rate of precipitation is exactly equal to the rate of dissolution.

$$Ca^{+2} + CO_3^{-2} \leftrightarrow CaCO_3 \tag{4.11}$$

This equilibrium reaction can be expressed mathematically by the equation for the equilibrium constant (K):

$$K = [Ca^{+2}][CO_3^{-2}]/[CaCO_3] \tag{4.12}$$

Recall that the bracketed values are expressed in concentration units, usually mol/L.

For the dissociation of electrolytes in water, the degree of ionization can be calculated, as shown for the reactions in Table 4.4.

Reaction	Degree of Ionization
$NaCl \leftrightarrow Na^+ + Cl^-$	0.85
$Na_2CO_3 \leftrightarrow 2Na^+ + CO_3^{-2}$	0.70
$HCl \leftrightarrow H^+ + Cl^-$	0.92
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	0.0017
$NaOH \leftrightarrow Na^+ + OH^-$	0.91
$NH_4OH \leftrightarrow NH_4^+ + OH^-$	0.013

TABLE 4.4 Degree of Ionization of Electrolytes [0.1 Normal Solution at 64°F (18°C)], Showing That Some Compounds Are Highly Ionized and Others Are Only Slightly Ionized in Water

Strong electrolytes, such as sodium chloride, completely ionize in freshwater, so that the equilibrium constant is of no value in calculations involving this particular salt. However, calculations involving weak electrolytes rely on the equilibrium constant to show the distribution of the reacting materials and products both in their ionic and nonionized forms. This provides data useful in selecting chemical processes for removal of various contaminants from water. For example, the equilibrium constants for gases that ionize in water, such as hydrogen sulfide and ammonia, make it possible to calculate the optimum pH values for removal of these materials from water in their gaseous form. Typical dissociation constants are shown in Table 4.5.

Compound	Formula	Dissociation Constant
Calcium hydroxide	$Ca(OH)_2$	$3.74 \cdot 10^{-3}$
Phosphoric acid	H_3PO_4	$7.5 \cdot 10^{-3}$
Lead hydroxide	$Pb(OH)_2$	$9.6 \cdot 10^{-4}$
Ammonium hydroxide	NH_4OH	$1.8 \cdot 10^{-5}$
Acetic acid	CH_3COOH	$1.8 \cdot 10^{-5}$
Carbonic acid	H_2CO_3	$4.3 \cdot 10^{-7}$
Hypochlorous acid	$HOCl$	$3.5 \cdot 10^{-8}$
Boric Acid	H_3BO_3	$5.8 \cdot 10^{-10}$

TABLE 4.5 Dissociation Constants of Weak Acids and Bases

Solid Reactants

There are two distinctive mechanisms by which materials dissolved in water react with solids: adsorption and ion exchange.

Adsorption

Adsorption is the adhesion of a layer of molecules or colloidal particles to the surface of a solid, which is usually porous. The gas mask is a common illustration of the use of this process. The mask contains a canister of adsorbent material, usually activated carbon, capable of removing and storing hazardous or toxic gases, so that the person wearing the mask can safely breathe in a contaminated atmosphere. In water systems, activated carbon removes organic molecules that cause taste and odor problems. Another example is the adsorption of silica (SiO_2), a negatively charged colloid, on freshly precipitated magnesium hydroxide [$Mg(OH)_2$].

The amount of adsorbent required for effective removal cannot be universally determined for all waters from a single equation. However, for any given system, experimental data are easily plotted on a semi-logarithmic graph, producing a straight line. This graph is known as the Freundlich isotherm (Figs. 4.18 and 4.19). An equation unique to a given system can be determined from the graph and then used for dosage adjustment.

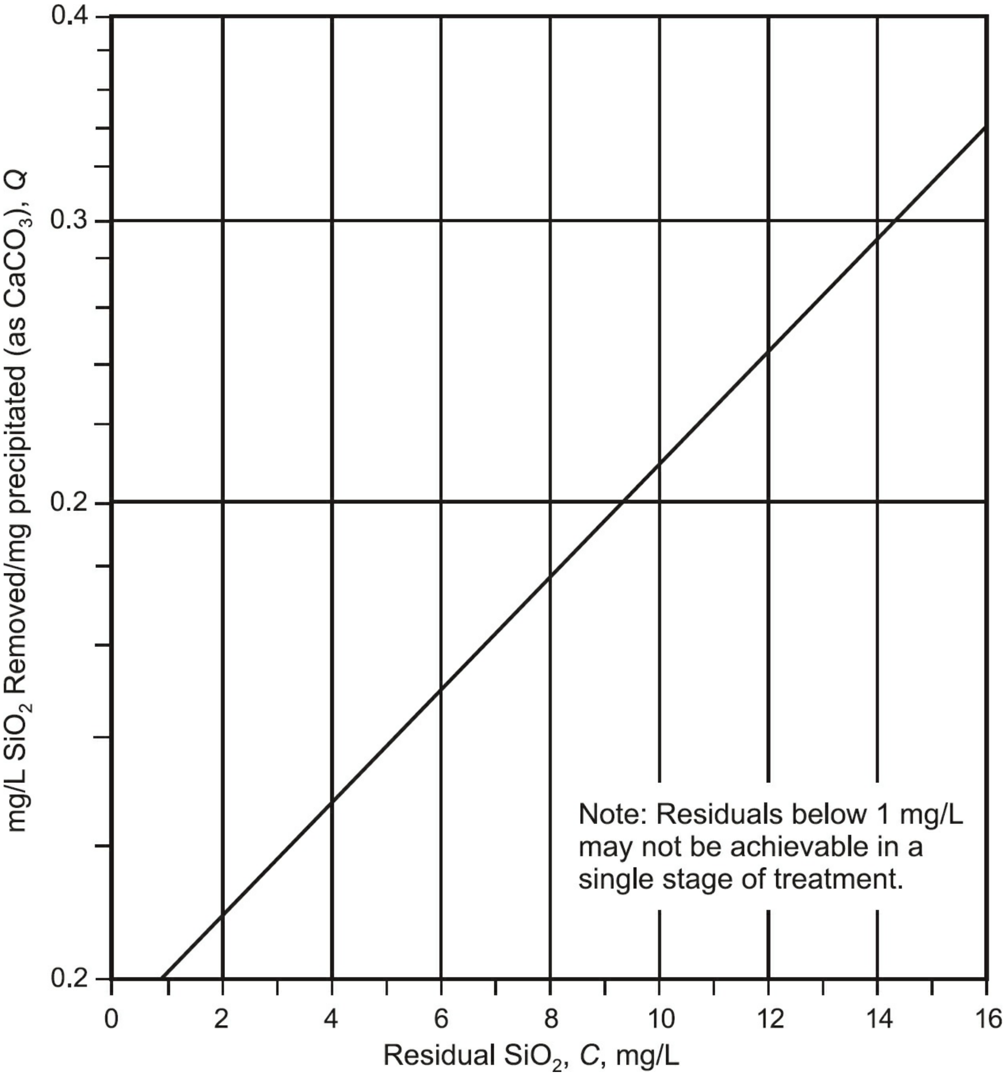


FIGURE 4.18 Freundlich isotherm showing effectiveness of SiO_2 adsorption by $Mg(OH)_2$. The formula for the isotherm is $Q = kC^{1/N}$.

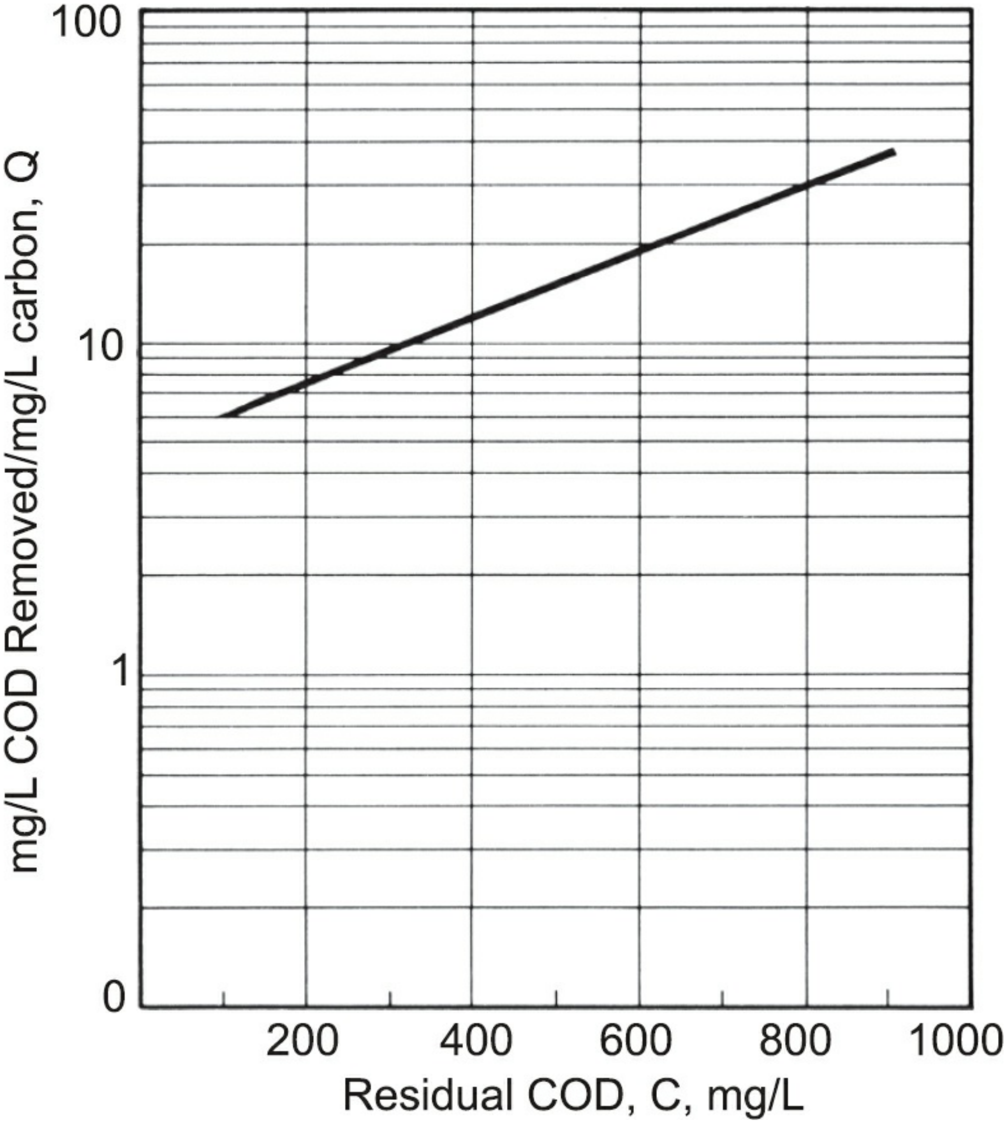


FIGURE 4.19 Freundlich isotherm showing effectiveness of organic adsorption (COD) by activated carbon. The formula for the isotherm is $Q = kC^{1/N}$.

Ion Exchange

Ion exchange is the process of removing unwanted ions from solution by an equivalent exchange for preferred ions supplied by a solid having a special structure. The solid is an ion exchange material that has a stronger binding affinity for the unwanted ion. This ion exchange material must be recharged periodically with the preferred ions. In this regeneration, the accumulated, unwanted ions are flushed to waste. Removal of calcium ions by sodium ion exchange is shown by the following reaction, where the letter X represents the cation exchange solid:

$$Ca^{+2} + Na_2X \rightarrow CaX + 2Na^{+} \tag{4.13}$$

Many types of clay have ion exchange properties. This is an important aspect of soil chemistry and plant nutrition. One of these clays, clinoptilolite, is used to remove ammonia from wastewater. However, most ion exchangers are synthetic organic materials formulated for specific applications.

Complexing Agents

A complex is a species formed by the association of two or more simpler species, each capable of independent existence. When one of these species is a metal ion, the resulting entity is known as a metal complex. Complexing agents are called ligands (or sequestrants or chelants) that act as an electron donor in a complex reaction. The ligand must have at least one pair of electrons to donate to the metal ion, forming a shared electron pair bond (coordinate covalent bond). A characteristic feature of such a complex is that the metal ion occupies a central position in the matrix.

A ligand with one electron pair donor site is an undentate ligand. An example is ammonia (NH_3) as shown in Fig. 4.20. The water molecule (H_2O) is shown as a ligand. A bidentate ligand has two electron pair donor sites, such as ethylenediamine ($NH_2CH_2CH_2NH_2$). The donor sites are the nitrogen atoms, when complexed with copper (Cu^{2+}). The ethylenediamine forms a five-member ring with copper. This is a chelate ring. When this ring system forms, it adds stability to the complex. A multidentate ligand has two or more electron pair donor sites. Examples of common chelates used in water treatment are nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). Both form multiple chelation rings with metal ions.

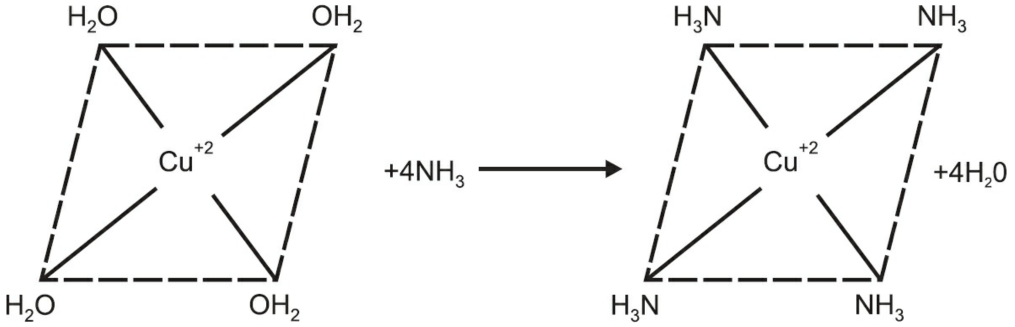


FIGURE 4.20 Example of a Cu^{+2} complex with ammonia.

A chelating agent is usually an organic molecule, which is soluble in water and undergoes reactions with metal ions that maintain the complexed ions in solution. A common chelate is the sodium salt of EDTA. Added to water, this chelant first reacts with a coordination site on the calcium cation, which forms a coordinate covalent bond, pulling the rest of the molecule into the coordination sphere. These interactions prevent the formation of $CaCO_3$ scale in water as follows:

$$Ca^{+2} + Na_4EDTA \rightarrow CaEDTA^{-2} + 4Na^{+} \tag{4.14}$$

Figure 4.21 shows the coordination complex formed with calcium. The bonding is through the nitrogen atoms of the ethylenediamine backbone of the chelant and through the oxygen atoms of the four acetic acid functional groups.

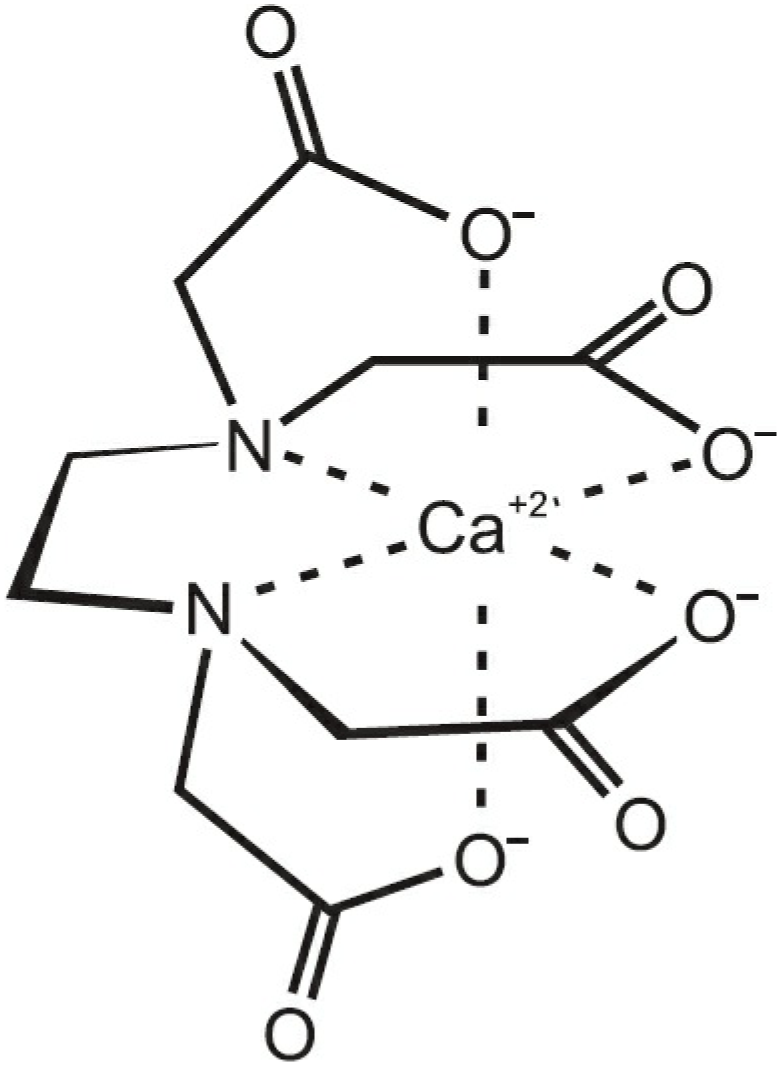


FIGURE 4.21 Calcium-EDTA complex, with the coordinate covalent bonds shown by the dashed lines.

Low molecular weight polyacrylate-based polymers can complex hardness ions in water by the same mechanism as chelates. The molecular weight of these polymers is typically in the range of 1000 to 10 000 g/mol, although other size polymers can be used. Example reactions are:

$$\mathrm{Ca^{+2} + (polymer)^{-40} \rightarrow Ca(polymer)^{-38}} \tag{4.15}$$

$$\mathrm{Ca^{+2} + Ca_9(polymer)^{-22} \rightarrow Ca_{10}(polymer)^{-20}} \tag{4.16}$$

Although at room temperature, polyacrylates form weaker complexes than EDTA and NTA, based on experimental and field boiler results, it has been found that they form stronger complexes at elevated temperatures. The synthetic polyacrylate polymers are significantly less corrosive to boiler internals than chelates.

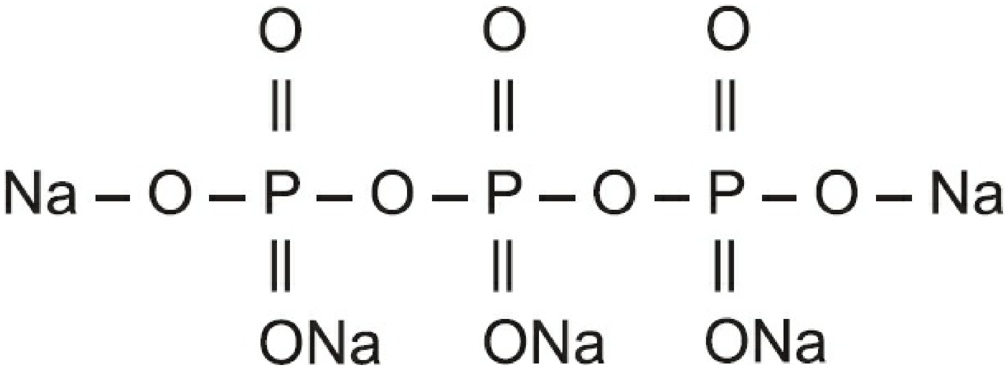
Low molecular weight polymers are excellent dispersants, which may operate by complexation. When compounds precipitate, they are usually deficient in one of the counter ions. This causes an imbalance of charge for a hydrophilic particle or colloid. Iron hydroxides are an excellent example. In industrial applications, iron corrodes to form ferrous hydroxide and ferric hydroxide. When this occurs, the system is usually deficient in hydroxide ions, resulting in an ineffectively shielded central metal ion, creating a positive surface attraction. Negatively charged polymers are attracted and adsorbed, shielding the central metal ion and increasing the surface partial negative charge. Like charge particles repulse each other, leading to dispersion.

On the other hand, very high molecular weight polymers (molecular weight in the millions) are used to neutralize surface charge on suspended material in water, leading to coagulation and settling of particles. This process is used in pretreatment for both industrial and municipal applications, as well as waste treatment operations.

A number of natural organic materials in water such as humic acid, tannins, and lignin have complexing ability. Because of their complexing abilities, some organic materials interfere with certain water softening processes.

Somewhat related to complex formation is the process of threshold treatment. A variety of phosphate compounds called polyphosphates is used in this process to prevent formation of deposits. $CaCO_3$ scale can be prevented in scale-forming water treated with only 0.5 mg/L of polyphosphate. The amount of polyphosphate required for effective scale control is far less than that required for complex formation on a stoichiometric basis, hence the name threshold treatment. Polyphosphates can hold iron (Fe) and manganese (Mn) ions in solution in an environment where they would otherwise precipitate, for example, in the presence of oxygen or chlorine at pH over 8.

Polyphosphates are produced by dehydration of one or more orthophosphate (PO_4^{-3}) compounds. Using different mixtures of orthophosphates can vary the kinds of condensed phosphates formed. Condensed phosphates form chains containing the P - O - P group, as shown in Fig. 4.22 for tripolyphosphate. See Chap. 19 for more details on polyphosphates and other materials used to prevent scale and deposition.



$$\begin{array}{ccccccccccccc} & & & & O & & & & O & & & & O \\ & & & & \| & & & & \| & & & & \| \\ Na & - & O & - & P & - & O & - & P & - & O & - & P & - & O & - & Na \\ & & & & \| & & & & \| & & & & \| \\ & & & & ONa & & & & ONa & & & & ONa \end{array}$$

FIGURE 4.22 Polymer-like structure of tripolyphosphate.

Application of Water Chemistry

Several key aspects of water are critical for the water chemist or anyone working with water system operation in municipal, industrial, or institutional applications. These include an understanding of the actions of various cations in water, alkalinity and pH relationships, mineral solubility, and oxidation and reduction concepts. A water chemist or system operator must know how these dynamic factors affect the systems that use water.

Hardness and Analysis of Water

One common denominator in the majority of water problems is hardness, which is a folk term inherited from the past with its origins in household use of water for washing. In some places, surface or well waters were hard to use for the family laundry. More soap was needed to produce suds in these hard waters, and clothes would not be cleaned as desired. To improve this, many houses had a rain barrel or a cistern to collect soft rainwater for washing. Indeed, this relation between hardness and soap demand was so fundamental that a standard solution of soap was used for many years to determine the hardness of water. Thus, tradition defines hardness as the soap-consuming capacity of water. For practical purposes, hardness equals the calcium and magnesium content of water, although heavy metals such as iron and manganese also consume soap.

Hardness then, is the sum of calcium and magnesium cations in water, independent of the nature of the anions present. The quantity has traditionally been expressed in terms of calcium carbonate equivalents, that is, mg/L as $CaCO_3$. This is a fortuitous choice because the molecular weight of $CaCO_3$ is 100, and its equivalent weight is 50, providing a convenient unit for expressing all ions in water, rather than showing each with its own equivalent weight. Historically, water analyses reported all constituents using the calcium carbonate equivalent concept.

The practice of reporting all components as $CaCO_3$ equivalents is still a widely, but not universally, used form for reporting a water analysis. There are two other forms also used around the world: elemental concentrations, usually in mg/L or ppm; and equivalents per million (epm) or equivalents per liter (eq/L). Equivalents per liter are calculated by dividing the concentration of each ion in mg/L by the equivalent weight. Table 4.6 compares these three methods of reporting a water analysis.

Component	Concentration, (mg/L as Ion)	Concentration, epm or eq/L	Concentration, (mg/L as $CaCO_3$)
Calcium	46	2.30	115
Magnesium	14	1.15	57.7
Sodium	32	1.40	69.8
Potassium	2.7	0.07	3.5
Total cations	94.7	4.92	246
Bicarbonate	154	2.53	126
Sulfate	67	1.39	69.7
Chloride	34	0.96	47.9
Nitrate	3.6	0.06	2.9
Total anions	258.6	4.94	246.5
Total hardness		3.45	172.7
Total dissolved solids (TDS)	362		
Conductivity, µS/cm	483		
pH (pH units)	7.5		
Silica	8.3		
Iron	0.03		
Color, APHA* units	15		

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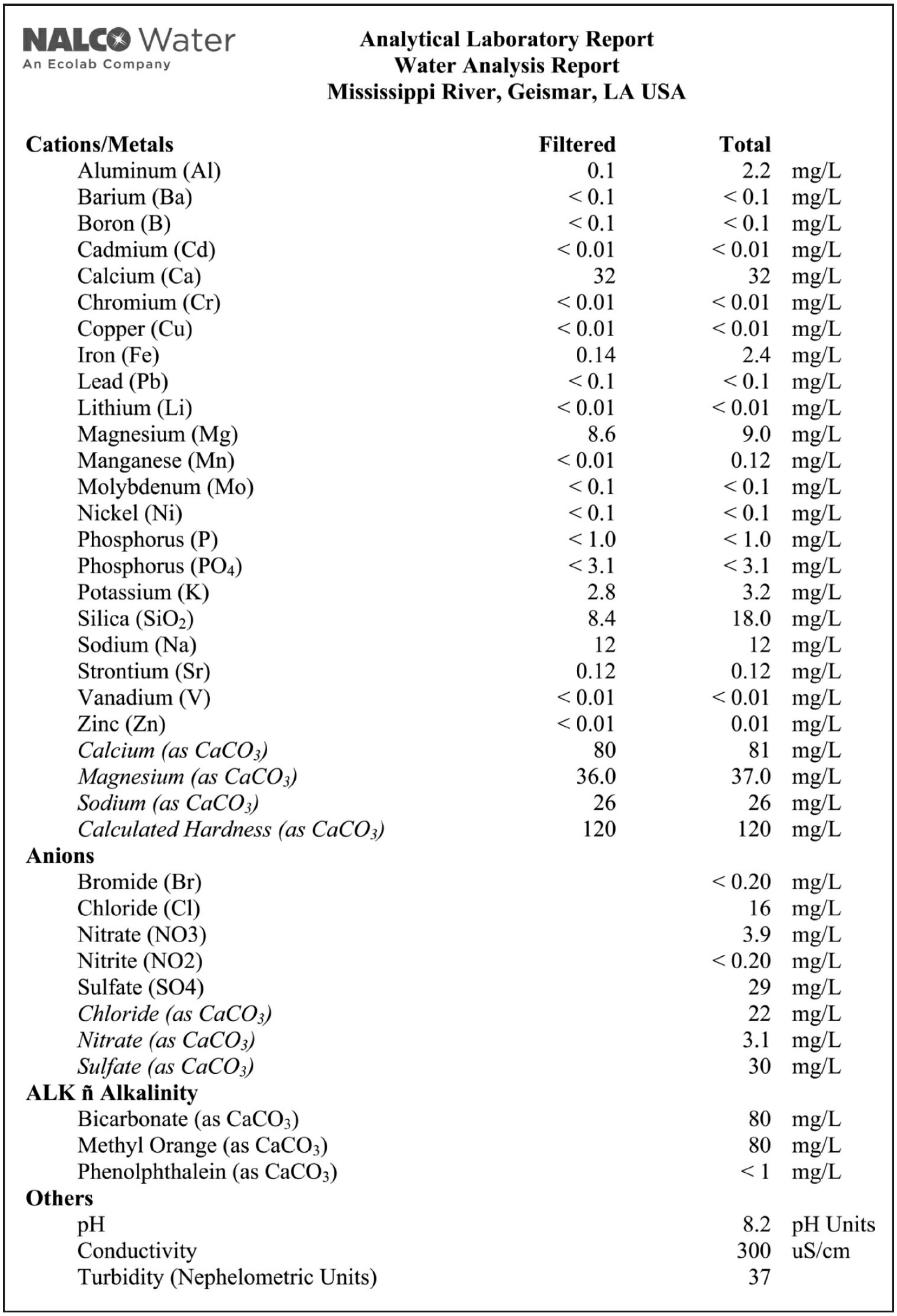
*American Public Health Association.

TABLE 4.6 Comparison of Water Analysis Reporting Methods on Mississippi River Water at Vicksburg, Mississippi

In the third column, the sum of all the anions determined by analysis is 4.94 epm. This slightly exceeds the total cations as determined by analysis (4.92 epm). Since the water must be electrically neutral, the sum of the cations should equal the sum of the anions; however, it is not unusual to find a modest discrepancy, because some minor constituents (perhaps ammonia, a cation) have not been reported, or because of limitations of individual ion tests.

Modern analytical methods make it easier to report the analyses in terms of elemental concentrations. These methods make possible the detection of many more components found in water. Nalco includes the concentrations of the major components like calcium, magnesium, alkalinity, sodium, and chloride reported in $CaCO_3$ equivalents. Compare the modern analysis of the

Mississippi River shown in Fig. 4.23 to that in Table 4.6.



NALCO Water
An Ecolab Company

Analytical Laboratory Report
Water Analysis Report
Mississippi River, Geismar, LA USA

Cations/Metals	**Filtered**	**Total**	
Aluminum (Al)	0.1	2.2	mg/L
Barium (Ba)	< 0.1	< 0.1	mg/L
Boron (B)	< 0.1	< 0.1	mg/L
Cadmium (Cd)	< 0.01	< 0.01	mg/L
Calcium (Ca)	32	32	mg/L
Chromium (Cr)	< 0.01	< 0.01	mg/L
Copper (Cu)	< 0.01	< 0.01	mg/L
Iron (Fe)	0.14	2.4	mg/L
Lead (Pb)	< 0.1	< 0.1	mg/L
Lithium (Li)	< 0.01	< 0.01	mg/L
Magnesium (Mg)	8.6	9.0	mg/L
Manganese (Mn)	< 0.01	0.12	mg/L
Molybdenum (Mo)	< 0.1	< 0.1	mg/L
Nickel (Ni)	< 0.1	< 0.1	mg/L
Phosphorus (P)	< 1.0	< 1.0	mg/L
Phosphorus (PO_4)	< 3.1	< 3.1	mg/L
Potassium (K)	2.8	3.2	mg/L
Silica (SiO_2)	8.4	18.0	mg/L
Sodium (Na)	12	12	mg/L
Strontium (Sr)	0.12	0.12	mg/L
Vanadium (V)	< 0.01	< 0.01	mg/L
Zinc (Zn)	< 0.01	0.01	mg/L
Calcium (as $CaCO_3$)	80	81	mg/L
Magnesium (as $CaCO_3$)	36.0	37.0	mg/L
Sodium (as $CaCO_3$)	26	26	mg/L
Calculated Hardness (as $CaCO_3$)	120	120	mg/L
Anions			
Bromide (Br)		< 0.20	mg/L
Chloride (Cl)		16	mg/L
Nitrate (NO3)		3.9	mg/L
Nitrite (NO2)		< 0.20	mg/L
Sulfate (SO4)		29	mg/L
Chloride (as $CaCO_3$)		22	mg/L
Nitrate (as $CaCO_3$)		3.1	mg/L
Sulfate (as $CaCO_3$)		30	mg/L
ALK ñ Alkalinity			
Bicarbonate (as $CaCO_3$)		80	mg/L
Methyl Orange (as $CaCO_3$)		80	mg/L
Phenolphthalein (as $CaCO_3$)		< 1	mg/L
Others			
pH		8.2	pH Units
Conductivity		300	uS/cm
Turbidity (Nephelometric Units)		37	

FIGURE 4.23 Analysis of Mississippi River water using modern instrumental methods of analysis.

Wastewaters usually contain a number of ions that may not be shown in this illustration. Wastewater composition depends on the kind of plant operations through which the water has passed. For example, heavy metals such as zinc and copper may be present in waste from plating operations, organics are present in sewage treatment plant effluent, and fluoride may be present as an anion or an anionic complex in wastewater from glass manufacturing.

Alkalinity and pH Relationships

A working knowledge of the basics of pH and alkalinity relationships is necessary for any water system operation. The relationships between the forms of alkalinity as a function of pH can be determined with simple equations. This information can help diagnose problems with pH measurement equipment and as a check of whether a pH measurement is reasonable, based on the alkalinity.

The pH of Water

Certainly, pH is one of the most fundamental symbols for water treatment specialists. It is the convention used to specify given water along the range of acidity-alkalinity. A good understanding of the effect of pH on systems to be treated is valuable. Applying these concepts to the practice of water treatment is the objective.

The equilibrium reaction at the heart of an understanding of pH is the dissociation of the water molecule into hydrogen and hydroxyl (hydroxide) ions:

$$H_2O \leftrightarrow H^+ + OH^- \tag{4.17}$$

Dissociation of water into hydrogen and hydroxyl ions is governed by the dissociation constant in Eq. (4.18). This book will use the hydrogen ion (H^+) for simplicity rather than the more correct hydronium ion (H_3O^+).

$$K_w = [H^+][OH^-] = 10^{-14} \tag{4.18}$$

This means that as the hydrogen ion concentration decreases, the hydroxide ion concentration increases proportionally. At neutrality, where $[H^+]$ and $[OH^-]$ are equal, there are only 10^{-7} mol/L of each ion. This H^+ ion concentration equates to a concentration of only 0.005 mg/L as $CaCO_3$. Since dealing with such low concentrations is inconvenient, the pH scale was devised. The term pH is defined as the negative logarithm of the hydrogen ion concentration $[H^+]$:

$$\mathrm{pH} = -\log[\mathrm{H}^+] \tag{4.19}$$

The pH of 7.0, where both concentrations are equal, is the neutral point. Numbers below 7.0 indicate an increasing concentration of $[H^+]$ and thus an increase in acidity. Above 7.0, the $[OH^-]$ and hence the alkalinity is increasing. The pH scale is an indicator of the balance between hydrogen and hydroxide ions. It is not a quantitative measure of the level of acid or alkaline substances dissolved in water. Other ions like dissolved carbon dioxide, bicarbonate, and carbonate can affect the acidity or alkalinity of water. These materials affect the pH only to the extent that they liberate H^+ or OH^-.

The dissociation constant K_w changes with temperature and concentration of salts in the water. This must be taken into account when interpreting data involving pH. For example, many water applications operate at high temperature, and samples from the system are usually cooled before analysis. The H^+ and OH^- concentrations measured on the cooled sample, even though different from those in the hot system, are often used for control purposes. This practice can cause a system to operate at the wrong pH. Table 4.7 shows the variation of the pK_w ($-\log K_w$) as a function of temperature. Since K_w decreases as temperature increases, the pH of water decreases as it is heated to higher temperature (assuming no change in gas concentration, such as carbon dioxide).

Temperature, °F (°C)	pK_w
32 (0)	14.93
41 (5)	14.73
50 (10)	14.53
59 (15)	14.35
68 (20)	14.17
77 (25)	14.00
86 (30)	13.83
122 (50)	13.26

TABLE 4.7 Change of Dissociation Constant of Water versus Temperature

The hydrogen ion concentration can be measured with a pH meter. It can also be titrated, when the concentration becomes large enough to be detectable by chemical analysis. Since pH is a logarithmic function, the hydrogen ion concentration increases by a factor of 10 for each unit of pH reduction.

When the pH drops below approximately 5, the hydrogen ion begins to reach mg/L concentrations, enough to be determined by titration, using the correct organic dye indicator. The chemical indicator originally used for this purpose was methyl orange, changing color at pH 4.2 to 4.4. The color change of this indicator was so subtle that a new indicator was found to give a more pronounced color change. The new indicator produces a blue color on the alkaline side and red on the acid side, with gray at the endpoint. Even though this special indicator has replaced methyl orange, the measurement of total alkalinity by this titration is still called methyl orange alkalinity or M alkalinity. Total or M alkalinity exists above the approximate pH range of 4.2 to 4.4. Below this pH, free mineral acidity (FMA) exists. An approximate relationship between pH value and mineral acidity is shown in Table 4.8.

H^+, mg/L as $CaCO_3$	pH
2–3	4.3
4–5	4.0
6–7	3.9
8–9	3.8
10–11	3.7
12–13	3.6
14–16	3.5
17–20	3.4
21–25	3.3
31–40	3.1
41–50	3.0

TABLE 4.8 Mineral Acidity Shown as the Concentration of H^+ Ions versus pH

A pH meter can also determine the hydroxyl ion concentration, since the following relationships hold:

$$\text{pOH} = 14 - \text{pH} \tag{4.20}$$

$$\text{pOH} = -\log[\text{OH}^-] \tag{4.21}$$

When the pH of a water solution exceeds about 9.6 to 9.8, a measurable concentration of hydroxyl ions begins to appear. The hydroxyl alkalinity (caustic or OH^- alkalinity) can be determined either by using a pH meter or by titration. The relationship between hydroxyl alkalinity and pH is shown in Fig. 4.24. The hydroxyl ion does not have an appreciable effect on alkalinity until pH is above 9.3, where the OH^- concentration is above 1 mg/L as $CaCO_3$.

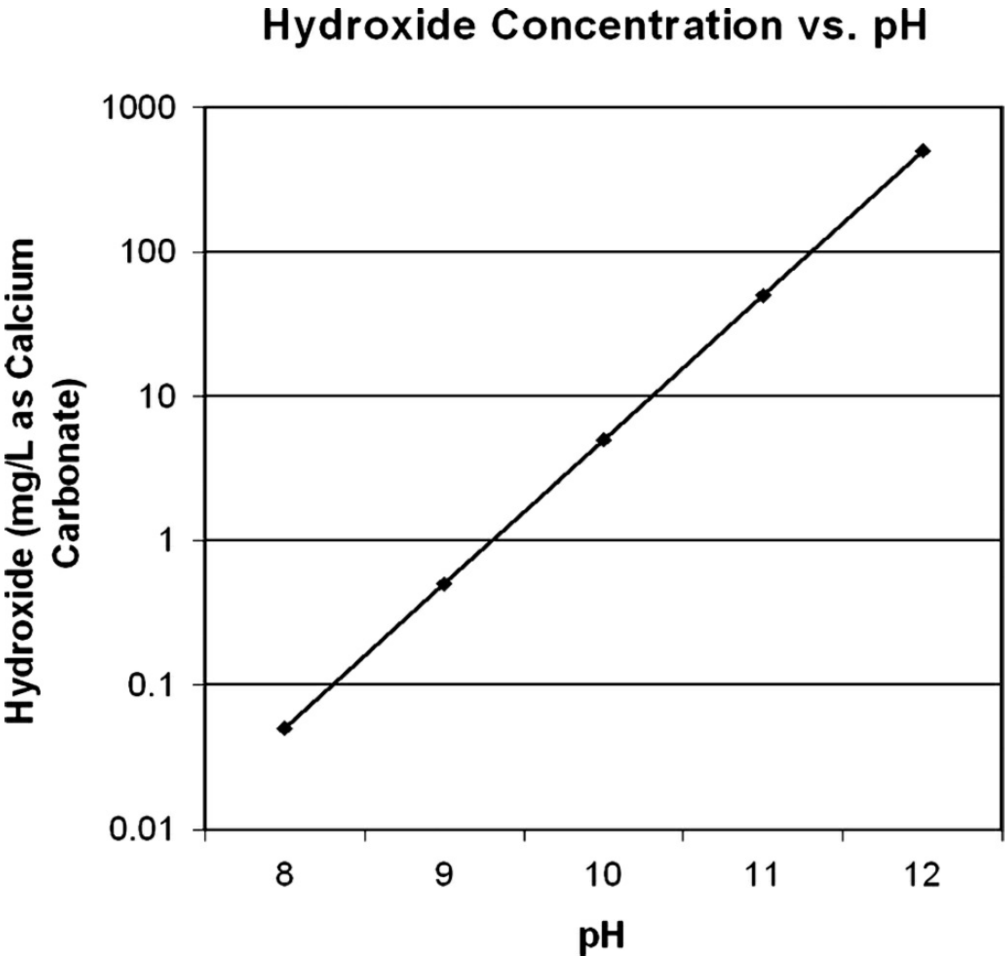


FIGURE 4.24 Concentration of hydroxide (in $CaCO_3$ equivalents) as a function of pH. Note that the hydroxide concentration is an insignificant part of alkalinity below pH 9.3.

An understanding of these concepts is necessary to put these acidity-alkalinity relationships into perspective. To the theoretical chemist, a pH of 7 is considered neutral; to the water chemist, a pH of 7 in itself means very little. We must also know how much total alkalinity and how much free or combined CO_2 may be present. For the water chemist then, the dividing point between acidity and alkalinity is not pH 7.0, but rather the M alkalinity endpoint, corresponding to a pH of 4.2 to 4.4.

Another measure is P alkalinity (phenolphthalein alkalinity), which exists when the water is above pH 8.2 to 8.4. P alkalinity can be determined by titration with phenolphthalein indicator, which changes from pink or red above pH 8.4 to colorless below pH 8.2. In most natural water supplies, the pH is less than 8.2, and there is no P alkalinity. Very few natural waters have pH below about 5.0; strong mineral acids are seldom found in freshwater. The pH range between the M endpoint and the P endpoint defines the bicarbonate alkalinity range, where weak acids may be present, like carbonic acid.

Impact of Carbon Dioxide in Water

Dissolved carbonate salts in most natural water supplies, result from the action of carbon dioxide in water. At the normal atmospheric level of 0.04% CO_2, less than 1 mg/L CO_2 dissolves in rainwater. However, once rainwater penetrates soil, it is exposed to CO_2 gas levels much greater than in the atmosphere, created by respiration of soil organisms as they convert organic food into energy and CO_2. Well waters, which have percolated through this CO_2-rich zone, may contain from ten to several hundred mg/L dissolved CO_2. When CO_2 dissolves in water, it reacts with water to form carbonic acid, which dissociates into the hydrogen ion and the bicarbonate ion according to Eq. (4.4).

The reaction between acidic groundwater and limestone minerals is shown in Eq. (4.22). Magnesium and calcium are dissolved from a common mineral, dolomite [$CaMg(CO_3)_2$], to produce hardness and alkalinity in groundwater.

$$2H_2O + 2CO_2 + CaMg(CO_3)_2 \rightarrow Mg(HCO_3)_2 + Ca(HCO_3)_2 \qquad (4.22)$$

In most waters, some excess CO_2 remains dissolved in the water. This creates a balance between pH and alkalinity as shown in Fig. 4.25. The amount of dissolved CO_2 in water depends on the pH value and the alkalinity. The graph shows the ratio of carbon dioxide to total alkalinity as a function of pH. Since the amount of CO_2 given by Fig. 4.25 is proportional to total (M) alkalinity, water with 1 mg/L CO_2 and 10 mg/L alkalinity has the same pH as water with 10 mg/L CO_2 and 100 mg/L alkalinity. Both of these waters have a ratio of 1:10 for the concentration of CO_2 to total alkalinity. The water with

100 mg/L alkalinity has a greater buffering capacity, however. If another 1 mg/L CO_2 were added to each water, the effect on pH would be greater in the first water with low CO_2 and alkalinity. The higher alkalinity in the second water moderates or buffers any pH change.

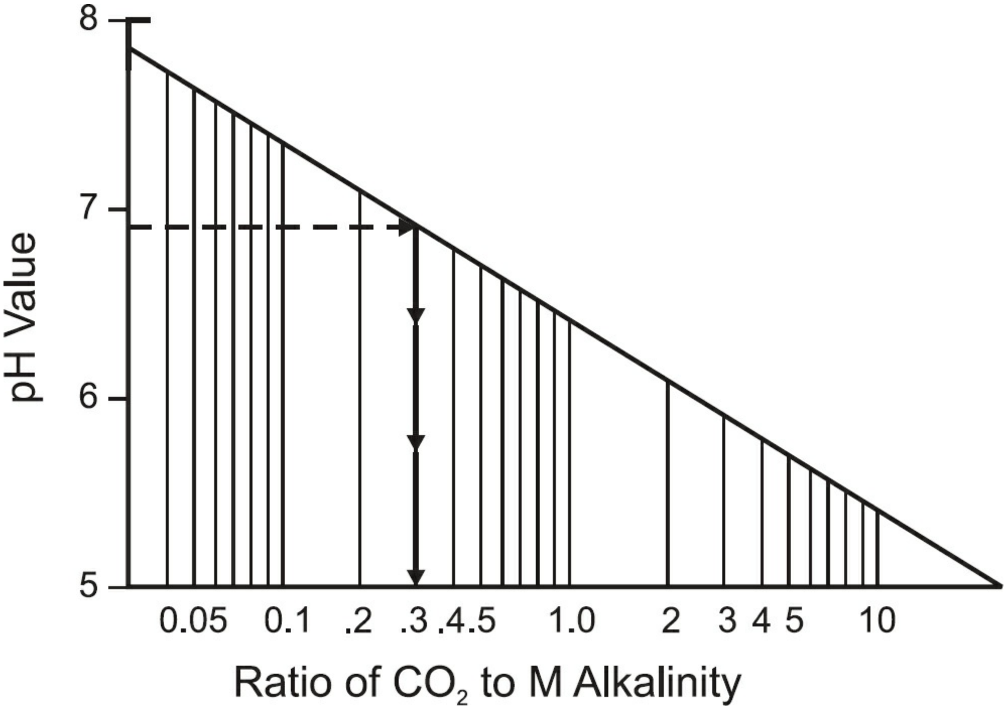


FIGURE 4.25 Approximate relationship of carbon dioxide, alkalinity, and pH in water. Both CO_2 and alkalinity are expressed in $CaCO_3$ equivalents.

The graph in Fig. 4.25 can be used to determine the CO_2 concentration in water with a given pH and alkalinity. Using the example in Fig. 4.25, shown by the line with arrows, at pH 6.9, the ratio of CO_2 to total (M) alkalinity is 0.3. If the total alkalinity is 150 mg/L as $CaCO_3$, then the CO_2 concentration is 45 mg/L as $CaCO_3$. Using the conversion factor of 1.14, we can determine the carbon dioxide concentration as CO_2:

$$1.0 \text{ mg/L } CO_2 \text{ as } CO_2 = 1.14 \text{ mg/L } CO_2 \text{ as } CaCO_3 \qquad (4.23)$$

Thus, 45 mg/L CO_2 as $CaCO_3$ is equal to 39.5 mg/L as CO_2. Note that this graph is limited to pH and alkalinity values where CO_2 is above a negligible concentration.

This demonstrates the balance between pH, alkalinity, and carbon dioxide in natural water. This balance depends upon a number of conditions, such as temperature, partial pressure of CO_2, and total alkalinity. Many well waters have a very high concentration of dissolved CO_2. In this case, even if the water has a high alkalinity, the pH is low. Figure 4.25 illustrates that as the ratio of CO_2 to total alkalinity increases, the pH of the water decreases.

It is essential to understand that this balance is affected by exchange of CO_2 between water and air. Under normal pressure, CO_2 establishes an equilibrium concentration in water, based on the pH and alkalinity of the water. Well water supersaturated with CO_2 loses carbon dioxide to the air when pumped out of the ground and exposed to lower pressure.

Distribution of Alkaline Species in Water

The relationship between pH, carbon dioxide, and alkalinity describes the general conditions of water, but it is still important to know the amount of individual alkalinity species in water. The equilibrium reactions and corresponding equilibrium constants for the carbonate system are:

$$\mathrm{H_2O + CO_2(aq.) \leftrightarrow H_2CO_3} \qquad K_H = 10^{-2.8} \quad \text{(Henry's Law)} \tag{4.24}$$

$$\mathrm{H_2CO_3 \leftrightarrow H^+ + HCO_3^-} \qquad K_{a1} = 10^{-6.3} \tag{4.25}$$

$$\mathrm{HCO_3^- \leftrightarrow H^+ + CO_3^{-2}} \qquad K_{a2} = 10^{-10.3} \tag{4.26}$$

From these equations, the fraction of inorganic carbon species as a function of pH can be determined as shown in Fig. 4.26.

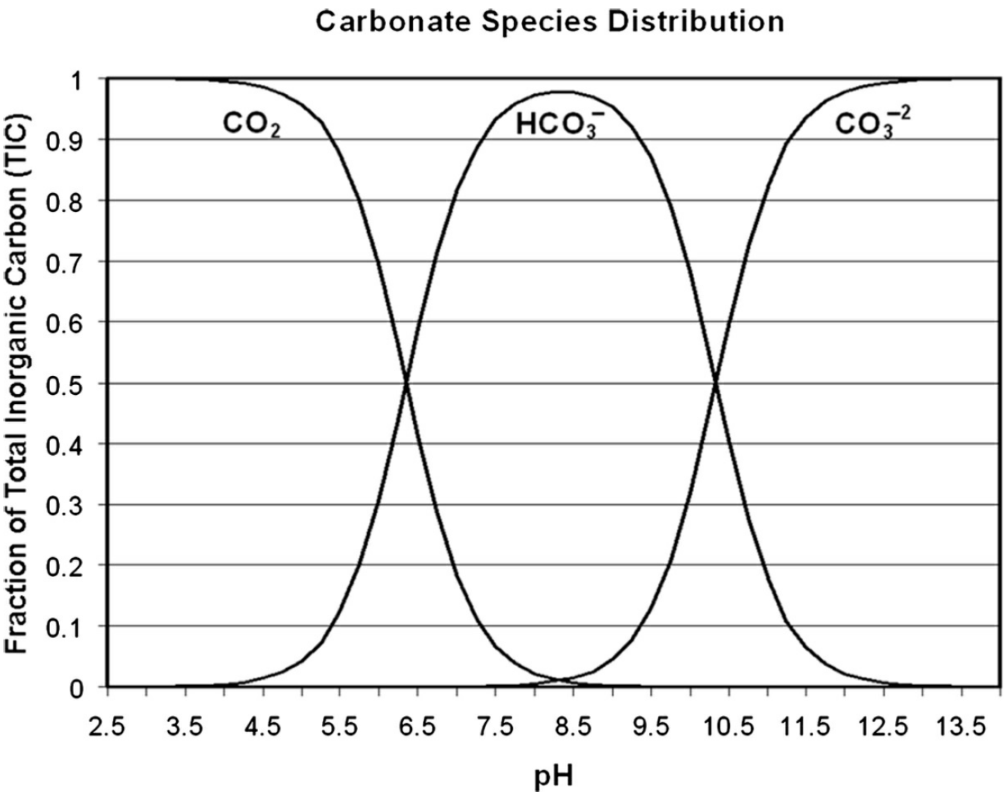


FIGURE 4.26 Fraction of inorganic carbon species versus pH.

Figure 4.26 shows that two inorganic carbon species exist between pH 4.3 and 12.3. Below pH 4.3, only CO_2 is significant, while above pH 12.3, only CO_3^{-2} is significant. Below pH 8.3, only HCO_3^- and dissolved CO_2 exist in water. Above this pH, HCO_3^- and CO_3^{-2} are the predominant species. Of course, above pH 7, the OH^- concentration increases and contributes to alkalinity. The concentration of OH^- must be known to describe the alkalinity of water completely. As shown earlier in Fig. 4.24, OH^- does not have an appreciable effect on alkalinity until pH is above 9.3, where the OH^- concentration is above 1 mg/L as $CaCO_3$.

Using these relationships, along with titration measurements of alkalinity described earlier, three types of alkalinity can be defined:

1. Total or M alkalinity at the methyl orange end point (pH about 4.3)
2. P alkalinity at the phenolphthalein end point (pH about 8.3)
3. Hydrate or caustic alkalinity, which can be calculated from the other two

The ionic species represented by each type of alkalinity can be described as follows:

$$M = OH^- + HCO_3^- + CO_3^{-2} \tag{4.27}$$

$$P = OH^- + \tfrac{1}{2}CO_3^{-2} \tag{4.28}$$

$$O = OH^- \tag{4.29}$$

These three equations are only valid when alkalinity is due to carbonate species hydroxide, and other species, like phosphate and ammonia, are negligible. Historically, this has been simply represented as shown in Fig. 4.27. In this diagram, some approximations have been made. The clear transition points are at pH 8.3, where carbonate is near zero, and at pH 4.3, where all alkalinity is near zero. However, two of the transitions shown at pH 10 are not so sharply defined. Figure 4.27 shows that bicarbonate exists above pH 10, and measurable quantities of OH^- exist between pH 9.2 and 10, although the concentration is very small. However, in the relationships shown in Fig. 4.27, both OH^- below pH 10 and HCO_3^- above pH 10 are considered negligible. These assumptions, although not strictly true, are commonly used as rules-of-thumb in the relationships that follow.

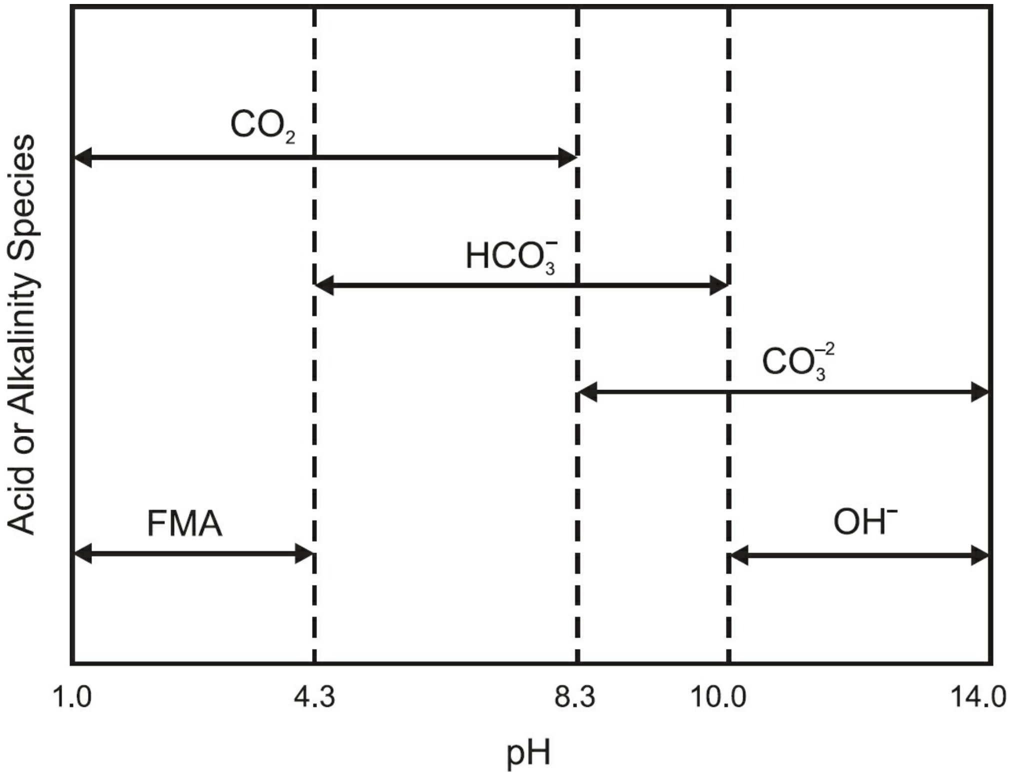


FIGURE 4.27 Simplified relationship between pH and alkalinity species.

By definition, alkalinity ceases to exist at pH 4.2 to 4.4, and further reduction of pH produces free mineral acidity (FMA). Therefore, Fig. 4.27 leads to the following commonly used definitions and assumptions:

- Below pH 4.3, M = 0
- Below pH 8.3, $CO_3^{-2} = 0$
- Above pH 10, HCO_3^- is considered negligible
- Below pH 10, OH^- is considered negligible

Using the equations given above for the alkalinity species and these definitions from Fig. 4.27, a set of rules can be developed to determine the concentration of each species. The rules differ, depending on whether OH^- or HCO_3^- is present in measurable quantities. A complete set of these relationships can be developed, depending on the results of the M and P titrations (Table 4.9).

Result of Titration	**OH^- as $CaCO_3$**	**CO_3^{-2} as $CaCO_3$**	**HCO_3^- as $CaCO_3$**
P = 0	0	0	M
P < ½ M	0	2P	M-2P
P = ½ M	0	2P	0
P > ½ M	2P-M	2(M-P)	0
P = M	M	0	0

TABLE 4.9 Relationship between P and M Alkalinity and the Hydroxide, Carbonate, and Bicarbonate Concentrations in Water

These approximations are very useful, but they may be subject to interferences, especially in contaminated waters where ammonia may be high. Wastewater may contain ions in addition to HCO_3^- and CO_3^{-2}, which are alkaline such as bisulfides, sulfides, and phosphates. Other ions like borate and silicate can affect alkalinity measurements. When dealing with such waters, M and P titrations are inadequate to determine HCO_3^- and CO_3^{-2} relationships; therefore, acid evolution of CO_2 must be used.

Remember that these are only approximations. For example, at pH 10, bicarbonate is set to zero, but it can be as much as 25% of the alkalinity based on Fig. 4.26. This practice tends to overstate carbonate alkalinity in the presence of OH^-. Therefore, these relationships work better as the pH of the system moves away from 10, either higher or lower. They remain convenient relationships that work reasonably well under most conditions encountered in water systems.

Buffer Capacity

A final consideration is the importance of the buffer effect of alkaline waters, a critical factor where careful control of pH may be necessary in treating either raw water or wastewater. As an example, compare the neutralization of sodium hydroxide (NaOH) to the neutralization of sodium carbonate (Na_2CO_3), as shown in Fig. 4.28. Control at pH 7 is virtually impossible in the NaOH neutralization, since there is a vertical drop between pH 9 and 4.3. Very little acid is required to change the pH from a value of 9 to 4.3 in water containing only NaOH. Controlling the addition of small amounts of acid and responding to a rapid pH change is very difficult. Water that is buffered with alkalinity (carbonate curve in Fig. 4.28) has a very gradual change in pH as more acid is added. This makes pH control in natural waters (with typical alkalinity concentrations) much easier to accomplish than in unbuffered water. As a corollary to this, it is considerably easier to control the pH of an acidic waste with Na_2CO_3 than with NaOH, provided the CO_2 generation can be controlled without excessive foaming.

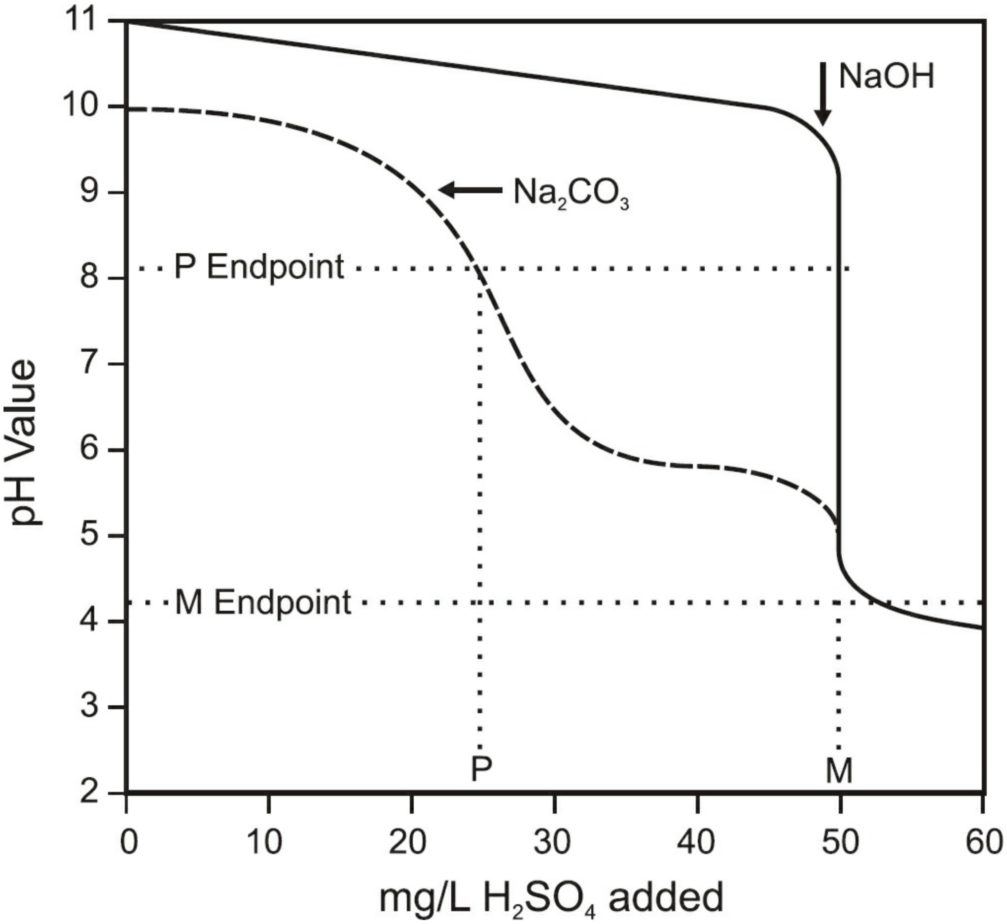


FIGURE 4.28 Neutralization with sulfuric acid (H_2SO_4) of alkaline water containing 50 mg/L alkalinity from either sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3).

Practical Aspects of Mineral Solubility

Examination of acidity-alkalinity relationships in water reveals that the solubility of minerals such as calcium carbonate and magnesium hydroxide is more complicated to predict than the solubility product concept suggests. The numerous equilibrium reactions that describe calcium carbonate precipitation make this prediction difficult. For that reason, water chemists usually rely on empirical data based on reported plant experiences to estimate results of a precipitation reaction.

Solubility in Softening Reactions

Figure 4.29 shows data used for predicting calcium carbonate solubility, specifically related to precipitation in a lime softening operation. The difference in results between hot process softening [above approximately 212°F (100°C)] and cold process softening (ambient temperatures) is considerably beyond what would be predicted by simple solubility data, which show a decrease of only about 2 mg/L solubility at the higher temperature. The empirical temperature effect must be caused by other factors, such as rate of reaction, which approximately doubles for each 18°F (10°C) temperature increase, the nature of the precipitate (crystalline or amorphous), and the possible effect of coagulating organic materials at higher temperature.

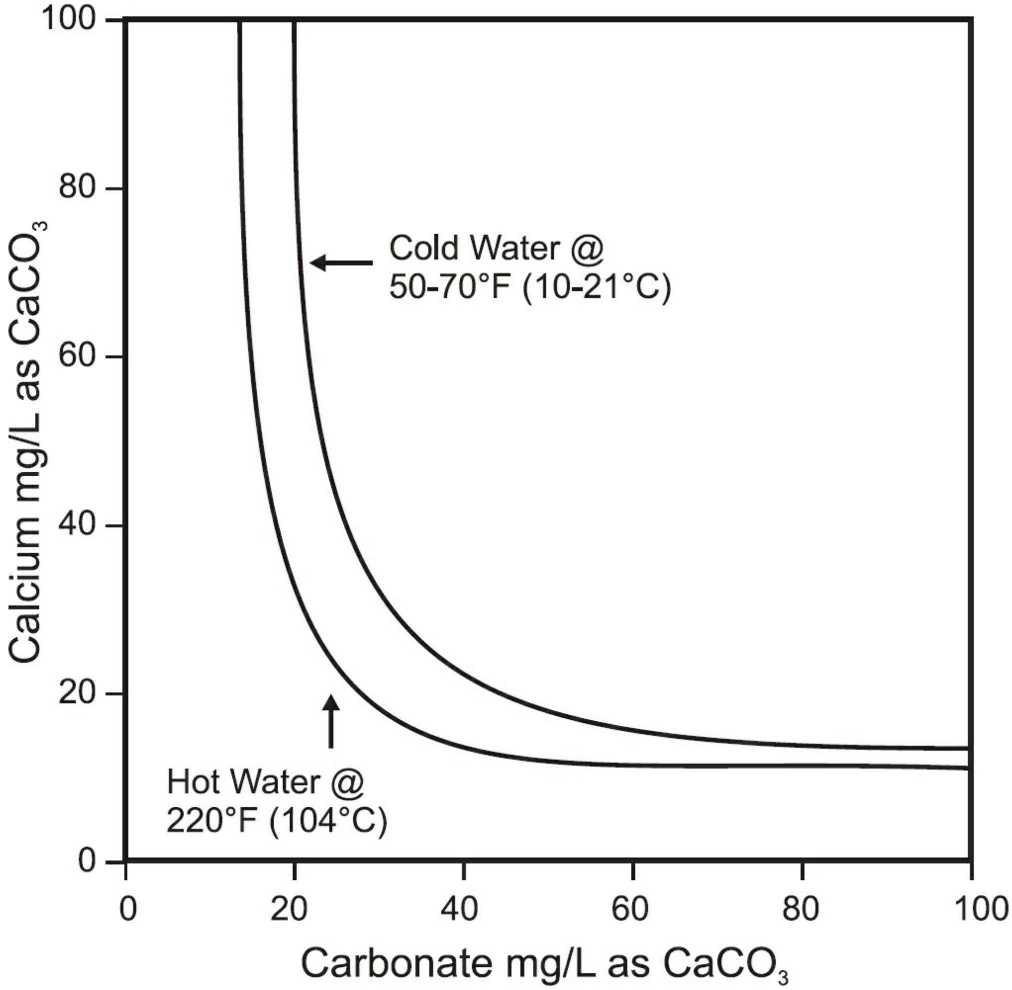


FIGURE 4.29 $CaCO_3$ solubility in hot and cold systems. (*Empirical data based on 60–90 min reaction and settling time.*)

Organic matter affects cold lime softening of municipal sewage, where residual calcium carbonate is invariably higher than when the same process is used in the treatment of freshwater. This is illustrated in Fig. 4.30. However, if sewage is heated above approximately 160°F (71°C), residual calcium carbonate after softening approaches that achieved in freshwater.

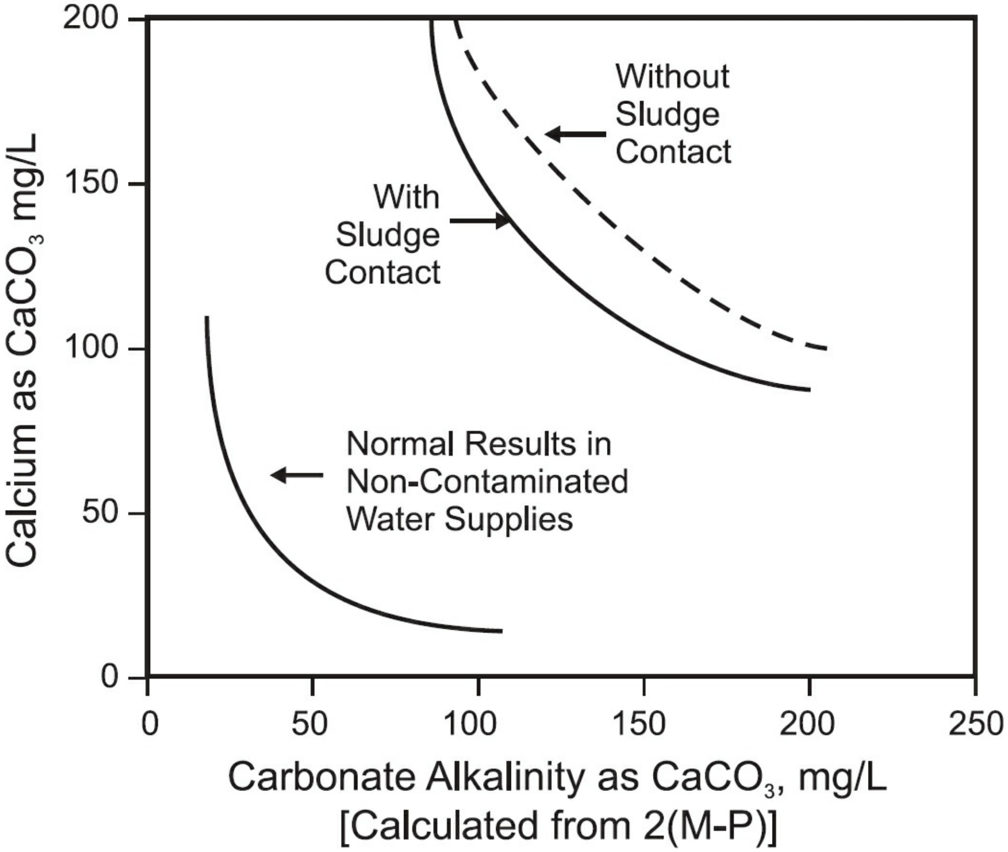


FIGURE 4.30 Cold lime softening of sewage (upper two curves) compared to raw water.

If magnesium precipitates with calcium carbonate, residual calcium in solution may be higher than if just calcium carbonate precipitates. Inclusion of other impurities, such as strontium, has been shown to increase solubility of calcium carbonate. Empirical data from a variety of plants should be used cautiously in estimating the results of lime treatment of an unknown water supply, especially if contamination levels are not fully defined. Actual bench testing to determine the response of that water to lime treatment is the best approach.

Magnesium solubility is as difficult to predict with accuracy as calcium solubility, for the same general reasons. The solubility of magnesium hydroxide is reported to be 30 to 40 mg/L at 77°F (25°C). Because of the difference in solubility product relationships, magnesium concentration is affected more by changes in hydroxyl concentration than calcium is by changes in carbonate concentration.

$$K_{Ca} = [Ca^{+2}][CO_3^{-2}] \tag{4.30}$$

$$K_{Mg} = [Mg^{+2}][OH^-]^2 \tag{4.31}$$

An increase in carbonate produces a corresponding decrease in calcium in Eq. (4.30). However, an increase in hydroxyl concentration affects the magnesium concentration in Eq. (4.31) in a squared relationship. Thus, a doubling of the $[OH^-]$ will result in the $[Mg^{+2}]$ to drop to one-fourth its original value.

When water is softened with lime, in the pH range of 9.5 to 10.5, magnesium precipitates as the hydroxide, and the precipitate is positively charged. In the same pH range, $CaCO_3$ precipitate is negatively charged. Furthermore, silica in the system is usually present as a strong negatively charged colloid. Sodium aluminate may be introduced in the system as a strong anionic complex. All of this may account for the coprecipitation of magnesium with calcium, the strong adsorption of silica on $Mg(OH)_2$ precipitate, and the low residual magnesium often achieved by the treatment of water with sodium aluminate in addition to lime.

In conventional softening operations, lime treatment of freshwater produces a $CaCO_3$ solubility of approximately 35 mg/L in cold water and 25 mg/L in hot water, and a residual magnesium hydroxide solubility of approximately 35 mg/L in cold and 2 to 3 mg/L in hot water.

Calcium carbonate and magnesium hydroxide are precipitated in the lime softening operation; however, these can precipitate from unstable water (water containing these materials in a supersaturated condition), if anything is done to the system to upset the equilibrium. The equilibrium shift could be caused by an increase in temperature, a decrease in pressure, turbulence, or contact with surfaces that seed the chemical precipitation. The most common product of instability of freshwater is $CaCO_3$; in seawater, the usual precipitate is $Mg(OH)_2$ or one of its complex carbonate-hydroxide salts.

$CaCO_3$ Stability Indexes

Historically, a variety of empirical and theoretical scaling index calculations have been used to predict the probability of mineral scale formation. Early methods of predicting the scale-forming tendency of water range from simple equilibrium saturation indexes to empirical indexes based on experimental or field data. The two key examples of these are the Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI).

These first indexes were an attempt to simplify the evaluation of the effect of water chemistry on scaling and corrosion in municipal drinking water systems. Both are based on calculations of the solubility of calcium carbonate, with minor corrections for temperature and ionic strength. These scaling indexes have many inherent limitations because of their simplified nature and do not consider all the complex factors in natural water that affect mineral solubility.

LSI was the first index calculation to come into wide usage (1920s). It is based on the saturation pH (pH_s), at which point a given water is saturated with calcium carbonate. LSI is determined by the difference between the actual pH and pH_s to define a saturation index:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH_s} \tag{4.32}$$

Positive LSI indicates the water solution is oversaturated with respect to calcium carbonate, while negative LSI indicates the water is undersaturated.

Based on studies of reported conditions of scaling and corrosion in a variety of municipal systems, Ryznar created an empirical index to predict scale-forming or corrosion tendency, based on pH and pH_s:

$$\mathrm{RSI} = 2\mathrm{pH_s} - \mathrm{pH} \tag{4.33}$$

A water solution is considered to be corrosive when the RSI exceeds approximately 6.0 and to be scale forming when the index is less than 6.0.

Other indexes, like the Stiff and Davis index, try to compensate for higher conductivity but are still limited in scope. None of these methods can consider all the factors in natural water that affect mineral solubility. The inherent limitations of these simplified indexes can give erroneous predictions of the scaling or corrosive tendency of water. The limitations of indexes are due to a variety of assumptions made in the calculations, including:

- The effects of temperature and ionic strength were either ignored or severely limited.
- The solubility of other scaling species (besides $CaCO_3$) was ignored.
- The effects of soluble complexes (ion pairing) were not calculated.
- A limited set of conditions was examined.
- Simplifying assumptions were made about the carbonate equilibria.

An example of the effect of ionic strength and ion pairing is illustrated by the difference between the predicted and actual solubility of $CaSO_4$ in a highly concentrated recirculating cooling water system (Fig. 4.31). The predicted solubility of Ca with increasing SO_4 concentration, shown by curve A, continues to decrease as conductivity increases. The actual solubility, in curve B, shows that a Ca concentration of 800 to 900 mg/L as $CaCO_3$ can be maintained, even at SO_4 concentrations in excess of 25 000 mg/L as $CaCO_3$.

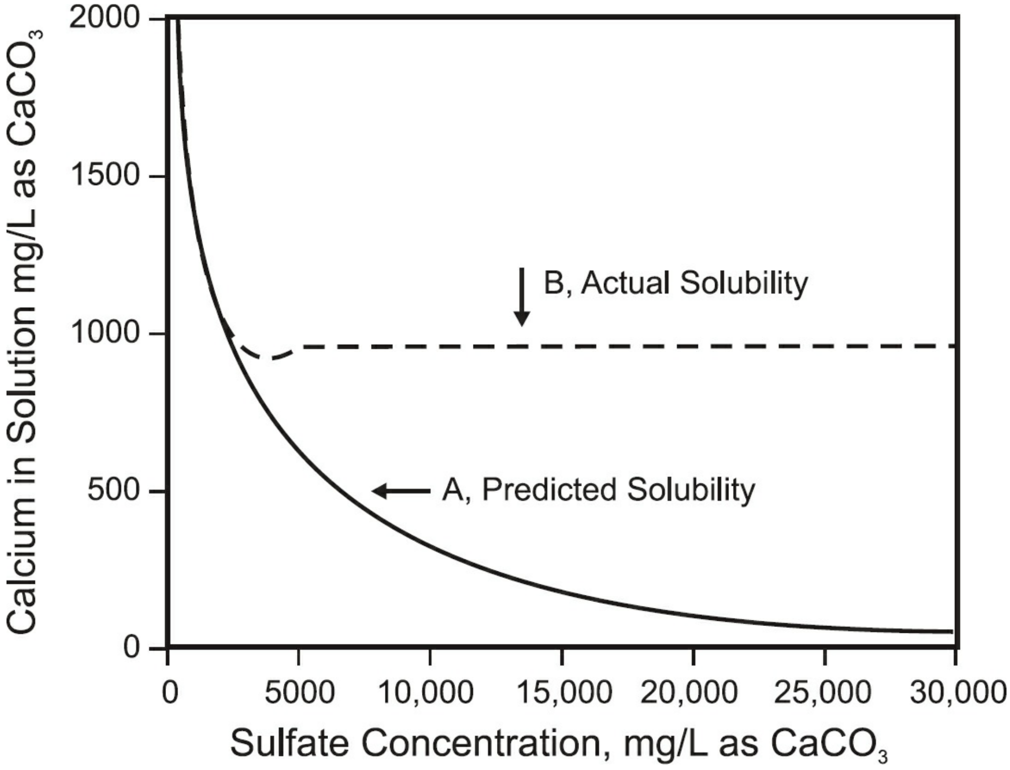


FIGURE 4.31 Effect of ionic strength on the solubility of $CaSO_4$ in highly concentrated cooling water.

Limitations of simple indexes are not due to lack of understanding of the problem, but rather to efforts to simplify the equations for easy use. Now, computer models that can run on any computer make rigorous calculations easily and quickly and include the effect of a wide variety of conditions. See Chap. 15 for more detail on models for solubility calculations.

Oxidation/Reduction Reactions

Oxidation and reduction reactions, also known as redox reactions, are important in water chemistry. A few examples of redox reactions include water disinfection, corrosion, precipitation of iron and manganese from water, and oxidation of sulfide for odor removal from water.

Basic Concepts

Redox reactions involve the transfer of electrons. In an oxidation reaction, electrons (e^-) are lost from a chemical reactant, like the oxidation of iron metal in corrosion, which releases two electrons:

$$Fe^{\circ} \rightarrow Fe^{+2} + 2e^{-} \tag{4.34}$$

In this oxidation reaction, iron is an electron donor, and a reducing agent, since it supplies the electrons, which can reduce other reactants in water. This reaction is called a half-cell reaction, because the electrons must be accepted by another half-cell reaction. To maintain electrical neutrality, every oxidation reaction in a system must be accompanied by a reduction reaction. In this reduction reaction, another reactant gains the electrons donated by the reducing agent, as in the half-cell reaction below:

$$\tfrac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \tag{4.35}$$

In this case, oxygen is an electron acceptor, and is reduced, since it gains the electrons. Oxygen can also be called an oxidizing agent or an oxidant. The two negative hydroxide ions produced in this reaction balance the positive charge on the ferrous ion (Fe^{+2}) to maintain neutrality.

These reactions should be familiar, since they are the corrosion reactions for iron-containing metals in water. They are called electrochemical reactions, since redox reactions involve the transfer of electrons. The power, or potential, of redox reactions can be determined from the electrochemical series (shown earlier in Table 4.2). In redox reactions, chemicals at the extremes of the series are more powerful oxidants or reductants. Sodium metal is a very strong reducing agent with a negative potential of -2.7 V. Fluorine is a very strong oxidizing agent with a positive potential of 2.87 V. There would be a very strong driving force for a reaction between sodium and fluorine.

Oxidizing or Reducing Conditions

Chlorine, bromine, and ozone are familiar in water chemistry as oxidizing biocides. They are applied to municipal water or treated sewage to kill pathogenic organisms; they control slime-forming bacteria and algae in cooling systems, clarifiers, and softeners.

Another important role for these chemicals is as oxidizing agents, especially for removal of iron and manganese from well water used for municipal water supply, and from acid mine drainage in coal producing regions. Iron and manganese are soluble in a reducing environment, such as deoxygenated well water, and found as the ferrous (Fe^{+2}) and manganous

(Mn^{+2}) ions. Oxidation to ferric (Fe^{+3}) and manganic (Mn^{+4}) ions reduces solubility substantially.

Redox potential is measured using a pH instrument with special electrodes. In the absence of a redox electrode in field-testing, there are several simple methods for qualitatively judging the redox state. The following can identify a reducing condition:

- Sulfide may be present; the sample may have a sulfide odor or may react to lead acetate paper (turn white lead acetate paper black).
- The color of methylene blue indicator disappears.
- A test for oxygen is negative.
- Test for presence of reducing agent is positive, such as the boiler water test for sulfite, using the same method.

Similarly, an oxidizing condition is indicated by a few conditions:

- Color of methylene blue dye persists.
- Oxygen test is positive.

Common Oxidizing and Reducing Agents

Although chlorine or hypochlorite is most frequently chosen as the oxidizing agent, it is not always the best. Table 4.10 shows a listing of various available oxidizing agents and their comparable oxidizing powers. Sometimes, the chemistry of the aqueous environment rules out the use of chlorine, as in the case of water high in ammonia, which consumes the chlorine to produce chloramines (still an oxidizer but weaker than chlorine). Oxidizing agents like permanganate, chlorine dioxide, and ozone are not affected by ammonia, and are better oxidants in this case.

Element or Compound	Half-Cell Reactions	Standard Electrode Potential (V)
Oxygen (in neutral water)	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
Oxygen (acidic)	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68
Hypobromite	$OBr^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	0.76
Hydrogen peroxide (basic)	$H_2O_2 + 2e^- \rightarrow 2OH^-$	0.87
Hypochlorite	$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.89
Bromine	$Br_2 + 2e^- \rightarrow 2Br^-$	1.08
Ozone (basic)	$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	1.24
Chlorine	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
Permanganate (acidic)	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68
Hydrogen peroxide (acidic)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77
Ozone (acidic)	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.07
Fluorine	$F_2 + 2e^- \rightarrow 2F^-$	2.87

TABLE 4.10 Table of Standard Electrode Potentials for Common Oxidizing Agents. Oxidation Potential Increases as the Potential Becomes More Positive

Some heavy metals are best removed by reduction. Mercury salts can be reduced to mercury metal by strong reducing agents like the borohydrides and then filtered from solution. When metals have been oxidized (or reduced) to an insoluble form, most become colloidal particles and are then removed from water by coagulation, flocculation, and filtration. If the metal concentration is over 2 to 5 mg/L, sedimentation is included before filtration to avoid rapid plugging of the filter.

Oxidation-reduction reactions can be very slow, especially compared to acid-base neutralization reactions, which are essentially instantaneous. Solution pH is important because it influences solubility and reaction rates. Oxidation reactions of iron and manganese are faster at high pH, when an oxidizing agent can increase the potential of the water. Therefore, at pH 5, a large detention basin is usually needed to provide time for these oxidation reactions; at pH 8.3 to 8.5, iron can be oxidized in-line and filtered with less than five minutes contact time with an oxidant. Certain materials catalyze the rate of oxidation. Fortunately, MnO_2 is such a catalyst, easily applied as potassium permanganate ($KMnO_4$), which also acts as an oxidant.

CHAPTER 5

Impurities in Water

Contaminants in water sources are related to rainfall, the geologic nature of the watershed or underground aquifer, biological activity in the ground or in the water, and the activities of human population. As described in the previous chapter, many contaminants are due to the unique solvent properties of water. The electrical polarity of the water molecule aids dissolution of many ionic and covalent compounds. Substances like salts, sugars, acids, and alkalis are very soluble in water. Many gases, including oxygen (O_2) and nitrogen (N_2), are soluble in water. Other gases that dissolve in water, like carbon dioxide (CO_2) and ammonia (NH_3), react with the water molecule to form weak acids or bases. Polar organic materials, like alcohols and sugars, dissolve in water to a high extent, depending on the properties of the molecule. The presence of polar organics in water can act as a cosolvent to dissolve small amounts of nonpolar organic compounds. The action of biological processes in water can increase or decrease the solubility of inorganic and organic materials in water.

The density and viscosity properties of water, combined with the power of flowing water, can keep in suspension, a wide variety of materials. These suspended particles can be inorganic solids, insoluble organic substances, or biological organisms.

Water supports all life forms known on Earth. The solvent properties allow fluids like blood to carry nutrients to the cells in a body. Water participates in many metabolic processes necessary for life. An example is photosynthesis, where energy from the sun is used by plants to convert CO_2 and water into sugar.

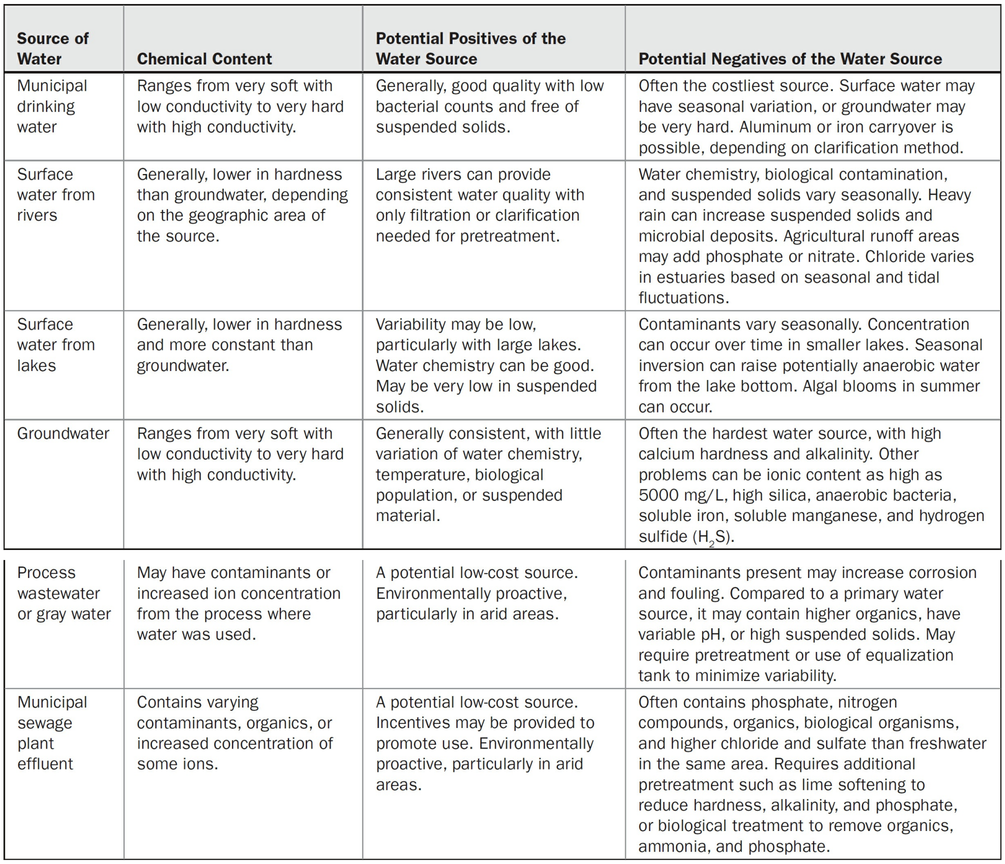
The result is that water can contain many substances, both living and nonliving. The materials in water may be either inert or reactive. The specific type of contaminant and its concentration depends upon the type and source of water. Understanding the various contaminants that can be found is the first step in water treatment for any use, from potable water to industrial applications.

The goal of this chapter is to present various impurities found in water and their effect on industrial processes. This is not an exhaustive list of impurities but includes many that are commonly found.

Characteristics of Water Sources

Chapter 2 on Water Sources and Stressors provided many examples of ground and surface water sources around the world. The rivers and lakes described in that chapter are typical of waters used for industrial purposes as well as for municipal drinking water. However, other sources of water are used for industrial and institutional purposes. Reclaimed wastewater is sometimes used and creates additional challenges, depending on contaminants remaining in the water, the particular industry, and the intended use of the water. Seawater may be used in a variety of applications and is commonly used for cooling in power utilities in coastal areas. Each source has an individual chemical composition that is specific to the nature of the source and the surrounding area, yet there are several general characteristics of water sources that are unique to each type of water.

One of the key factors that affect the quality of water is the geological nature of the area where the groundwater or surface water exists. Surface water composition is affected by contact with the soil or rock of the watershed that supplies either a river or lake. Groundwaters are dependent on the type of rock through which rainwater permeates when entering the aquifer. In addition, CO_2 created by the action of bacteria in soil, and absorbed from air by rainwater, can make water slightly acidic. If subsurface rock contains limestone, groundwater in that area can be high in hardness (calcium and magnesium) and alkalinity. General characteristics of some of the main sources of water used for industrial and institutional processes are shown in Table 5.1.



Source of Water	Chemical Content	Potential Positives of the Water Source	Potential Negatives of the Water Source
Municipal drinking water	Ranges from very soft with low conductivity to very hard with high conductivity.	Generally, good quality with low bacterial counts and free of suspended solids.	Often the costliest source. Surface water may have seasonal variation, or groundwater may be very hard. Aluminum or iron carryover is possible, depending on clarification method.
Surface water from rivers	Generally, lower in hardness than groundwater, depending on the geographic area of the source.	Large rivers can provide consistent water quality with only filtration or clarification needed for pretreatment.	Water chemistry, biological contamination, and suspended solids vary seasonally. Heavy rain can increase suspended solids and microbial deposits. Agricultural runoff areas may add phosphate or nitrate. Chloride varies in estuaries based on seasonal and tidal fluctuations.
Surface water from lakes	Generally, lower in hardness and more constant than groundwater.	Variability may be low, particularly with large lakes. Water chemistry can be good. May be very low in suspended solids.	Contaminants vary seasonally. Concentration can occur over time in smaller lakes. Seasonal inversion can raise potentially anaerobic water from the lake bottom. Algal blooms in summer can occur.
Groundwater	Ranges from very soft with low conductivity to very hard with high conductivity.	Generally consistent, with little variation of water chemistry, temperature, biological population, or suspended material.	Often the hardest water source, with high calcium hardness and alkalinity. Other problems can be ionic content as high as 5000 mg/L, high silica, anaerobic bacteria, soluble iron, soluble manganese, and hydrogen sulfide (H_2S).
Process wastewater or gray water	May have contaminants or increased ion concentration from the process where water was used.	A potential low-cost source. Environmentally proactive, particularly in arid areas.	Contaminants present may increase corrosion and fouling. Compared to a primary water source, it may contain higher organics, have variable pH, or high suspended solids. May require pretreatment or use of equalization tank to minimize variability.
Municipal sewage plant effluent	Contains varying contaminants, organics, or increased concentration of some ions.	A potential low-cost source. Incentives may be provided to promote use. Environmentally proactive, particularly in arid areas.	Often contains phosphate, nitrogen compounds, organics, biological organisms, and higher chloride and sulfate than freshwater in the same area. Requires additional pretreatment such as lime softening to reduce hardness, alkalinity, and phosphate, or biological treatment to remove organics, ammonia, and phosphate.

TABLE 5.1 Types and Characteristics of Water Sources

In addition, there are some general differences between groundwater and surface water. Many of these properties are direct opposites. Groundwater typically has these characteristics:

- Temperature remains constant throughout the year.
- Dissolved solids concentration is generally higher than surface water at the same locale. Groundwaters are often high in hardness and alkalinity, if those minerals are present in the substrate. In some areas, salt water or connate water (water trapped underground) intrusion may add considerable amounts of sodium chloride and other salts. Some areas overlie underground soda ash (sodium carbonate) formations; these waters contain very high levels of sodium and alkalinity but very little hardness.
- Dissolved gases such as hydrogen sulfide (H_2S) and CO_2 may be present in well water at levels above saturation. Both gases can cause

the water to be corrosive. When the water is brought to atmospheric pressure, these gases can be released. When CO_2 is released, the resulting pH increase of the water may cause scale formation. Release of H_2S can cause odor problems in the area surrounding the water source.

- Alkalinity and pH remain constant in groundwater. The water can be highly acidic (pH as low as 4.3) or very alkaline (pH as high as 9.8) depending on the minerals present.
- Metal ions like iron and manganese are often present as soluble ions in groundwater sources. They may be oxidized to insoluble forms after the water contacts air.
- In most cases, turbidity of groundwater is generally very low.

Surface water quality is not generally as uniform as groundwater. In fact, the variability of surface water can be a challenge for industrial water treatment applications.

- Temperature can vary seasonally but also in much shorter periods, depending on conditions upstream from point of use. Temperature and weather changes can cause inversion of a lake, where water from the bottom of the lake is raised to the lake surface. Lake bottom water can contain anaerobic bacteria and high levels of iron and manganese.
- Total dissolved solids (TDS) are generally lower than in groundwater. Depending on other industrial processes located upstream, there might be significant variability.
- Dissolved gases are present because the water is continuously in contact with air; however, excess dissolved gases are not generally present.
- Alkalinity and pH vary seasonally due to precipitation and runoff. There can be geographic variations in the TDS, pH, and various contaminants from discharge of municipal waste, industrial waste, or farm runoff into the river or lake.
- Metal ions may be present in surface water supplies because of industrial pollution. Most metals in surface waters are commonly

present as insoluble particulate metal oxides. In some cases, the soluble form may be present.

- Suspended solids and turbidity in surface water can be high, particularly in rivers, and varies seasonally with rainfall and runoff. Rapid changes are possible, depending on upstream or climatic events.

Classes of Impurities

There are many ways to group impurities found in water sources, most of which are arbitrary classifications. Impurities can be grouped by different ranges of concentrations, by ranges of the solubility of the materials, or by type of material, such as inorganic and organic compounds. The most common way is probably to group matter by whether it dissolves in water (soluble) or whether it is not soluble in water (insoluble). However, even with this classification, further breakdown or special groups are probably needed. For example, many gases dissolve in water and may have significant interaction with other species in water, because the gases like CO_2 or NH_3 may react with water. Organic compounds should be in a separate category, because even low concentrations of some organics can cause serious problems in many industrial systems or are health hazards in drinking water, whether they are soluble or insoluble. Biological growth, such as bacteria, algae, or macroorganisms, should also be a separate category, due to the complex nature of these living creatures and the by-products they release.

In this chapter, grouping the impurities as follows allows a logical discussion of each group of materials and their effect on industrial systems:

- Soluble matter
- Insoluble matter (suspended material)
- Organic contaminants
- Biological contaminants
- Dissolved gases
- Radioactive materials

The variety of materials in this list show the complexity of water-based systems and the challenges that are involved when using natural water in industrial, institutional, or municipal water systems.

Dissolved Substances

Dissolved substances can be found at very high concentrations, like sodium and chloride in ocean waters, or as trace components, like selenium and titanium. The components may be completely dissolved and soluble in the source water but become insoluble when used in an industrial or institutional process. Insolubility may be caused by temperature and ion concentration changes in the process where the water is used. Solubility of various ions is governed primarily by the solubility product constant for any compound that may form. The solubility of carbonate with various positive ions is shown in Fig. 5.1. Examples of the solubility of various hydroxide and oxide compounds are shown in Fig. 5.2. However, many other processes, like common-ion effects or ion pairing, can affect solubility of a mineral. Therefore, the prediction of mineral solubility in an industrial or institutional process is not a simple matter that can be calculated by common indexes. (See Chap. 15 on Cooling Water Deposition for more detail on factors affecting solubility in cooling water systems.)

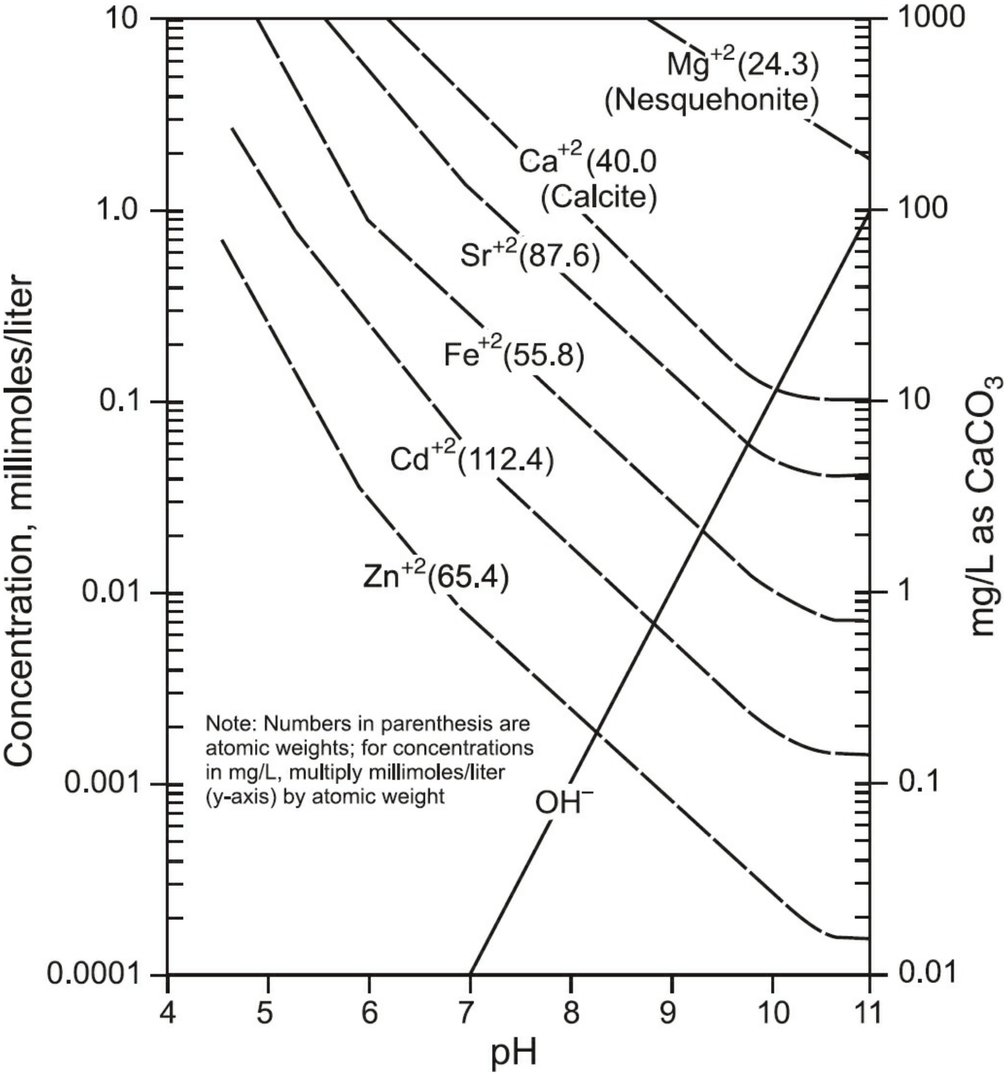


FIGURE 5.1 Theoretical solubility of carbonate compounds in a water system closed to an external CO_2 environment. (*Source: Stumm and Morgan, 1970*.)

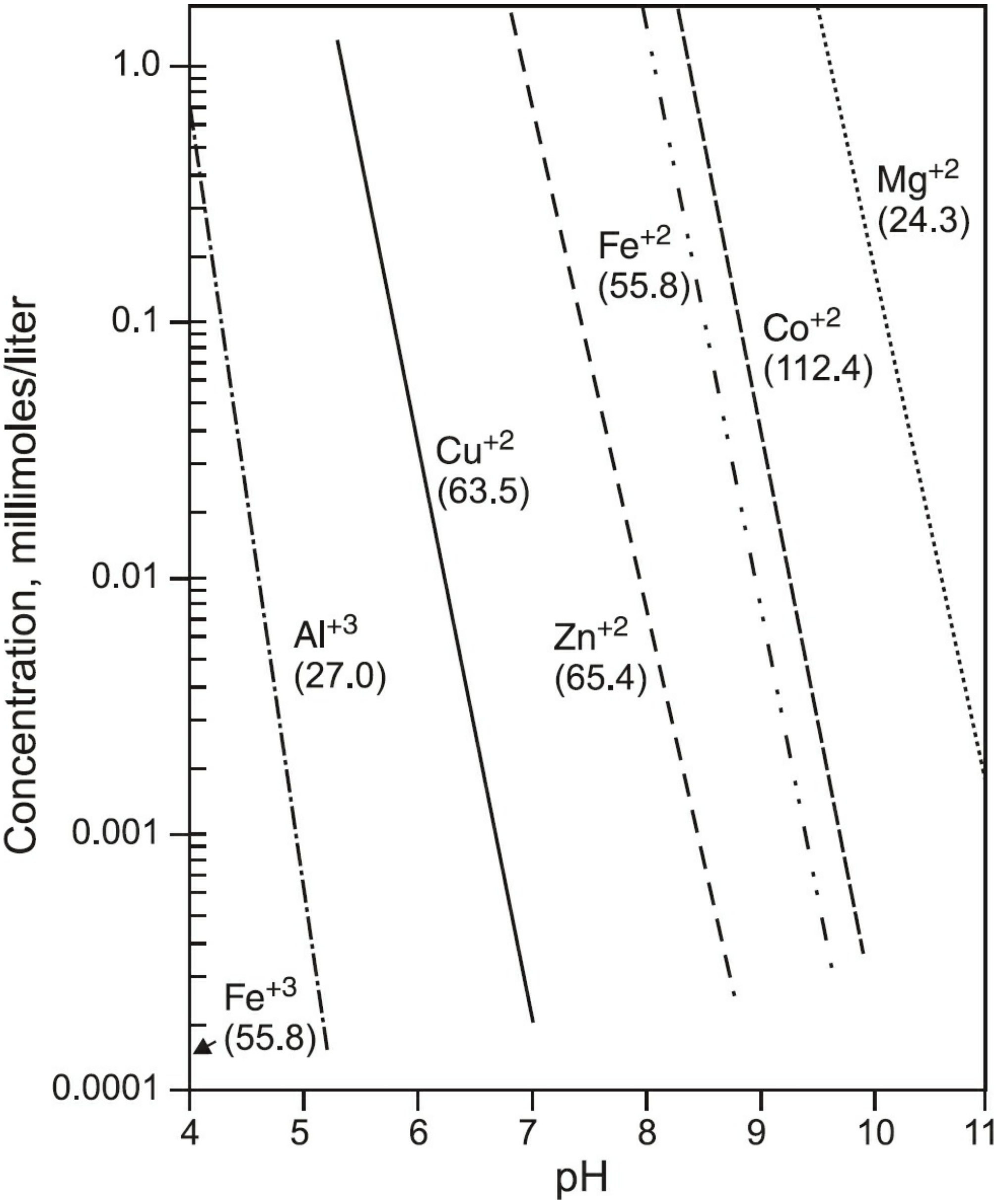
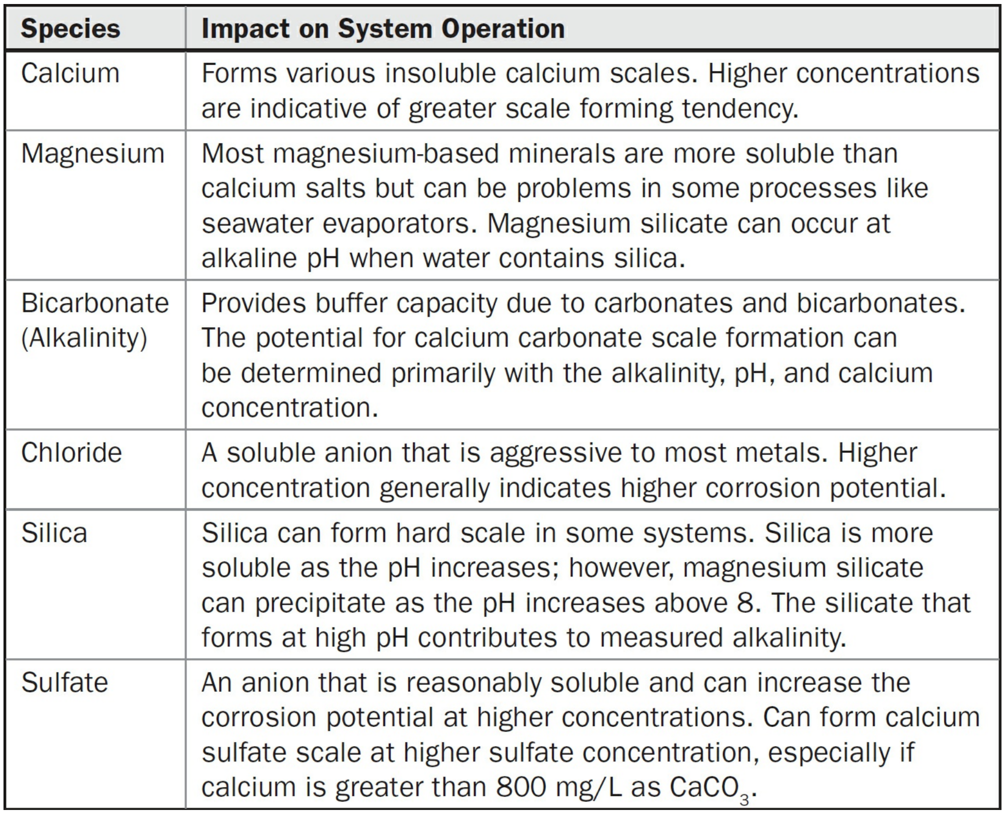


FIGURE 5.2 Theoretical solubility of oxides and hydroxides in water at 25°C. (*Source: Stumm and Morgan, 1970.*)

TDS is the sum of all materials dissolved in water and is usually in the range of 25 to 5000 mg/L. The suggested limit for public water supplies, based on potability, is 500 mg/L. The principal effect of dissolved solids on industrial processes is to limit the extent to which water can be concentrated before it must be discarded. High concentrations can cause scale formation, affect the taste of beverages, or cause other problems depending on the manufacturing process. The related electrical conductivity of high TDS tends to accelerate corrosion. The conductivity of water can be used as a relative indicator of TDS.

Dissolved matter in water can be present as a compound like ethanol or as dissolved ions from a mineral or salt. These dissolved ions can be divided into two groups based on concentration. The major constituents that are generally present in high concentration (> 5 mg/L) are shown in Table 5.2.



Species	Impact on System Operation
Calcium	Forms various insoluble calcium scales. Higher concentrations are indicative of greater scale forming tendency.
Magnesium	Most magnesium-based minerals are more soluble than calcium salts but can be problems in some processes like seawater evaporators. Magnesium silicate can occur at alkaline pH when water contains silica.
Bicarbonate (Alkalinity)	Provides buffer capacity due to carbonates and bicarbonates. The potential for calcium carbonate scale formation can be determined primarily with the alkalinity, pH, and calcium concentration.
Chloride	A soluble anion that is aggressive to most metals. Higher concentration generally indicates higher corrosion potential.
Silica	Silica can form hard scale in some systems. Silica is more soluble as the pH increases; however, magnesium silicate can precipitate as the pH increases above 8. The silicate that forms at high pH contributes to measured alkalinity.
Sulfate	An anion that is reasonably soluble and can increase the corrosion potential at higher concentrations. Can form calcium sulfate scale at higher sulfate concentration, especially if calcium is greater than 800 mg/L as $CaCO_3$.

TABLE 5.2 Major Components That Affect Water Chemistry

Bicarbonate (HCO_3-)

The bicarbonate ion is the principal alkaline constituent of almost all water supplies. Bicarbonate concentration is generally 5 to 500 mg/L as calcium carbonate ($CaCO_3$). One cause of bicarbonate in natural water is the presence of limestone rock in the watershed or subterranean rock. Normal activities of the human population introduce alkaline materials into water, evidenced by a typical increase of alkalinity of sewage plant effluent of 100 to 150 mg/L above the alkalinity of the municipal water supply. Much of this is due to the alkalinity of industrial and domestic detergents. Alkalinity in drinking water supplies seldom exceeds 300 mg/L. Control of alkalinity is important in many industrial applications, because of its significance in calcium carbonate scale formation. Alkalinity control is important in both concentrated boiler water and cooling water in evaporative cooling systems. Makeup water for these systems must often be pretreated for alkalinity reduction, or by direct acid addition. Alkalinity is objectionable in certain other industries, such as the beverage industry, where it neutralizes the acidity of fruit flavors; and in textile operations, where it interferes with acid dyeing.

Total alkalinity (also called M alkalinity) is a measure of all titratable species that neutralize acid. If the relationship between pH and alkalinity is outside the norm, M alkalinity may include other species besides bicarbonate and carbonate, like phosphate, silicate, or ammonia.

Calcium ($Ca+^2$)

Calcium is the major component of hardness in water and usually is in the range of 5 to 500 mg/L as $CaCO_3$ (2–200 mg/L as Ca). Calcium, along with alkalinity, is a major factor in determining the scale forming or corrosive tendency of water. It is present in many minerals, principally limestone and gypsum. Limestone deposits are often the residues of the fossils of tiny aquatic organisms, such as polyps, that have taken calcium from seawater in which they lived and used it for their skeletons. This is but one of many cycles in nature whereby some component of the environment is continually withdrawn by living things and eventually returned directly or indirectly.

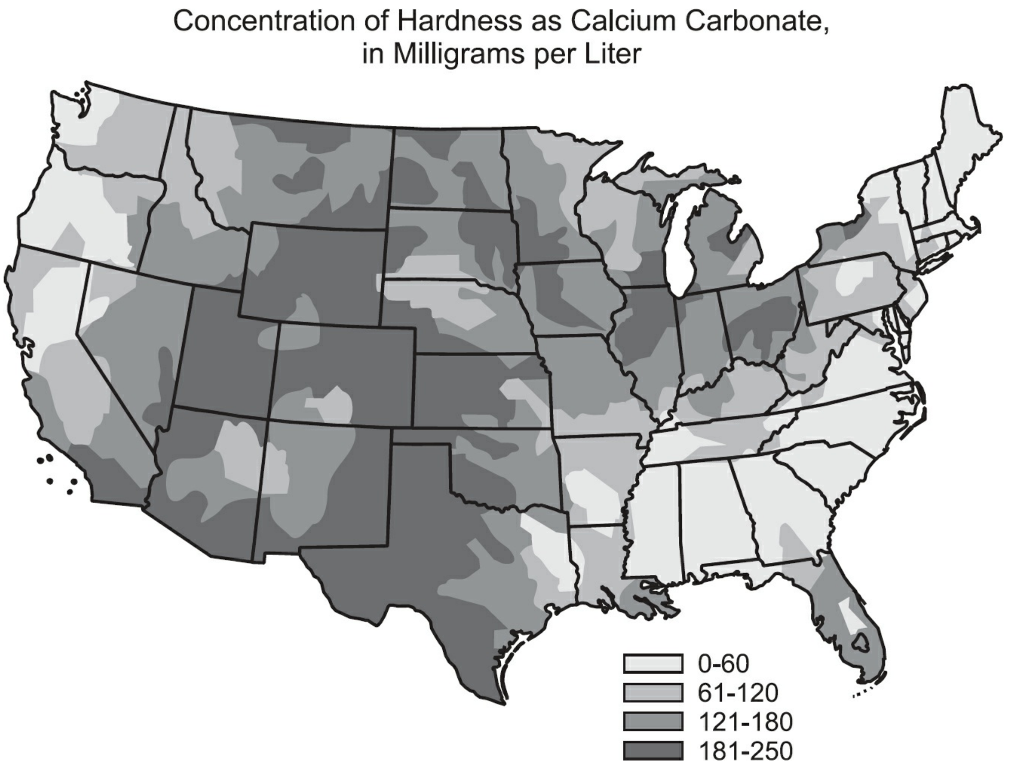


FIGURE 5.3 The calcium hardness of water can vary significantly depending on location because of the minerals in the soil that contact groundwater or surface water. (*Adapted from content provided by the United States Geological Survey*.)

Chloride (Cl-)

Since almost all chloride salts are highly soluble in water, chloride is common in freshwater supplies, ranging from 10 to 100 mg/L. Seawater contains over 30 000 mg/L as sodium chloride (NaCl), and certain underground brine wells may actually be saturated (approximately 25% NaCl). Many geologic formations were once sedimentary rocks in the sea, and it is not surprising they contain residues of chlorides that are continually leaching into freshwater sources. The chloride content of sewage can be 200 mg/L above the concentration of the municipal water supply, accounting in part for the gradual increase in salinity of rivers as they proceed from headwaters to the sea. The recommended upper limit for chloride in drinking water is 250 mg/L, based entirely on taste, not on any known physiological hazards.

Magnesium ($Mg+^{2}$)

The magnesium hardness of water is usually about one-third of the total hardness, the remaining two-thirds being calcium hardness. Magnesium typically ranges from about 40 to 200 mg/L as $CaCO_3$ (10–50 mg/L as Mg). In seawater, the magnesium concentration is about five times that of calcium on an equivalent basis. The production of magnesium hydroxide from seawater is the starting point in the manufacture of magnesium. Magnesium is a prominent component of many minerals, including dolomite, magnesite, and numerous varieties of clay.

Since magnesium carbonate is appreciably more soluble than calcium carbonate, magnesium is seldom a major component in scale, except where silicate is present in the water or in seawater evaporators. However, magnesium must be removed along with calcium, where soft water is required for boiler makeup or for process applications.

Silica (SiO_2)

Silica is present in almost all minerals, and is found in freshwater at 1 to 100 mg/L as SiO_2. The skeletons of diatoms are pure silica, and the silica content of surface waters may be affected by seasonal diatom blooms. Silica may be dissolved, but is often colloidal because of its reaction with adsorbents like magnesium oxide (MgO) and ferric hydroxide [$Fe(OH)_3$], thereby having characteristics similar to typical colloids. There is probably equilibrium between the silica in colloidal form and the bisilicate ($HSiO_3^-$) anion. Because of this complexity, it is difficult to predict the solubility of silica as water concentrates by evaporation.

The term “colloidal silica” is loosely used by water chemists and can be confusing. Small polymeric silica chains can form in solution. Larger polymeric groups may not be measured when analyzing dissolved silica by the typical molybdate-reactive method. The undetected silica may be termed colloidal silica. A more accurate statement would be that inert (or nonreactive) silica is present, since most of the silica is colloidal, although of differing sizes. Silica is objectionable at high concentration in cooling tower makeup because of this uncertainty about its solubility limits.

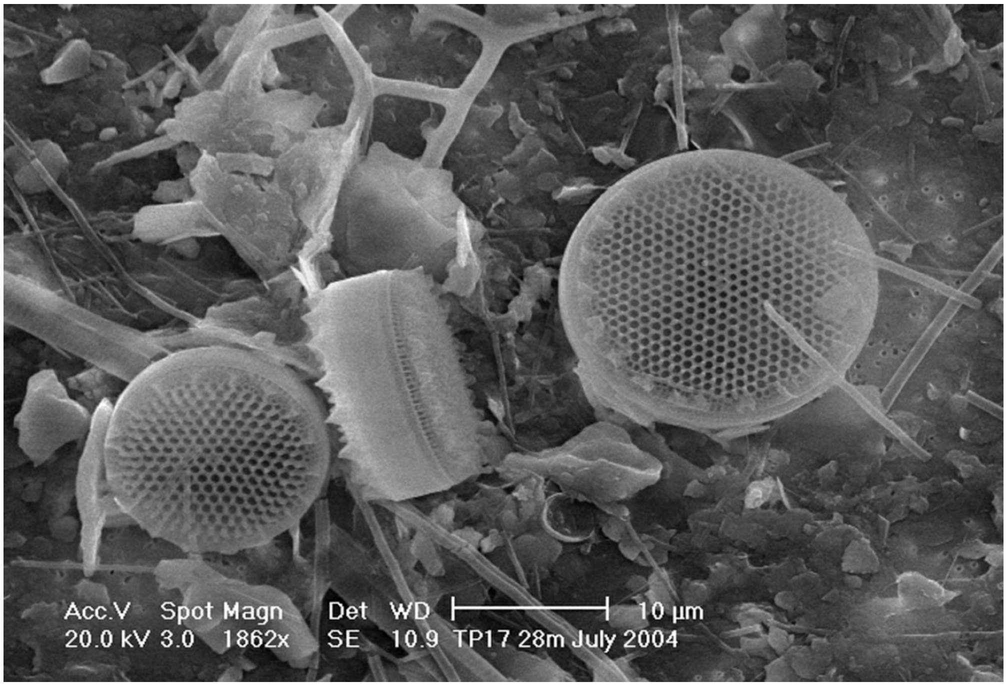


FIGURE 5.4 Diatoms create a skeleton of silica as seen by a scanning electron microscope (CC BY-SA 4.0, via Wikimedia Commons.)

Silica is objectionable in boiler feedwater makeup because it may form scale in the boiler itself, and because it volatilizes at high temperatures and redeposits on turbine blades. Treatment processes that remove silica include adsorption on magnesium precipitates in lime softening, adsorption on ferric hydroxide in coagulation processes using iron salts, anion exchange in the demineralization process, and reverse osmosis (RO).

Sodium (Na^+)

Sodium salts are highly soluble in water, although certain complexes in minerals are not. The high chloride content of brines and seawater is usually associated with the sodium ion. In freshwaters, its range is usually about 20 to 200 mg/L as $CaCO_3$ (10–100 mg/L as Na). Sodium is present in certain types of clay and feldspar. There is an increase of sodium in municipal sewage of 40 to 70 mg/L in excess of the municipal water supply. Its concentration is not limited by federal drinking water standards, and persons on low sodium diets may require special sources of potable water.

Sulfate (SO_4^{-2})

Sulfate dissolves in water from certain minerals, especially gypsum, or appears from the oxidation of sulfide minerals. It's typical range is 5 to 200 mg/L as SO_4. The suggested upper limit in potable water is 250 mg/L, based on taste and its potential cathartic effect. Because calcium sulfate is relatively insoluble (< 2000 mg/L), sulfate may be objectionable in water concentrating processes that are high in calcium, as in an evaporative system.

Aluminum ($Al+^3$)

Although aluminum constitutes a high percentage of the earth's crust as a common component of a wide variety of minerals and clays, its solubility in water is so low that it is seldom a cause for concern in either municipal supplies or industrial water systems. However, in industrial systems, the carryover of alum floc from a clarifier may cause deposit problems, particularly in cooling systems where phosphate is used for corrosion control. Aluminum found in treated water systems is usually due to colloidal residues of alumina (Al_2O_3) from coagulation of water, when alum or sodium aluminate is used as the coagulant. If the residuals are objectionable, they can be removed by improved filtration practices.

As shown by the solubility curves (Fig. 5.5), aluminum is amphoteric, meaning soluble at both low and high pH. In water, soluble aluminum is present as Al^{+3} or lower valence hydroxyl forms at low pH and the aluminate anion $[Al(OH)_4^-]$ at higher pH values. As might be expected from this amphoteric nature, alumina particles are positively charged at low pH and negatively charged at high pH, as indicated by Fig. 5.6. The effectiveness of alum in precipitating negatively charged colloids, such as clay particles from water, is more likely related to the charge on the precipitated alumina than the charge on the aluminum ion itself, since the aluminum ion is not soluble in the typical coagulation pH of 5 to 7. Its strong negative charge at pH 10.0 to 10.5 helps explain the effectiveness of sodium aluminate in precipitating magnesium hardness, which is positively charged at this pH.

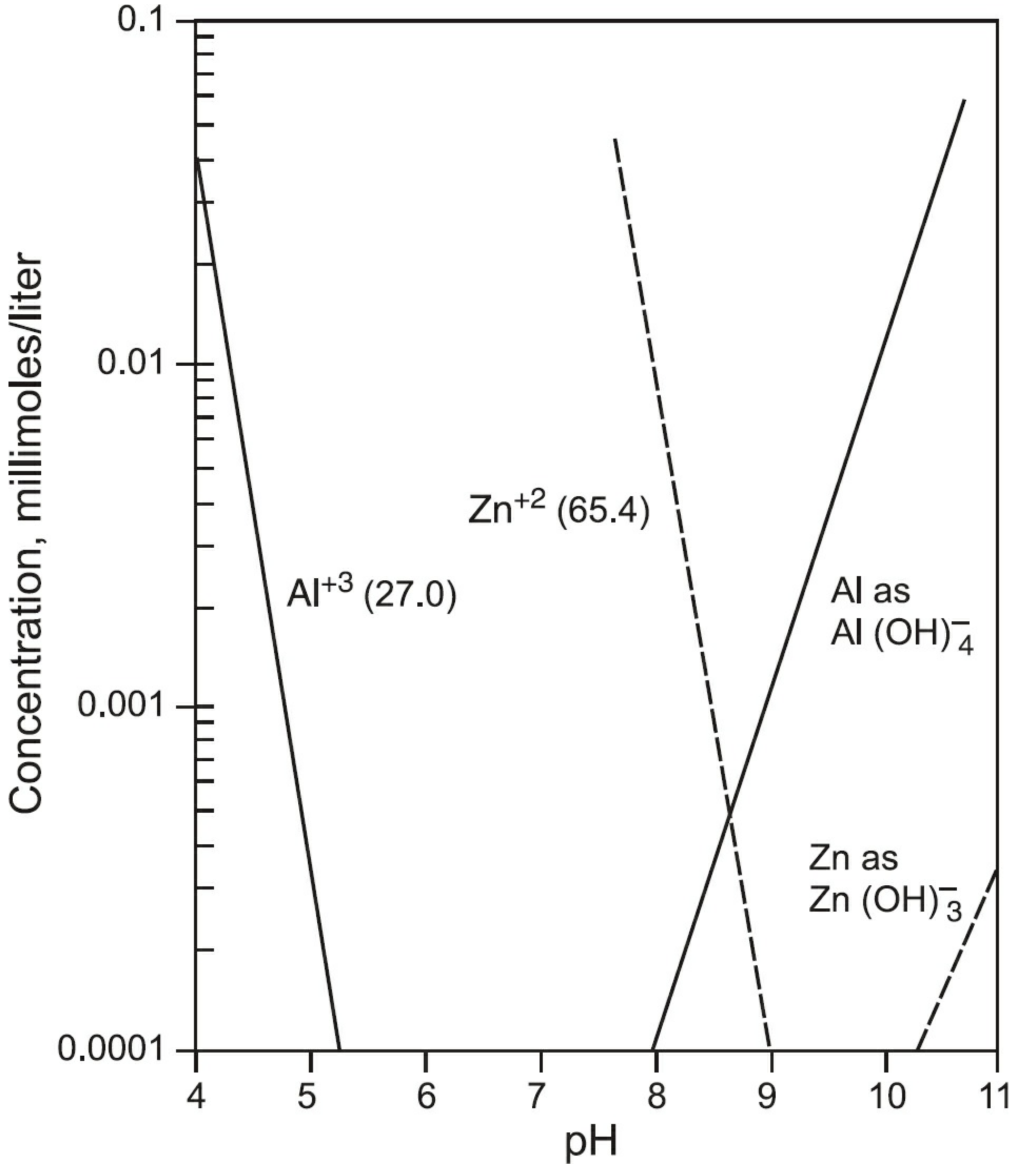


FIGURE 5.5 Theoretical solubility of aluminum and zinc in water at 25°C, showing the amphoteric nature of both metal ions. (*Source: Stumm and Morgan, 1970.*)

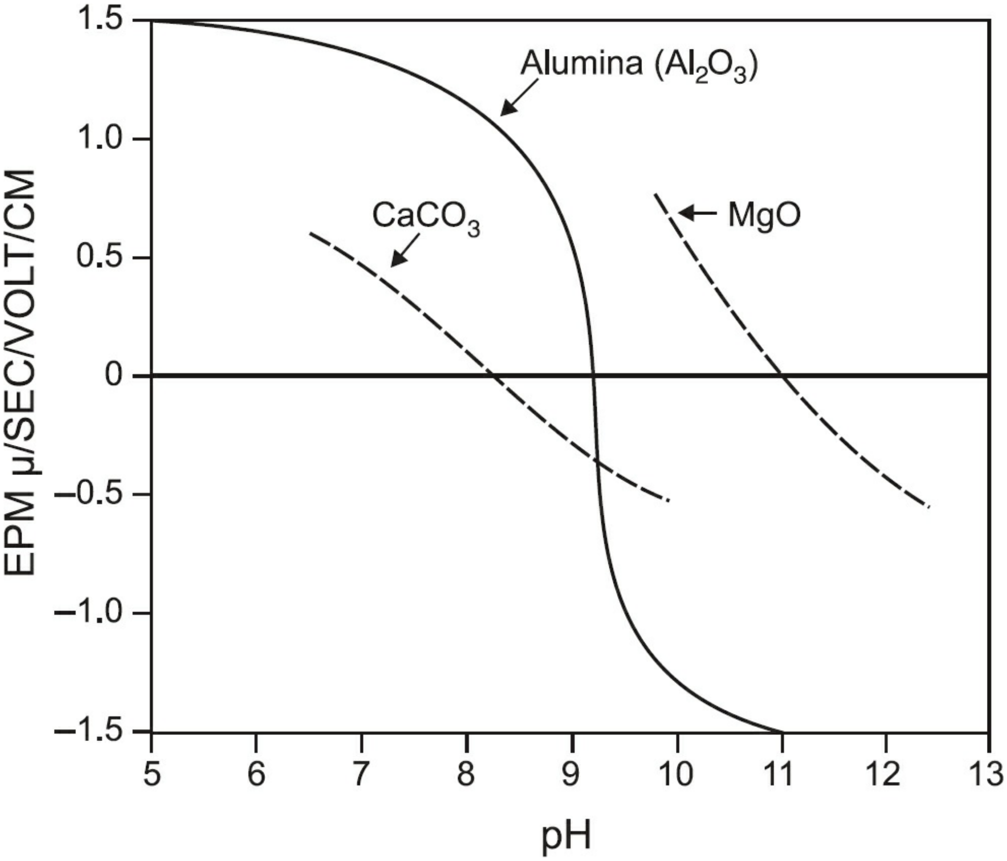


FIGURE 5.6 Variation of particle charge with particle type and solution pH. (*Source: Stumm and Morgan, 1970.*)

Arsenic (As)

The solubility of arsenic in water is so low that its presence is usually an indicator of either mining or metallurgical operations in the watershed or runoff from agricultural areas, where arsenical materials have been used as industrial poisons. If in colloidal form, it would be removed by conventional water treatment processes. Federal regulations limit the content in public water supplies to 0.01 mg/L total arsenic. If the material is present in organic form, it may be removed by oxidation of the organic material and subsequent coagulation or by an adsorption process, such as passage through granular activated carbon.

Barium ($Ba+^2$)

In natural waters containing bicarbonate and sulfate, the solubility of barium is less than 0.1 mg/L as Ba, and it is seldom found at concentrations exceeding 0.05 mg/L. Removal to low residuals can be expected in conventional lime treatment processes. There are instances of barium being added to water for the specific purpose of sulfate reduction. The reaction is hindered because the barium reagent itself is so insoluble that considerable time is needed for the reactions to occur; furthermore, sulfate deposition on the surface of the barium reagent makes the process inefficient. Barium is limited in drinking water to a maximum concentration of 2 mg/L.

Borate [$B(OH)_4$-]

Most of the world's boron is contained in seawater at 5 mg/L as B. Pure supplies of sodium borate occur in arid regions where inland seas evaporated to dryness, especially in volcanic areas. Boron is frequently present in freshwater supplies from these same geologic areas. It is present in water as nonionized boric acid [$B(OH)_3$]. At high pH (> 10), most of it is present as the borate anion [$B(OH)_4^-$]. Borate is used for pH adjustment and buffering in closed cooling systems. Its concentration is not limited in municipal waters by potable water standards. Borate can be damaging to citrus crops if present in irrigation water, and irrigation methods tend to concentrate the material in the soil. Although boron is in the same group on the periodic chart as aluminum, it behaves more like silica in aqueous systems.

Bromide (Br -)

Bromine is found in seawater at about 65 mg/L as the bromide ion; some connate waters produced with oil contain several hundred milligrams per liter and are the source of commercial bromine. Over 0.05 mg/L in freshwater may indicate the presence of industrial wastes, possibly from the use of bromo-organo compounds such as biocides or pesticides.

Copper (Cu+ and Cu+^{2})

Copper may be present in water from contact with copper-bearing minerals or mineral wastes from copper production. It is more likely, however, copper found in water is a product of corrosion of copper or copper alloy piping or fittings, or may have been added deliberately as copper sulfate to a water supply reservoir for algae control. When copper sulfate is added for algae control, because its solubility is limited, organic chelating materials may be added to the copper sulfate formulation to keep the copper from precipitating, and therefore maintain its effectiveness. Drinking water regulations limit the municipal water supply concentration to 1 mg/L. At higher concentrations, the water has an astringent taste. If a water supply is corrosive to copper, the first drawing or tapping of the supply from piping, which has been idle overnight, may contain relatively high concentrations, and ingestion of this water may cause immediate vomiting. In industrial supplies, the presence of copper can be objectionable, as it is corrosive to aluminum. Copper is essential to certain aquatic organisms, being present in hemocyanin in shellfish, the equivalent of hemoglobin in humans.

Fluoride (F^-)

Fluoride is a common constituent of many minerals, including apatite and mica. It is common practice to add fluoride to municipal water to provide a residual of 1.5 to 2.5 mg/L as F, which is beneficial for control of dental caries. Concentrations above approximately 5 mg/L are detrimental, however, usually causing mottled, brittle tooth structure. Because of this, the concentration is limited by drinking water standards to 4 mg/L. High concentrations are present in wastewaters from glass manufacture, steel manufacture, and foundry operations. Lime precipitation can reduce this to 10 to 20 mg/L.

Iron (Fe^{+2} and Fe^{+3})

Iron is found in many igneous rocks and in clay minerals. In the absence of oxygen, iron is quite soluble in the reduced state, which is the ferrous form (Fe^{+2}). This can be seen in an analysis of well water containing iron. When oxidized to ferric ion (Fe^{+3}) at pH 7 to 9, iron is insoluble, and the concentration can be readily reduced to less than 0.3 mg/L as Fe, the suggested maximum set by drinking water standards. Because iron is so insoluble when oxidized completely, the actual residual iron after treatment is determined by how well the colloidal iron has been coagulated and filtered from the water. Because iron is a product of corrosion in steel piping systems, iron found in water from a distribution system is often from the pipes and does not represent iron left from the treatment process in the water treatment plant.

Lead (Pb^{+2})

The presence of lead in freshwater usually indicates contamination from metallurgical wastes or from lead-containing industrial poisons, such as lead arsenate. However, lead may appear in water because of corrosion of lead-bearing alloys, such as solder. Being amphoteric, lead is attacked in the presence of caustic alkalinity.

The limitation on lead in drinking water is 0.015 mg/L as Pb, which should be readily achieved with good filtration practice. In wastewaters where lead may be complexed with organic matter, it may be solubilized, and oxidation of the organic may be required for complete lead removal.

Lithium (Li+)

This alkaline earth element is rare in nature and seldom analyzed in water. There are no records of experience indicating that this material is of concern either in industrial or municipal water supplies. However, lithium salts are used in psychotherapy to combat depression, so there may be a concentration level in water that has a psychotropic effect. Lithium salts have a wide variety of uses, but the industrial consumption is so low that it is not likely to be a significant factor in wastewaters.

Manganese (Mn^{+2}, Mn^{+4})

Manganese is present in many soils and sediments as well as in metamorphic rocks. In water free of oxygen, it is readily dissolved in the manganous (Mn^{+2}) state and may be found in deep well waters at concentrations as high as 2 to 3 mg/L as Mn. It is also found with iron in acid mine drainage. Wastewaters from metallurgical and mining operations frequently contain manganese. It is an elusive material to deal with because of the great variety of complexes it can form depending on the oxidation state, pH, bicarbonate-carbonate-hydroxide equilibria, and the presence of other materials, particularly iron. The suggested drinking water limit is 0.05 mg/L, because higher concentrations cause manganese deposits and staining of plumbing fixtures and clothing. However, even lower concentrations can cause similar effects, as it may accumulate in the distribution system as a deposit, to be released in higher concentrations later if the environment changes, such as by change in pH, CO_2 content, oxidation potential, or alkalinity. In industrial systems, it is as objectionable as iron, particularly in textile manufacture or the manufacture of bleached pulp, since small amounts of deposited manganese can slough off to stain products, which must be rejected. Certain textile finishing operations require reduction to levels as low as 0.01 mg/L.

In the oxidized manganic (Mn^{+4}) state, manganese is insoluble. Organic materials can chelate manganese much as they chelate iron and increase its solubility. Because manganese accumulates in sediments, it is common to find high levels of manganese in deep water, where none may be apparent at the surface. This should be studied in designing the proper intake structure for a plant water supply. An example of this is illustrated in Fig. 5.7, showing hypothetical manganese concentrations in a lake at various times of the year and at different depths.

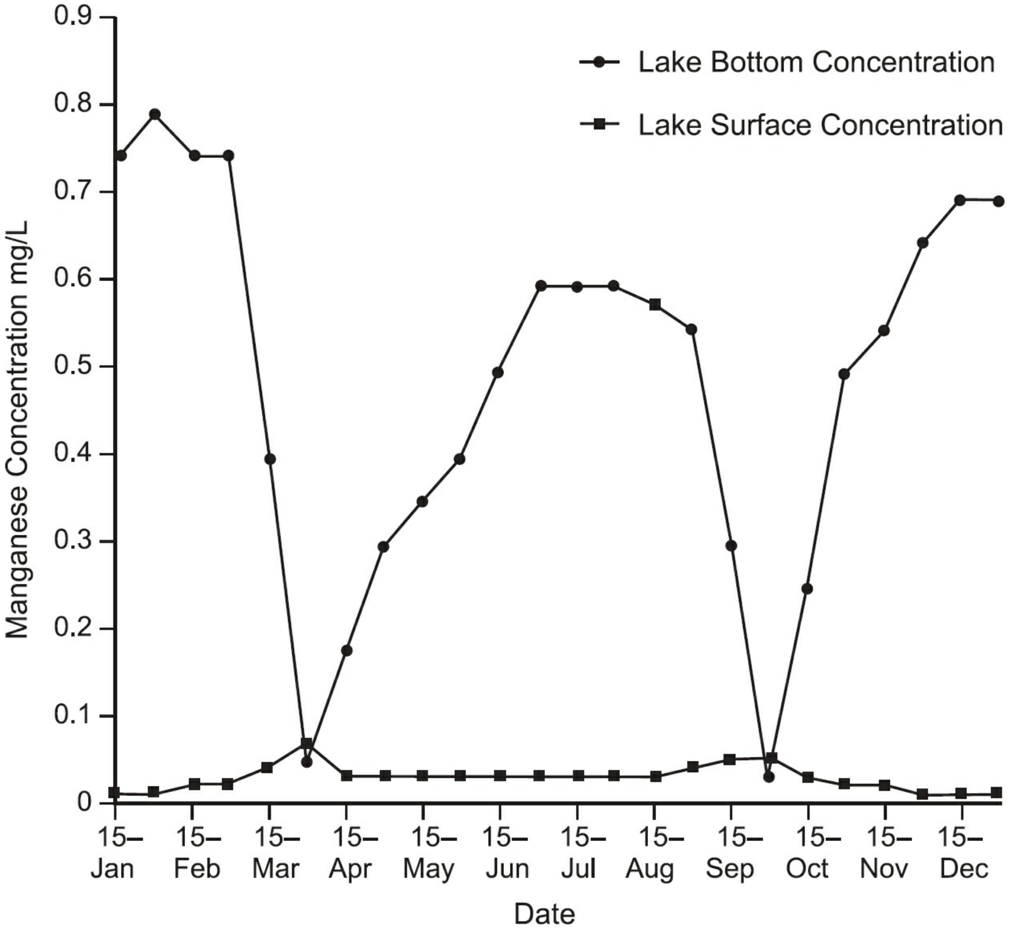


FIGURE 5.7 Hypothetical example of seasonal inversion of a lake that is 93 ft (28 m) deep. The soluble manganese concentration varies significantly at the bottom, but only slightly in the oxygenated surface layers of water.

Nitrate (NO3-)

Nitrate, like ammonia, comes into water via the nitrogen cycle, rather than through dissolving minerals. Its concentration is limited by drinking water standards to 10 mg/L as N for physiological reasons. There are no reported uses of water where nitrate is a restrictive factor. Total nitrogen in sewage plant effluent can increase 20 to 40 mg/L as N above the level in the municipal water supply. Sources of this nitrogen include nitrate and ammonia. Nitrate can be converted to nitrogen in a biological system by the action of nitrifying bacteria. The nitrate content of well water may be higher than surface water, unless the surface water is contaminated with agricultural fertilizers.

Phosphate (PO_4^{-3})

Phosphorus is found in many common minerals such as apatite, in the form of orthophosphate (PO_4^{-3}). Since phosphate compounds are widely used in fertilizers and detergents, it is common to find phosphate in silt from agricultural runoff, with high concentrations being found in municipal wastewater, generally in the range of 5 to 15 mg/L as PO_4, but it can be as high as 15 to 30 mg/L as PO_4. Since phosphate is a primary cause of excessive algal growths, which lead to eutrophication of lakes and streams, legislated reduction of phosphate from all sources continues in many parts of the world.

Phosphate may be present in water as HPO_4^{-2} and $H_2PO_4^{-}$ as well as the higher pH form PO_4^{-3}. The distribution as affected by pH is shown in Fig. 5.8. Phosphate can be reduced to very low levels by treatment with alum, sodium aluminate, or ferric chloride, which causes formation of insoluble aluminum phosphate or iron phosphate. It can also be precipitated with lime at pH > 10 to produce residuals less than 2 to 3 mg/L in the form of hydroxyapatite; in a hot process system, the residuals would be less than 0.5 mg/L. These phosphate precipitates are often colloidal, and filtration is required to achieve low residuals.

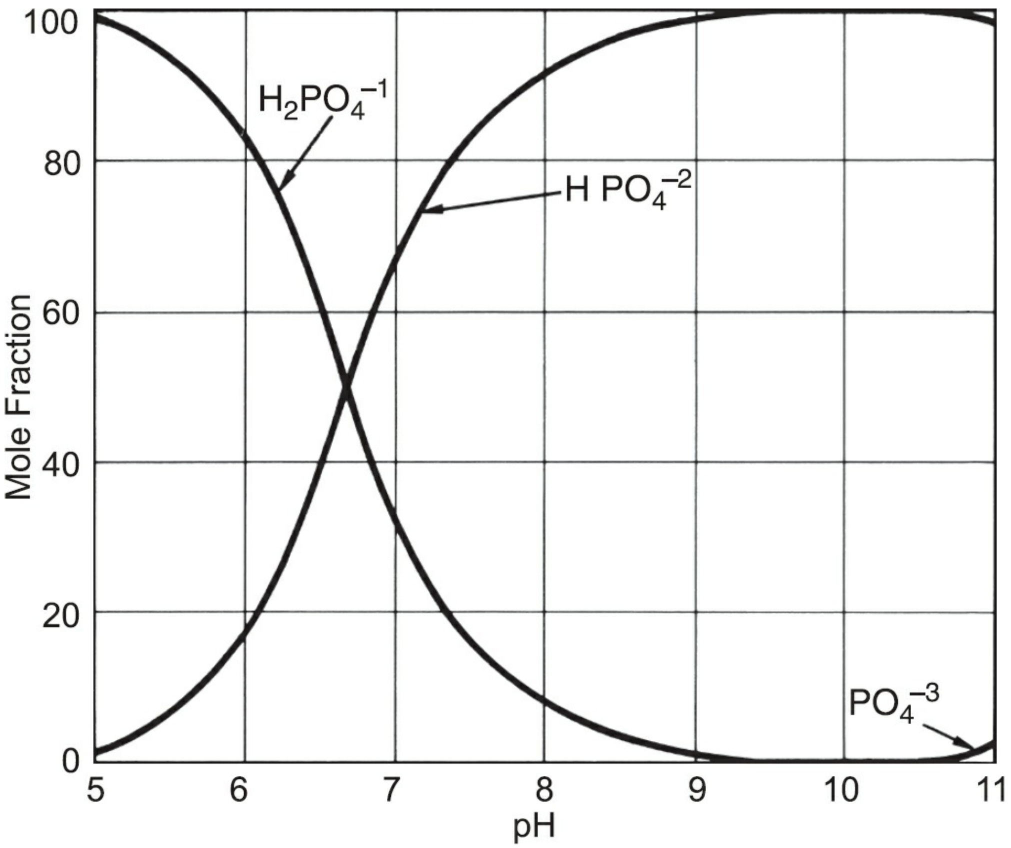


FIGURE 5.8 Effect of pH on the distribution of phosphate ions in solution.

Potassium (K+)

Potassium is closely related to sodium, so much so that it is seldom analyzed as a separate constituent in water analysis. Its occurrence is less widespread in nature, and for that reason, it is found at lower concentrations than sodium. It has no significance in public water supplies or in water used for industrial purposes. As with sodium, it can be removed chemically only by cation exchange or by physical processes such as evaporation and reverse osmosis. Potassium salts are highly soluble in water, but as a common constituent of clays, potassium is kept from dissolving by the nature of the structure of clay. For that reason, when water-formed deposits contain significant levels of potassium, it is probably caused by silt, in which case the deposit would also be high in Al_2O_3 and SiO_2.

Strontium ($Sr+^2$)

Strontium is in the same family as calcium, magnesium, and barium and has low solubility in the presence of bicarbonate (about half that of calcium).

Strontium is only found in areas of geologic formations where lead ores occur, and therefore its concentration in water is typically quite low. It is completely removed by any process used for calcium removal. If not removed by softening, in scale-forming water, it is a contributor to the scale problem.

Zinc (Zn^{+2})

Zinc is a metal, behaving quite like calcium in solution, although zinc has considerably lower solubility than calcium in natural waters with a neutral pH and bicarbonate alkalinity. Figure 5.5, shown earlier, illustrates zinc solubility characteristics. Zinc is seldom found at concentrations over 1 mg/L as Zn, with a typical concentration being approximately 0.05 mg/L. Because it tends to have an astringent taste, its concentration in public water supplies is recommended as 5 mg/L maximum.

Zinc may be present in water because of waste discharges from mining, metallurgical, or metal finishing operations. It may also appear because of corrosion of galvanized steel. Zinc is often included in proprietary corrosion inhibitors, where its effect on steel piping is similar to that of galvanizing.

Suspended Matter

A variety of matter can be suspended in water, particularly flowing water. Silt, sand, and soil are perhaps the first things that one thinks of as suspended matter in water. Pictures of the great rivers of the world illustrate the brownish, muddy appearance of the water. Aerial photos of the mouth of the Amazon River in Brazil show suspended matter carried for long distances out into the Atlantic Ocean by the powerful flow of the river. While most of the suspended matter in rivers is probably soil removed from the drainage basin, other suspended matter can be organics and metal ions. Decaying organic material, bacteria, algae, protozoa, etc. can all contribute to suspended matter in natural waters. In the open oceans, plankton is the major component of suspended material. Metal ions such as iron and manganese in their oxidized states can contribute to suspended matter in water. While these metal ions are soluble in many groundwater sources, iron and manganese are insoluble metal oxides present in particulate form in oxygenated waters.

Lake water can contain suspended material, depending on the characteristics of the body of water. Generally, lake water has much lower suspended solids than river waters. A young lake in a mountainous region, with a rocky bottom, may be very clear and have less than 1 mg/L suspended matter. An older lake, which has significant bottom sediment, can have higher suspended solids content, partly consisting of biological organisms. Seasonal turnover in lakes can temporarily increase the suspended solids concentration.

While suspended particles in water are not true colloids (like milk), colloidal properties help to keep the particles suspended in the water. Electrostatic forces between particles can determine whether particles repel each other or are attracted to each other. In most cases, particles in water have a natural, negative charge on the surface. This electrical charge serves to repel other like particles when two or more particles interact. Another force that affects particle interaction is the van der Waals force, which is a weak, short-range, attractive force. The fluctuating negative charge on a particle surface can create a temporary dipole moment in a particle. This dipole can induce another opposite dipole in a nearby particle. In this case, the particles are attracted to each other. These surface charges are the basis for the functioning of both dispersant and coagulation technology. Anything that increases or reinforces the surface charge helps keep the particles suspended, while anything that neutralizes the surface charge causes the particles to agglomerate and settle out of solution.

Organic Matter (Carbon, C^{+4})

Since organic material makes up a significant part of the soil and because it is used by aquatic organisms to build their bodies and produce food, it is inevitable that water-soluble organic products of metabolism should be present in all water supplies. Analytical data on the many organic compounds in most water sources are not generally available. Therefore, indexes such as those described in Table 5.3 are used. There are literally hundreds of thousands of known organic compounds, many of which might find their way into the hydrologic cycle. Methods of analysis exist for organic materials of interest, especially those considered toxic or carcinogenic, such as polychlorinated biphenyls (PCB) and absorbable organic halogen (AOX). In general, indirect measures of organics in water are used instead. Examples include biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC).

Test	Description
BOD	Biochemical oxygen demand measures the ability of common bacteria to digest organic matter, usually in a five-day incubation at 20°C, by analyzing depletion of oxygen. This measures biodegradable organic matter, expressed as mg/L O_2.
COD	Chemical oxygen demand measures the ability of hot chromic acid solution to oxidize organic matter. This analyzes both biodegradable and nonbiodegradable (refractory) organic matter, expressed as mg/L O_2.
Color	Color is a rough measure of tannin, lignin, and other humic matter in surface waters and certain wastes, such as Kraft pulping wastes. Reported in American Public Health Association (APHA) color units related to cobalt and platinum standards.
DOC	Dissolved organic carbon is a measure of the total dissolved organic matter in water. The sample is filtered through a 0.45 μm or 0.22 μm membrane to remove undissolved organics, then acidified, and purged to remove inorganic carbon. Analysis by TOC follows, reported as mg/L C.
Solvent extractables	Extractables measures the organic matter directly extractable from water, using an organic solvent, usually hexane (C_6H_{14}), although carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) may be used. Reported as mg/L.
TOC	Total organic carbon measures the CO_2 produced from organics, when a water sample is atomized into a combustion chamber. The CO_2 equivalent to the alkalinity may be removed first, or this equivalent may be subtracted from the total CO_2 to determine organic carbon. Reported as mg/L C.

TABLE 5.3 Commonly Used Methods for Determination of Organic Matter in Water

Many waters have a yellowish or tea color due to decayed vegetation leached from the watershed by runoff. These organic materials are broadly classified as humic substances, further categorized as humic acid (a water-soluble compound), fulvic acid (alkali-soluble material), and humin (high molecular weight, water-insoluble matter). These organic compounds are molecules having many functional groups containing oxygen and hydrogen atoms in various proportions, so that when organic matter is reported as carbon, as in TOC determination, it is probable that the molecular weight of these humic organic molecules is 2.0 to 2.5 times greater than the value reported as carbon. A survey of 80 municipal supplies in the United States showed an average TOC content in the finished water of 2.2 mg/L as C, and the organic matter was probably about 5 mg/L.

Organic matter in a river can vary significantly over the length of the river. Figure 5.9 shows the dissolved organic carbon (DOC) along the length of the Mississippi River. DOC is a measure of the total dissolved organic matter. Most organic matter is from natural sources, and wastewater contributes small amounts of DOC. The concentration of DOC is dependent on volume and flow of the river, as evidenced by decreasing concentration downriver near New Orleans. Absorbable organic halogen (AOX) is a measure of halogenated organics dissolved in water. Some AOX may be natural, but many AOX compounds result from chlorination or bromination of water, including drinking water, wastewater before discharge, and process applications that require bleaching, such as in the paper industry. AOX compounds may be volatile or nonvolatile, and some may be toxic. The concentration of AOX along the Mississippi River varies significantly, but in no specific pattern, along the length of the river (Fig. 5.9).

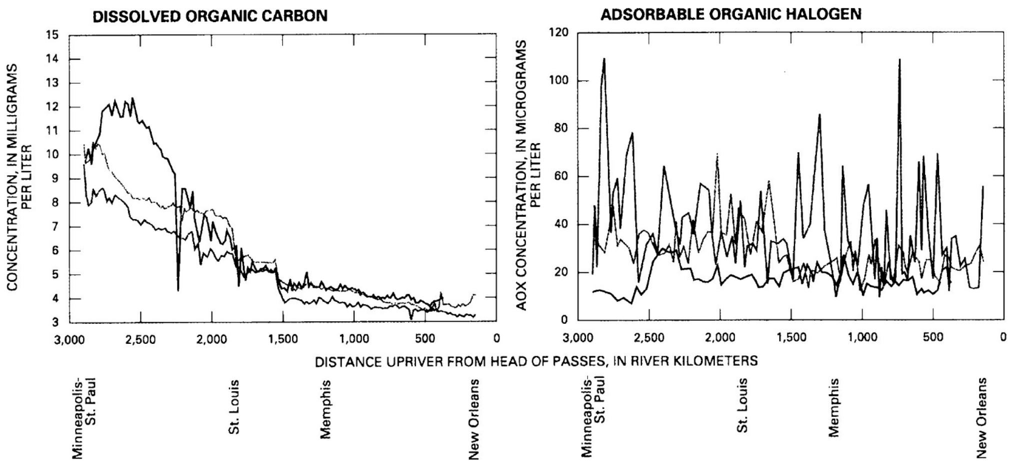


FIGURE 5.9 Dissolved organic carbon and absorbable organic halogen along the Mississippi River. (*Source: Figure 54 in USGS Circular 1133, 1995; Courtesy of the U.S. Geological Survey.*)

Because some of the functional groups in humic compounds have ion exchange properties, they tend to form soluble complexes with heavy metals. In spite of this, there is no correlation whatever between the color of water and its total heavy metal concentration.

A study of the Rhine River showed that humic substances comprised from 25% at 1000 m^3/s to 42% at 3500 m^3/s of the dissolved organic matter; sulfonic acids ranged from 41% at 1000 m^3/s to 17% at 3500 m^3/s; a third category, chloro-organics, ranged from 12% at low flow to 5% at high flow. Chloro-organics are refractory, or nonbiodegradable classes of organic matter. The significance of this information is simply that each investigator selects the most practical categories to study and the simplest methods of analysis. There is usually no purpose in identifying 30 to 40 specific organic compounds in water (a rather costly procedure), if rough indexes such as TOC or DOC suffice for the study.

Some organic materials are truly soluble, but many, like humic matter, are colloidal and can generally be removed by coagulation (Fig. 5.10). Alum coagulation at pH 5.5 to 6.0 typically reduces color to less than five APHA units. Organic matter found in domestic sewage often inhibits calcium carbonate precipitation. If natural color exceeds about 50 APHA units, it must be partially removed for lime softening to occur. Organic matter may be removed by activated carbon treatment, which is widely practiced in municipal treatment plants when organic matter causes objectionable tastes or odors in the finished water. Generally, these tastes and odors are produced by algae, each species having its characteristic odor or taste just as with land plants. Like land plants, algae produce organic compounds, and may be toxic if enough is ingested by fish or animals. Organic matter is objectionable in municipal water chiefly for aesthetic reasons. It can be troublesome in industrial supplies by interfering with treatment processes. It is a major factor in the fouling of anion exchange resins, degrading effluent quality of demineralized water, and requiring early replacement of resin.

FIGURE 5.10 A clarifier can effectively remove the majority of suspended solids and humic matter from raw water as illustrated by the output water.

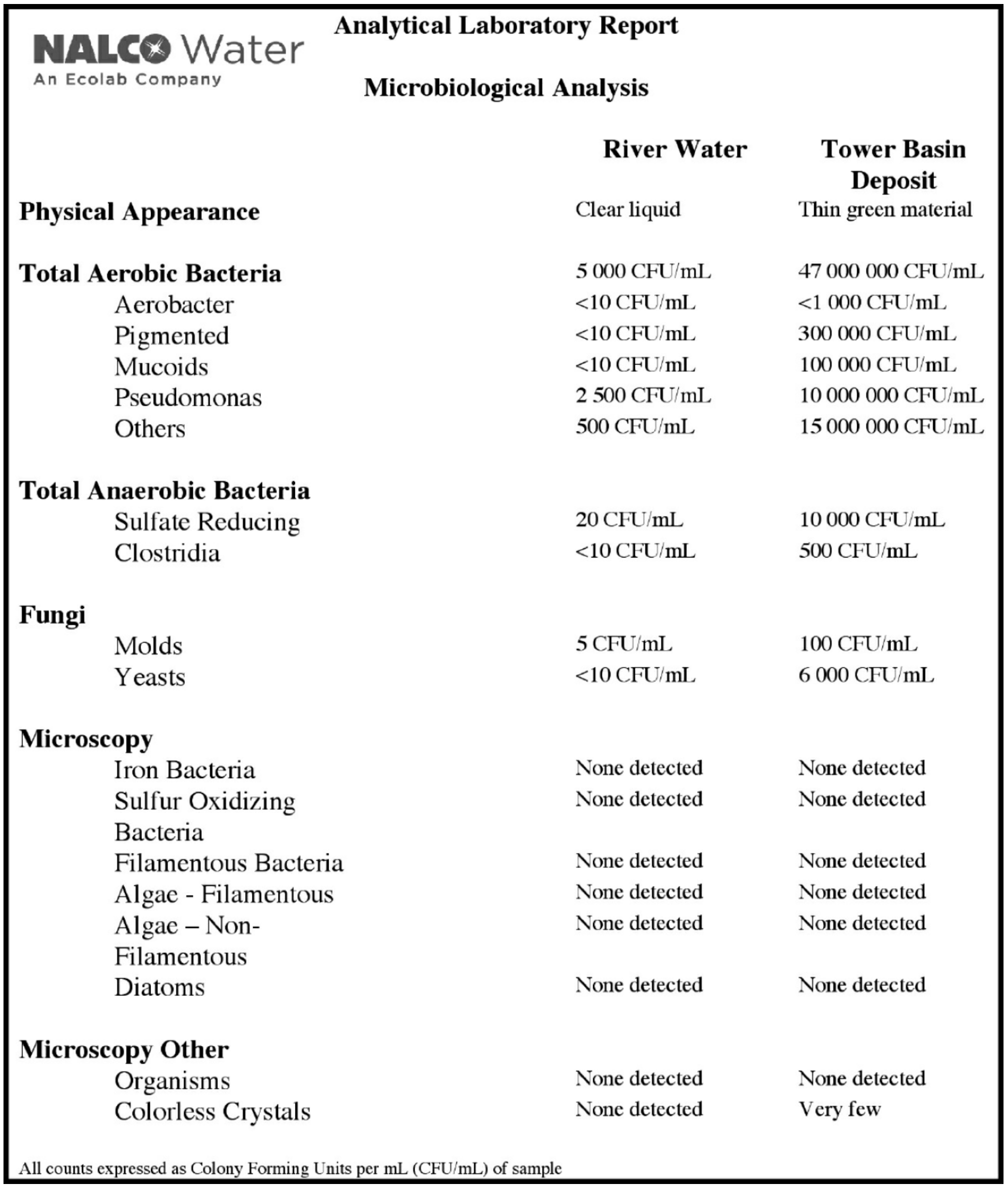
Many organic compounds found in nature are the result of human activity and carried by wastewater discharge into bodies of water. For example, caffeine can be found in rivers (ng/L concentrations) below municipal wastewater plant discharges. Pharmaceutical compounds have been found at very low levels in lakes and rivers. Certain organic materials in water polluted by agricultural runoff (eg, pesticide residues) or by industrial wastes in concentrations below 1 mg/L can exert a significant effect on the biota of the receiving stream. Even when the effect is not dramatic, such as a fish kill, it may have long-term consequences, such as affecting reproduction or disrupting the food chain.

Biological Organisms

Water is essential for life and there are many organisms, large and small, that make their home in water. Generally, microorganisms are considered troublesome contaminants in either drinking water or industrial water. However, several macroorganisms like zebra mussels can cause trouble for systems that use water directly from rivers or lakes. Describing all organisms that may be troublesome in systems that use water is beyond the scope of this book. Therefore, only an introduction to biological organisms is presented.

Other chapters have details on organisms for biological digestion of wastewater, cooling water biological fouling, and pathogenic organisms like *Legionella*.

Microbial analyses are conducted to pinpoint problems in domestic and industrial water systems. There are thousands of species of microbes, and a variety of methods exists to identify troublesome organisms. The most common is the plate count, where bacteria from a water sample are grown on special types of agar containing nutrients specific to different species. The result of the plate count is a number of organisms per volume of sample. Bacteria, fungi, and molds can be determined by plate count methods. Other organisms like algae, iron-depositing bacteria, and protozoa may be identified visually by microscopic inspection. Figure 5.11 illustrates analyses of a river water sample and a cooling tower basin deposit sample. The categories in the analyses are described briefly in the following paragraphs.



NALCO Water
An Ecolab Company

Analytical Laboratory Report

Microbiological Analysis

	River Water	Tower Basin Deposit
Physical Appearance	Clear liquid	Thin green material
Total Aerobic Bacteria	5 000 CFU/mL	47 000 000 CFU/mL
Aerobacter	<10 CFU/mL	<1 000 CFU/mL
Pigmented	<10 CFU/mL	300 000 CFU/mL
Mucoids	<10 CFU/mL	100 000 CFU/mL
Pseudomonas	2 500 CFU/mL	10 000 000 CFU/mL
Others	500 CFU/mL	15 000 000 CFU/mL
Total Anaerobic Bacteria		
Sulfate Reducing	20 CFU/mL	10 000 CFU/mL
Clostridia	<10 CFU/mL	500 CFU/mL
Fungi		
Molds	5 CFU/mL	100 CFU/mL
Yeasts	<10 CFU/mL	6 000 CFU/mL
Microscopy		
Iron Bacteria	None detected	None detected
Sulfur Oxidizing Bacteria	None detected	None detected
Filamentous Bacteria	None detected	None detected
Algae - Filamentous	None detected	None detected
Algae – Non-Filamentous	None detected	None detected
Diatoms	None detected	None detected
Microscopy Other		
Organisms	None detected	None detected
Colorless Crystals	None detected	Very few

All counts expressed as Colony Forming Units per mL (CFU/mL) of sample

FIGURE 5.11 Illustration of the types of organisms typically found in water and deposit samples.

Bacteria

At the head of the list are aerobic bacteria. The total count is a measure of the variety of bacteria living together in a water sample. One of the most common is *Pseudomonas*, a slime-forming variety, which reproduces by fission. Others include spore-forming bacteria that can secrete a thick coating to encapsulate the cell and help it survive changes in temperature, food supply, and other shocks from the environment. Aerobic bacteria require oxygen and produce CO_2 as a by-product of energy production. These exist and survive only in oxygenated water. Some bacteria are facultative, meaning that they can live both in the presence and absence of dissolved oxygen. In lakes and rivers, oxygen content can vary by depth of the water, with the highest concentration at the surface.

The next major classification includes common anaerobic (oxygen-free environment) organisms. These bacteria use fermentation processes to breakdown food sources and produce energy. Some use sulfate in the water and produce sulfide that can cause corrosion in metal piping and equipment, especially beneath deposits where they are shielded from contact with dissolved oxygen. The bottom of deep lakes can be totally devoid of oxygen. Swamps, bogs, and some rivers may have low oxygen at the bottom of the water column, and deposits of decaying vegetation lead to fermentation of the organic matter. By-products of anaerobic bacteria are carbon dioxide, methane, hydrogen, ammonia, and hydrogen sulfide.

Other troublesome bacteria may be determined by microscopic observation of the water or deposit sample. These include iron-depositing bacteria, sulfur-oxidizing bacteria, and filamentous bacteria. When organisms other than those shown on the standard analytical form are found, these are noted in the appropriate location. For example, *Escherichia coli* is reported as aerobic, non–spore-forming bacteria.

Fungi and Algae

Fungi are molds and yeasts. They are important because of their ability to attack cooling tower lumber, deteriorate paper or textile products, and affect use of water in food production. Algae produce tastes and odors and interfere with flocculation and sedimentation processes for clarification of water. Like their larger plant relatives, they have certain blooming seasons during the year.

Identification of species of algae is done with the microscope. The analyst must be able to recognize the large varieties of blue-green and green algae and the delicately patterned diatoms that are part of this family of microorganisms.

Other Organisms

Organisms other than bacteria, fungi, and algae include protozoa and rotifers that are often found grazing on the floc containing other microorganisms. Protozoa are larger, single-celled organisms, and rotifers are multi-celled organisms. The presence of these species in a water sample generally indicates a higher level of biological contamination.

When wastewater is analyzed, it is generally necessary to determine fecal coliform and fecal streptococci to establish the need for final disinfection. Coliform bacteria and particularly fecal coliform are generally an indicator of the presence of pathogenic organisms that can be a health hazard. Effluent should be tested regularly and have coliform counts below a maximum value for a statistically significant number of samples to be considered safe for discharge.

If a bioassay is made of a stream to assess its health, a census must be made of many larger organisms. Macroorganisms, visible to the unaided eye, include a variety of worms, crustaceans, and larvae. A healthy stream contains a large number of species with relatively low populations. These provide food for higher forms of life, such as fish, crawfish, and shrimp.

Macrofouling

Surface water presents problems from growth of mollusks like clams or mussels in plant intake pipes and cooling system (Fig. 5.12). Macrofouling is the attachment of these complex organisms to piping and other surfaces of plant intake piping and cooling system. Macrofouling is most common in, plant intake pipes, once-through cooling systems or system water intakes using surface water, like lakes, rivers, or oceans. Shells of adult clams or mussels can plug heat exchanger tubes as shown in Fig. 5.13. Macrofouling costs are estimated to be in the billions of dollars on an annual basis for worldwide industries. This cost is related to plugged pipes and heat exchanger tubes, reduced water flow, under-deposit corrosion, damage to pumps, and the high cost of prevention or mechanical cleaning of macrofouling deposits.

FIGURE 5.12 A variety of Zebra mussels, which are typically about 5/8 inch (15 mm) in length. (*Courtesy of the United States Geological Survey*.)

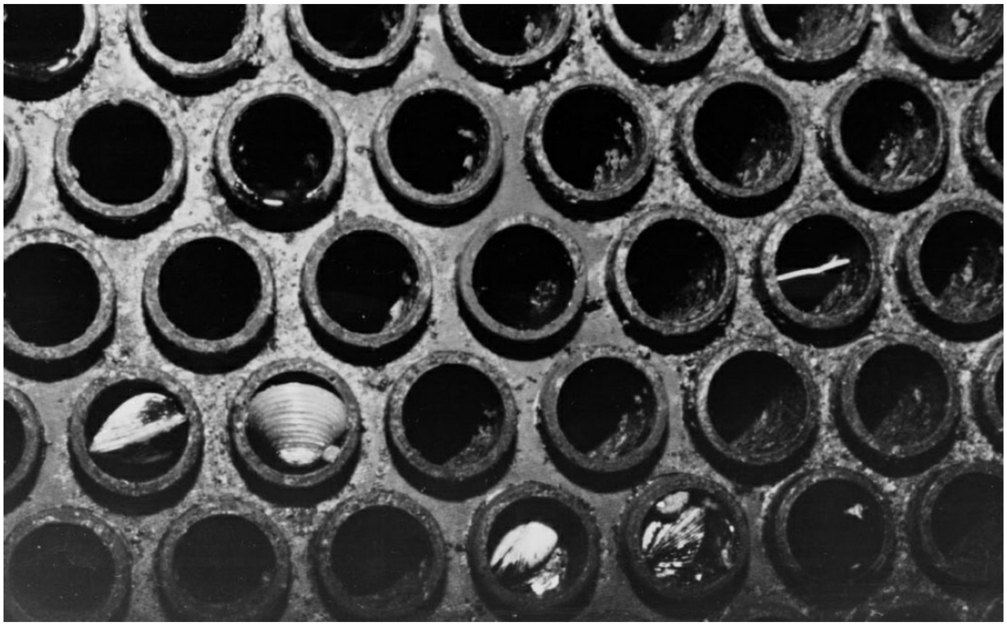


FIGURE 5.13 Small clams lodged in heat exchanger tube inlet end, preventing water flow through those tubes, reducing exchanger efficiency.

The various species of mollusks that cause macrofouling differ between freshwater, brackish, and seawater systems. Barnacles, bryozoa, oysters, and brown-, blue-, and green-lip mussels are examples of seawater and brackish water mollusks responsible for cooling water macrofouling. In fresh water systems, the most common species of concern are Asiatic clams, zebra mussels, gastropods, and bryozoa. Macrofouling can be caused by different species depending on location of the cooling system in the world. The species that receive the most attention as major problem sources are zebra mussels, Asiatic clams, and blue mussels.

Mollusks are invertebrates, characterized by a soft body, and most but not all have an outer shell. The Asiatic clam, blue mussel, and the zebra mussel are bivalves with a hinged, hard shell that covers a soft body. Two tubes channel water to and from a central cavity where there is a single pair of gills. Bivalves filter an average of 7.5 L of water per hour for respiration and feeding. Closure of the shell enables the bivalve to withstand adverse physical and chemical factors for a period. The organism can tolerate anaerobic conditions during the period that the shell is closed.

The life cycle of the blue mussel is shown in Fig. 5.14. This cycle is typical for most bivalves beginning with the larvae or veliger stage and continuing to the mature adult. A complete cycle occurs in about 6 to 9 months for most species, leading to rapid multiplication. When adult organisms in the water spawn, juvenile organisms called veligers are produced. The veligers are free-floating organisms and may be drawn into the water intake of a plant or a once-through system. The veligers can attach to system surfaces and grow into adult mollusks. When adults die, the shell may be released and plug tubes in heat exchangers.

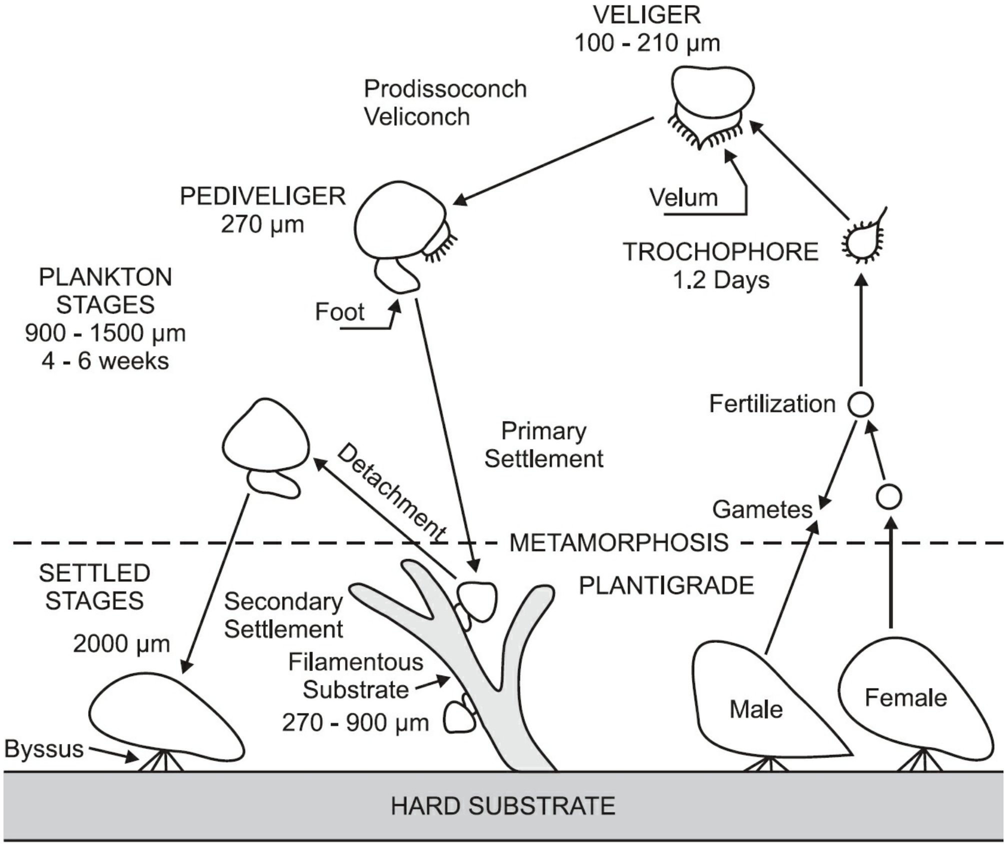


FIGURE 5.14 Life cycle of blue mussels.

The Asiatic clam was first observed in the United States in the 1930s having arrived from Asia. This species is also found in Mexico, Latin America, and Europe, and therefore, Asiatic clams are a global problem. The organisms multiply rapidly in waters with temperatures between 35 to 95°F (2–35°C). In the spring, the adults are able to release about 300 larvae on a daily basis. These mature within 6 to 9 months, and then as adults, are able to reproduce. The larvae and juveniles initially attach to surfaces and later tend to burrow into accumulated mud and silt in low-flow zones.

The zebra mussel is similar to the Asiatic clam in many respects. Zebra mussels reproduce when the adult releases mobile larvae into the environment. A mature adult may release as many as 40 000 larvae per year. The larvae are small and mobile and are able to pass through screens and settle on virtually any surface. Zebra mussels attach themselves to the surface through a sticky byssal thread. The ideal temperature for growth is lower than the Asiatic clam in that zebra mussels prefer water temperature of 68 to 77°F (20–25°C).

The blue mussel is an edible seawater organism and prefers to settle in low-flow environments in cooling systems. The shell of the adult is the main source of fouling problems.

Dissolved Gases

Dissolved gases like oxygen, carbon dioxide, nitrogen, oxides of nitrogen, and oxides of sulfur can significantly affect the quality of any water. For example, a deep well can contain anaerobic bacteria because oxygen has been depleted from the water. A healthy river or stream contains adequate amounts of dissolved oxygen to support a variety of species of fish. Biological activity can affect the balance of dissolved gases in water. For example, algae can cause an increase in the pH of a lake by consuming much of the dissolved carbon dioxide in the water. Several of these gases can affect the pH of groundwater or lake water.

The typical pH of almost all natural waters is 6 to 8, controlled mostly by the presence of bicarbonate alkalinity and some CO_2 dissolved in the water. All waters in contact with geologic formations, including limestone and dolomite minerals, tend to reach this equilibrium pH range as the result of chemical reactions that cause weathering of rocks, and oxidation-reduction reactions which are mediated by aquatic organisms. Because of this, the few exceptional streams that contain free mineral acidity (ie, have a pH below about 4.5) usually dissipate this condition by accelerated weathering of the alkaline components of the rocks they contact. Likewise, when the pH exceeds 8 and carbonate alkalinity begins to appear, this is brought into balance by reaction with carbon dioxide from the atmosphere or from respiration of aquatic life.

Uncontrolled discharge of industrial wastes can damage this natural buffering effect of the equilibrium between the aquatic environment, the atmosphere, and the lithosphere. In most parts of the world, legislation prohibits such discharge; therefore, the only circumstances that normally cause waters to fall outside the natural conditions are accidental spills of large volumes of strong chemicals, seepage of acid mine drainage into a stream, or acid rain from air pollution.

Acid rain is caused by the dissolution of acidic gases from the environment, chiefly the oxides of sulfur, like sulfur dioxide (SO_2) and sulfur trioxide (SO_3), and aggravated by nitrogen oxides (NO_x). The most prominent source appears to be emissions of sulfur from coal-fired power plants. When acid rain falls on alkaline rock or into rivers or lakes in limestone basins, there may be enough reserve alkalinity in the rock or dissolved in the water to neutralize the acidity. However, often rain falls in forested areas where vegetative litter has developed a soil high in humus. There is no natural alkalinity then to counteract acidity of the rainfall, and the runoff is acidic. If the drainage leads to a lake in a granite basin (or a formation free of limestone), the lake itself becomes acidic, and normal aquatic life disappears.

Water Reuse and Recycle

Whether it is called reuse, cascading, or recycle, the use of water that has already been used in another application brings added challenges along with potential savings in water and cost. Many factors must be evaluated when planning to reuse or recycle water in an institutional or industrial application. The first step is to determine the environmental and economic goals. Various water sources and the quality and variability of those sources must be evaluated to match the sources to water quantity and quality requirements of systems. Options for recycle should be optimized for both system performance and cost savings.

One of the major challenges is the use of low-quality water sources for recycle (Table 5.4). Often, water that has been discharged from domestic or industrial applications contains higher contaminant concentrations or additional contaminants that increase the potential for the typical problems in water treatment applications:

Source	Ground Water	Surface Water	Municipal Wastewater	Refinery Wastewater	Sour Water Stripper Bottoms
Aluminum (Al)	<0.1	<2	0.1–0.5	<0.1	0.1–0.5
Iron (Fe)	<5	<2	0.1–1	0.1–2	0–10
Phosphate (PO_4)	<2	<3	6–12	1–10	0–3
Sulfate (SO_4)	10–100	5–50	100–200	100–2000	1–300
Chloride (Cl)	5–100	5–50	100–400	300–700	2–300
Nitrate (NO_3)	<2	<4	2–11	0–4	<3
Ammonia (NH_3)	<1	<1	5–25	0–20	5–70
Hydrogen sulfide (S)	0–2	<0.1	<0.1	<1	0–50
Phenols (C_6H_5OH)	<0.1	<0.1	<0.1	<0.1	200–400
Conductivity µS/cm	<1000	<500	1200–1600	2000–6000	200–1100
Suspended solids (Total at 105°C)	<2	1–25	<5	10–110	<2
COD(C)	<2	<5	20–80	20–280	430–4300
TOC(C)	<2	<10	10–20	10–130	65–1200

All values are in mg/L except conductivity, which is µS/cm.

TABLE 5.4 Comparison of General Ranges of Troublesome Contaminants in Three Wastewater Sources to Typical Concentrations Found in Reasonable Quality Ground and Surface Water Sources That May Be Used for Industrial or Domestic Uses

- Corrosion due to increased chloride, sulfate, ammonia, or sulfide
- Scale due to increased calcium, magnesium, alkalinity, sulfate, phosphate, or silica
- Fouling from increased suspended solids, iron, manganese, aluminum, or organics
- Microbial growth from increased phosphate, ammonia, and organics

These problems can be made more severe by variability of the concentrations of various contaminants in the water stream to be reused. The result is that some type of pretreatment or intermediate treatment must be used to clean the water before it is reused or recycled. In other cases, additional treatment chemicals or methods may be required to minimize corrosion, scale, fouling, or microbial growth in the system that is using the recycled water. Pretreatment methods may be as simple as filtration or as extensive as membrane separation like reverse osmosis.

Finally, to achieve the desired goal, a strategy for reuse and recycle should be developed. The simplest options should be considered first, before progressing to successively more complex reuse and recycle methods. Water conservation should be one of the first options considered. Cascading water from one process in a plant to another, that has less critical water requirements, is the next option. This may be possible without intermediate treatment in some cases. Reuse of another wastewater source from outside the plant or recycle of a wastewater stream within the plant is generally the last consideration. These sources generally require some type of pretreatment before they can be used in industrial applications. Evaluating all the options gives the best opportunity to achieve the desired goal at the lowest cost.

SECTION 3.1

Applications—Impurity Removal

CHAPTER 6

Raw Water Clarification and Filtration

The processes of coagulation and flocculation are employed to separate suspended solids from water, whenever natural subsidence rates are too slow to provide effective clarification. Water clarification, lime softening, sludge thickening, and dewatering depend on correct application of the theories of coagulation and flocculation for success. Depending on the water quality required, water treatment plants usually provide some degree of treatment, such as softening and water clarification. Water softening is the process of removing or reducing water hardness and possibly alkalinity. Water clarification is the process of removing suspended solids from water.

Taking surface water clarification as an example, raw water contains impurities in varying amounts. Before this water can be used for common industrial and household applications, it requires treatment to remove these impurities. Turbid water contains suspended matter with varying particulate sizes. Settleable solids are particles large enough to settle quiescently, while dispersed solids are particles that do not readily settle. A rule of thumb is that settleable solids are greater than about 10 μm, while dispersed solids are 1 to 10 μm. True colloidal solids are less than 1 μm.

A significant portion of non-settleable solids may be colloidal, and the colloidal and dispersed solids are the targets of coagulant addition. Each particle is stabilized by negative electrostatic charges on its surface, causing it to repel neighboring particles, analogous to magnetic poles repelling each other. Since this prevents particles from colliding to form larger agglomerates, termed *flocs*, the particles do not settle. Coagulation is the destabilization of these colloids by neutralizing the forces that keep them apart. This is generally accomplished by adding chemical coagulants with appropriate mixing energy.

Aluminum salts, iron salts, and polyelectrolytes are the chemicals usually used.

Figure 6.1 illustrates how these chemicals reduce the electric charges on colloidal surfaces, allowing the colloidal particles to collide and agglomerate into floc particles. These initially small flocs join, creating larger and larger agglomerates that become large enough to settle. The destabilization step is coagulation (charge neutralization); the floc-building stage is flocculation.

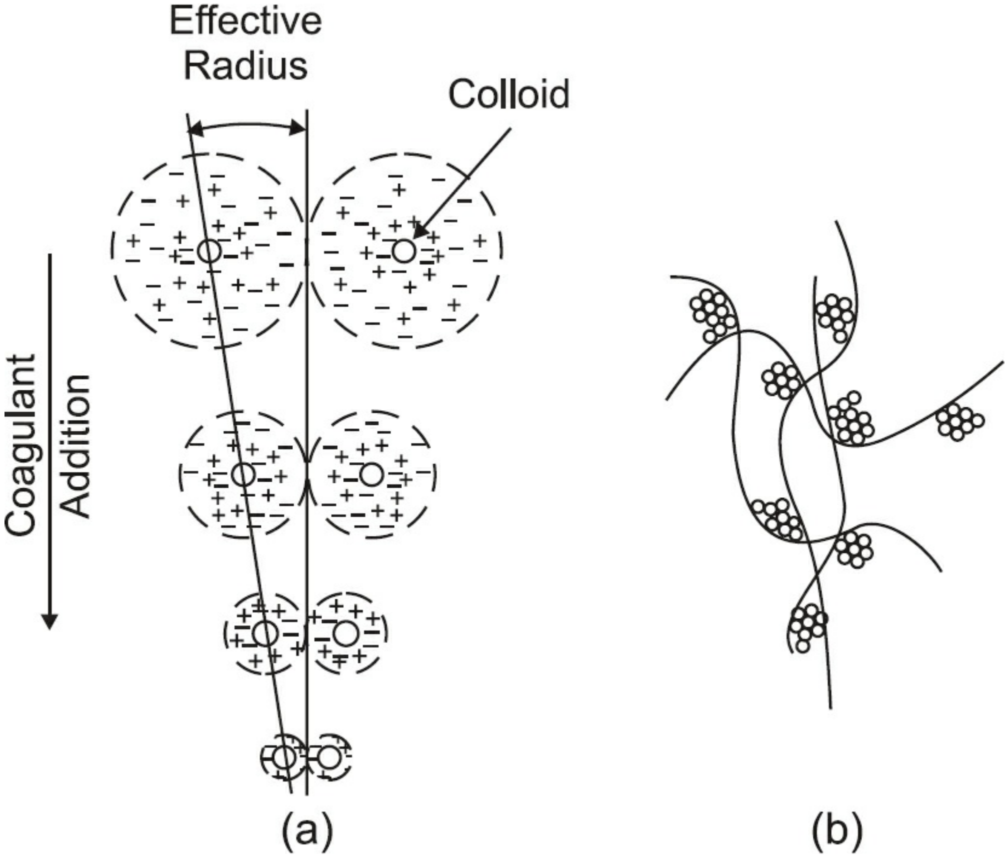


FIGURE 6.1 (a) Coagulation: Addition of a coagulant neutralizes charges, collapsing the “cloud” surrounding colloids, so that they can agglomerate. (b) Flocculation: Bridging by the flocculant chemical among agglomerated colloidal particles forms large, settleable flocs.

The terms coagulation and flocculation are often used interchangeably; however, when viewed as two different mechanisms, a better understanding of clarification and dewatering is provided. From a practical viewpoint, coagulants and flocculants are different, since flocculant polymers are very high molecular weight and require an inversion or dissolution step before being used to bridge particles. Coagulants are smaller molecules designed to neutralize the surface charge on the particle. Thus, they can be fed as a concentrated solution or diluted.

Water treatment plants provide efficient coagulation and flocculation of raw water by adding chemicals that provide a positive surface charge, as well as turbulent mixing of the chemically treated water.

Water filtration is the process of removing suspended solids from water during passage through porous granular materials. Sand filters are typical granular filtration units in both municipal and industrial water treatment plants, as a final polishing step before the water proceeds to the user. Granular filters can be single or multimedia and are available in three categories: gravity (several types), pressure, and upflow filters. Discussions of each filter category show the variety of designs available.

Coagulation

Water clarification depends on the application of the principles of coagulation and flocculation. At common water pH greater than the isoelectric point (>3), the surface of each particle in the water develops a negative electrostatic charge, repelling neighboring particles. Coagulation involves the neutralization of the electrostatic charge, enabling the particles to collide and form agglomerates.

These collisions, in turn, combine the particles into small groups, called flocs. The formation of flocs is called flocculation. Ideally, flocculation proceeds until the flocs become large enough to settle from suspension within a reasonable time (about 20 minutes).

Colloidal species encountered in raw water and wastewater include clay, silica, iron and other heavy metals, color, and organic solids. Colloids may also be produced in precipitation processes such as lime softening. Oil in wastewater is frequently colloidal.

Among the wide variety of colloidal materials in water, there is a broad distribution of particle sizes. Table 6.1 is based on Stokes' Law [Eq. (6.1)], which shows how particle size, density, and water viscosity relate to the settling rate.

$$V_o = \frac{G(\rho_1 - \rho_2)D^2}{18\mu} \tag{6.1}$$

where V_o = settling velocity, cm/s

G = gravitational force, cm/s^2

ρ_1 = particle density, g/cm^3

ρ_2 = liquid density, g/cm^3

D = particle diameter, cm

μ = liquid viscosity, $dyne \cdot s/cm^2$

Typical Suspended Solid	Diameter (mm)	Diameter (μm)	Total Surface Area for Equal Mass	Settling Time to Fall 1 m
Gravel	10	10 000	314 mm^2	1 s
Coarse sand	1	1000	3140 mm^2	10 s
Fine sand	0.1	100	31 400 mm^2	125 s
Silt	0.01	10	0.314 m^2	108 min
Bacteria	0.001	1	3.14 m^2	180 h
Colloids	0.0001	0.1	31.4 m^2	755 d

Particles larger than 100 μm are visible to the naked eye and are considered settleable solids. In the range 10 to 100 μm, particles are considered turbidity. Below 10 μm, particles are considered colloidal. Particles larger than 0.1 μm are visible by light microscope; below 0.1 μm, the electron microscope is used for detection.

TABLE 6.1 Sedimentation of Small Particles of Silica (Specific Gravity = 2.65)

Equation (6.1) assumes hard, spherical particles. Note that the water viscosity affects settling (i.e., when the water is cold, the settling speed is slower). Table 6.1 shows that 10 μm particles settle in a reasonable period of 108 minutes. Colloids always require coagulation to achieve an effective size and settling rate; but even larger particles, which are not truly colloidal and would settle if given enough time, may require coagulation to form larger, faster settling floc.

When insufficient settling time is available in a treatment plant to remove suspended solids, coagulation and flocculation may cause them to grow in size and settle more rapidly to overcome the physical limitation of the plant design. In this case, the chemicals are being used as settling or sedimentation aids.

Colloids are categorized as hydrophobic (water hating) or hydrophilic (water loving). Hydrophobic colloids do not react with water; most natural clays are hydrophobic. Hydrophilic colloids react with water; organics causing color are hydrophilic. Of importance in water treatment, hydrophilic colloids may chemically react with coagulants used in the treatment process. Therefore, hydrophilic colloids require more coagulant than hydrophobic colloids, which do not chemically react with coagulants.

Several theories have been advanced to describe the colloidal particle and the forces surrounding it. For practical purposes, the determination of the nature and strength of the particle charge is all that is needed to define the colloidal system. The particle charge strength, illustrated as the layer surrounding the colloid in Fig. 6.1, affects how closely colloids can approach each other.

Contaminants Removed

Suspended solids and color are the two major impurities removed during clarification. Through various clarification techniques, iron, manganese, and silica may also be partially removed, but total dissolved solids (TDS) are not reduced. TDS may actually increase when using clarification aids containing aluminum or iron salts. Organic materials contributing to taste and odor problems may be reduced through proper chemical treatment.

Water quality objectives of municipal and industrial water treatment plants vary greatly, depending on the quality of the incoming water, the intended uses for the finished water, and the economics of the treatment processes used. The following sections discuss major impurities in water in terms of problems each impurity can cause, and the importance municipal and industrial plants place on its removal.

Suspended Solids (Turbidity)

Many water supplies are turbid, containing suspended matter varying in concentration from a trace in deep wells to thousands of mg/L in some rivers. Suspended solids include such materials as fine sand, silt, clay, decomposed vegetation, bacteria, algae, and other microbiological organisms.

The amount of these impurities varies significantly in some water sources. In a river after rain, suspended solids due to sand, silt, and clay may increase rapidly. During rainy periods, such as in the spring, rivers may run very turbid for several weeks, only to be extremely low in turbidity during the driest days of summer. Algae and other microorganisms may be present at certain times of the year, making treatment more difficult, and at other times may be so low that they have no effect on clarification.

The most common measure of the amount of suspended solids in water is turbidity, which is a measure of the clarity of the water and may be obtained in several ways.

The preferred turbidity unit is the nephelometric turbidity unit (NTU). Drinking water must contain less than 0.5 NTU, as required by state and federal government standards, although some plants have requirements that are more stringent. Most surface water sources are less than 100 NTU, though a muddy river may rise as high as 4000 NTU for brief periods.

Note that the Jackson turbidity unit (JTU) is an obsolete turbidity method that measures when a candle can no longer be seen through a standardized cell and clay suspension. In general, there is no correlation between JTU and NTU, although site-specific correlations are possible.

The most widely used turbidity measurement technique is the nephelometric or light scattering method. A nephelometer employs an incandescent light source directed into a water sample. The suspended particles scatter light as the beam passes through the sample, with the intensity of the scattered light being related to the number, size, and color of the particles. A photodetector is placed at right angles to the light beam and detects the intensity of light scattered.

Another method is the Helige Comparator. The operator makes a turbidity measurement based on a visual comparison. As with all visual comparator methods, the results are extremely operator dependent. In addition, the unit is not as sensitive as the nephelometer, especially at low turbidity readings; consequently, the comparator is no longer commonly used.

Some spectrophotometers have a turbidity measurement using the formazin turbidity unit (FTU). This measurement is different from NTU, as the instrument detects how much light passes through the water sample. Light that did not reach the detector is assumed to be scattered light. This method is acceptable, and the correlation between NTU and FTU is linear. Either instrument can be used to measure turbidity, as long as the units are reported. The exception is in waters that are highly colored, where absorbed light is assumed scattered light, and FTU results tend to be higher than NTU results for the same sample. In addition, since FTU measures lost photons, it measures a larger number of lost photons versus NTU, which detects scattered photons at a 90° angle from the light source.

Municipal water systems produce potable water, and in the United States, they are affected by the guidelines of the Safe Drinking Water Act. All around the world, water plants must meet certain water quality requirements to assure the production of safe, healthful water. One line of defense against bacteria and other detrimental materials entering the water system is good coagulation in the water plant. The clarity of water is the easiest measure of complete coagulation. In the United States, the law varies with region, but a rule of thumb is a turbidity limitation of 0.5 NTU for finished water. Many plants produce water less than 0.5 NTU and use their historical turbidity level as the standard for good water. Note that these turbidities are measured immediately after the filter (in the clearwell). Home tap water turbidities can be higher due to distribution system contamination, disinfection, etc.

Many industrial plants making non-potable water often require 1 NTU quality. Generally, a plant wants to produce less than 5 NTU water from the sedimentation basin. This water can be acceptable for various processes, depending on the specific process requirements. However, excessive turbidity may cause fouling of heat transfer surfaces and reduce efficiency of some systems. If filtration is utilized, finished turbidity of less than 1 NTU is often obtained. In some cases, low turbidity is imperative to good plant operation, such as in boiler pretreatment where ion exchange or reverse osmosis (RO) precedes boiler makeup, following clarification or cold lime softening. Turbidity can foul ion exchange media, leading to channeling through the media bed. In RO systems, high turbidity causes a high silt density index (SDI), which leads to colloidal fouling of RO membranes. Excessive fouling could lead to expensive increased cleanings, or in the worst-case scenario, could lead to very expensive membrane replacement. Low turbidity water does not guarantee low SDI for the RO water influent, because particles smaller than 1 µm do not scatter light and are thus, not detected using turbidity measurements.

Another means of measuring suspended solids is particle counting. Particle counters are increasingly popular due to reduced costs and improved reliability (especially with the commercial development of diode lasers and low-cost computing). In addition, particle counters are more sensitive to changes in finished water quality compared to turbidity. For example, it is common to monitor sand filters for turbidity breakthrough as a measure of effluent quality, since many filtrate specifications involve turbidity, it is often used to trigger a filter backwash. Particle counters are more sensitive than turbidimeters and can be an early warning for systemic filter issues. Generally, particle counts start to increase before turbidity increases, indicating the filter capacity has been reached and a backwash should be initiated.

Particle counters generally measure individual particles; therefore, they are limited to relatively clean (<1 NTU) water. They are also different from particle sizers. Because particle sizers can handle higher solids (even slurries), sizers measure particle size via indirect methods. True particle counters measure individual particles.

There are two types of particle counters: light scattering and light extinguishing. Light scattering is similar to nephelometric turbidity, except the excitation wavelength is well defined and the scattered light is measured as a function of the observation wavelengths. From the scattered light intensity as a function of wavelength, the particle size distribution is determined using complex equations that are beyond the scope of this book. Light scattering is extremely sensitive, being able to measure sub-micron size particles. Due to the data processing and sensitivity, these particle counters are suitable for clean water applications.

Light extinguishing particle counters function, by blocking light as a single particle passes through a light beam, which is usually a laser beam. The larger the particle, the more light is blocked. This reduction in light is calibrated to a particle size. While the particle may be irregular, the counter reports the particle as an average circular cross-section spherical equivalent. Because individual particles are counted, these instruments are limited to approximately 20 000 particles/mL. In addition, for optical and electronic reasons, light extinguishing particle counters can measure down to approximately 2 µm in diameter.

Color

Surface water runoff carries organic material leached from vegetation into streams and lakes, adding color to the water. Color is usually associated with naturally occurring tannins and lignins and is measured by a visual comparator procedure against platinum cobalt color standards or using color meters. These standards are solutions prepared from platinum and cobalt salts and are the bases for the American Public Health Association (APHA) color scale. Color is reported in APHA color units.

The majority of industrial plants do not put a specification on color in the finished water. For plants with highly colored water sources (>30 APHA), a color specification of 10 APHA is often established, especially if the water is going to demineralizers or used in making white paper.

Zeta Potential

Zeta potential is a measurement of the electrostatic charge on a particle. For colloids in natural water sources in a pH range of 5 to 8, the zeta potential is generally −14 to −30 mV; the more negative the number, the stronger the particle charge. As the zeta potential approaches zero, particles can approach one another more closely, increasing the likelihood of collision.

In a conventional clarification system at pH 6 to 8, coagulants provide positive charges to reduce the negative zeta potential. Coagulation usually occurs at a zeta potential that is still slightly negative; complete charge neutralization is not required. The optimal zeta potential required for coagulation varies, depending on the chemical coagulant mechanism and the measurement technique used. If too much coagulant is added, the particle surface becomes positively charged (a positive zeta potential), and the particles are redispersed; this is called charge reversal.

Coagulants may be required in high pH water treatment systems, such as in lime softening. Calcium carbonate ($CaCO_3$) particles carry a negative charge, and cationic coagulants are useful in reducing residual colloidal hardness, presumably by agglomerating colloidal $CaCO_3$. Magnesium hydroxide [$Mg(OH)_2$], on the other hand, carries a positive charge until the pH exceeds 11. In lime or lime-soda softening processes, where both $CaCO_3$ and $Mg(OH)_2$ precipitate, the oppositely charged particles coprecipitate. This coprecipitation in past geologic periods produced the mineral dolomite ($CaCO_3 \cdot MgCO_3$). In waters that are severely acidic ($pH < 3$), the natural particulate charge could be cationic, and then anionic coagulants would be needed for charge neutralization.

Zeta potential is determined indirectly from data obtained in observing particle motion under a microscope. Zeta potential measurements have been used successfully to monitor plant coagulant dosages. However, for selecting the best coagulant, zeta potential readings alone are not reliable. Observation of results in a jar test remains the best method of coagulant selection.

Somewhat related to zeta potential in a qualitative way is streaming current, an electric current produced when colloidal particles are trapped in a capillary tube or confined space with water flowing past them at high velocity.

The adsorbed charges, or counter-ions, are stripped from the surface of the colloid and pass along with the water, until the velocity is dissipated. The flow of ions constitutes an electric current that is measurable by an instrument called a streaming current detector (SCD). As is true with zeta potential, if coagulants have neutralized the charge on the colloids, the current is reduced. Note that an SCD is only sensitive to particles that transiently adsorb to the piston's wall. Particles that do not adsorb are not detected. This may partially explain why optimal coagulation usually occurs at a slightly negative surface charge, because particles are neutralized but not detected.

Streaming current detectors require frequent maintenance to control plugging of the close clearances in the water passages and are sensitive to pH swings. In many cases, the head of the detector (a piston or plunger reciprocating in a closed cup) can be kept clear by an ultrasonic cleaning device. SCD can produce an output signal to control the coagulation process. One of the variables that need study in each system is the time factor; the speed or rate of charge neutralization varies with the type of colloid present and with temperature. Therefore, a sample taken immediately after coagulant addition is usually inadequate. Typically, an equilibration time of 5 to 10 minutes is needed before putting the sample through the SCD.

Mixing is required to supplement coagulant addition to destroy stability in the colloidal system. For particles to agglomerate, they must collide, and mixing promotes collision. Brownian movement, the random motion imparted to small particles through bombardment by individual water molecules, is always present as a natural mixing force. However, additional mixing energy is usually required. High-intensity mixing, which distributes the coagulant and promotes rapid collisions, is most effective. The frequency and number of particle collisions are important in coagulation. In low-turbidity water, the addition of solids such as clay, or the recycle of previously settled solids, may be required to increase the number of particle collisions.

Flocculation

The floc formed by the agglomeration of several colloids may not be large enough to settle or dewater at the desired rate. This is termed pin floc because of its small size. In such situations, a flocculant gathers together floc particles into a net, bridging from one small agglomerate to another and binding the individuals into large agglomerates as shown in Figs. 6.2 and 6.3. The increase in size also increases the probability that small, unreacted primary particles can adsorb onto the large, net-like agglomerate surface. High molecular weight polymers are common flocculants. Flocculation is promoted by slow mixing, which brings the flocs gently together. Excessive mixing velocity shears the floc, and they seldom reform to their optimum size and strength without additional polymer treatment. Flocculation not only increases the size of floc particles, but it also affects the physical nature of the floc. Sludges and slurries, when flocculated, dewater at faster rates on sand beds and in mechanical dewatering equipment, because of the less gelatinous structure of the floc.

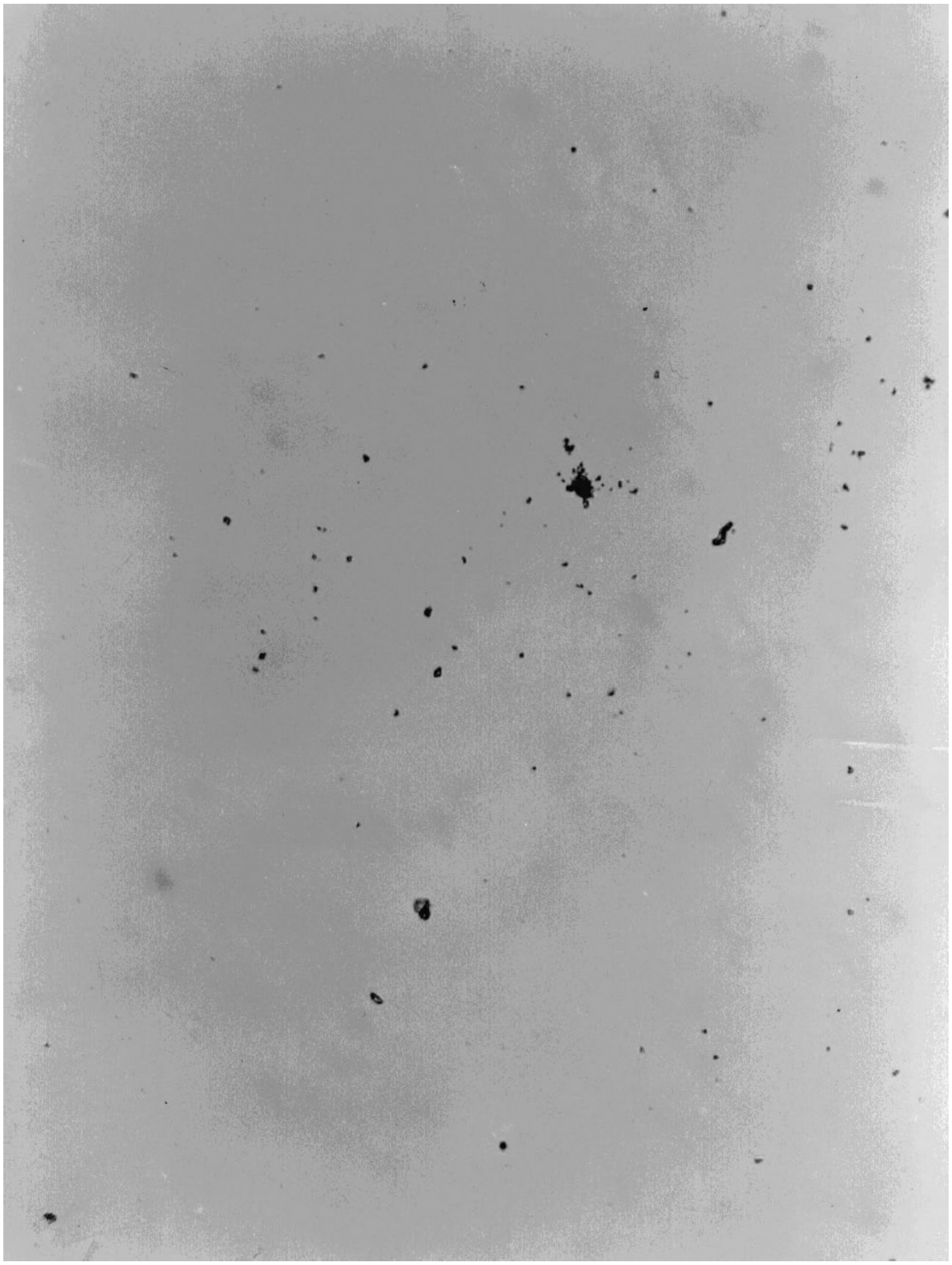


FIGURE 6.2 Turbid river water photomicrograph showing fine dispersion of tiny particles.

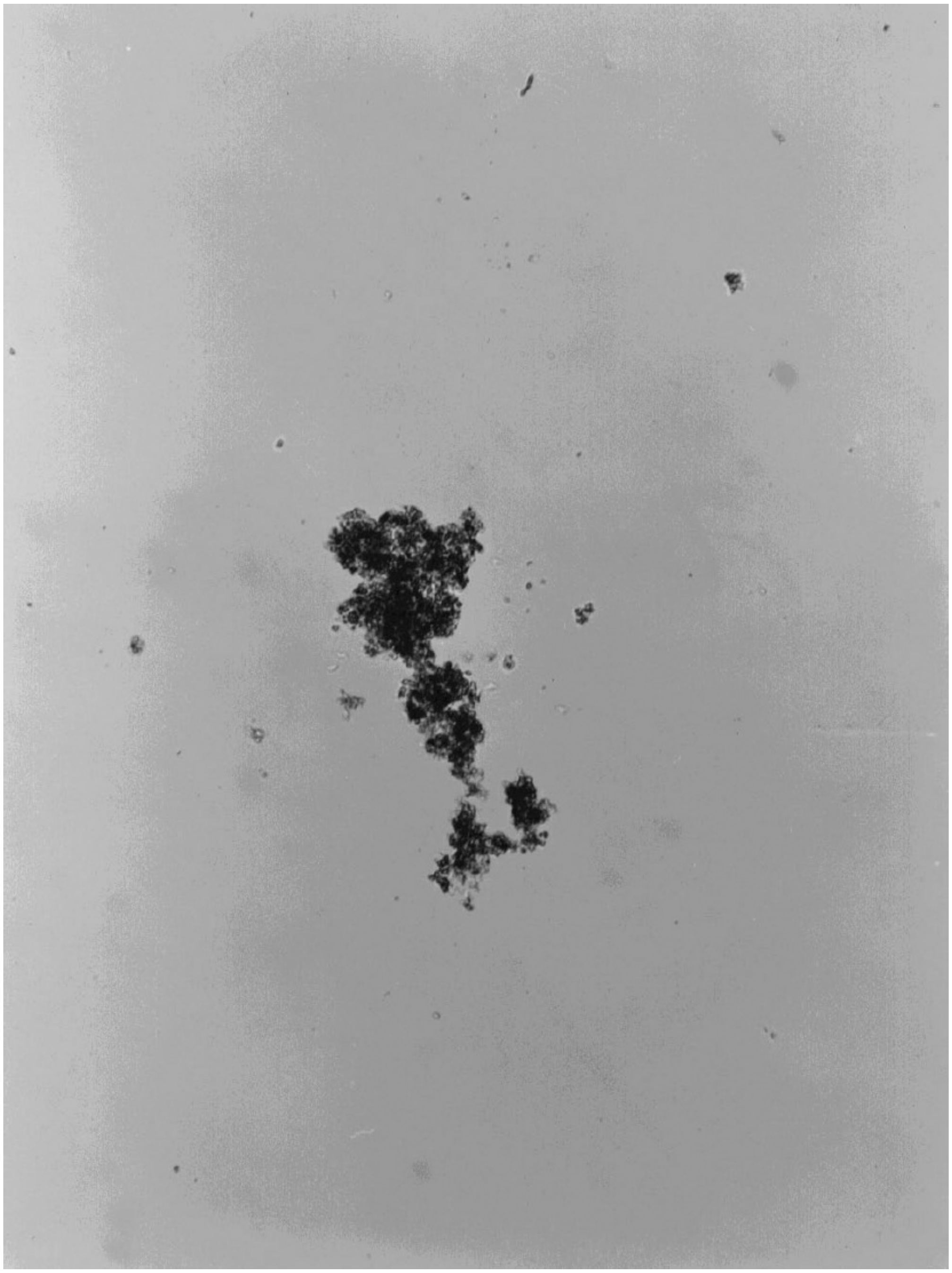


FIGURE 6.3 The same water treated with coagulant. Particles are collected in the floc (130×).

It is apparent that the processes of charge neutralization, or coagulation, and floc building, or flocculation, are so different that each system containing the chemically treated solids being processed has its own physical constraints. These are outlined in Table 6.2.

Variable	Coagulation	Flocculation
Nature of solids	Numerous, fine particulates	Scattered, large gels
Type of chemical applied	Low molecular weight charge neutralizer	High molecular weight particle binder
Energy requirement	Rapid mixing	Slow stirring
Velocity gradient	High	Low
Time in process	Seconds	Minutes

TABLE 6.2 Constraints between Coagulation and Flocculation

In an attempt to develop a mathematical procedure to express some of these variables, hydraulic engineers developed the concepts of velocity gradient and shear rate, or *G* factor. Figure 6.4 illustrates the basis of these concepts. In this illustration, the differential velocity between two particles 0.01 ft (3 mm) apart is 0.25 ft/s (76 mm/s), and the shear rate is 25/s. Obviously, it is impractical to measure the *G* factor in this way, but fortunately, further development of the mathematical model shows that shear rate is also related to the rate of energy input (power) per unit volume (equivalent to detention time in the process) and water viscosity. The latter has a direct bearing on the frequency of particle collisions and explains, in part, the strong influence of water temperature on both coagulation and flocculation. Equation (6.2) shows the formula for *G* factor:

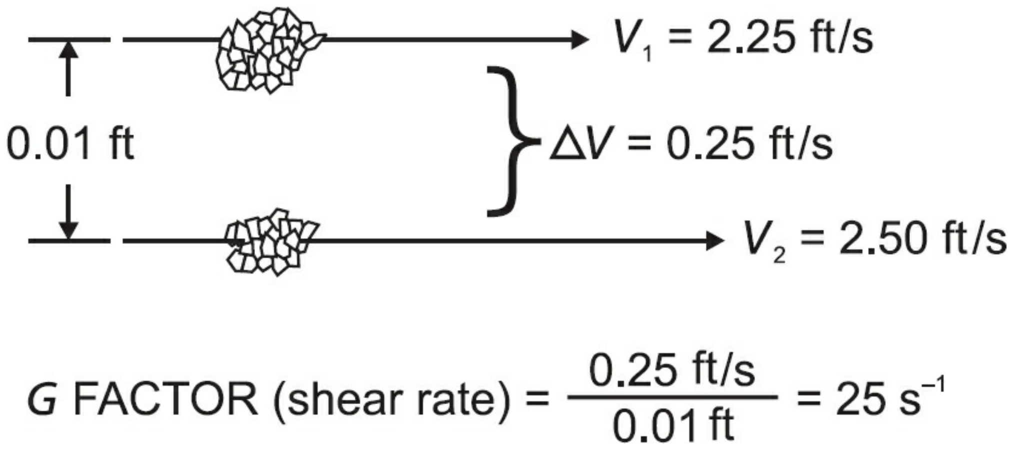


FIGURE 6.4 Illustration of velocity gradient and shear rate.

$$G\ \text{factor} = \left(\frac{P}{[V \cdot \mu]}\right)^{0.5} \tag{6.2}$$

where G factor = velocity gradient, s^{-1}
P = power input, $ft \cdot lb/s$ (W)
V = volume, ft^3 (m^3)
μ = viscosity, $lb \cdot s/ft^2$ ($Pa \cdot s$)

The G factor usually recommended for most coagulation units is about 900/s for a 30-s mixing time, varying inversely with time. The required mixing time is usually established by bench tests, as described later. The recommended G factor for flocculation is lower, varying from about 50/s for cold, colored water carrying a very fragile floc to about 200/s for a solids contact lime softener on warm river water. Again, the G factor for flocculation must be determined by bench testing, and this should lead to a flocculator design that can be varied in speed and power input, as water conditions change, leading to fluctuations in solids concentration and sensitivity of floc to shear.

Coagulation and Flocculation Chemicals

Historically, metal coagulants (aluminum and iron salts) have been most widely used in water clarification. These products function primarily as coagulants. When added to water, they form positively charged species in the typical pH range for clarification (about 6–7). The hydrolysis reaction produces insoluble gelatinous aluminum or ferric hydroxide:

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4 \tag{6.3}$$

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl \tag{6.4}$$

Note that the by-products are hydroxide precipitates and mineral acids, which react with alkalinity to reduce system pH and produce carbon dioxide (CO_2) as a secondary by-product. Sometimes, the gaseous CO_2 by-product interferes with the coagulation process by forming small bubbles, which adsorb onto the hydrous precipitate and cause floc flotation rather than settling. Dissolved gasses can also be an issue when water is warming, as water releases some of its dissolved gas during the settling portion of clarification, which can take hours.

Even if there are no suspended solids in the water initially, metal coagulants form floc, which enmesh destabilized colloids. However, the voluminous sludges produced by addition of metal coagulants create disposal problems, because they are usually difficult to dewater. This is why aluminum and iron salts are not often used to improve efficiency of centrifuges, filter presses, and other dewatering devices.

Metal coagulants are particularly sensitive to pH and alkalinity. If pH is not in the proper range, clarification is poor, and iron or aluminum may be solubilized and cause problems to the water user. The lower the coagulant dosage, the more sensitive the floc is to pH changes (Fig. 6.5). Table 6.3 lists some important properties of common coagulants.

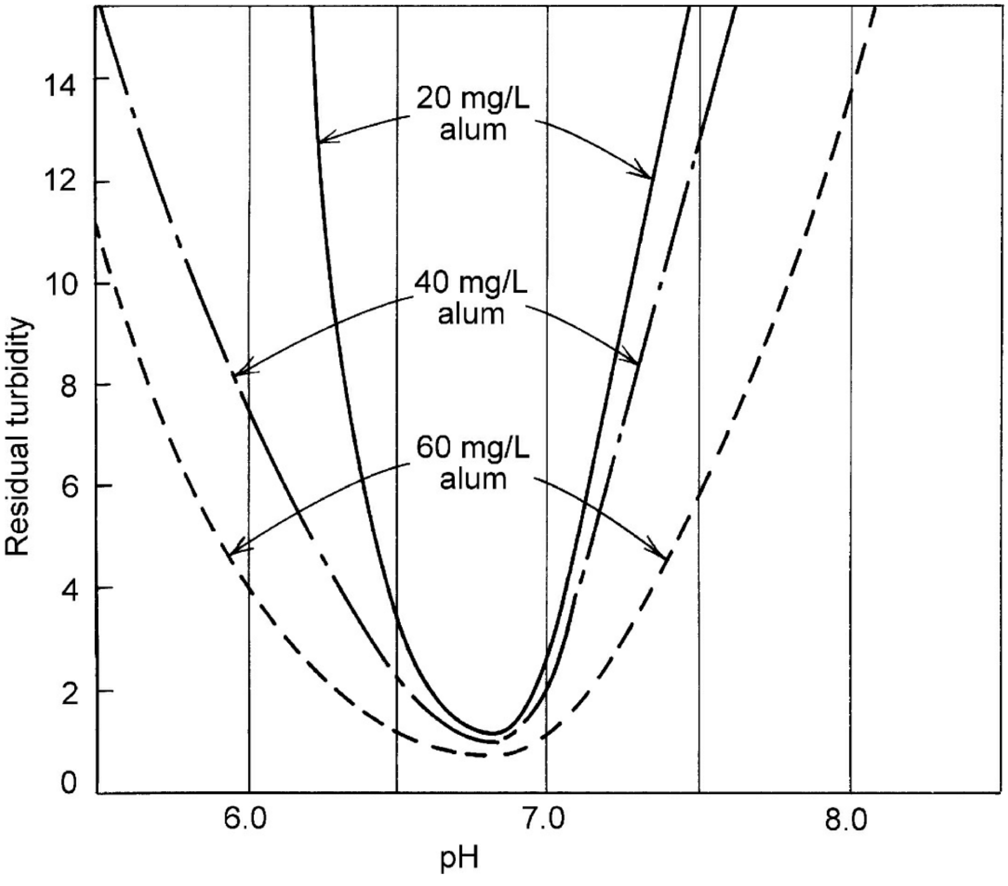


FIGURE 6.5 Effect of coagulant dosage on pH range limitations. The optimum pH remains almost constant, but the pH range becomes less restrictive as the coagulant dosage increases.

Common Name	Formula	Formula Weight	Equivalent Weight	pH of 1% Solution
Alum	$Al_2(SO_4)_3 \cdot 18H_2O$	666	111	3–4
Ferric chloride	$FeCl_3 \cdot 6H_2O$	270	90	3–4
Ferric sulfate	$Fe_2(SO_4)_3 \cdot 3H_2O$	454	75.7	3–4
Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	278	139	3–4
Sodium aluminate	$Na_2Al_2O_4$	164	27.3	11–12

TABLE 6.3 Properties of Common Inorganic Coagulants

The introduction of activated silica in the 1940s significantly improved performance of aluminum and iron salts in water clarification. The subsequent development of a variety of organic polymers called polyelectrolytes in the 1950s was an even more spectacular contribution to water treatment technology.

Polyelectrolytes are large water-soluble organic molecules, made up of small building blocks called monomers, repeated in a long chain. They usually incorporate ion exchange sites, which give the molecule an ionic charge. Those having a positive charge are cationic, and those with a negative charge are anionic. These molecules react with colloidal material in the water by neutralizing charge, or by bridging (tying together) individual particles to form a visible, insoluble precipitate or floc.

Polyaluminum chloride (PACl) is a generic term for a range of products that were initially developed in Japan in the 1970s. PACl minimizes the alkalinity consumption problem, because these materials incorporate some of the required alkalinity to form aluminum hydroxide. These products are essentially partially neutralized aluminum chloride and have the empirical formula $Al(OH)_xCl_{(3-x)}$.

From the empirical formula, aluminum hydroxide would have "x" equal to 3 with the aluminum +3 valence completely neutralized by hydroxide. Zero hydroxide is simply aluminum chloride ($AlCl_3$). Aluminum hydroxide (three hydroxides and zero chlorides) has a basicity of 100% with basicity defined as:

$$\text{Basicity} = \frac{x}{3}(100) \tag{6.5}$$

where x = moles of OH^- and moles of $Al^{+3} = 1$.

The basicity of a given PACl product is an averaged parameter with the actual aluminum speciation being a complex mixture that can vary from monomeric aluminum (Al^{+3}) to a range of partially neutralized PACl molecules. Precise aluminum distribution is complex and the subject of much debate that is beyond the scope of this book.

Tailoring Polyelectrolytes

The performance of these materials can be modified to suit the nature of the colloidal matter to be removed from water. These modifications include variations in molecular weight and ion exchange capacity. These materials can also be produced without an ionic charge; these are called nonionic polymers. Although they are not, strictly speaking, polyelectrolytes, nonionic polymers exhibit many of the same flocculating properties in solution, and are considered as part of the general polyelectrolyte family of compounds.

Although most polyelectrolytes are synthetic organic materials, nature produces an endless variety of such materials. Some of these are chemically processed to improve performance and are commercially available. The cationic polyelectrolytes are either polyamines or quaternary amines. In water, a polyamine hydrolyzes as follows:

$$RNH_2 + HOH \Leftrightarrow RNH_2H^+ + OH^- \tag{6.6}$$

Because the hydrolysis yields hydroxide (OH^-), at high pH, the equilibrium reaction is forced to the left, and the polymer becomes nonionic. This is illustrated by Fig. 6.6, which shows loss in exchange capacity for a specific polyamine as pH increases. In contrast, the quaternary polymers are but slightly affected by pH, remaining positively charged over a broad pH range.

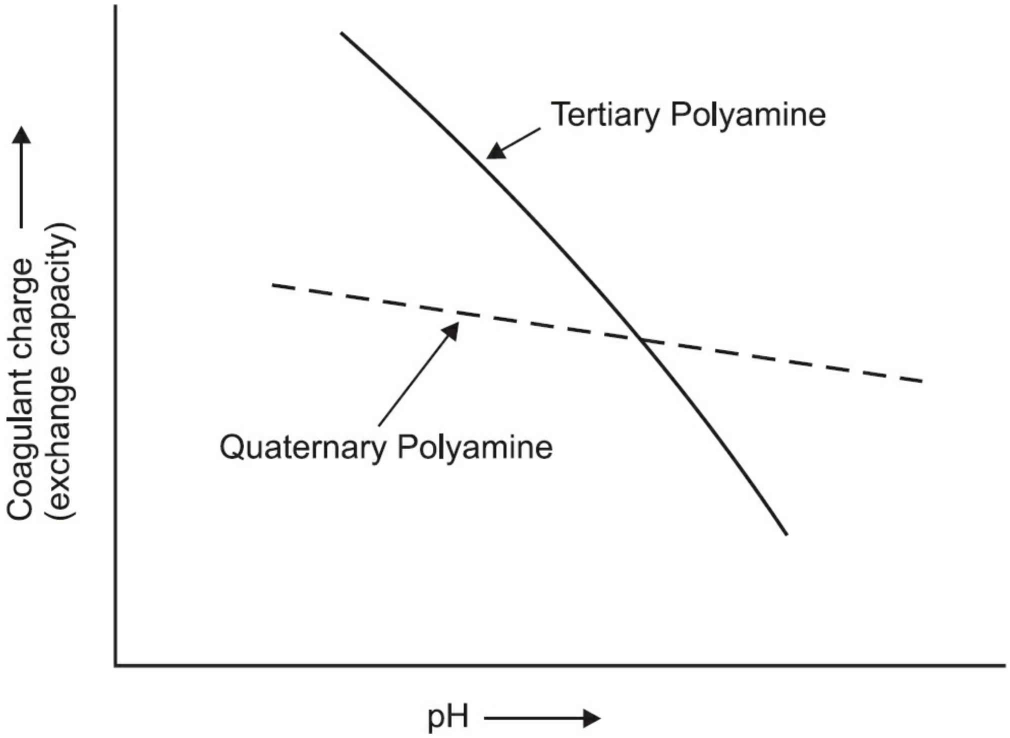


FIGURE 6.6 Generalized plot showing loss of cationic strength for tertiary polyamines as pH increases and relative pH independence of quaternary amine coagulants.

Anionic polymers incorporate a carboxyl group (COOH) in their structure. These ionize in the following manner:

$$\mathrm{RCOOH} \Leftrightarrow \mathrm{RCOO^-} + \mathrm{H^+} \tag{6.7}$$

The hydrogen ion forces the equilibrium reaction to the left, and anionic polymers become nonionic at low pH.

The ionic nature of polyelectrolytes is only one factor determining the performance of these materials as coagulants and flocculants. Other factors, such as the polar nature of nonionic bonds in the molecule, molecular size, and molecular geometry, play a large part, and may in some cases, overshadow the effects of charge and charge density. Hence, high molecular weight nonionic polymers are effective flocculants in many systems, because of their ability to attract and hold colloidal particles at polar sites on the molecule. Furthermore, because of their molecular size, they can bridge together many small particles. Less sludge is generated by organic polymers than by inorganic salts, since they do not add weight or chemically combine with other ions in the water to form a precipitate. Organic polymers do not affect the pH of the water and generally do not require pH adjustment for effective use.

As a rule, cationics are designed to work at lower pH values, anionics at higher. Nonionics and quaternaries are only slightly influenced by pH. The general rule should not be interpreted to mean that anionic polymers do not work at low pH; it simply means they are no longer ionic. They may produce good results in flocculating solids at low pH simply because of their nonionic bonds. The same applies to cationics; even though they are not charged at high pH, they may act as effective coagulants because of their polar groups.

Organic polymers overcome many of the problems inherent in the use of aluminum or iron salts. Depending on the selection of monomers and processing methods, a wide variety of polymers can be made of various configurations and molecular weights. Molecular weight is proportional to polymer chain length; the wide selection of structures and molecular weights makes it possible to design a polymer specifically for a given coagulation or flocculation problem, but this is seldom practical for economic reasons.

Organic polymers used in water treatment are of two major types, coagulants and flocculants. Coagulants are positively charged molecules of relatively low molecular weight. Although they exhibit some ten dency for bridging, they are not particularly effective flocculants. Flocculant polymers have much higher molecular weight, providing long bridges between small flocs to enhance particle growth. Flocculants are cationic, anionic, or nonionic. The flocculant that works best in any system can be determined only through laboratory screening and in-plant testing. Polymer flocculants, unlike coagulants, are not selected for neutralization, but rather for the ability to bridge and entangle pin floc.

Unlike inorganic salts, polymers do not produce voluminous, gelatinous floc. In applications where additional solids improve results, inorganic coagulants or clay may be required to supplement polymers. Polymers do not affect pH, nor is their performance as sensitive to the pH of the treated water as metal coagulants.

Activated Silica

Some inorganic compounds can be polymerized in water to form inorganic polymer flocculants. Activated silica (sometimes identified as SiO_2) is an example. When sodium silicate, which contains alkali, is diluted to 1.5 to 2.0% and then partially neutralized (usually with chlorine or sodium bicarbonate), the silica becomes colloidal and then begins to slowly polymerize. After aging for 15 to 30 minutes, the solution is diluted to about 0.5 to 1.0% SiO_2, arresting further polymerization and producing activated silica. Although this preparation procedure is complicated, this is a very effective flocculant for such applications as assisting alum treatment for color removal, and improving the softening of organic-containing waters.

Coagulation and Flocculation Applications

A sample of turbid water in a graduated cone separates into two layers, the settleable and the colloidal solids (Fig. 6.7). In raw water clarification, a coagulant is usually used, since the colloidal haze must be removed to produce the low turbidity demanded by most water-using processes. In wastewater clarification, a coagulant is required only where the suspended solids create a problem in meeting effluent guidelines; here a flocculant may be required to speed the settling rate.

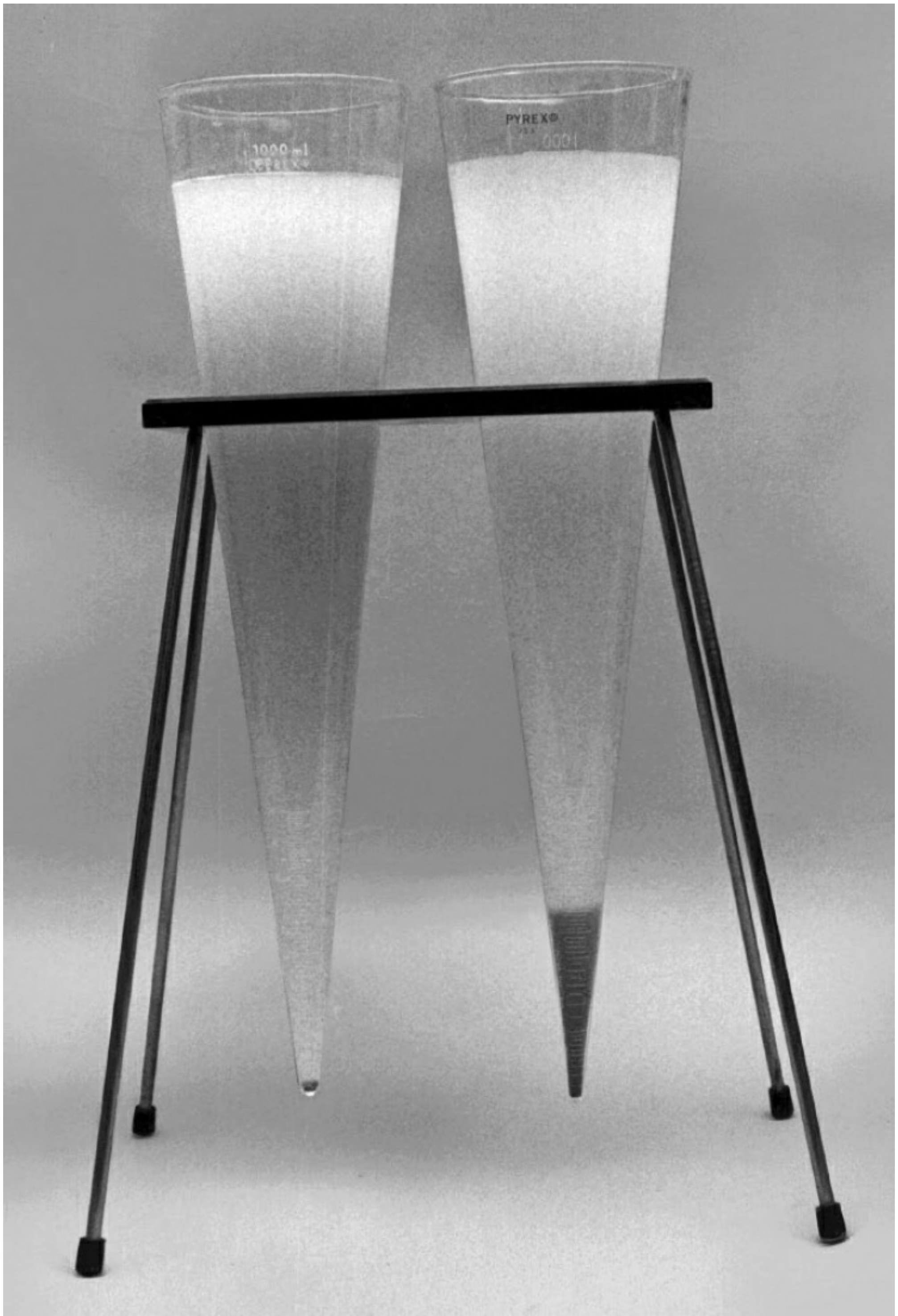


FIGURE 6.7 Solid particles in the left cone are a conglomeration of materials of various particle sizes, identified as suspended solids. After settling for 30 minutes, two fractions are obtained (right cone), settleable solids and turbidity.

Two types of laboratory tests are used to select the best chemical and approximate dosage level required for clarification: jar test and cylinder test. The jar test is used when the stream to be clarified has less than approximately 5000 mg/L suspended solids. Raw water clarification, settling of biological solids, and most primary waste streams are in this category. The cylinder test is used for heavy slurry streams where suspended solids exceed approximately 5000 mg/L. Coal and mineral processing wastes and the sludge resulting from a primary clarification are examples of heavy slurries.

The jar test simulates the types of mixing and settling conditions found in a clarification plant. The laboratory unit for running these tests (Fig. 6.8) allows up to six individual tests to be run simultaneously. The jar tester has a variable speed motor allowing control of the mixing energy in the jars. A basic jar testing procedure would have a brief fast mix (about one minute) to properly disperse treatment chemicals. Then a slow mix time, about ten times longer than the fast mix duration, is used to promote agglomerates. Finally, a settling period at least as long as the slow mix is performed to simulate settling. The purpose of jar testing is to simulate plant performance and the combination of fast/slow/settling times is adjusted to approximately match the full-scale system performance.

FIGURE 6.8 This type of gang stirrer is widely used for jar testing, as both a research tool and a plant

control device.

Clarification results are sensitive to chemical dosage, mixing energy, and length of mixing. Figures 6.9 to 6.12 show a typical sequence in jar testing where a colloidal haze is removed. The coagulant is added with high energy to disperse it in the water and promote an increased frequency of collisions. The duration may be short, less than one minute. The actual mixing time is refined as the test regimen proceeds, in essence defining the optimum *G* factor. A polymer flocculant, if required, is added during the last few seconds of the rapid mix. In the slow-mix period that follows, floc-building proceeds until the floc becomes so big that shear forces finally over come the bridging forces, breaking the floc apart. This limits the size of the floc. After slow mixing for an optimum period, found only by repeated tests (usually 5–20 minutes), the jars are allowed to settle for 5 to 10 minutes.

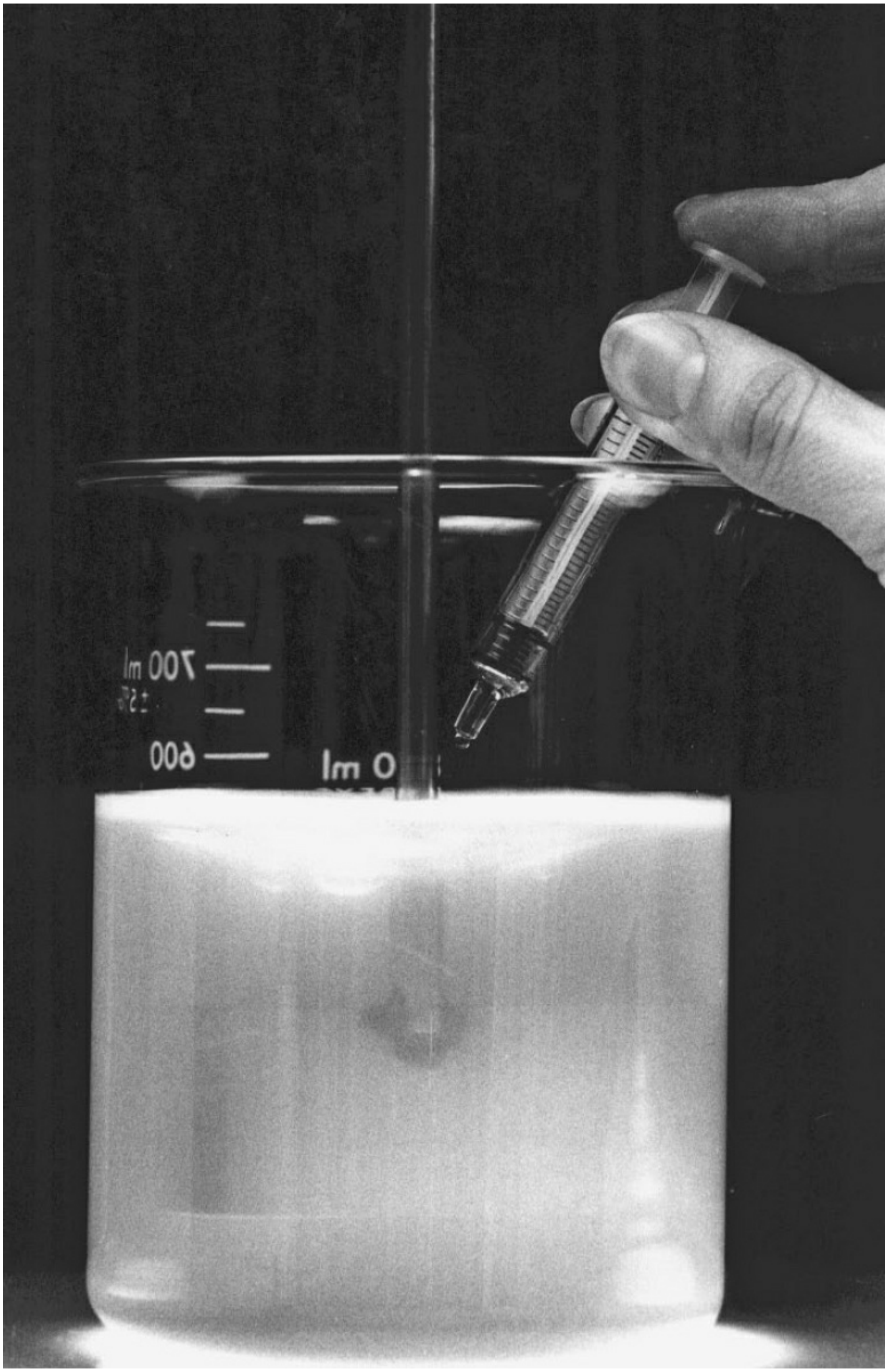


FIGURE 6.9 Coagulant is measured into a sample of turbid water with a high degree of mixing.

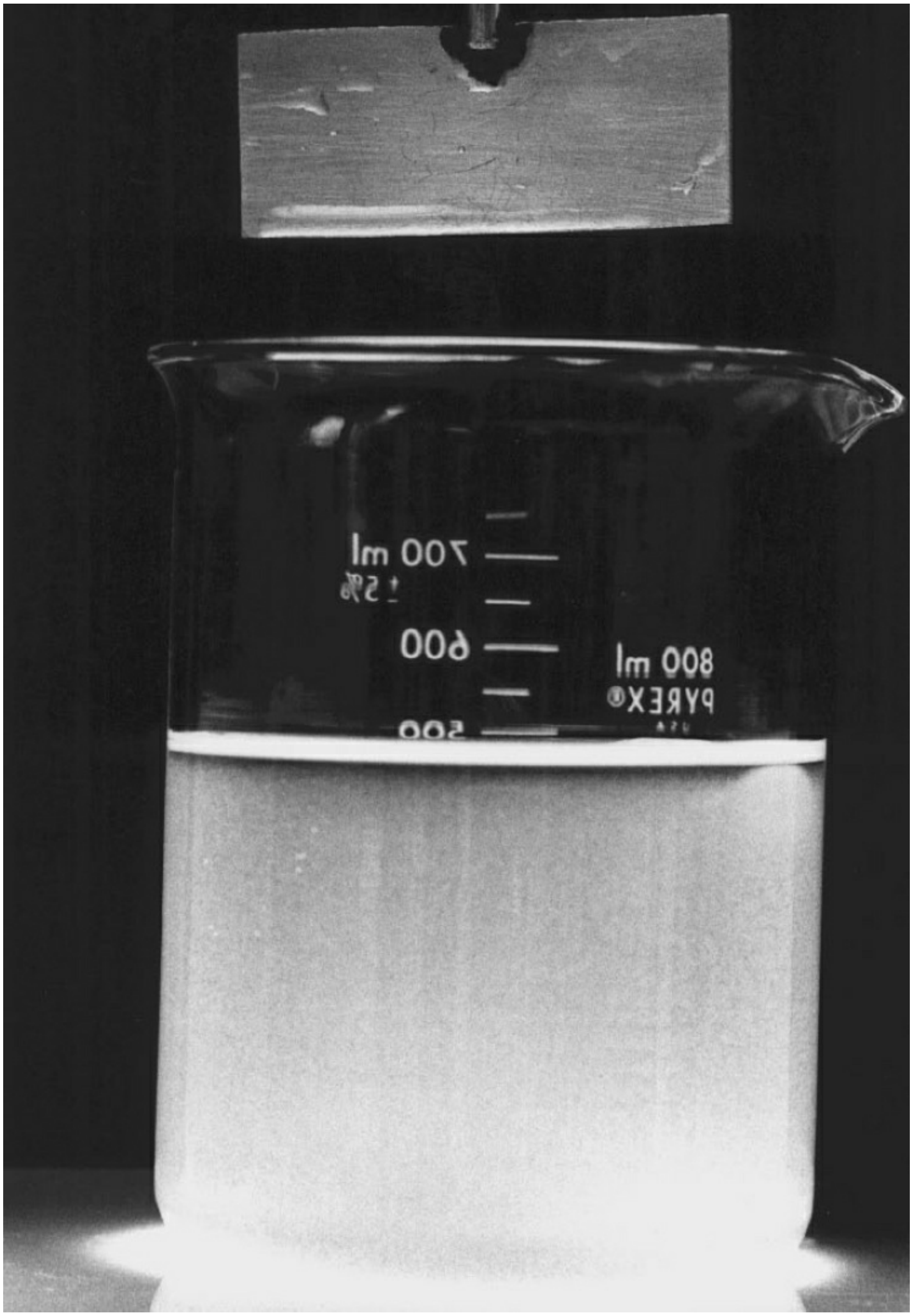


FIGURE 6.10 After coagulant addition, particle growth occurs because of charge neutralization. Additional coagulant or a high molecular weight flocculant may then be added.

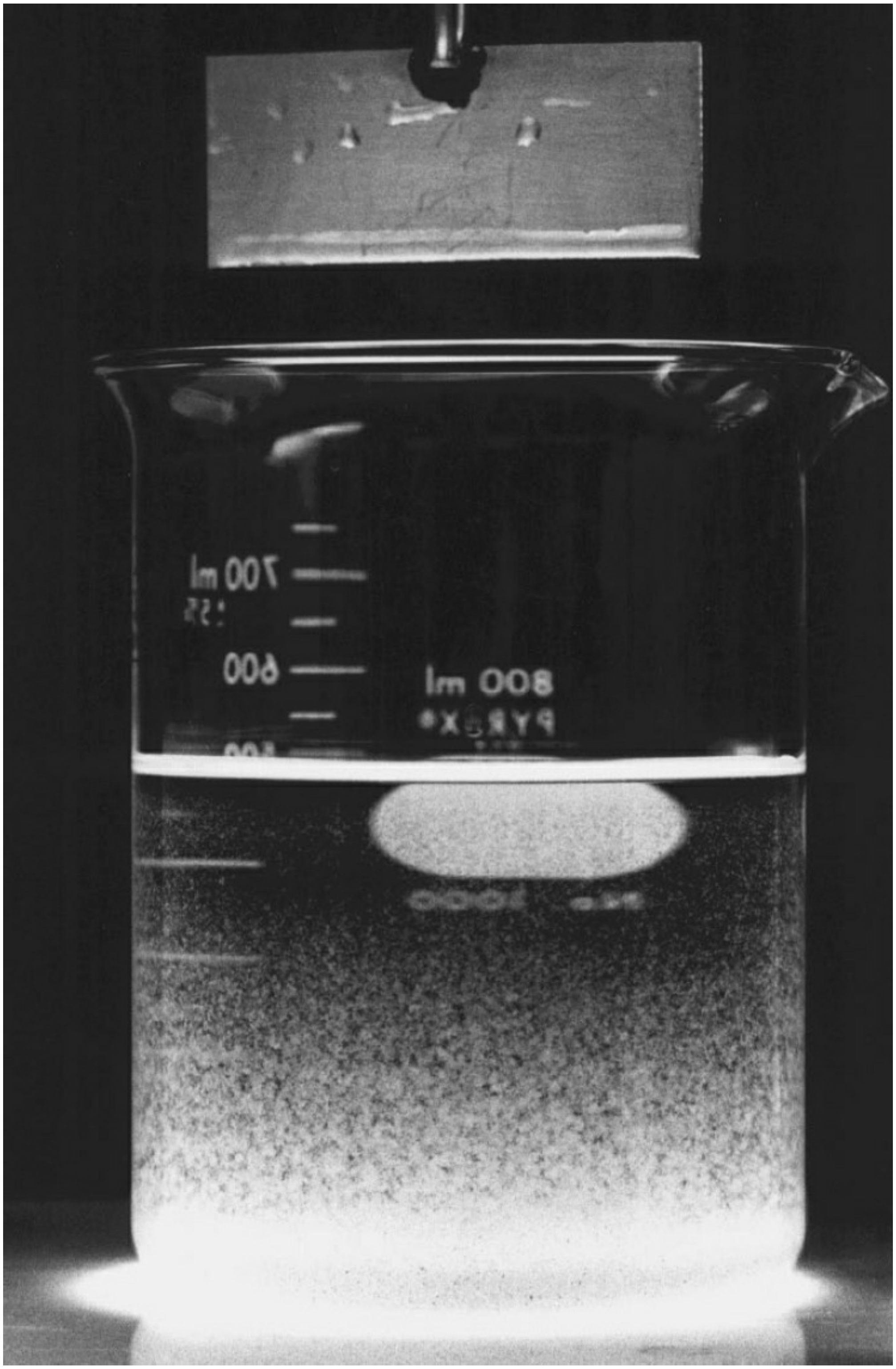


FIGURE 6.11 After flocculation at a very low stirring speed (typically 10–15 rpm), the sample is examined after an established time. Note the fine pin floc, which has escaped entrapment by the larger floc.

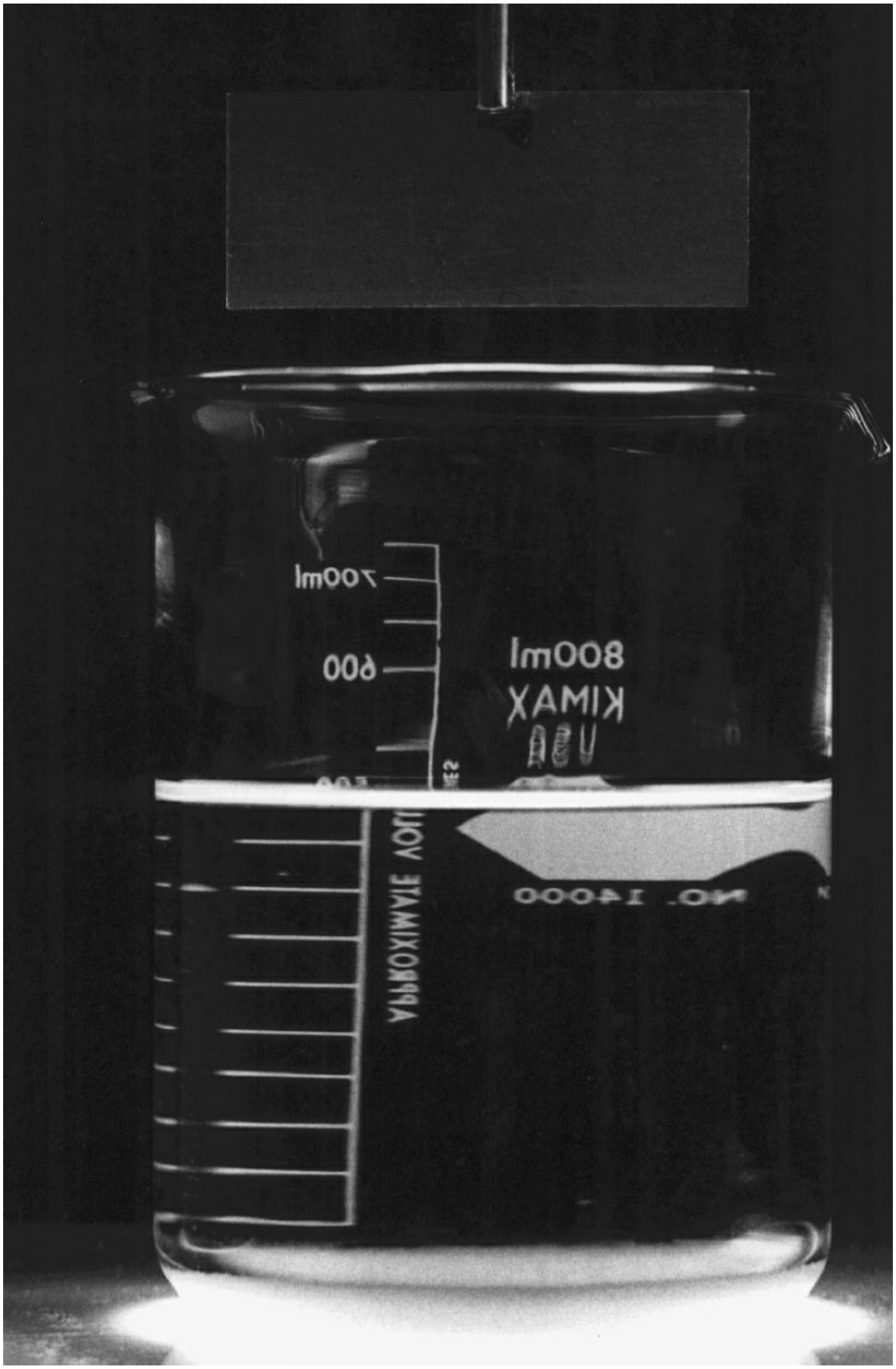


FIGURE 6.12 The supernatant is examined and tested after 5 to 10 minutes settling time, and the nature and volume of the floc is recorded.

Jars with different chemicals, or the same chemical at different dosages, are run side-by-side and the results compared. Floc settling rate, final clarity or suspended solids, and volume of sludge produced (if measurable) are contrasted among jars. Although the eye can judge clarity, the more accurate standard measurement is made with a turbidimeter. Other quality tests such as pH, biochemical oxygen demand (BOD), color, chemical oxygen demand (COD), particle counting, and soluble metals, can be run on the settled water to establish performance standards.

A dosage series should always be performed to ensure accurate, relative test results. Figure 6.13 shows a generic dosage profile using a coagulant such as alum, which is represented by the dashed line. At a critical concentration, the water quality response (such as turbidity) quickly changes, and levels out with increasing dosage. In this situation, adding more alum does not improve performance, it only wastes chemical and increases treatment costs.

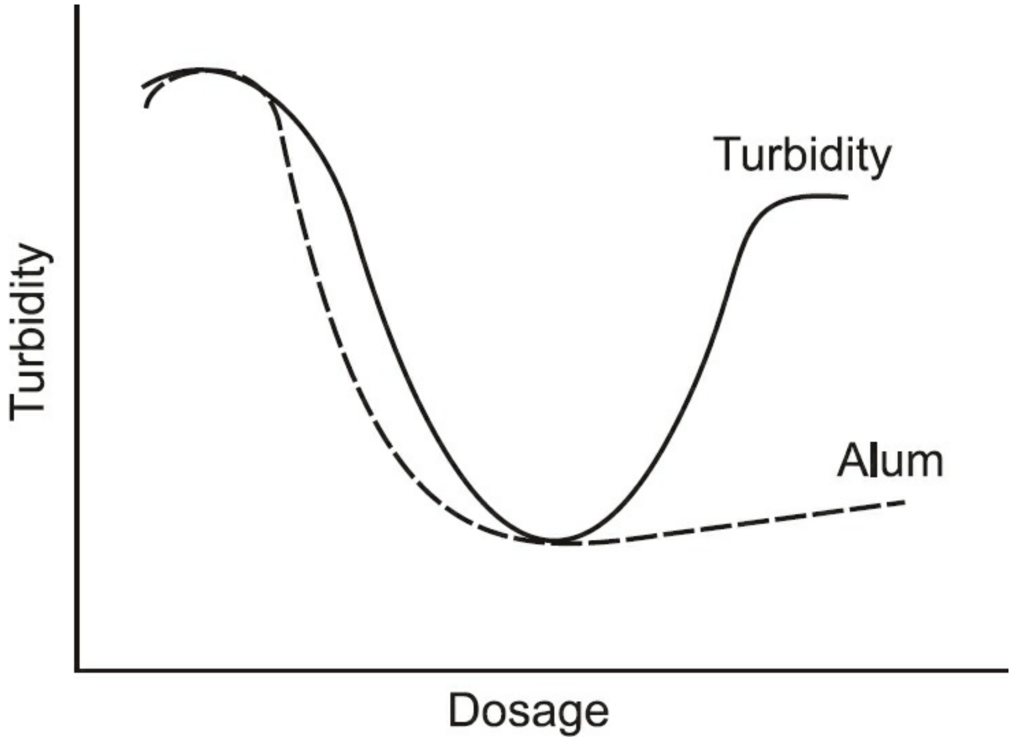


FIGURE 6.13 Typical jar test dosage profile.

The same figure shows the dosage profile for a polymeric coagulant (solid line), and it illustrates distinctly different behavior. Here, there is the same critical concentration, but with increasing dosage, the finished water quality degrades due to redispersion of the solids. With some treatment chemistries, there is a potential false minimum at a higher dose; therefore, a dosage profile is critical for proper coagulant selection.

The cylinder test, designed to indicate how fast the suspended solids settle, employs a 1000-mL graduated cylinder, stopwatch, and lab ware for dosing the chemical being evaluated. The slurry sample is placed in the cylinder, chemical is added, and the cylinder gently inverted several times. Mixing is much less severe than in the jar test, because solids are present at much higher levels and frequent collisions can occur at the lower mixing energy. After mixing, the cylinder is set upright, and the interface between the water and the settling solids observed. Time and solids level are recorded, and the data are plotted on a graph. As in the jar test, a number of analytical tests can be run on the clear water; however, rapid settling rate is usually the goal. By running coagulants and flocculants at different dosages and comparing settling rates, the most effective products are selected. Figure 6.14 illustrates the results of cylinder tests.

FIGURE 6.14 Cylinder test showing the stages of mixing and settling.

Color Removal

The selection of an effective chemical program for the removal of color from water, is accomplished by jar testing. The floc produced from coagulated organic matter is fragile, and the jar test device must be operated in a manner that duplicates mixing energy and flocculation shear corresponding to full-scale equipment.

For the most part, color in water is a mixture of colloidal organic compounds that represent breakdown products of high molecular weight substances produced by living cells. These materials are analogous to the polyelectrolytes used in water treatment. In fact, natural organics like starch have been used as both dispersants and flocculants since the earliest days of water treatment. Natural organics are variously identified as humic acid (a polymer containing phenolic groups), polysaccharides (polymers similar to sugar and cellulose), polypeptides (protein polymers), and lignins and tannins (relatives of cellulose). For the most part, these substances are anionic or nonionic polymers. It is not surprising that cationic materials coagulate them, and the amount of coagulant needed tends to be proportional to the color.

Alum is commonly selected as the first coagulant to be evaluated in the jar test. After the alum demand has been satisfied, excess alum produces a floc that ties the coagulated particles together. The pH range is extremely narrow, usually about 5.0 to 5.8, and variation in pH usually disperses the floc and creates a haze. Most natural colored waters are low in alkalinity, and the alum used for coagulation often destroys the natural alkalinity. The addition of an alkali may be needed for pH adjustment. After coagulation and formation of the alum floc, an anionic polymer is usually used to strengthen the floc and aid sedimentation. A complicating factor is temperature; many colored waters are found in Canada, the northern United States, and Northern Europe where the selected program must be effective at 32°F (0°C), where viscosity greatly increases shear forces, and hinders sedimentation, complicating the jar test procedure. Another potential complication is the usual need for pH correction of the finished water to render it less corrosive than water at pH 5.5. The color matter in water behaves much like an acid-base indicator, and an increase in pH usually results in a color increase.

Certain cationic polyelectrolytes are useful for partial replacement of alum in the color removal process, permitting treatment at higher pH and reducing alkalinity destruction by the high alum dosage otherwise required. Table 6.4 compares the results of a conventional alum program to alum-polyamine treatment.

	Conventional Alum Program	Alum-Polyamine Program
Alum dosage, mg/L	55	35
Aluminate dosage, mg/L	40	30
Nonionic polymer, mg/L	0.5	None
Polyamine, mg/L	None	5
Final pH	5.2	6.5
Final color	5–10	5–10

Florida swamp drainage at 400 APHA color.

TABLE 6.4 Chemical Treatment of Colored Water

PACl can be used in partial alum replacement strategies, which are based on treatment costs in addition to performance. This is especially important in situations where significant finished water pH adjustment is required. Here, the cost of pH adjustment can be significant, especially if the safety aspects of handling large amounts of corrosive chemicals are considered. In addition, sludge disposal costs can be significantly reduced by reducing alum usage. Sludge is a factor to be considered during discussion of water treatment, because the amount and type of sludge are direct results of water treatment processes. Sludge disposal can be a major economic factor associated with the total cost of operation (TCO).

Wastewaters containing color, such as pulp and paper mill discharges, are sometimes even more difficult to treat than natural water sources. Experience and ingenuity are needed to screen potential coagulants; this is an area of water treatment that is still more an art than a science. An example of this was a study of a textile wastewater, where the color could not be removed by alum treatment followed by pH correction with alkali, but it could be treated by aluminate, followed by pH correction with acid.

Plant Design

For water clarification, water treatment plant designs are classified as either conventional clarification or direct filtration. A conventional clarification plant is capable of handling a wider range of impurities in influent raw water and usually involves sedimentation followed by filtration for raw water applications. Wastewater processes commonly use only sedimentation. Direct filtration is used when the incoming water does not contain many solids. A rule of thumb would be when influent is consistently greater than 10 NTU, sedimentation is cost-effective; less than 5 to 10 NTU can economically operate with only filtration. Both classes of water clarification plants can provide softening treatment, as necessary, using the lime softening process.

The design flow of a surface water clarification plant shows how the principles of coagulation and flocculation apply to actual plant design. Generally, the lower the suspended solids in the process stream, or the higher the required effluent clarity, the more critical is mixing to the final results. Surface water is relatively low in suspended solids, and removal to a low concentration of residual solids is usually required. For this reason, many water plants are designed with both flash mixing and flocculation mixing. The jar test protocol of rapid and slow mixing, which works best for raw water clarification, is duplicated on the plant scale. Flash mixing is accomplished in two ways: in-line hydraulic mixing (Fig. 6.15) and high-speed mixing in a small mixing basin (Fig. 6.16). The coagulant is added at or before the flash mix. Mixing can also be accomplished by hydraulic jumps in open channels, venturi flumes, and pipelines with tortuous baffles. However, these do not maintain the necessary *G* factor at low flows and are somewhat limited in application. In many situations, there is a practical benefit to having serial flash mixers (usually two) to improve coagulant dispersion, or to promote initial primary particle agglomeration. This has been especially useful in filter aid feed systems for maximum particulate removal and filter run length. Sequential flash mixing also provides flexibility in adapting to future plant requirements.

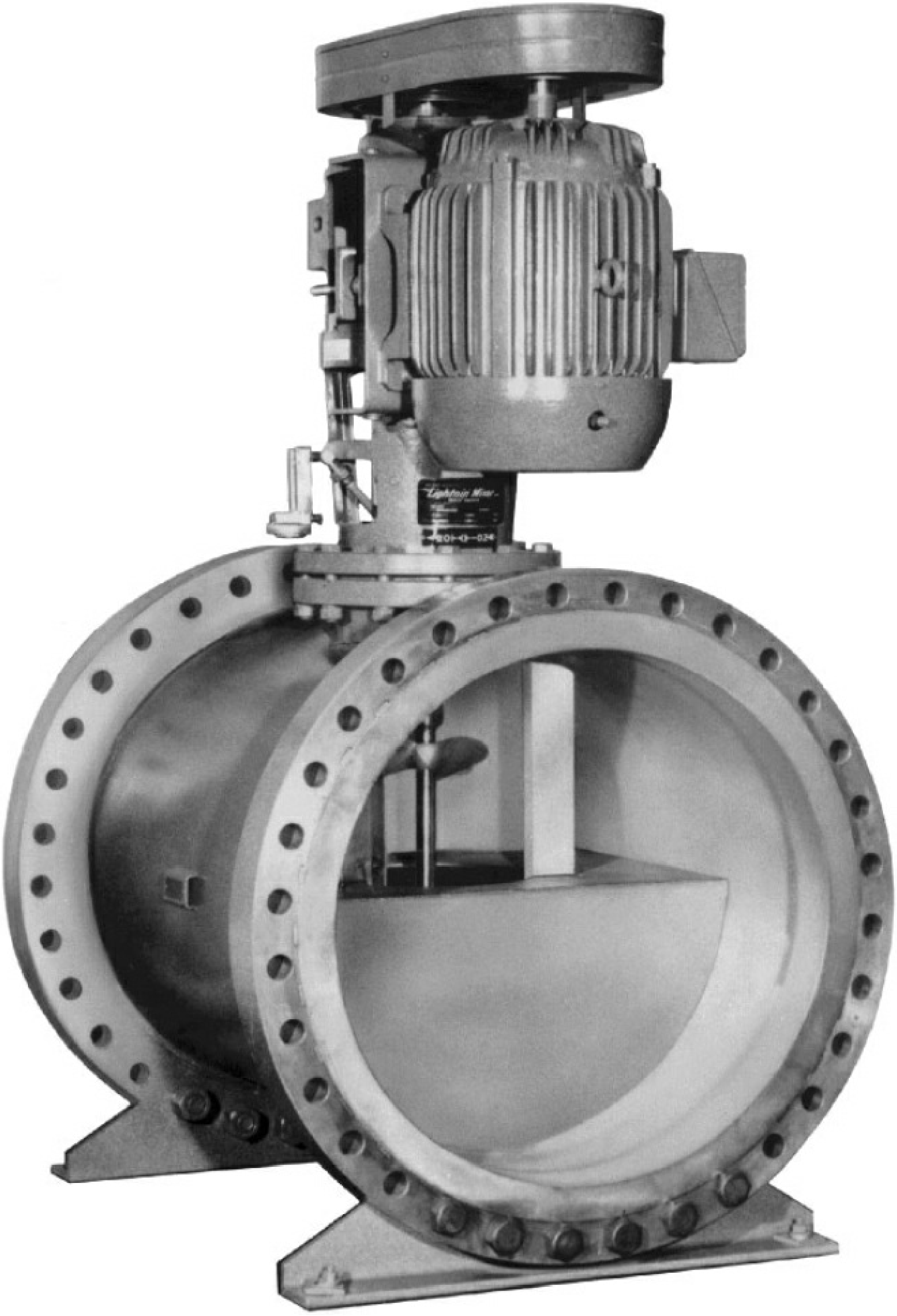


FIGURE 6.15 High-energy in-line mixer. (*Courtesy of Mixing Equipment Company*.)

FIGURE 6.16 Flash mixers are designed to disperse chemicals throughout the water instantaneously, before flocculation. (*Courtesy of FMC Corporation*.)

Flocculation mixing occurs in gently stirred compartments. Two common flocculator designs are the horizontal reel (Fig. 6.17) and the turbine mixer (Fig. 6.18). Variable speed motors may be provided to allow variation in mixing energy. Some plants employ hydraulic flocculation mixing, but this has limited use because the effectiveness decreases at reduced flows.

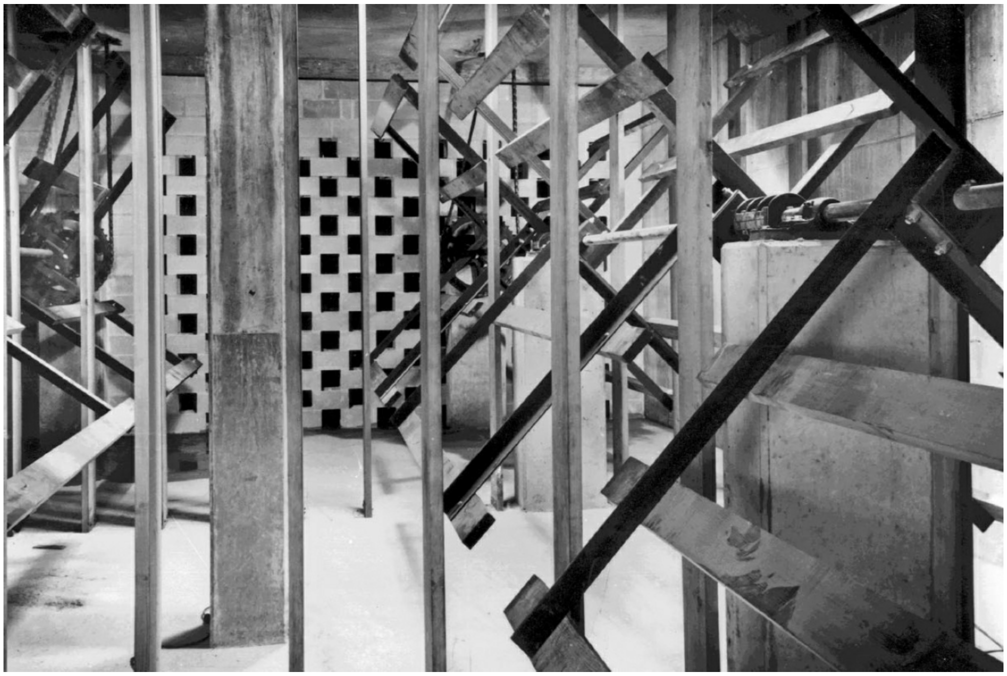


FIGURE 6.17 Reel-type paddle flocculator. (*Courtesy of Envirex, a Rexnord Company.*)

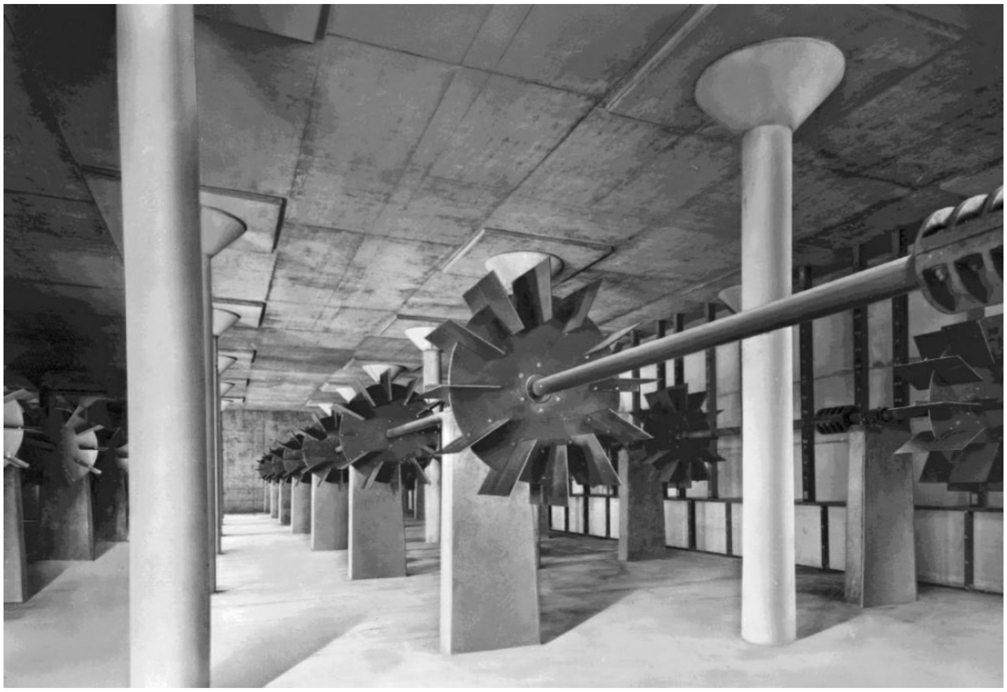


FIGURE 6.18 Turbine-type flocculators. (*Courtesy of Envirex, a Rexnord Company.*)

Silt or color removal in raw water is accomplished using two basic treatment schemes: conventional clarification or direct filtration. The most common plant operation is conventional with rapid mix, slow mix, sedimentation, and filtration (Fig. 6.19). Historically, alum has been most widely used, because the optimum pH is often below 6. It is fed at the head of the plant, sometimes in conjunction with alkali for pH control. Iron salts are seldom used, since the optimum pH is greater than 7. Because alum floc is light, a polymeric flocculant is usually required to reduce carryover from the settling basin to the filters.

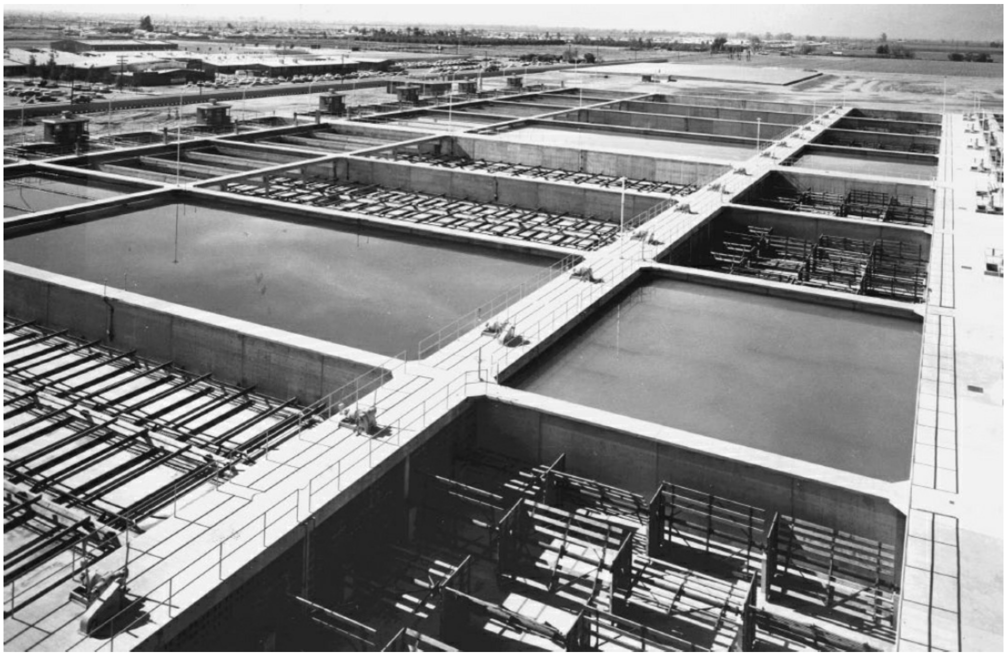


FIGURE 6.19 Conventional water treatment plant showing reel-type flocculation units, rectangular sedimentation basins in parallel with common wall construction, and sludge collection flights. Final filtration is not shown. (*Courtesy of FMC Corporation*.)

Polymer coagulants often are used to either replace or reduce inorganic salts. The polymer coagulant is added at the flash mix. Sometimes, alum can be replaced only if clay is fed to ensure high collision frequency, and to add weight to the floc. An alternate method is to return sludge from the bottom of the settling basin to the rapid mix. These methods essentially add solids to increase collisions. Adding solids can be beneficial during the initial startup of a clarifier. This increases agglomeration in low turbidity water and accelerates sludge blanket formation.

When the color or turbidity is very low in the raw water, direct filtration is often practiced. In a direct filtration plant, water passes through flash mixing, sometimes a flocculator, and then directly to the filters. There are so few solids in the water that the filters do not plug excessively. A polymer or a blend is used as the primary filter aid (coagulant) in this process, since inorganic salts add solids that could blind the filter.

High molecular weight flocculant polymers are not normally used as filtration aids because these excel at bridging, which is undesirable in the microscopic spaces between sand particles.

Wastewater streams usually have higher solids than raw water, and the required suspended solids removal may not be as stringent. Generally, for wastewater clarification, hydraulic mixing has been widely used in the past; but newer plants are being designed with mechanical mixing similar to raw water clarification plants, in order to improve removal of suspended solids.

Filtration

Water filtration is essentially a batch-type liquid-solids separation process for the removal of suspended material by passing it through a porous bed of sand or other granular materials. Granular media filtration is used to remove filterable solids from raw water, recycled water, floc particles from pretreated water, precipitates from the effluent of a lime or lime-soda ash process, iron and manganese precipitation products, and as a tertiary treatment step in wastewater treatment. Filtered suspended solids are usually removed from a filter by taking the filter out of service and backwashing the media, with the waste backwash water going to drain.

Granular media filtration, as used in water treatment, is generally applicable for removal of suspended solids in the 5 to 50 mg/L range, where an effluent of less than 1 NTU is required. Sand filters have been used for many years as a final polishing step in municipal and industrial water plants, where the clarifier effluent contains 5 to 20 mg/L of suspended solids. In areas where a very low turbidity raw water source is available, some water treatment plants use granular media filtration along with chemical conditioning as the only treatment process for solids removal, particularly for industrial process water. This is referred to as direct filtration.

Filtration Mechanisms

Granular media filtration is considered to include both physical and chemical mechanisms. Some particle removal, especially larger particles, may be considered mechanical straining, and as such, occurs mainly in the upper portion of a stratified media. For a granular media filter to remove other particles, especially smaller particles, these particles must be transported to a media grain and attach to that media grain or other particles previously deposited. Particle transport mechanisms within the media may include gravitational settling, interception, diffusion, hydrodynamic effects, and inertial forces.

Colloid chemical forces bring about particle attachment. As the particle approaches the media surface, or the surface of a previously deposited particle, the removal of that particle is dependent upon attachment mechanisms that may involve chemical bridging, specific adsorption, and electrostatic interaction. Increasing particle size enhances inertial impaction, hydrodynamic action, and gravity settling. Decreasing particle size enhances diffusion.

Figure 6.20 illustrates particle transport mechanisms. Gravity settling (a) is related to particle settling in the range of 2 to 10 µm. Diffusion (b) is related to Brownian diffusion for particles of 1 µm or less. Interception (c) relates to the collision of a particle with the media. Hydrodynamic effects (d) relate to the crossing of fluid streamlines due to an existing shear gradient and impacting the media. Inertia (e) relates to a particle having a greater density than the liquid; this particle then experiences inertial forces, which cause the particle to cross the fluid streamlines before it flows past the media grain.

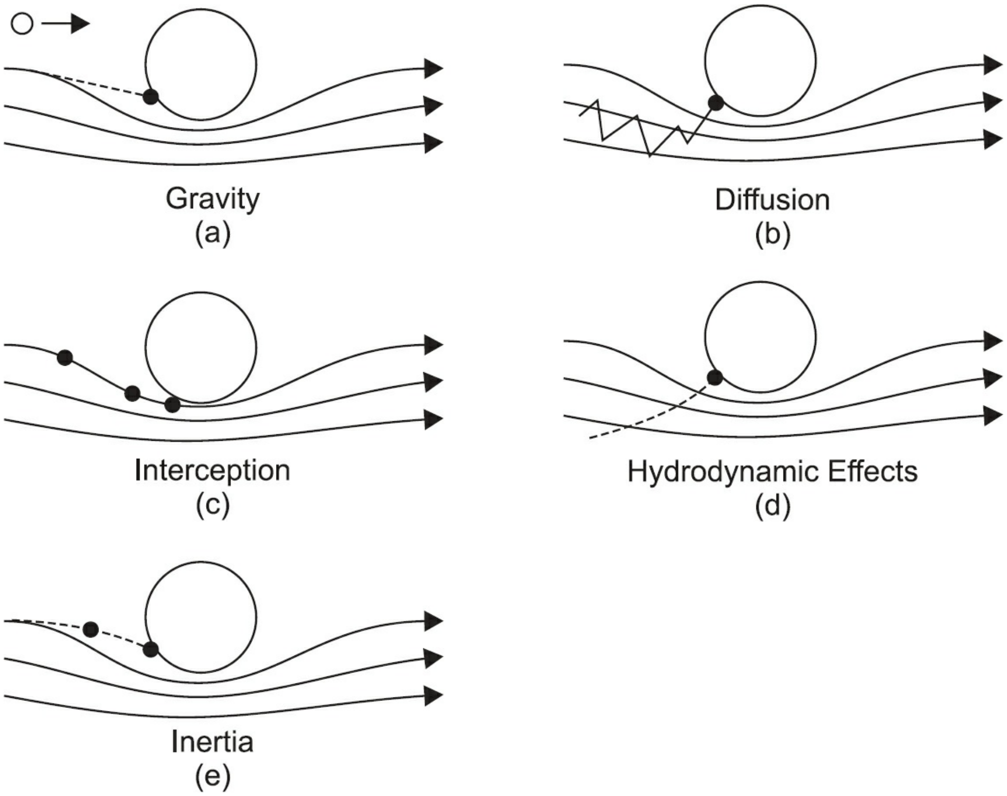


FIGURE 6.20 Particle transport mechanisms.

Usually a pretreatment step, often using a coagulant or flocculant, precedes filtration. If the floc particle is too large, it will blind (plug) the filter surface. If it is not properly treated or coagulated, it will completely pass through the filter. If the floc particle strength is too strong (Fig. 6.21), the service run may be shortened due to a high head loss. If the floc particle strength is too weak (Fig. 6.22), the service run may be shortened due to turbidity breakthrough.

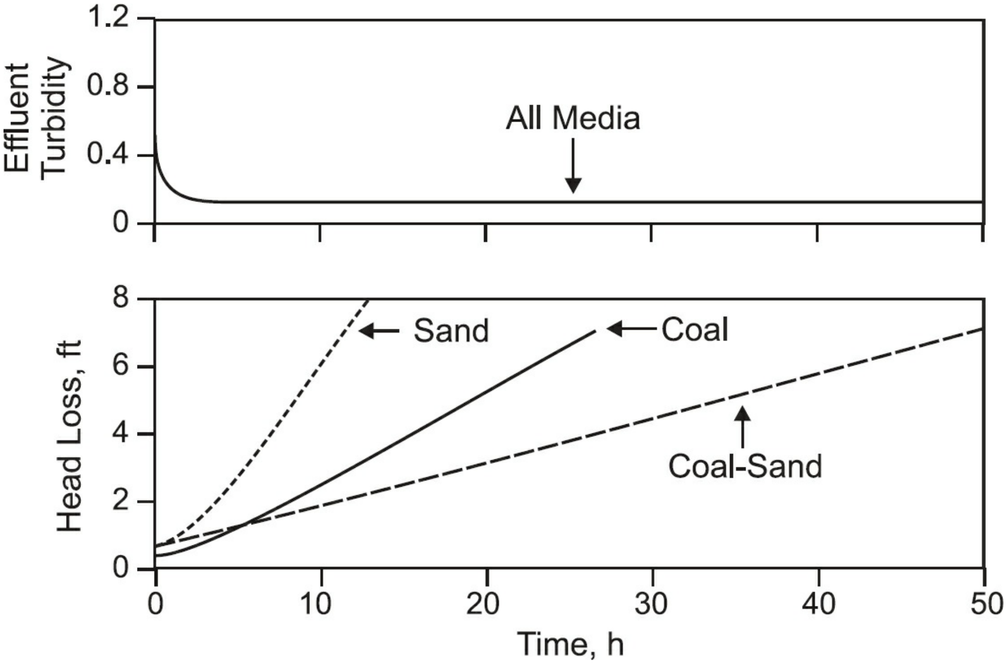


FIGURE 6.21 Strong floc effect on filter run length with various media.

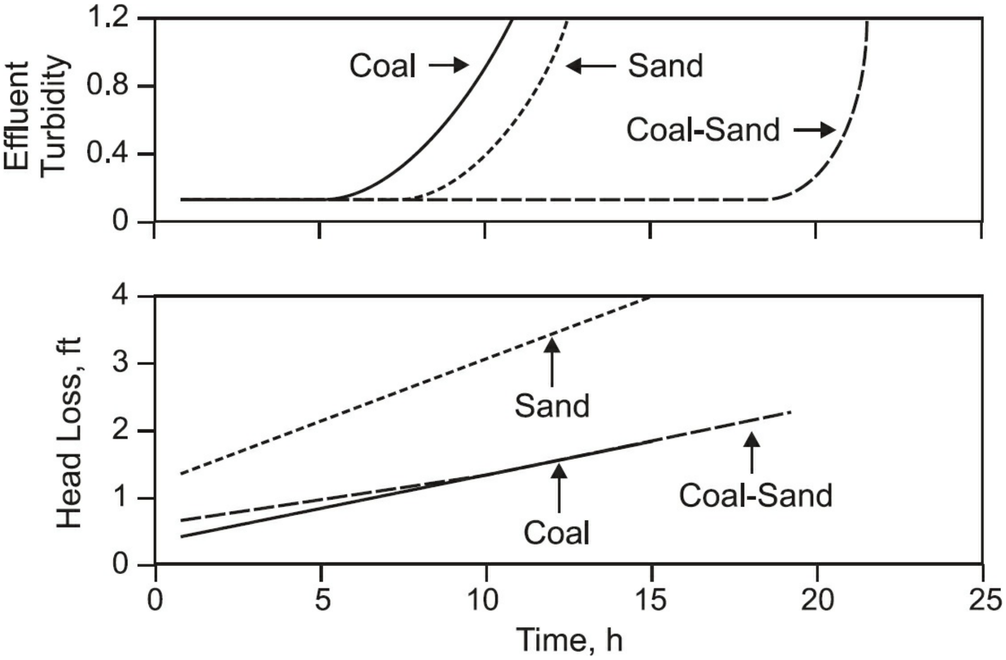


FIGURE 6.22 Weak floc effect on filter run length with various media.

Once the particles have contacted the media, they are retained by an attractive force. To remove these particles and those removed by straining, the filter bed is fluidized by upflowing the bed with water. The addition of an air scouring or surface wash agitation step in the backwash cycle greatly improves particle removal efficiency.

Granular Media Filters

Granular media filters are generally of the following three types:

- Gravity (conventional rapid sand, self-backwashing, or continuously cleaned)
- Pressure
- Upflow

The most widely used granular media filter in the municipal raw water treatment field is the conventional rapid sand type filter with either a single media (sand) or a dual media (anthracite-sand) bed. Pretreatment filters used in industry for large-scale applications are usually of the conventional type with dual media. Smaller industrial type filtration applications, such as boiler water pretreatment and recycle, are usually of the pressure filtration type.

Media, media depth, filter operational control method, backwash method, and underdrain design vary between the types of filters and within a type of filter. Therefore, a brief discussion of a conventional rapid sand filter configuration (Fig. 6.23), before highlighting the various filter types, will aid in understanding the operation of granular media filters.

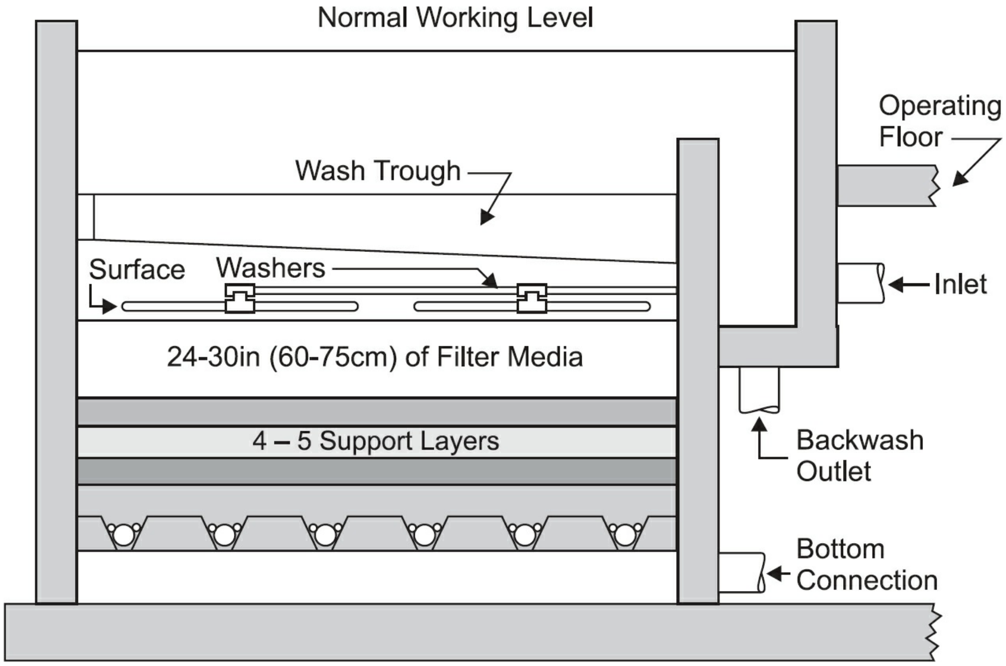


FIGURE 6.23 Conventional rapid sand filter.

The major portion of a filter configuration is determined by interrelated components such as filter area, filter depth, filter operational control method, backwash method, and to a minor extent the filter conditioning method, if used.

Filter area is determined by the actual flow rates expected and the selected design unit flow rate. The overall dimensions of a filter bay or cell are usually limited by the backwash water requirements such as storage, recovery, and the required backwash water rate.

Filter depth as measured from the top of the filter wall to the underdrain-supporting slab, provides for the necessary freeboard, submergence, media depth, and underdrain design.

Freeboard is as required by regulations or the plant hydraulic profile.

Submergence includes the depth of water provided for loss of head and the water depth required to prevent air binding in the media during a service run. Adequate submergence is also necessary to minimize inlet velocity above the filter bed surface. Note that part of the filter head loss includes the head loss through the underdrain system, including nozzles, effluent piping, and valves. The head loss through the underdrain system becomes critical if the unit filtration rate is increased substantially. Media depth and the underdrain system depth allowances are self-explanatory. Dual media and single media (stratified or unstratified) filters each have different depth requirements. The type of underdrain system selected has an additional gravel support bed depth requirement, ranging from none to several gradations of gravel. The placement of the wash water troughs or outlet above the media, depending upon the backwash water method used, determines any additional filter depth requirement for media expansion during the backwash cycle.

Operational control methods available are constant rate and variable declining rate. The filter configuration varies as to inlet and outlet structure, control valves, level sensing devices, etc., depending upon the control method selected.

In the constant rate mode, flow through the filter can be controlled by one of the following methods:

- Inlet flow, split between each filter cell, usually by means of weirs with a constant water level across the filter, maintained by an effluent line automatic throttling valve controlled by a level sensing device located in the water above the filter bed.

- Inlet flow, split between each filter cell, with the water level in each filter cell varying with the loss of head through the filter. An effluent weir arrangement properly positioned is usually provided for initial submergence of the media.
- Rate of flow controller in the filter effluent piping, to maintain a constant flow rate through the filter, by gradually opening up to a point, as the filter head loss increases.

Variable declining rate filtration operation requires multiple filter cells and results in a higher unit filtration rate (gpm/ft^2 or m^3/[h · m^2]) at the beginning of a service run than at the end of the service run. For this mode of operation, the water level is essentially the same in all operating filter cells at all times. As filtration continues, flow through the dirtiest filter tends to decrease, causing the influent flow to be redistributed to all filters automatically, so that cleaner filter cells pick up the capacity lost by the dirtiest filter cell. This method causes a gradual declining rate toward the end of a filter cell run. The advantage is that there is less hydraulic disturbance to the other filter cells in service, when a filter cell is taken off-line for backwashing, as that filter cell is already operating at a diminished proportion of the total inlet flow. Filter cells are generally cleaned on a selected time interval basis. Influent or effluent control (such as an orifice in the filtered water line) is used to restrict abnormally high unit filtration rates through a filter cell, when a cleaned filter cell is returned to service.

Storage capacity determines if the filtration system can be operated on a consistent basis in a true constant rate or variable declining rate mode.

Backwash methods in general vary, but the usual practice is to fluidize single (stratified) and dual media filters with an upflow of water to flush captured solids out of the filter. Auxiliary scouring devices such as surface washers or air scouring systems are frequently provided, especially with dual media filters, to remove impacted solids by increasing the number of collisions within the media.

Single media filters (unstratified) are simultaneously air-water backwashed at low subfluidizing backwash rates, followed by a low backwash water flow only. This method, used to flush out suspended solids and accumulated air, also keeps the media in the desired unstratified state, and is used in certain proprietary designs and deep bed filters.

Self-backwashing filters use on-line stored filtered effluent as the backwash water source, or when properly designed, the filtered effluent from the other filter cells in the cluster. Continuously cleaned filters usually use a central airlift device with baffles to clean a small portion of the media continuously and return the cleaned media to the top surface of the filter.

Filter conditioning is used to minimize the initial surge of filtered water turbidity that occurs when a backwashed filter is returned to service (Fig. 6.24). Methods used to overcome this initial water quality problem are:

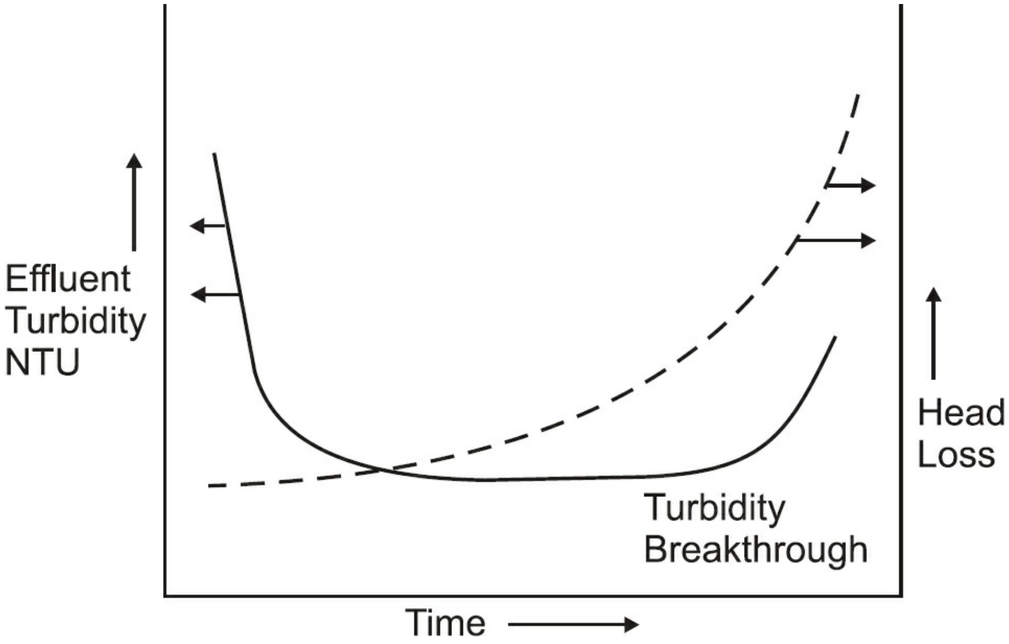


FIGURE 6.24 Filtered water turbidity and head loss profile versus time.

- Filter to waste—piping arrangement
- Lower initial flow rate—instrumentation
- Polymer addition—chemical feed station

In filter to waste, the filtered water is wasted to drain until the desired quality is obtained. This method has the disadvantage of contributing to waste water volume. The lower initial flow rate method involves slowly opening the filter service valve over a period of time, until the filter bed is hydraulically stabilized with regard to suspended solids retention. Disadvantage is loss of full service flow for a period. Polymer addition during the last few seconds of a backwash conditions the filter media to retain suspended solids. This is an effective and flexible method to condition a filter.

Conventional Rapid Sand Filter

Figure 6.23 shows a gravity filter of the conventional rapid sand type. The great majority of municipal water treatment plant filters are of this type.

Water enters the filter through the influent valve, passes through the filter bed, collects in the filter underdrain, and is discharged through the effluent valve. The filtered water flow is controlled by an effluent rate of flow valve. At the start of a backwash cycle, the water level is drained to within a few inches (millimeters) of the surface sweep arms. The drain valve is closed, the backwash wastewater valve is opened, and the surface wash is initiated.

After sufficient scouring occurs, the surface wash system is stopped. The backwash water supply valve is opened, and the water flows up through the bed at a rate high enough to fluidize the bed and dislodge accumulated solids. Backwash water overflows the wash water trough and flows to drain. The backwash water rate is much higher than the service flow rate for this type of filter. Backwashing usually takes 8 to 15 minutes or until the waste backwash water runs clear.

Granular Media Filter Beds

Granular media bed classifications include the media composition and arrangement, media size distribution, and filter depth. Common media compositions and arrangements used in water filtration (Fig. 6.25) include single media (a), using either sand or anthracite; dual media (b), using anthracite and sand; and mixed media (c), using anthracite, sand, and garnet.

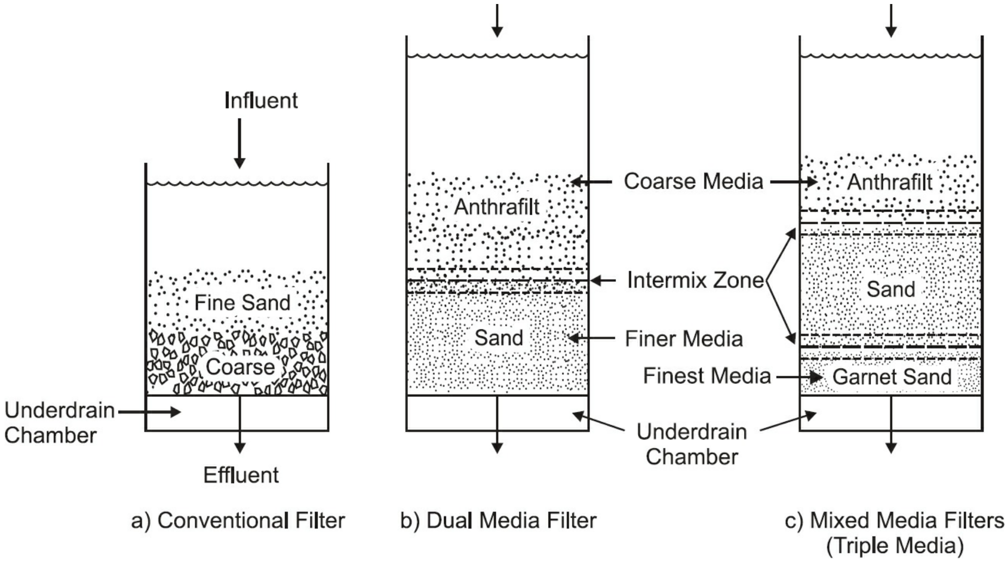


FIGURE 6.25 Filter media compositions and arrangements.

The heights of the intermix zones, shown in Figs. 6.25*b* and *c*, are dependent in part on each media's effective size (ES) and uniformity coefficient (UC).

The UC characterizes the fine and coarse grain distributions in the media, and is by definition the 60% size divided by the 10% size. The ES by definition is the 10% size. Sizes are determined by plotting on log normal probability paper, the cumulative weight percent of the media retained on various US standard sieves versus the separation size (mm).

The intermix zone occurs because the larger size anthracite in the lower portion of the stratified anthracite bed mixes with the finer sand in the upper portion of the stratified sand bed. Media grain size distributions for the various media compositions and arrangements are illustrated in Fig. 6.26.

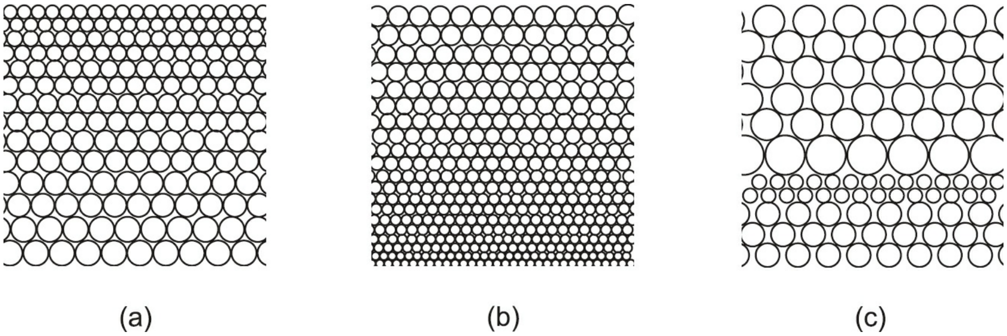


FIGURE 6.26 Media arrangements and grain size distributions.

By using larger media particle sizes of a lower density than the succeeding layer, the general media gradation for filter beds (Figs. 6.26*b* and *c*) can be made coarser-to-finer, as opposed to the media bed shown in Fig. 6.26*a*, which is finer-to-coarser.

The advantage of a coarse-to-fine grain distribution, or a uniform grain size distribution, is that of in-depth filtration [filtration across the majority of the media depth rather than filtration just in the first few inches (millimeters)] of the bed, as is characterized by the grain size distribution of the stratified filter bed of Fig. 6.26*a*.

Depth of the media plays a part in effluent turbidity along with the media ES. The depth of the anthracite layer in a dual media filter provides storage for the coarser particles in the water, before final polishing by the lower finer sand bed. The unstratified bed acts in a similar manner, with solids captured across the depth of the bed rather than just in the upper few inches (millimeters) of a stratified sand bed or in the anthracite media, as in a dual media filter.

Figures 6.21 and 6.22 graphically illustrate the preceding discussion. The media are sand [0.45 mm E.S., 2 ft (0.6 m) deep]; coal [0.7 mm E.S., 2 ft (0.6 m) deep]; and dual media [coal: 1.05 mm E.S., 1.5 ft (0.5 m) deep] and sand [0.45 mm E.S., 0.5 ft (0.15 m) deep]. Clarifier effluent turbidity for the strong floc was 2 NTU, while that for the weak floc was 15 NTU.

Figure 6.21 shows the effluent turbidity for all arrangements being the same. This would be so, since the sand media is the same in the sand filter and the dual media filter. An ES of 0.7 mm anthracite approaches a 0.5 mm ES characteristic, because of the irregular shape of the anthracite. Head loss was higher for the sand media because of the initial solids capture in the first few inches (millimeters) of the stratified sand bed as previously discussed. Head loss for the coal media was greater than the dual media filter, because of the finer coal size used in the coal media filter.

In Fig. 6.22, effluent turbidity was greater for the coal filter, because of its larger pore size versus the smaller pore size in the sand filter. The dual media filter provided greater storage of the floc in the anthracite layer and finer polishing in the sand layer.

Head loss for the sand filter is greater, because of greater capture of solids. Equal head loss for the coal filter and the dual media filter reflects, in part, loss of solids through the anthracite filter, as evidenced by higher effluent turbidity.

Both Figs. 6.21 and 6.22 illustrate the overall effects that must be reviewed when considering backwash initiation on a turbidity, time, or head loss basis, using various types of filter media and treated influent water characteristics.

Filter Backwashing Systems

A filter bed can function properly only if the backwashing system used in conjunction with the filter design effectively cleans the material removed by the filter. The methods commonly used for backwashing granular media filter beds include:

- Water backwash only
- Water backwash with auxiliary surface wash
- Water backwash with auxiliary air scour
- Combined air-water backwashing

Note that the specific application of one of these methods to a filter depends upon the filter configuration, filter control, media, etc. as previously discussed.

Water backwash only—The idea in the system using water backwash only is to fluidize the filtering media, so that the shearing action of water as it moves past individual grains scours material that has accumulated. These systems have been used in water treatment plants, where solids and turbidity levels are relatively low.

Water backwash with auxiliary surface wash—Surface washers can be used to provide extra shearing force to improve cleaning of the grains. Operationally, the surface washing cycle is started for about one or two minutes after the water level is drained to the recommended level above the centerline of the surface sweep pipe arms. Then the backwash flow is started, and both cycles are continued for about two minutes, at which time the surface wash is terminated. Water usage is as follows:

- For a single-surface sweep backwashing system: 0.5 to 1 gpm/ft^2 (1.2–2.4 m^3/[h · m^2])
- For a combined surface sweep-subsurface backwashing system: 1.5 to 2 gpm/ft^2 (3.7–4.9 m^3/[h · m^2])

Water backwash with auxiliary air scour—Operationally, air is usually applied for three to four minutes after the water level has been drained to the recommended level above the media surface and before the water backwashing cycle begins. Typical airflow rates range from 3 to 5 cfm/ft^2 (0.9–1.5 $m^3/[min \cdot m^2]$). Because of the violent action of the air injected into the filter bed, conventional gravel underdrain systems cannot be used without additional restraints. Therefore, when air scour is used, the filtering medium is placed directly on a specially designed underdrain system. (See discussion of underdrain systems later in this chapter.)

Combined air-water backwash—The combined air-water backwash system is used in conjunction with the single media unstratified filter bed. Operationally, air and water (at a low rate) are applied simultaneously for several minutes. The specific duration of the combined backwash varies with the design of the filter bed. At the end of the combined air-water backwash, a two to three minutes water backwash at subfluidization velocity is used to remove air bubbles that remain in the filter bed. This last step is required to eliminate air binding within the filter.

Backwash water rates are dependent upon the media size, media type, backwash water temperature, and the type of filter backwash water system used, along with the filter configuration provided. The manufacturer's instruction book or the treatment plant's operation and maintenance manual should be consulted before changing an existing backwash water flow rate.

Filter Appurtenances

The principal filter appurtenances are:

- The underdrain system is used to support the filtering materials, collect the filtered effluent, and distribute the backwash water and air (where used).
- The wash water troughs are used to remove the backwash water from the filter.
- The surface washing systems, when used, help remove attached material from the filter media.

Underdrain systems—The type of underdrain system used depends on the type of backwash system. In conventional water backwash filters without air scour, it is common practice to place the filtering media on a support consisting of several layers of graded gravel and a coarser media layer. When there is to be a gravel layer, an underdrain system, such as the one shown in Fig. 6.27, is used. With air scour or combined air-water backwash systems, there is usually no gravel layer, and underdrain systems of the type shown in Fig. 6.28 are generally used. In the single-media unstratified filter bed, the grain size is sometimes larger, and the slot or screen size in the backwash nozzle can be larger.

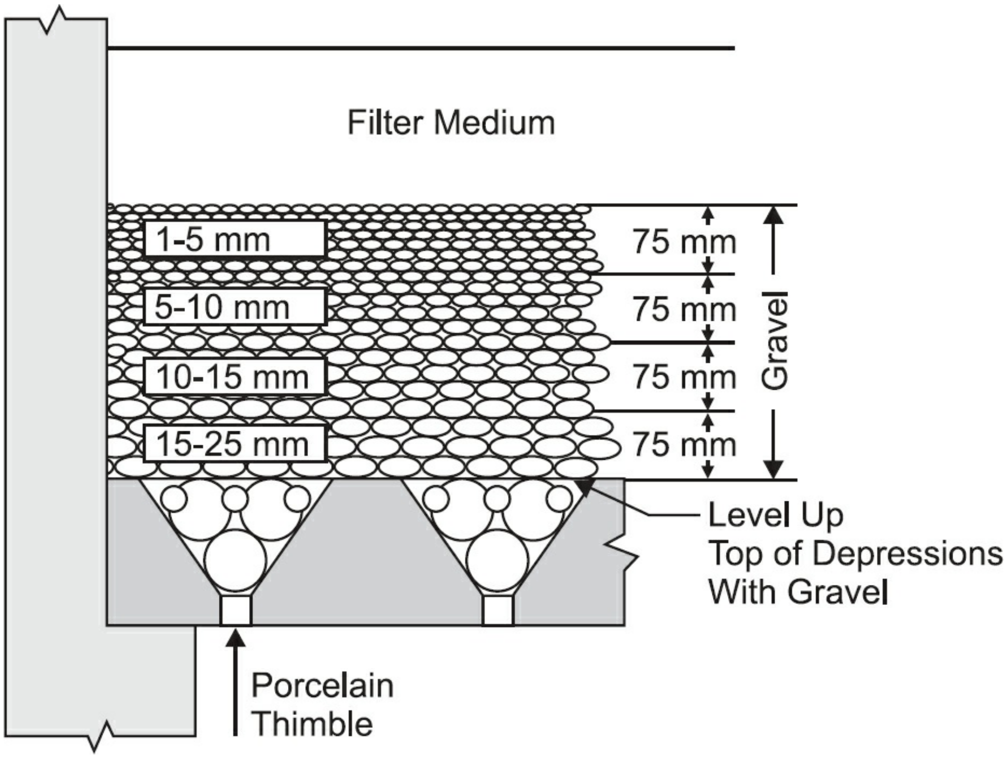


FIGURE 6.27 Filter underdrain systems with gravel sublayers.

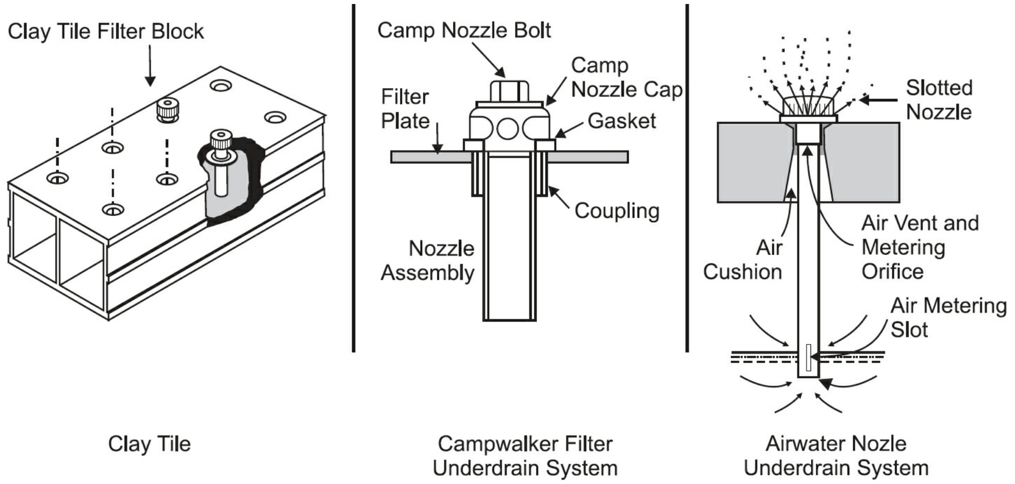


FIGURE 6.28 Underdrain nozzles used in filters without gravel sublayers.

Wash water troughs—Wash water troughs are now constructed of plastic, sheet metal, or concrete with adjustable weir plates. The particular design of the trough depends to some extent on the other equipment used in the design and construction of the filter.

Surface washers—Surface washers for filters can be fixed or mounted on rotary sweeps. According to data on a number of systems, rotary-sweep washers are the most effective.

Service Operating Parameters

Filters are designed and operated based on hydraulic loading or filtration rate expressed as gpm/ft^2 [m^3/(h · m^2)]. The parameter can be calculated from Eq. (6.8):

$$\text{Filtration rate} = F/A \tag{6.8}$$

where filtration rate = hydraulic loading, gpm/ft^2 or m^3/(h·m^2)
F = filter water flow rate, gpm or m^3/h
A = filter surface area, ft^2 or m^2

Normal operating rates vary with the type of filter system used (gravity or pressure filters). Unit filtration rates for conventional water treatment rapid sand type filters, are generally 2 to 4 gpm/ft^2 [4.9–9.8 m^3/(h · m^2)].

Normal operation is judged by two variables: quality of water produced and length of filter run. A time profile of turbidity (the measure of water quality) and head loss provides a picture of filter operation. Figure 6.21 shows typical changes in water quality when operating a filter at a constant rate over time. When the filter is first brought into service, relatively high turbidity is encountered in the filtered water. Filter conditioning can last from five minutes to two hours before turbidity drops and stabilizes. After a length of time, the turbidity rapidly increases. This sudden increase (turbidity breakthrough) occurs when the shear forces in the filter, which increase as head loss increases, become greater than the shear strength of the trapped floc. During the filtration process, head loss builds as shown in Fig. 6.21. There may be no correlation between breakthrough and head loss; breakthrough can occur at high or low head loss. If there is a sudden increase in influent flow to the filter, previously captured suspended solids may slough off the media and pass through the filter bed, thereby causing a higher effluent turbidity until the filter bed hydraulically restabilizes.

Water Quality

Turbidity or suspended solids in the filter effluent are the primary measure of filter efficiency. The effluent turbidity actually depends on the turbidity removal efficiency of the filter. The efficiency expressed as a percent is calculated using Eq. (6.9):

$$E = (100)(\mathrm{TSS}_I - \mathrm{TSS}_E)/\,\mathrm{TSS}_I \tag{6.9}$$

where E = removal efficiency, %
TSS_I = influent suspended solids, mg/L
TSS_E = effluent or filtrate suspended solids, mg/L

Effluent turbidity can be affected in two ways:

1. If filtration removal efficiency remains constant, a change in influent turbidity affects effluent turbidity.
2. If influent turbidity remains constant, a change in filtration removal efficiency affects effluent turbidity.

Most filtration operations run with at least 70% removal efficiency.

Many factors can affect influent turbidity; some are controllable, and some are not. If a clarification program precedes filtration, changes in the chemical or mechanical program can change the amount and nature of the incoming suspended solids. If no sedimentation type pretreatment step is present, there may be little that can be done to change the volume of influent solids.

The efficiency of the filter is also influenced by many factors, a number of which are controllable. Factors affecting filtration efficiency are:

Filterability of suspended solids—Colloidal solids are not readily filterable, because they are not easily adsorbed on the filter media. Other floc particles, such as alum floc, may be too large and tend to blind filter media. The strength of the floc trapped in the void spaces also affects turbidity removal efficiency. Chemical and mechanical changes before filtration can affect floc filterability.

Type of media—The finer the media, the higher the efficiency. Generally, a mixed-media or dual-media filter is more efficient than a single-media filter, especially as filtration rates increase.

Physical condition of the media—If some of the media is missing or if it is dirty after backwashing, efficiency decreases.

Chemical conditioning of the media—The surfaces of the media are charged; just as colloidal particles are charged. Generally, if the media is positively charged by cationic polymer addition, electrokinetic forces of attraction exist between the media surface and the floc particles, enhancing solids capture.

Flow rate—As the flow rate increases, the possibility of floc passing through the filter also increases.

Changes in flow rate—Any increase in flow rate disturbs the floc accumulated in the bed. Some flocs are shear sensitive and are dislodged during flow changes.

Length of filter runs—The other major measure of filter operations is length of filter runs. Filter runs are measured by the number of hours the filter is on line, although gallons (m^3) of water produced are a better measure. A filter operating for 20 hours at 5 gpm/ft^2 [12.2 $m^3/(h \cdot m^2)$] processes more water between backwashes than one operating for 30 hours at 3 gpm/ft^2 [7.3 $m^3/(h \cdot m^2)$]. Another measure is the percentage of treated water required to backwash filters. A well-operated plant uses less than 3% of its treated water for backwash. It is desirable to extend filter runs, since backwashing can be expensive in terms of personnel, water usage, and electrical cost.

A filter is backwashed for three reasons:

1. *Breakthrough occurs*—Where effluent turbidity standards govern, particularly in municipal plants, turbidity breakthrough rather than time or head loss is the main criterion for backwash initiation.
2. *Head loss exceeds maximum desired level*—When pressure drop exceeds some predetermined level, the filter is backwashed. Usually, this level is determined by experience, so that the filter is backwashed before turbidity breakthrough occurs.
3. *Time*—Many plants, particularly industrial plants, arbitrarily choose to backwash filters at a convenient interval, usually every 24 hours or once per shift. They find that water quality is maintained at an acceptable level, while providing a defined procedure for shift operators.

Filter run length is affected by several variables. The factors affecting turbidity breakthrough have already been discussed. Head loss is most commonly affected by the volume of solids in the influent water. The more influent suspended solids, the shorter the filter runs. The nature of the solids and the coagulation program used in pretreatment, as discussed before, may result in a floc that is so large or adhesive that it blinds the surface, causing rapid head loss. The deeper the average floc penetration into the bed, the less head loss for a given volume of floc removed. Dual and mixed-media filters give longer filter runs, since the coarse material is stored in the top anthracite layer and the finer material stored in the finer sand layer.

The cleaner the bed after backwash, the lower the initial head loss, and a clean bed can accumulate more solids before reaching the maximum head loss.

Chemical Treatment

Chemical treatment in raw water filtration can be accomplished by any of several techniques. Coagulants and flocculants can be added as filter aids to improve the filtration process. Generally, coagulants are used in direct filtration chemical treatment for process performance improvement. Chemical cleaner programs can be used on media during or before backwash, to reduce solids retained in or on the filter media in the backwash cycle and to improve overall treatment performance.

Filter aids are chemical treatments for improving filter efficiency. The most common application, and what is usually meant as a filter aid, is the continuous feed of polymer, either a flocculant or a coagulant, at low dosage directly to water going to the filter. A second application is to the backwash water to aid filtration during the first minutes that the unit is on stream. Figure 6.29 shows effluent turbidity during a filter run with and without a filter aid. With addition of a filter aid, filter turbidity comes down faster after backwash, reaches a lower level, and breakthrough is postponed. Lower average turbidity during the run indicates the filter aid has increased filtration efficiency.

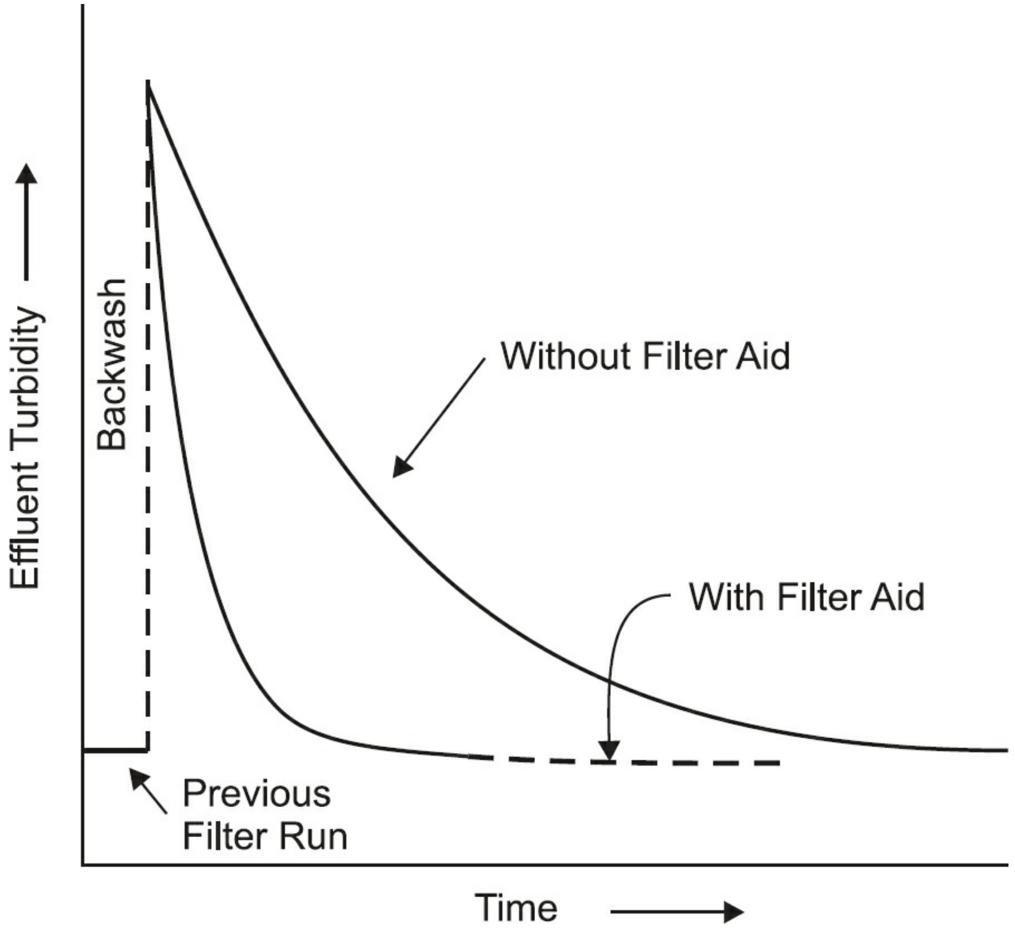


FIGURE 6.29 Filter efficiency improvement with filter aid.

Two types of products are used as filter aids:

1. Coagulants
2. Flocculants

Generally, coagulants are used since they are easier to feed. In addition, they provide more flexibility if the turbidity coming to the filter is under-coagulated, since the coagulant neutralizes the charge and increases removal. Coagulants are fed at 0.25 to 1 mg/L as filter aids. Over feeding can cause filter blinding. Filter aids can be fed dilute or as concentrated as 30%. In some cases, solution application strength toward the more concentrated levels improves performance.

High molecular weight flocculants work by strengthening floc trapped in the filter, thus improving shear sensitivity. Flocculants are fed at lower dosages of 10 to 100 µg/L and provide better shear resistance and economics but are more difficult to handle than coagulants. Overdosage of flocculants quickly causes filter blinding.

Flocculants can be used, if the filter is experiencing breakthrough without high loss of head. If the filter is experiencing both breakthrough and high head loss, a flocculant should not be used as a filter aid, because head loss will increase even more. In this case, the better choice is a coagulant. Flocculants must be fed at very dilute solution concentrations, because of the low dosages required. Feed at the same location as indicated for a coagulant.

To bring filters on-line faster (reduce initial turbidity faster), a coagulant can be fed to the filter backwash water. This can be done as a quick test to show the activity of a coagulant as a filter aid and filter conditioner. Be careful when applying this slug feed, if ion exchange units follow filtration, because cationic coagulants can foul cation resin.

Direct Filtration

Direct filtration lacks a precise definition, but in general it means that the overall treatment process does not include a sedimentation step prior to filtration and that all of the raw water suspended solids plus those added by treatment chemicals must be stored in the filter during its service run.

This definition would include those direct filtration plants, where coagulant is added to untreated raw water upstream of the filter and where definite rapid mix and flocculation stages precede the filter. It would also include those plants with separate rapid mix and flocculation steps ahead of a grossly hydraulically overloaded clarifier and those plants where low seasonal raw water turbidity either allow the settling function to be taken out of service or render the clarifier non-functional.

With separate coagulation and flocculation stages, chemical conditioning is targeted toward obtaining a floc designed to penetrate the filter bed in-depth and to resist shear forces. In other words, neither a strong floc nor a weak floc is desired.

In direct filtration where the coagulant is added upstream of the filter, the filter can be considered as a reactor with the chemical with physicochemical reactions occurring within the media bed.

The direct filtration potential for any raw water is related to the amount of chemical treatment required to destabilize the turbidity and color, so that they can be reduced by filtration to meet required levels. The method of determining the direct filtration potential of raw water is jar testing to determine a workable chemical program, followed by a No. 40 Whatman paper filtration test to determine the optimum chemical dosage and filtered water turbidity. If the results warrant, pilot plant testing is conducted.

Direct filtration is most suited for raw waters that seldom exceed 5 NTU turbidity or 20 APHA color, although higher levels can be handled, especially in industrial plants where maximum turbidity or color removal is not required. Upflow filters can handle much higher levels, but are generally used only in industrial plants.

Even though a conventional filtration plant may have some design limitations for direct filtration, such as mixing and filter media, conventional plants have flexibility not available in a direct filtration design. Having flocculation and a sedimentation basin available can be a great advantage. The flocculator can provide additional mixing, which may improve direct filtration results. In addition, the plant can return to conventional operation, when raw water turbidity and color increase. In most cases, even in direct filtration operation, some floc is removed across the basin, reducing load on the filters.

CHAPTER 7

Ion Exchange

For as long as water has been used in industrial processes, deposits from undesirable ionic species have been precipitating on equipment. Deposits result in reduction in heat transfer at a minimum, and up to and including catastrophic loss at the extreme. Some of the earliest attempts to remove undesirable ions occurred with the use of naturally occurring inorganic sodium aluminosilicates. Much has changed since the early years of ion exchange. This chapter explores various synthetic ion exchange resins and the mechanical systems that are in use to shape ionic characteristics of water, in order to minimize operational problems in target water systems.

While the ion exchange system is often named for its equipment configuration, it is the resin contained within the vessels that governs the changes in water chemistry. Water quality at the vessel outlet is primarily a function of the type of resin and regenerant utilized, and secondarily how the equipment is performing.

The ion exchange process is exactly that, an exchange of one ion for another, utilizing a synthetic resin in order to accomplish transfer. As water passes through resin, ion exchange occurs, removing targeted ions from the water and replacing them with more desirable ions that have been loaded on the resin. Which ions are loaded on the resin and which ions are exchanged are determined by the regenerant used and the type of resin loaded in the vessel. The process is reversible, meaning that the resin bed can be recharged once exhausted. Recharging the bed is accomplished through a process called regeneration.

Ion Exchange Resins

Synthetic ion exchange resins are a copolymer of divinylbenzene (DVB), and styrene or acrylic polymers. When these are reacted chemically during manufacture, they achieve desired ion exchange characteristics and properties. Finished resin is comprised of small, insoluble, and permeable beads of varying particle sizes. Each bead contains water that makes up approximately 50% of the bead's weight. During the manufacturing and activation process, each resin is given either cation or anion exchange properties by permanently locking positively or negatively charged exchange sites into the polymer skeleton. The styrene skeleton of the resin bead is a wraparound structure much like a ball of twine. Water flows not just over the surface, but also through the permeable bead. Since exchange sites are all along the skeletal structure, both inside and outside the bead, exchange capacity is significantly higher than if just the external surface of the bead exchanged ions.

Cation resin exchanges desirable cations to the water from negative permanent sites on the resin; anion resin exchanges desirable anions to the water from positive permanent sites. Thus, resins are named for ions they exchange, not charges on the resin itself. Figure 7.1 illustrates a cation exchange resin. Negatively charged permanent sites are loaded with the sodium cation ready to exchange.

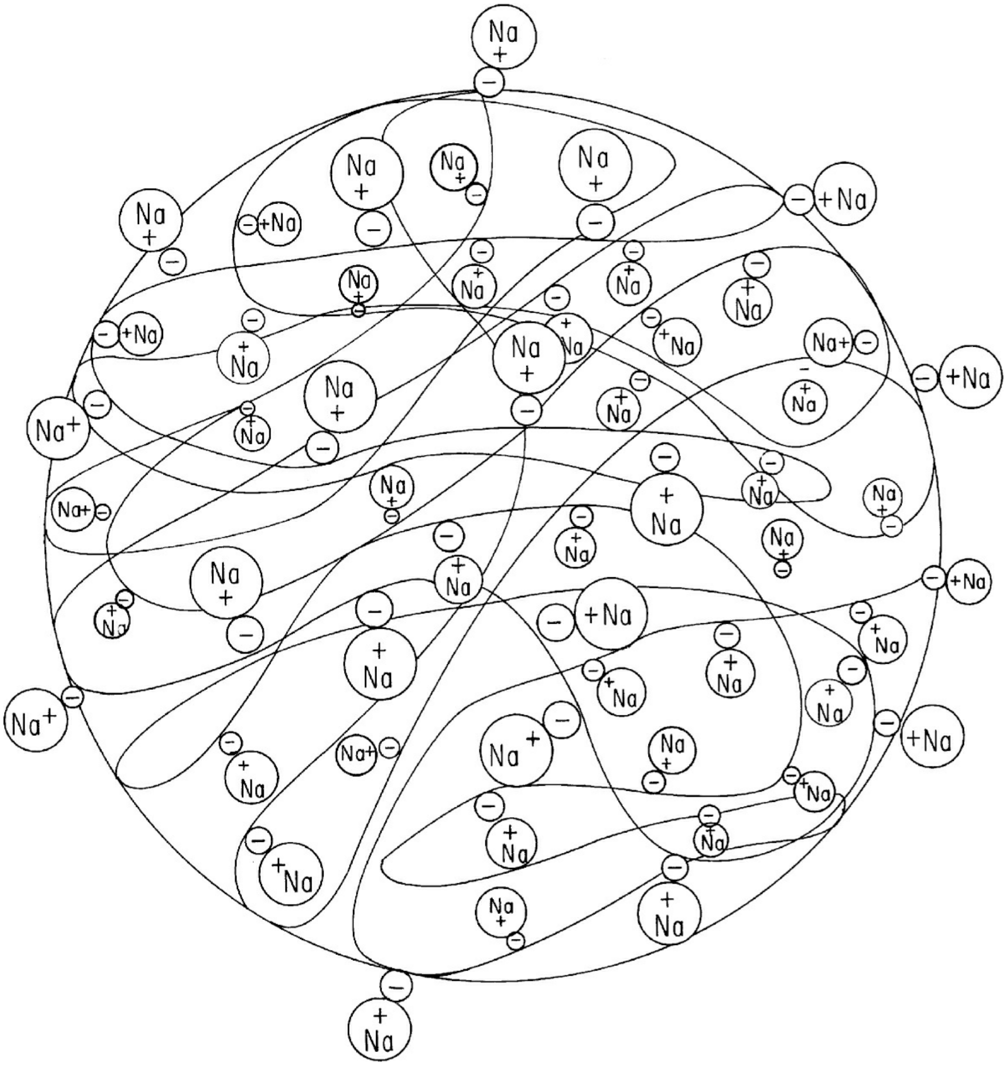


FIGURE 7.1 Illustration of cation exchange resin showing negatively charged exchange sites holding sodium ions.

These permanent sites are capable of retaining ions of opposite charge taken from the surrounding water. Ion exchange is reversible, and ions removed from water can be regenerated, or displaced, from resin by contact with a solution containing other ions of similar charge. Ions released or eluted from resin sites are discharged to waste during the regeneration process. Equation (7.1) illustrates the exchange process of a strong cation resin in sodium form, exchanging sodium ions for calcium ions.

$$2\mathrm{RNa} + \mathrm{Ca(HCO_3)_2} \xrightarrow{\text{flow}} \mathrm{R_2Ca} + 2\mathrm{NaHCO_3} \tag{7.1}$$

where R = active ion exchange site on resin (single valence)
2RNa = resin charged with sodium available to exchange other cations
R_2Ca = resin with calcium exchanged for sodium

Ion Affinity

Resin affinity is a reflection of relative selectivity for ions by resins. Generally, affinity is strongest with higher valence and higher atomic mass (Fig. 7.2). There are exceptions to these general rules, particularly with ions that form complexes or insoluble compounds, such as high molecular weight organic acids for anion exchange resins.

Cations	**Anions**	**Affinity**
Fe^{+3}	CrO_4^{-2}*	Highest
Al^{+3}	SO_4^{-2}*	↓
Pb^{+2}	SO_3^{-2}*	
Ba^{+2}	HPO_4^{-2}*	
Sr^{+2}	CNS^{-}	
Cd^{+2}	CNO^{-}	
Zn^{+2}	NO_3^{-}	
Cu^{+2}	NO_2^{-}	
Fe^{+2}	Br^{-}	
Mn^{+2}	Cl^{-}	
Ca^{+2}	CN^{-}	
Mg^{+2}	HCO_3^{-}	
K^{+}	$HSiO_3^{-}$	
NH_4^{+}	OH^{-}	
Na^{+}	F^{-}	
H^{+}		
Li^{+}		Lowest

*These ions may be displaced as they are protonated at low pH to $HCrO_4^{-}$, HSO_4^{-}, HSO_3^{-}, and $H_2PO_4^{-}$.

FIGURE 7.2 General order of ion selectivity in water below 1000 mg/L total dissolved solids (TDS).

Resin Bead Structure

A combination of both the chemical and physical structures govern to some degree or another, kinetics, capacity, strength, and life span of resin beads.

Chemical Structure

Two basic chemical structures used in the manufacture of resins are styrene and acrylic acid. Styrene-based materials are aromatic hydrocarbons, while acrylic-based resins are straight-chained hydrocarbons based on polyacrylate or polymethacrylate. However, resins of both types use DVB as a cross-linking agent to physically strengthen the resin beads.

Strong acid cation (SAC) exchange resins are styrene, and their exchange sites are derived from sulfonic acid (H_2SO_3). Weak acid cation (WAC) exchange resins are acrylic, and their exchange sites are carboxylic acid (–COOH).

Strong base anion (SBA) exchange resins may be either styrene or acrylic based. Styrene-based materials receive their functionality from quaternary ammonium exchange sites. Type I resins differ from Type II in that the amine used for chemical activation in Type I resins has three methyl groups, while the amine used in Type II has one ethanol and two methyl groups. Weak base anion (WBA) exchange resins may be either styrene or acrylic-based materials.

Physical Structure

There are two physical structures in ion exchange resins based on styrene: gel and macroporous. Gel is the most common structure, which is a homogeneous crosslinked polymer in which exchange sites are distributed evenly throughout the bead. Physical strength of gel resins depends on the percentage of DVB cross-linking used in the manufacturing process. Standard SAC resins use 8% cross-linking; this is the most common cation resin and the one used in water softening applications. However, additional physical strength is gained by increasing cross-linking percentage, with an upper limit of 20%. Increased strength generally comes at the expense of slower kinetic exchange rates, lower exchange capacity, and higher cost. Gel resins are generally translucent in appearance (Fig. 7.3).

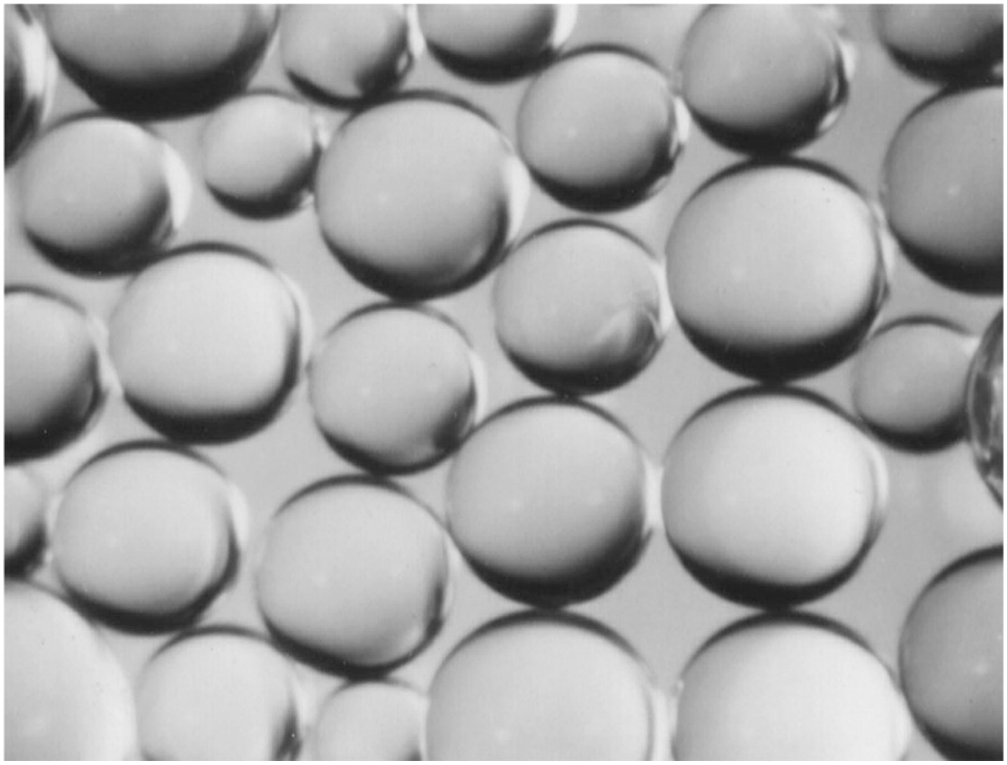


FIGURE 7.3 Typical gel resin (magnified).

A macroporous (sometimes referred to as macroreticular) bead structure provides harder and stronger resins more resistant to oxidative and physical stress attack. Unlike gel resins, macroporous resins have a definite pore distribution in a sponge-like formation. Because of the pores in the active portion of the polymer, very high percent cross-linking is possible, but manufacturers do not state the actual percentage. Pores can constitute 10 to 30% of the bead volume, which causes a proportionate reduction in ion exchange capacity. Macroporous resins are typically opaque (Fig. 7.4).

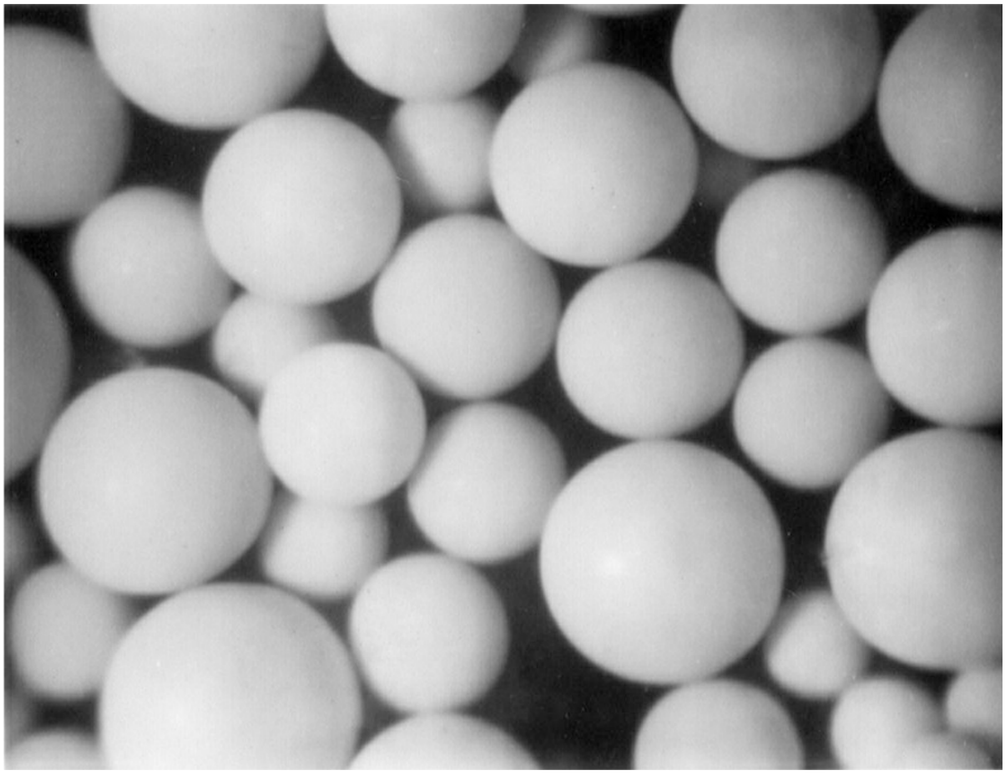


FIGURE 7.4 Typical macroporous resin (magnified).

Particle Size and Size Distribution

Historically used manufacturing processes resulted in resin bead particle sizes ranging from 16 to 50 mesh (1.19–0.30 mm) and a uniformity coefficient of 1.5 to 1.7, with the majority of beads being in the center of a typical Gaussian bell curve.

To optimize service and regeneration of ion exchange operations, a special process that results in more than 90% of beads being the same mesh size produces a newer class of resins. Such resins are called uniform particle size (UPS) resins (Fig. 7.5). During service, exchange kinetics are optimized because film diffusion is the controlling rate, and the consistent surface area per unit volume in UPS beads facilitates this principle. In the rinse step, particle diffusion is the controlling rate, and with UPS resins, the longer rinse time and larger waste volume required to rinse large beads is eliminated. Figure 7.6 illustrates this concept. Observed advantages are higher regeneration efficiency, increased operating capacity, and reduced rinse volumes. In mixed bed demineralizers, where the effectiveness of the separation backwash is a key to regeneration success, separation is improved because the UPS beads are more precisely engineered. As a result of this a

1980s innovation of using an inert resin layer to facilitate cation and anion bead separation is more rarely seen now.

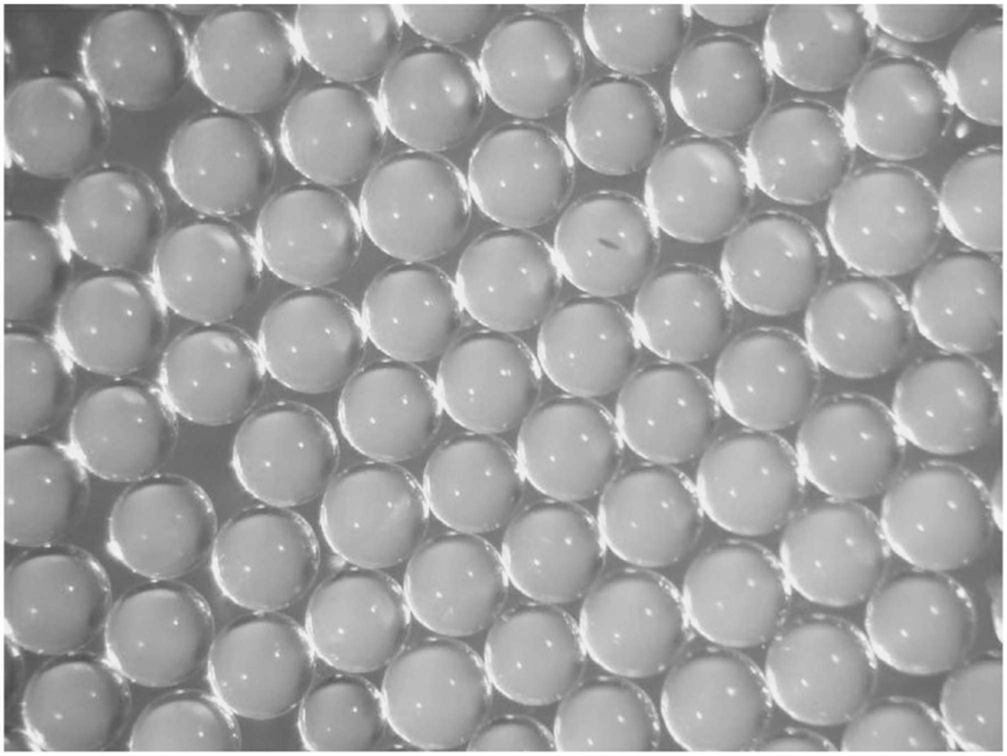


FIGURE 7.5 Uniform particle size (UPS) resin (magnified).

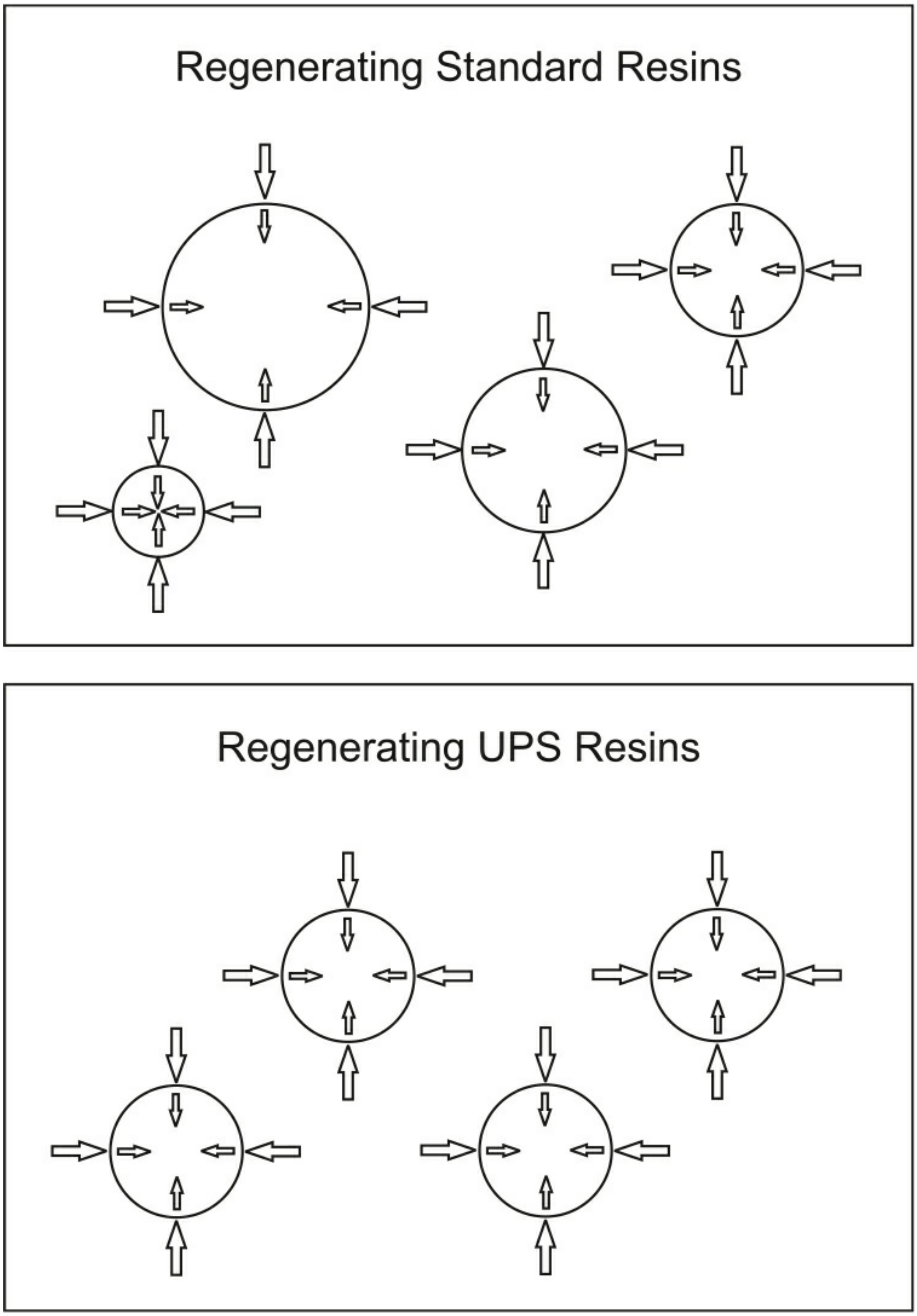


FIGURE 7.6 Regeneration difference between standard resin and UPS resin.

Resin Capacity

Units for expressing resin capacity are equivalents per liter (eq/L), milliequivalents per milliliter (meq/mL), kilograins per cubic foot (kgr/ft^3), and grams per liter (g/L). Generally, chemists use the first two units; the last two are practical units used by designers, engineers, and system owners.

When calculating the ionic load for resin, individual ions must first be expressed as their calcium carbonate ($CaCO_3$) equivalents in terms of mg/L. Applicable ions are then totaled and converted to ionic load expressed as grains per gallon (gr/gal) or grams per liter (g/L). Table 7.1 shows conversion factors to express ionic concentration in $CaCO_3$equivalents.

Ion	Expressed as	Multiply by for $CaCO_3$ Equivalent
Barium	Ba^{+2}	0.78
Strontium	Sr^{+2}	1.14
Calcium	Ca^{+2}	2.50
Magnesium	Mg^{+2}	4.12
Potassium	K^{+}	1.28
Ammonia	NH_3	2.94
Sodium	Na^{+}	2.18
Carbonate	CO_3^{-2}	1.67
Sulfate	SO_4^{-2}/Na_2SO_4	1.04/0.70
Nitrate	NO_3^{-}	0.81
Chloride	$Cl^{-}/NaCl$	1.41/0.85
Bicarbonate	HCO_3^{-}	0.82
Hydroxide	OH^{-}	2.94
Fluoride	F^{-}	2.66
Carbon dioxide	CO_2	1.14*
Silica, reactive	SiO_2	0.83*

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*These values are for ion exchange applications only and are one-half the values used for lime softening calculations.

TABLE 7.1 Calcium Carbonate Conversion Factors for Common Ions

A typical raw water analysis expressed as $CaCO_3$ equivalents allows determination of several items that are important in understanding the ionic load that needs to be removed through ion exchange. Total cations (TC) is the sum of all cations present including calcium, magnesium, sodium, potassium, and any others found through analysis to be significant. Total hardness (TH) is a subset of TC and is just the sum of calcium, magnesium, barium, and strontium ions. These are the targeted species for removal with softener operation. Calcium and magnesium ions are the major hardness concerns. Total anions (TA) is the sum of all anions present including alkalinity, chloride, sulfate, nitrate, and any others found through analysis to be significant.

Once TC and TA are known, ionic load can be determined by evaluating which ions are removed through the ion exchange process. Total exchangeable cations (TEC) is the sum of all cations removed by cation resin. Total exchangeable anions (TEA) is the sum of anions removed by anion resin. For SBA resin, the TEA number includes carbon dioxide (CO_2) and silica (SiO_2). For WBA resin, carbon dioxide and silica are not included in the TEA calculation.

The total exchangeable ions definition can change depending on resin type and regenerant chemical used. For instance, SAC resin in the sodium form SAC (Na^+) only exchanges sodium for TH (Ca^{++}, Mg^{++}, Ba^{++} and Sr^{++}), while the same resin operating in the hydrogen form SAC (H^+) also removes sodium, potassium, and any other cation present. Table 7.2 is a typical raw water analysis showing TH, TC, and TA.

Constituent	**Concentration***
Calcium	194.0
Magnesium	70.2
Sodium	14.4
Potassium	1.5
Total hardness (TH)	264.2
Total cations (TC)	280.1
Bicarbonate	220.0
Chloride	5.2
Sulfate	54.0
Nitrate	0.9
Total anions (TA)	280.1
TMA†	60.1
P alkalinity	—
M alkalinity	220
Carbon dioxide, CO_2	11
Silica (reactive), SiO_2	0.7
TDS, mg/L‡	428
Conductivity, µS/cm	564
pH, units	7.6

*All mg/L as $CaCO_3$ except if noted otherwise.
†Theoretical mineral acidity (sum of anions less alkalinity, carbon dioxide, and silica).
‡Total dissolved solids.

TABLE 7.2 Raw Water Analysis Indicating Total Hardness, Total Cations, and Total Anions

Ionic loading for resin is expressed as mass per unit volume. Typical conventions are grains per gallon (gpg) in U.S. units and g/L (or mg/L) in metric units. Using the data in Table 7.3, this raw water has a TH ionic load of 15.45 gpg or 0.2642 g/L for a SAC (Na^+) unit and a TC ionic load of 16.38 gpg or 0.2801 g/L for a SAC (H^+) unit.

Constituent	Concentration, mg/L $CaCO_3$	Concentration, gpg* $CaCO_3$
Calcium	194.0	11.35
Magnesium	70.2	4.11
Sodium	14.4	0.84
Potassium	1.5	0.09
Total hardness (TH)	264.2	15.45
Total cations (TC)	280.1	16.38
Bicarbonate	220.0	12.87
Chloride	5.2	0.30
Sulfate	54.0	3.16
Nitrate	0.9	0.05
Total anions (TA)	280.1	16.38
TMA	60.1	3.51
P alkalinity	—	—
M alkalinity	220	12.87
Carbon dioxide, as CO_2	11	0.64
Silica (reactive), as SiO_2	0.7	0.04

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*Grains/gallon (1 lb = 7000 grains; 1 gpg = 17.1 mg/L)

TABLE 7.3 Raw Water Ionic Constituents Expressed in Common Ion Exchange Units

The theoretical exchange capacity of any given resin is a design feature based on brand and resin type. Practical or use capacity varies based on a variety of factors including regenerant mass and concentration, resin degradation, and fouling to name a few. Resin specifications list capacity based on type and dosage of regenerants. Capacity is expressed in kgr/ft^3 in U.S. units and g/L in metric units, where 1 kgr/ft^3 = 2.29 g/L.

The amount of water that can be serviced by any given unit volume of resin is its capacity divided by ionic load. Equation (7.2) illustrates the relationship.

$$\text{Service water volume} = \frac{\text{exchange capacity}}{\text{ionic load}} \tag{7.2}$$

where Service water volume = volume that can be treated, gal (L)
Exchange capacity = resin ion exchange ability, gr as $CaCO_3$ (g as $CaCO_3$)
Ionic load = ion equivalents to be exchanged, gpg as $CaCO_3$ (g/L as $CaCO_3$)

In order to establish the amount of water that can be serviced by a particular vessel, the amount of resin in the vessel is incorporated into the equation as shown in Eq. (7.3).

$$\text{Service water volume} = \frac{\text{resin capacity} \times \text{resin volume}}{\text{ionic load}} \tag{7.3}$$

where Service water volume = volume that can be treated, gal (L)
Resin capacity = resin ion exchange ability, gr $CaCO_3/ft^3$ (g $CaCO_3$/L)
Resin volume = volume of active resin in vessel, ft^3 (L)
Ionic load = ion equivalents to be exchanged, gpg as $CaCO_3$ (g/L as $CaCO_3$)

While the above equation indicates optimum removal per vessel, the actual service run is usually lower due to kinetic and hydraulic inefficiencies.

Resin Regeneration

Ion exchange is a batch process. Once throughput capacity of the vessel is exhausted and undesirable ions start to leak into the outlet water flow, the unit must be taken off line and regenerated. This process reverses ion exchange that has been occurring in service and recharges resin back to the desired ionic form for service. Resin regeneration is usually accomplished in a co-current manner. The other method of regeneration is called counter-current. In the co-current regeneration process, there are four distinct phases (Fig. 7.7): backwash, regenerant addition, slow rinse, and fast rinse.

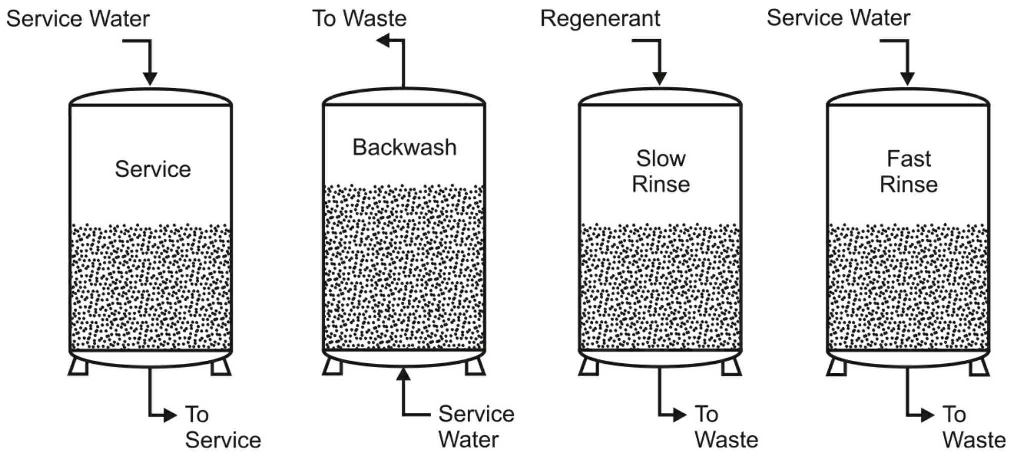


FIGURE 7.7 Four steps of co-current regeneration.

Backwash

Besides being a medium to exchange ions, resin is also a reasonably effective filter for suspended materials, which collect in the top section of the resin bed. Backwash is designed to expand the resin bed and remove accumulated suspended material. In addition, broken beads or resin fines migrate to the top of the bed during backwash, which removes them over time. Improper removal of this material not only fouls the resin bed, but it also increases pressure drop values, putting more mechanical stress on the remaining beads (Fig. 7.8).

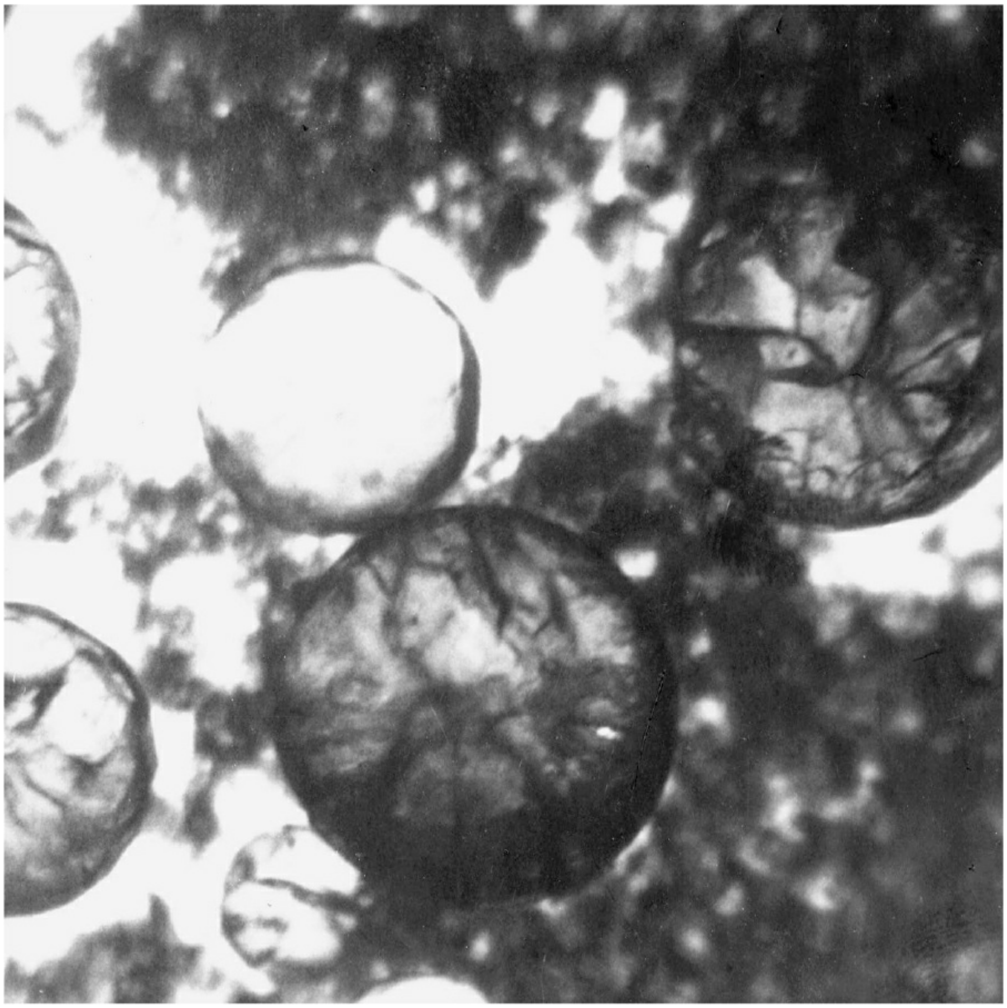


FIGURE 7.8 Gel-type resin containing a large amount of loose precipitate, indicating improper backwash. This condition is responsible for many problems with ion exchange equipment.

Flow and time are the two components that combine to make a good backwash. Flow must be adequate to fluidize the bed and expand it sufficiently to allow suspended material to be removed. Time allowed for backwash must be sufficient to allow removal of all suspended material. When backwash is complete, the bed is reclassified, and any channeling that formed during service is eliminated. Figure 7.9 shows a good backwash turbidity profile.

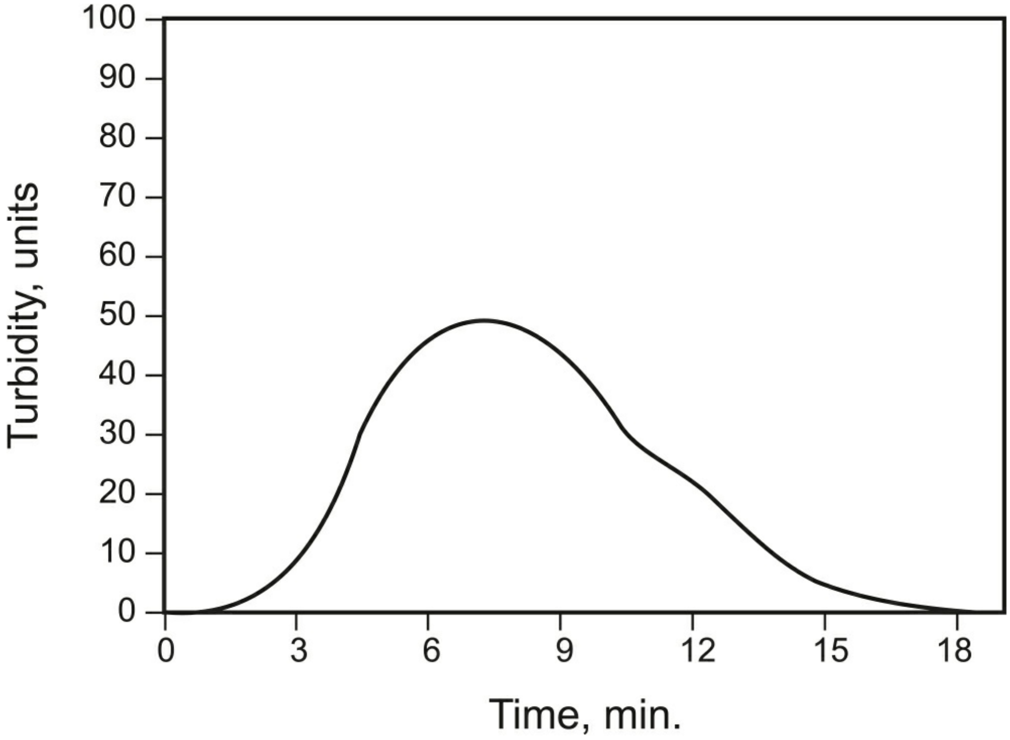


FIGURE 7.9 Turbidity profile of ion exchanger backwash.

Backwashing involves reversing the normal service water flow through the vessel. Backwash water enters the vessel at the bottom and leaves the vessel at the top through the service water inlet. During backwash, the resin bed is expanded. A minimum expansion of about 50% is required for cation resins to ensure good suspended material removal and bed reclassification. Anion resins tend to require a little more bed expansion; 75% is a common recommendation for them.

Waters that are subject to seasonal variation in temperature experience density changes. At the same flow rate, colder, denser water has more lifting capability than warmer, less dense water. Plants with seasonal fluctuations in water temperature should adjust the backwash flow rate to avoid losing resin during times when cold water is in use, or getting insufficient solids removal when the water is warmer. Figure 7.10 illustrates the effect of water temperature on bed lift.

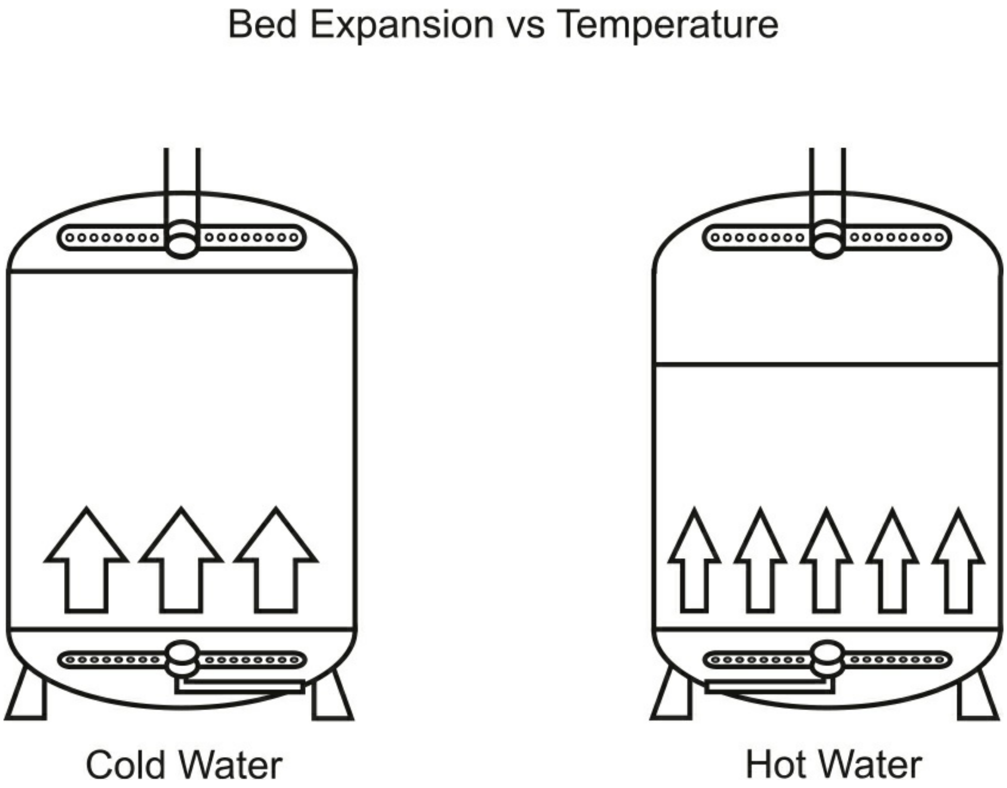


FIGURE 7.10 Bed expansion is governed not just by flow but also by water temperature.

Regenerant Addition

Concentrated regenerant chemicals are typically diluted continuously in-line by being injected into a flow of dilution water of acceptable quality. Simple systems may employ a dilute chemical tank from which regenerant is pumped or educted and further diluted to the required concentration. The resulting plug of regenerant is moved through the resin bed, exchanging desired ions for undesired ones.

It is a basic principle of ion exchange that all of the water used for backwashing, regenerating, and rinsing resins should be the same as the normal inlet flow to that vessel. For regeneration of all systems employing anion exchange resins, regenerant dilution water must be cation unit outlet quality to prevent precipitation of hardness in resin and to maintain desired effluent quality.

During any regeneration, it is extremely important that the correct combination of regenerant concentration, flow rate, and contact time is maintained to achieve the required exchanger working capacity. Specific conductance meters, calibrated in percent regenerant concentration, can be used to monitor and alarm dilute regenerant concentrations.

Slow Rinse

The displacement (slow) rinse is very important and is actually part of the regenerant injection step. It is usually a continuation of the dilution water flow after regenerant addition is terminated. The displacement rinse clears the regenerant solution from the piping systems and pushes the regenerant plug remaining in the vessel slowly through the resin bed, continuing the regeneration step. This ensures that all regenerant is utilized by maintaining the required flow rate for efficient ion exchange.

The volume of water used should be more than one bed volume of resin. This may be greater with some design configurations in order to allow diffusion of regenerating ions through the interior of the resin beads to the surface, where they can be released into the slow rinse flow. Larger slow rinse volumes may reduce the required fast rinse volume and reduce total wastewater generation.

Fast Rinse

This step flushes remaining regenerant from voids or pockets in the resin bed and from resin particles themselves. This rinse is discharged to waste until it is free of excess chemical and undesirable ions. The fast rinse should be continued until reaching required effluent quality, keeping in mind that resin fouling or degradation may increase rinse volume requirements.

In-line analytical instrumentation, such as hardness and silica analyzers or conductivity monitors, can be used to indicate and alarm the endpoint of ion exchange regeneration or service.

Counter-Current Regeneration

In this method of regeneration, dilute regenerant flows in the opposite direction to the service flow. With downflow service, regeneration is upflow; with upflow service, regeneration is downflow. The heel of incompletely regenerated resin is at the service inlet end of the regenerated resin, and leakage is much lower than achievable with co-current regeneration (see Fig. 7.11).

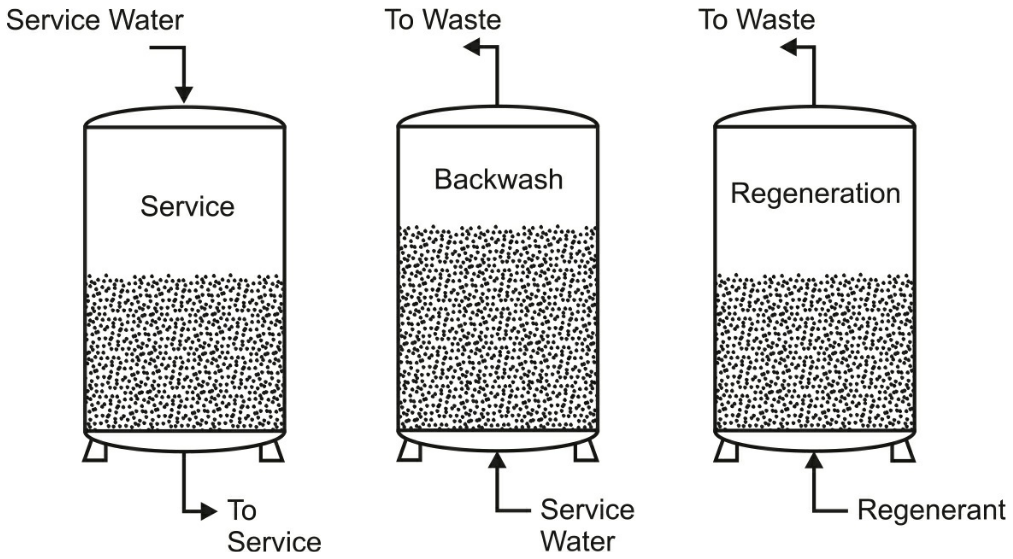


FIGURE 7.11 Counter-current regeneration. The backwash step only occurs periodically.

Counter-current regeneration performance is dependent on the resin bed being held in a compacted state, without it being allowed to fluidize. Fluidization allows resin to mix and results in the most completely exhausted beads populating the entire bed rather than remaining at the service inlet end of the bed. Fluidization is prevented by placing mechanical restrictions to movement, such as a regenerant collecting system buried in the resin bed approximately 6 inches (152 mm) from the service inlet end of the bed. This layer may be simply unregenerated working resin or inert beads. If the layer is working resin, it is not included in capacity calculations.

In addition, a blocking flow of water or compressed air is used in opposition to the regenerant flow to further prevent bed fluidization. Air block tends to dry and eventually break some resin particles, while water block increases the amount of wastewater generated.

These units are not backwashed with every regeneration but at intervals varying from every third to as little as every fortieth regeneration, depending on cleanliness of service water being treated. Once backwashed, resin must be regenerated at dosages double or triple normal levels to restore the service outlet end of the resin bed to a highly regenerated state. Failure to use increased dosage results in inability to produce the higher purity effluent expected.

Given all of these demands for successful counter-current regeneration it is not surprising that despite its benefits counter-current regeneration is used in only a small minority of ion exchange systems. Retrofitting or converting a conventionally regenerated system to counter-current operation is a considerable engineering project, and this should not be undertaken without a thorough understanding of the challenges that must be overcome.

Weakly functional resins such as weak acid cation and WBA derive little benefit from counter-current regeneration, and therefore, counter-current regeneration is rarely used in such units. Counter-current regeneration of strongly functional resins such as SAC and SBA offers a number of benefits:

- Dramatic reduction in ion leakage at lower regenerant dosage
- Increased regeneration efficiency
- Reduced chemical consumption
- Decreased waste treatment cost due to reduced regenerant waste

Resin Types

Modern synthetic ion exchange resins have different structures and functional groups. These differences allow the different resins to target different ions in water. Resins are categorized by function. Four basic types of resin used in water treatment are:

1. Strong acid cation (SAC)
2. Weak acid cation (WAC)
3. Strong base anion (SBA)
4. Weak base anion (WBA)

Strong Acid Cation

SAC resins operate across the entire pH range. Life expectancy of a quality SAC resin is 10 to 15 years, or even longer under ideal operating conditions. Life expectancy can be shortened due to a number of factors:

- Oxidation such as by free chlorine or chloramines
- Thermal shock
- Foulants such as iron, calcium sulfate, or aluminum as examples

SAC resins can remove all cations or just some cations, depending on regenerant used to recharge the resin. The amount of regenerant required for regeneration is considerably higher than stoichiometric levels. Common regenerant chemicals are sodium chloride (NaCl) and strong mineral acids such as sulfuric acid (H_2SO_4) and hydrochloric acid (HCl).

When a SAC unit is regenerated with NaCl, resin is put into the sodium form SAC (Na^+). In this form, resin exchanges sodium for the TH ions, mostly calcium and magnesium. When a SAC unit is regenerated with hydrogen from a strong acid such as H_2SO_4 or HCl, it is put into the hydrogen form SAC (H^+). In this form, resin exchanges for all cations.

Strong Acid Cation—Sodium Form

SAC (Na^+) softening is used in treatment of process water, boiler makeup, or any use involving removal of the scale forming ions, calcium and magnesium, and replacing them with completely soluble sodium ions. In the process, other cations with higher affinity for the resin than sodium are also removed. For instance, potassium is removed initially but is displaced from the resin as the ion exchange band containing hardness progresses down through the bed. This is the simplest ion exchange process, producing soft water, and is shown in Eq. (7.4) and Fig. 7.12.

$$\mathrm{Ca(HCO_3)_2} + 2\mathrm{RNa} \xrightarrow{\text{flow}} \mathrm{R_2Ca} + 2\mathrm{NaHCO_3} \tag{7.4}$$

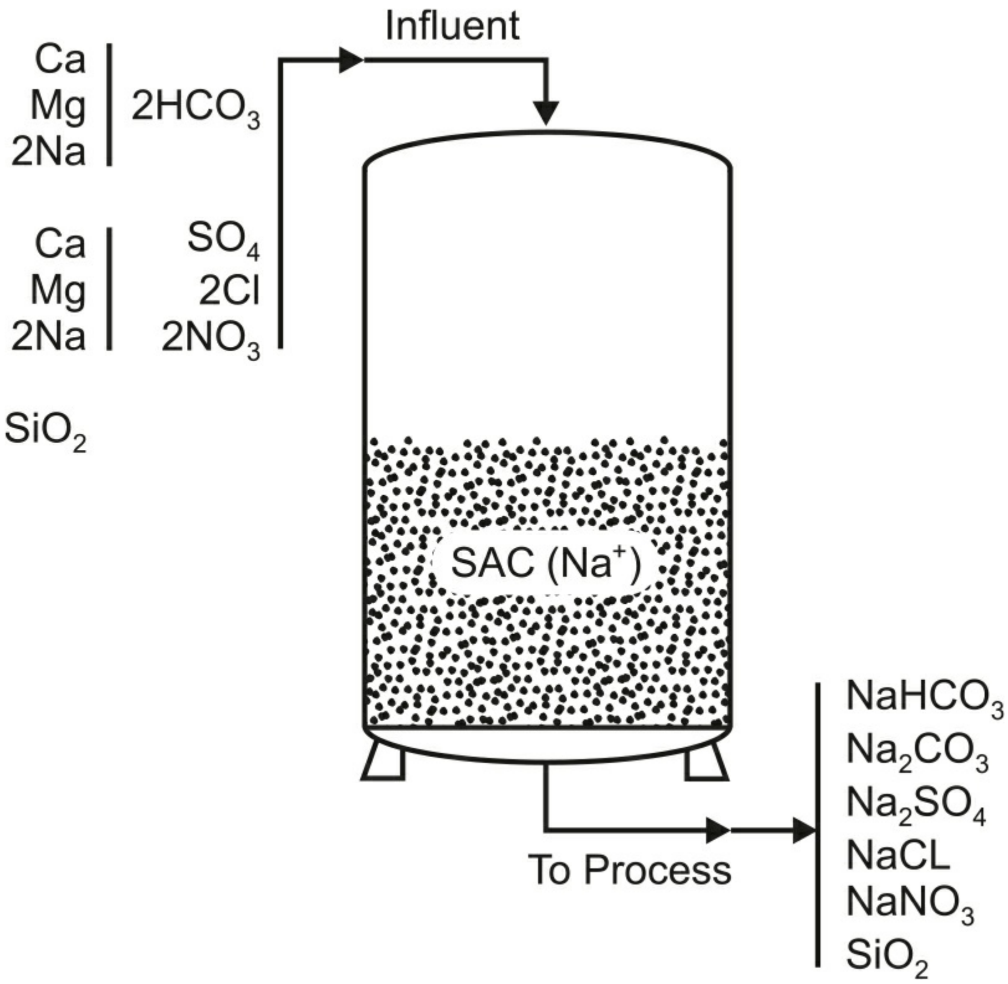


FIGURE 7.12 Typical SAC (Na^+) exchanger (sodium softener).

As ion exchange is a batch process, resin continues to exchange sodium for calcium and magnesium until its capacity is exhausted. Regeneration is then required with a solution of sodium chloride brine at a concentration sufficiently high to overcome the inherent affinity of the resin for calcium and magnesium ions. The regeneration reaction is shown in Eq. (7.5).

$$2NaCl + R_2Ca \xrightarrow{\text{flow}} 2RNa + CaCl_2 \tag{7.5}$$

Reactions for magnesium are the same as Eqs. (7.4) and (7.5). Calcium ions have a stronger affinity for SAC resin than magnesium; therefore, magnesium ions leak first at service break. These reactions are the same whether the softener is a primary unit, polishing unit, or installed after cold or hot lime softening systems.

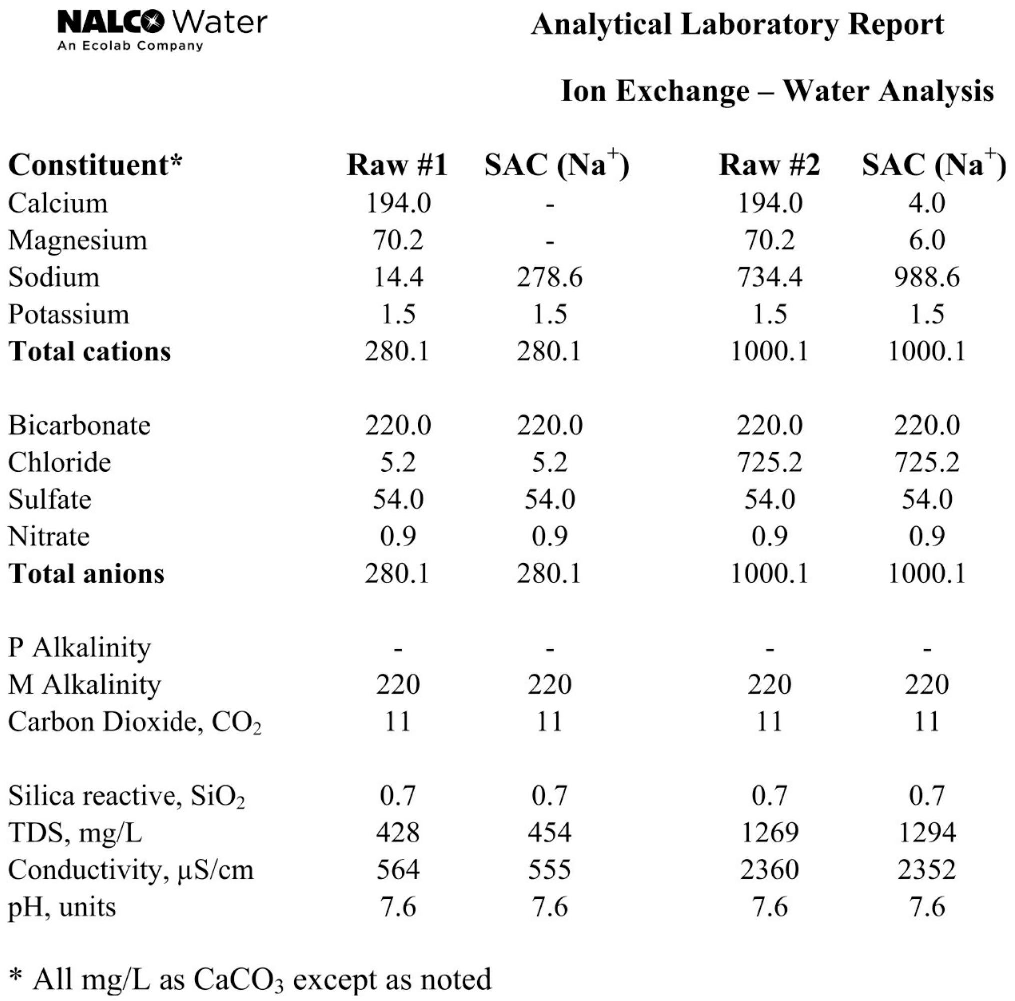
Achievable working exchange capacities are dependent upon applied regeneration dosages and allowable hardness leakage. Working capacity is best determined from engineering data provided by resin manufacturers but can range from 20 to 30 kgr/ft^3 (46–69 g/L) of resin at 100% sodium chloride dosages ranging from 6 to 15 lb/ft^3 (96–240 kg/m^3) of resin. Working capacity and regenerant dosage should be selected to provide required service throughput between regenerations at reasonable regeneration efficiency and resin volume.

This process may be used in units or combinations of units employing:

- Co-current or counter-current regeneration
- Single unit or primary plus polishing unit train
- Normal or thoroughfare regeneration
- Conventional configuration for all applications or packed bed design (except following lime softening processes where packed beds should not be used)

Regeneration conditions for flow rates, regenerant concentration, and contact time should be set as required for the particular application and dissolved solids concentration in the water to be treated. Hardness leakage increases as background total dissolved solids (TDS) concentration increases. Compensation requirements start when TDS exceeds 500 mg/L, and the degree of compensation is obtained from resin engineering data.

Figure 7.13 shows typical softening results using SAC (Na^+) for two different waters. Note the impact of the elevated sodium concentration in the second raw water.



NALCO Water
An Ecolab Company

Analytical Laboratory Report

Ion Exchange – Water Analysis

Constituent*	**Raw #1**	**SAC (Na^+)**	**Raw #2**	**SAC (Na^+)**
Calcium	194.0	-	194.0	4.0
Magnesium	70.2	-	70.2	6.0
Sodium	14.4	278.6	734.4	988.6
Potassium	1.5	1.5	1.5	1.5
Total cations	280.1	280.1	1000.1	1000.1
Bicarbonate	220.0	220.0	220.0	220.0
Chloride	5.2	5.2	725.2	725.2
Sulfate	54.0	54.0	54.0	54.0
Nitrate	0.9	0.9	0.9	0.9
Total anions	280.1	280.1	1000.1	1000.1
P Alkalinity	-	-	-	-
M Alkalinity	220	220	220	220
Carbon Dioxide, CO_2	11	11	11	11
Silica reactive, SiO_2	0.7	0.7	0.7	0.7
TDS, mg/L	428	454	1269	1294
Conductivity, µS/cm	564	555	2360	2352
pH, units	7.6	7.6	7.6	7.6

* All mg/L as $CaCO_3$ except as noted

FIGURE 7.13 Illustrates effects of high TDS and sodium on softener performance. These analyses are based on co-current regeneration in conventional units. To achieve hardness leakage shown in right most SAC (Na^+) column, sodium chloride regeneration level must be increased 20%.

Strong Acid Cation—Hydrogen Form

The SAC (H^+) process is one of the primary stages in demineralization, where it can be part of simple two-bed systems or more complex multiple-stage systems. It can be used as part of split stream dealkalization or as a single dealkalization process when combined with decarbonation.

The same resin used to remove hardness from water, when regenerated with sodium chloride, can be used to remove all cations from water, when regenerated to the hydrogen form with strong mineral acid. In acid form, the resin replaces all cations with hydrogen (H^+)ions. Chloride, sulfate, and nitrate are converted to corresponding strong mineral acids, while weakly ionized acids are created from bicarbonate and carbonate alkalinity and silica (see

Fig. 7.14).

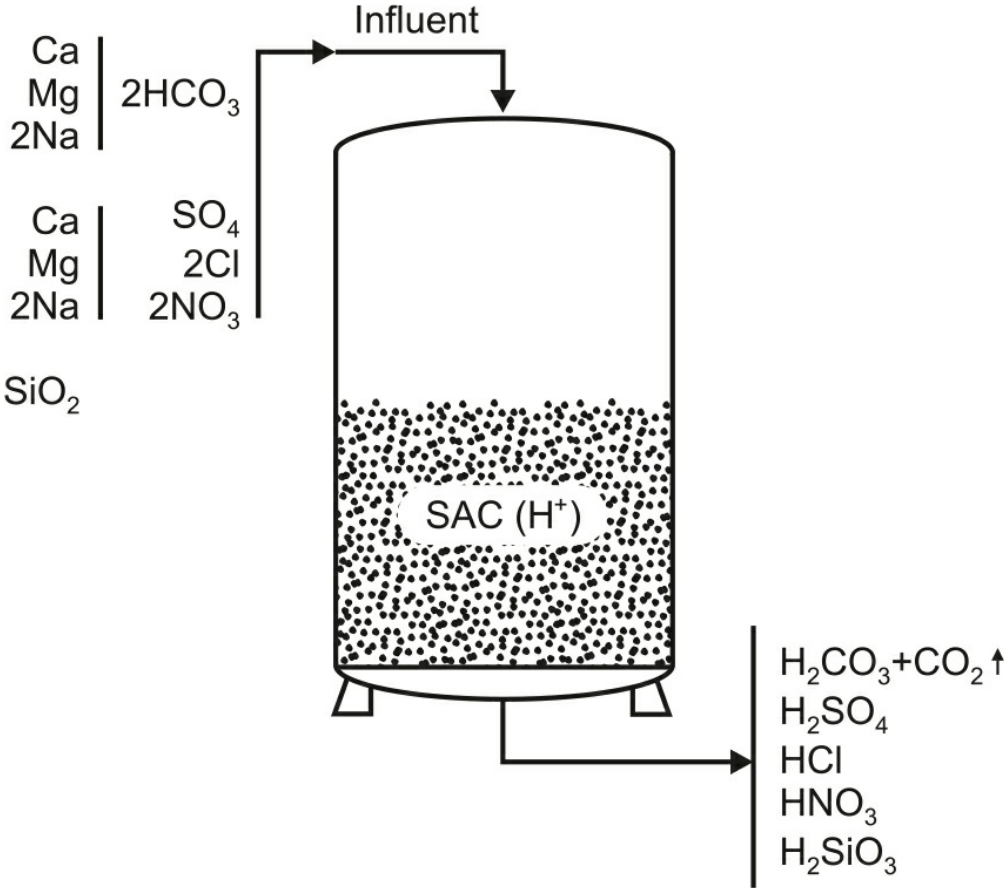


FIGURE 7.14 Typical SAC (H$^+$) exchange.

Typical chemical reactions for the exhaustion cycle are shown in Eqs. (7.6) to (7.8).

$$Ca(HCO_3)_2 + 2RH \xrightarrow{\text{flow}} R_2Ca + 2H_2CO_3 \tag{7.6}$$

$$MgCl_2 + 2RH \xrightarrow{\text{flow}} R_2Mg + 2HCl \tag{7.7}$$

$$Na_2SO_4 + 2RH \xrightarrow{\text{flow}} 2RNa + H_2SO_4 \tag{7.8}$$

Affinity of sodium for SAC (H$^+$) resin is lower than calcium and magnesium, and some sodium leakage always occurs. With effective counter-current regeneration, sodium leakage is less than 0.2 mg/L as CaCO$_3$. With co-current regeneration, the amount of sodium leakage is a function of:

- Ratio of sodium to TC—as percent sodium increases, sodium leakage increases.
- Ratio of alkalinity to TC—as percent alkalinity increases, sodium leakage decreases because less free mineral acidity (FMA) is created, decreasing the tendency to elute sodium ions. This is an important factor when SAC (H^+) resin is used for demineralization.
- Acid regeneration dosage—increasing acid dosage decreases sodium leakage.

However, when this process is used in co-current units for demineralizer applications, acid regeneration dosage is generally selected to ensure sodium leakage is less than 2 mg/L as $CaCO_3$. Increased sodium leakage presents as higher pH and conductivity values in the anion unit outlet stream. As with all ion exchange processes, the efficiency of regeneration and the amount and type of leakage are defined by the mechanical design of the internal distribution systems. Regeneration reactions are shown in Eqs. (7.9) to (7.11).

$$R_2Ca + H_2SO_4 \xrightarrow{\text{flow}} 2RH + CaSO_4 \tag{7.9}$$

$$2RNa + H_2SO_4 \xrightarrow{\text{flow}} 2RH + Na_2SO_4 \tag{7.10}$$

$$R_2Ca + 2HCl \xrightarrow{\text{flow}} 2RH + CaCl_2 \tag{7.11}$$

Equations (7.10) and (7.11) show formation of completely soluble salts, but Eq. (7.9) indicates the regeneration effluent contains calcium sulfate ($CaSO_4$) that has very low solubility in water and sulfuric acid. Its solubility is slightly better in hydrochloric acid, but even that must be heated to become truly effective in dissolving calcium sulfate.

SAC (H^+) units can be regenerated at higher concentrations of sulfuric acid; however, calcium sulfate precipitation remains a significant problem, requiring use of a stepwise regeneration technique that is not required when using hydrochloric acid for regeneration.

When regenerating SAC (H^+) resin with sulfuric acid, to avoid $CaSO_4$

precipitation, the initial dilute acid concentration used must be selected based on influent water ionic concentrations. In addition, dilute acid flow rate for injection must be sufficiently high to ensure acid containing eluted calcium is discharged from the resin bed before $CaSO_4$ crystals can develop.

Stepwise regeneration meets two objectives. The first step elutes most of the calcium from the resin at a concentration, in the dilute acid, less likely to precipitate $CaSO_4$ rapidly. The second step, at higher concentration, is necessary to achieve the degree of regeneration necessary in order to provide desired resin working capacity.

Some resin manufacturers recommend using as many as four dilute sulfuric acid concentrations, however, two or three steps tend to be the norm. This method requires that hydrogen ions be exchanged onto resin at ever-increasing exchange rates, which becomes more difficult as resin sites become more fully converted. It is preferredthat stepwise regeneration be confined to two steps and that concentration be changed by decreasing dilution water flow rate. This method provides a constant rate of hydrogen ion exchange to resin exchange sites.

The minimum dilute acid flow rate required for the first step in stepwise regeneration or for single-step regeneration can be calculated from Table 7.4.

% Ca of Total Cations as $CaCO_3$	Minimum Dilute Sulfuric Acid Flow Rate, gpm/ft³ (m³/[h·m³])
0	0.5 (4)
25	0.5 (4)
50	1.0 (8)
75	1.5 (12)
100	2.0 (16)

TABLE 7.4 Minimum Flow Rates for Sulfuric Acid Regeneration to Avoid $CaSO_4$ Fouling

When regenerating with dilute hydrochloric acid, there are no problems of precipitate formation, and dilute regenerant may be injected at 5% concentration by weight. Higher concentrations can lead to osmotic shock due to rapid change in resin volume. Dilute acid injection time should be at least

15 minutes with HCl.

Hydrochloric acid is a more efficient regenerant but is more expensive than sulfuric acid in North America. In addition, vessel internals cannot be constructed of stainless steel but must be of Hastelloy C or of nonmetallic construction.

Resin working capacity varies widely depending on influent water chemistry and regeneration level. With sulfuric acid, capacity may range from 8 to 25 kgr/ft^3 (18–57 g/L) at dosages of 3 to 10 lb/ft^3 (48–160 kg/m^3) of 66° Bé (93% H_2SO_4) acid. With hydrochloric acid, capacity may range from 12 to 33 kgr/ft^3 (27–76 g/L) at dosages of 6 to 30 lb/ft^3 (96–480 kg/m^3) of 30% HCl. Highest capacities are obtained on water with very high alkalinity and sodium concentrations.

Minimum resin bed depths should be 30 inches (0.76 m) in conventional co-current units and 5 ft (1.5 m) in counter-current units to allow for exchange reactions to be completed.

Weak Acid Cation

Weak acid cation (WAC) resins operate under alkaline conditions. These resins remove only hardness cations calcium and magnesium associated with alkalinity. WAC resin can be regenerated at stoichiometric dosages. Common regenerants are strong mineral acids such as sulfuric and hydrochloric or sodium chloride. When regenerated in the sodium form, resin is primarily used for hardness reduction of brackish water or polishing the effluent stream of lime softened water. Average life expectancy of WAC resin is the same as that of SAC, 10 to 15 years. This resin is subject to many of the same degradation issues as SAC, such as oxidation by free chlorine or chloramines and fouling from iron, calcium sulfate, or aluminum.

Weak Acid Cation—Hydrogen Form

A major advantage of the WAC (H^+) process is that it produces consistent effluent alkalinity regardless of variations in influent water. WAC (H^+) resin, having properties of weak carboxylic acid, is capable of exchanging cations of alkaline salts, but has no exchange capacity with neutral salts as illustrated in the following equations:

$$2\mathrm{RCOOH} + \mathrm{Ca(HCO_3)_2} \xrightarrow{\text{flow}} \mathrm{(RCOO)_2Ca} + 2\mathrm{CO_2} + 2\mathrm{H_2O} \qquad (7.12)$$

$$\mathrm{RCOOH + CaCl_2 \xrightarrow{flow} no\ reaction} \qquad (7.13)$$

Affinity of cations for this type of resin is typically

$$\mathrm{H^+ >> Cu^{+2} > Fe^{+2} > Ca^{+2} > Mg^{+2} > NH_4{}^+ > Na^+}$$

From affinity data, it is apparent that

- Hydrogen has a very high affinity for WAC resin.
- Magnesium leaks in preference to calcium.
- Sodium associated with alkalinity reduces working capacity of WAC resins.

If TH exceeds alkalinity, hardness is reduced to exactly the same extent as alkalinity reduction when expressed as $CaCO_3$. When hardness is less than alkalinity, in addition to capacity reduction of the resin, it is important to realize that zero hardness is not achieved. Magnesium leaks at a concentration of 1 to 2 mg/L, and attempts to achieve zero hardness by artificially increasing alkalinity to exceed hardness have been unsuccessful.

Exhaustion chemical reactions are shown in Eqs. (7.14) and (7.15), and regeneration reactions are shown in Eqs. (7.16) and (7.17).

$$\mathrm{2RCOOH + Ca(HCO_3)_2 \xrightarrow{flow} (RCOO)_2Ca + 2H_2CO_3} \qquad (7.14)$$

$$\mathrm{2RCOOH + Mg(HCO_3)_2 \xrightarrow{flow} (RCOO)_2Mg + 2H_2CO_3} \qquad (7.15)$$

$$\mathrm{(RCOO)_2Ca + H_2SO_4 \xrightarrow{flow} 2RCOOH + CaSO_4} \qquad (7.16)$$

$$\mathrm{(RCOO)_2Ca + 2HCl \xrightarrow{flow} 2RCOOH + CaCl_2} \qquad (7.17)$$

As previously discussed, calcium sulfate has very low solubility in water and sulfuric acid, and only slightly higher solubility in cold hydrochloric acid. As a result, regeneration with sulfuric acid requires dilute acid (<0.8% by weight) to avoid precipitation of calcium sulfate in the resin bed and within resin beads. Use of hydrochloric acid eliminates the precipitation problem but imposes restrictions on materials of construction for internals. WAC (H^+) resin working capacity ranging from 30 to 38 kgr/ft^3 (69–87 g/L) is easily achieved while operating in starvation mode. Figure 7.15 is an example of a WAC exchanger in hydrogen form.

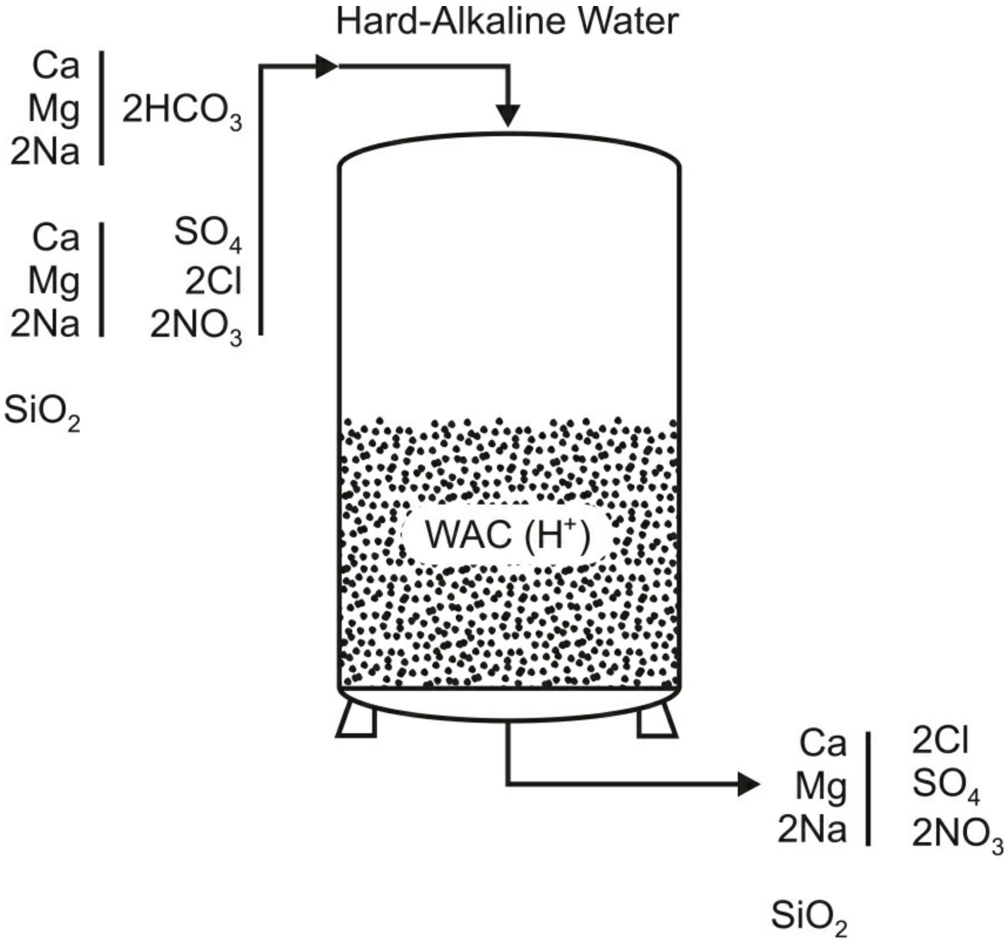


FIGURE 7.15 Weak acid cation in acid form.

Two methods are used for acid regeneration of weak acid resins. In the United States, the most common method uses approximately 20% over the stoichiometric dosage of acid, which produces effluent containing FMA and pH less than 4.3 for a good portion of the service run. This requires pH adjustment after the decarbonator using sufficient caustic to neutralize FMA and residual CO_2. Acid regeneration level and caustic dosage are both higher than with the alternative starvation method discussed in the following section. In addition, residual TDS of the effluent is higher than achieved with the starvation method.

Achievable working capacity of WAC resins is affected by service water temperature. In very cold water, achievable working capacity is reduced, and good design makes allowance for temperature variations. Automated starvation mode operation adjusts for such capacity changes as easily as it adjusts for alkalinity variations in influent water. A major advantage to starvation mode is that acid consumption is constant, virtually stoichiometric, even with varying water chemistry. The only changes would be in the service throughput per regeneration and the frequency of regenerations required for a unit.

Starvation Regeneration Method Outside of the United States, the most common method of regeneration uses only the stoichiometric acid dosage plus a minimal amount to neutralize alkalinity contained in acid dilution water. This method is referred to as starvation regeneration. With 110 mg/L M alkalinity in the water, using 0.8% by weight H_2SO_4 for regeneration at a resin rating of 36 kgr/ft^3 (82 g/L), the amount of excess acid required for starvation regeneration is about 2% above stoichiometric requirements.

With starvation regeneration, very little FMA is generated. This method is easily controlled and automated. Besides reducing acid consumed for the same treated water produced, caustic pH adjustment is required only to neutralize residual CO_2 from the decarbonator.

Acid injection is started at a constant service endpoint, for example, pH 5.8. Acid injection is terminated, either automatically or manually, when the effluent pH meter indicates a sudden drop in effluent pH. This occurs when the resin, which is very “hungry” for hydrogen ions, is fully regenerated, and acid breakthrough occurs. While a very small amount of FMA may be detected in the first few minutes of rinse, pH stabilizes with a small but positive alkalinity, typically from 2 to 5 mg/L as $CaCO_3$.

Automatic control of starvation regeneration simply involves shutting off the acid pump or acid ejector suction at acid breakthrough. The important objective is to terminate the service run at a constant pH and to control the volume of concentrated acid used for regeneration accurately.

Weak Acid Cation—Sodium Form

As mentioned earlier, WAC resin in sodium form is primarily used in treatment of brackish water or as a polisher for lime softening effluent. This ion exchange process of removing hardness ions from sodium chloride brine or brackish water solutions as concentrated as 2% by weight (20 000 mg/L) is shown in Eq. (7.18).

$$CaCl_2 + 2RCOONa \xrightarrow{flow} (RCOO)_2Ca + 2NaCl \tag{7.18}$$

The reaction for magnesium is the same, but affinity for calcium is higher. WAC resin in sodium form is at its most swollen state, which is 60% larger than in acid form. During the exhaustion step shown in Eq. (7.18), the resin bed shrinks by 30% of its sodium form volume. Figure 7.16 shows a WAC exchanger in sodium form.

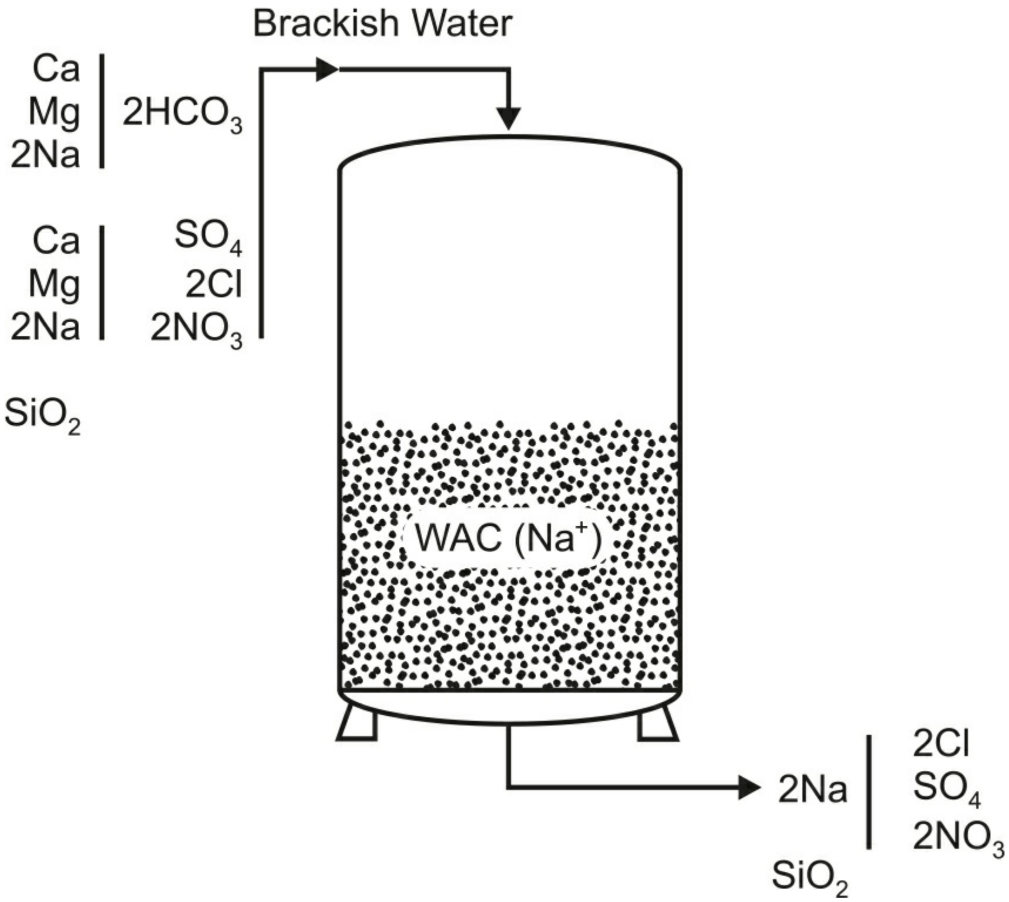


FIGURE 7.16 WAC exchanger in sodium form.

The resin continues to exchange sodium for calcium and magnesium until its capacity is exhausted. WAC resin cannot be regenerated from the exhausted state with sodium chloride or sodium hydroxide. However, WAC resin is readily converted to the sodium form if it is first regenerated to the acid (hydrogen) form. Regeneration is then required, first with a solution of strong mineral acid, hydrochloric or sulfuric, at an acceptable concentration. The acid regeneration reaction is shown below using sulfuric acid as the regenerant.

$$(RCOO)_2Ca + H_2SO_4 \xrightarrow{\text{flow}} 2RCOOH + CaSO_4 \qquad (7.19)$$

Following conversion to acid form, resin volume shrinks to approximately 35% of sodium form volume. The resin bed must now be regenerated to sodium form by a solution of sodium hydroxide. The caustic regeneration reaction is shown in Eq. (7.20).

$$RCOOH + NaOH \xrightarrow{\text{flow}} RCOONa + H_2O \qquad (7.20)$$

Following completion of this step, WAC resin again swells to its maximum state and is 60% larger than in acid form. Since WAC resin regenerated into sodium form undergoes such major changes in volume, special consideration must be given to system and unit design. In order to withstand stress caused by repeated change in volume, stronger macroporous resins are used in preference to gel resins.

In theory, WAC resin can be regenerated at stoichiometric dosages for both acid and caustic regeneration. In practice, it has been found necessary to maintain a substantial excess to ensure satisfactory effluent hardness levels. Regeneration dosages are commonly 12.5 lb/ft^3 (200 kg/m^3) of both 100% HCl and 100% NaOH. Resin working capacities for hardness are typically about 40 kgr/ft^3 (92 g/L) for primary units and 17.5 kgr/ft^3 (40 g/L) for polishing units.

Strong Base Anion

SBA resins have three sub categories: Types I, II, and III. SBA resins remove all anions, including weakly ionized anions like carbon dioxide (CO_2) and silica (SiO_2). Regenerant dosages are considerably higher than stoichiometric.

Type I: Although resin manufacturer information suggests possible operation with water temperatures up to 140°F (60°C), these resins can be most safely operated and regenerated at temperatures of 122°F (50°C) and are used effectively on high alkalinity and high silica bearing waters. Common regenerants are sodium hydroxide (NaOH) and occasionally potassium hydroxide (KOH).

Type II: These resins have a lower temperature limit of 95°F (35°C), but they have higher working capacity than Type I resins. Type II resins are effective with high concentrations of carbon dioxide and silica. Common regenerants are sodium chloride (NaCl), sodium hydroxide (NaOH), and occasionally potassium hydroxide (KOH). Type II SBA resins are most often used in dealkalizer service.

Type III: This type of anion resin is less common. It exhibits the higher working capacity of Type II with the silica removal capacity and temperature limits of Type I. Common regenerants are sodium hydroxide (NaOH) and occasionally potassium hydroxide (KOH).

Strong Base Anion—Hydroxide Form

SBA (OH^-) units remove both strong mineral acids and weak acids produced by a SAC (H^+) exchanger, including carbonic and silicic acid (see Fig. 7.17).

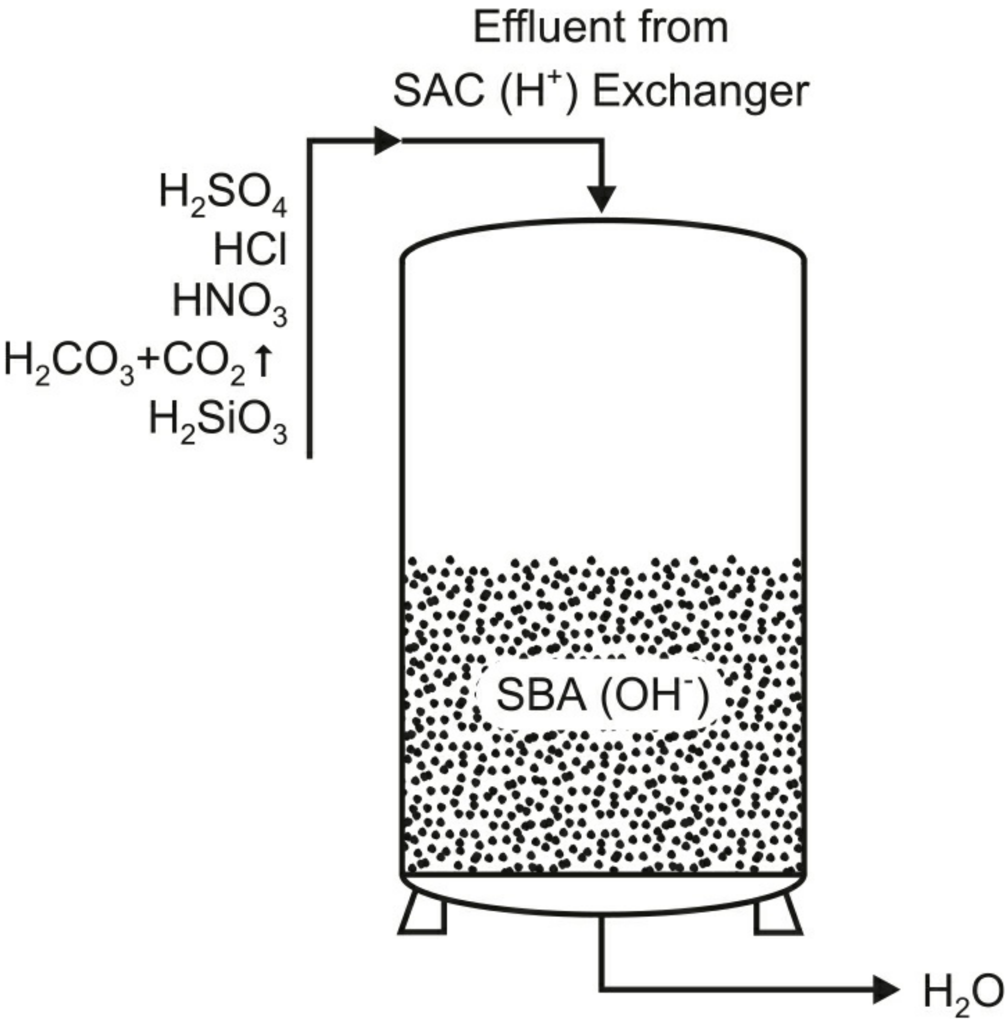


FIGURE 7.17 SBA exchanger in hydroxide form.

The combination of SAC (H^+) and SBA (OH^-) resins in a demineralizer system, either in separate units or combined in a mixed bed demineralizer, is capable of producing effluent water with purity acceptable for use as feedwater in the highest pressure utility boilers. Provided proper upstream pretreatment is utilized, when combined in a mixed bed unit, the ion exchange process is capable of producing water having silica less than 0.01 mg/L and a specific conductance below 0.055 μS/cm or a resistance above 18.2 MΩ. This water purity is required for microchip manufacture. Equations (7.21) to (7.24) show SBA (OH^-) exhaustion reactions.

$$H_2SO_4 + 2ROH \xrightarrow{\text{flow}} R_2SO_4 + 2H_2O \tag{7.21}$$

$$\mathrm{HCl + ROH \xrightarrow{flow} RCl + H_2O} \tag{7.22}$$

$$\mathrm{H_2SiO_3 + ROH \xrightarrow{flow} RHSiO_3 + H_2O} \tag{7.23}$$

$$\mathrm{H_2CO_3 + ROH \xrightarrow{flow} RHCO_3 + H_2O} \tag{7.24}$$

Regeneration must employ a strongly basic alkali such as caustic (NaOH).

$$\mathrm{R_2SO_4 + 2NaOH \xrightarrow{flow} 2ROH + Na_2SO_4} \tag{7.25}$$

$$\mathrm{RCl + NaOH \xrightarrow{flow} ROH + NaCl} \tag{7.26}$$

$$\mathrm{RHSiO_3 + NaOH \xrightarrow{flow} ROH + NaHSiO_3} \tag{7.27}$$

$$\mathrm{RHCO_3 + NaOH \xrightarrow{flow} ROH + NaHCO_3} \tag{7.28}$$

Because strong base resin is highly ionized, caustic regenerant utilization is incomplete. As described earlier, Type I and Type II SBA have different regeneration efficiency, and excess regenerant dosages of 200 to 300% of the stoichiometric amount required to drive the reactions.

Depending on influent analysis and regenerant dosage, Type I resins typically provide a working capacity of 9 to 13 kgr/ft^3 (21–30 g/L), but these values can be improved considerably when the beads are regenerated with caustic at 120°F (49°C). Type II resins are expected to provide 16 to 21 kgr/ft^3 (37–48 g/L). Type III capacity falls between Type I and Type II. However, Type I resin is more chemically stable than Type II, and normal capacity loss is slower and less extensive. In addition, Type II resins are service water temperature sensitive, and silica leakage is slightly higher than with Type I resins.

To improve chemical efficiency of the demineralizing process, carbon dioxide formed by the SAC (H^+) unit is often removed with decarbonation or vacuum deaeration to reduce ionic load on the SBA (OH^-) resin and save caustic. This reduces both the resin volume and vessel size required. Mechanical, rather than chemical removal, usually becomes economical when carbon dioxide content exceeds 25% of the TEA load.

Because the SBA (OH^-) unit does not exchange cations, any cations leaking from the SAC (H^+) unit are present in anion effluent as alkalinity. Leakage through the SAC (H^+) unit is usually sodium, which the SBA (OH^-) converts to NaOH. Each mg/L of NaOH, expressed as $CaCO_3$, in the effluent creates a specific conductance of 5 μS/cm.

Strong Base Anion—Chloride Form

When silica removal is not a concern, SBA resin can be utilized in chloride form. In this form, SBA resin is particularly good for alkalinity removal. This is a two-stage process, with the primary treatment stage being SAC (Na^+) exchange. Anion influent must be completely softened water to ensure hardness is not precipitated in the anion resin (Fig. 7.18).

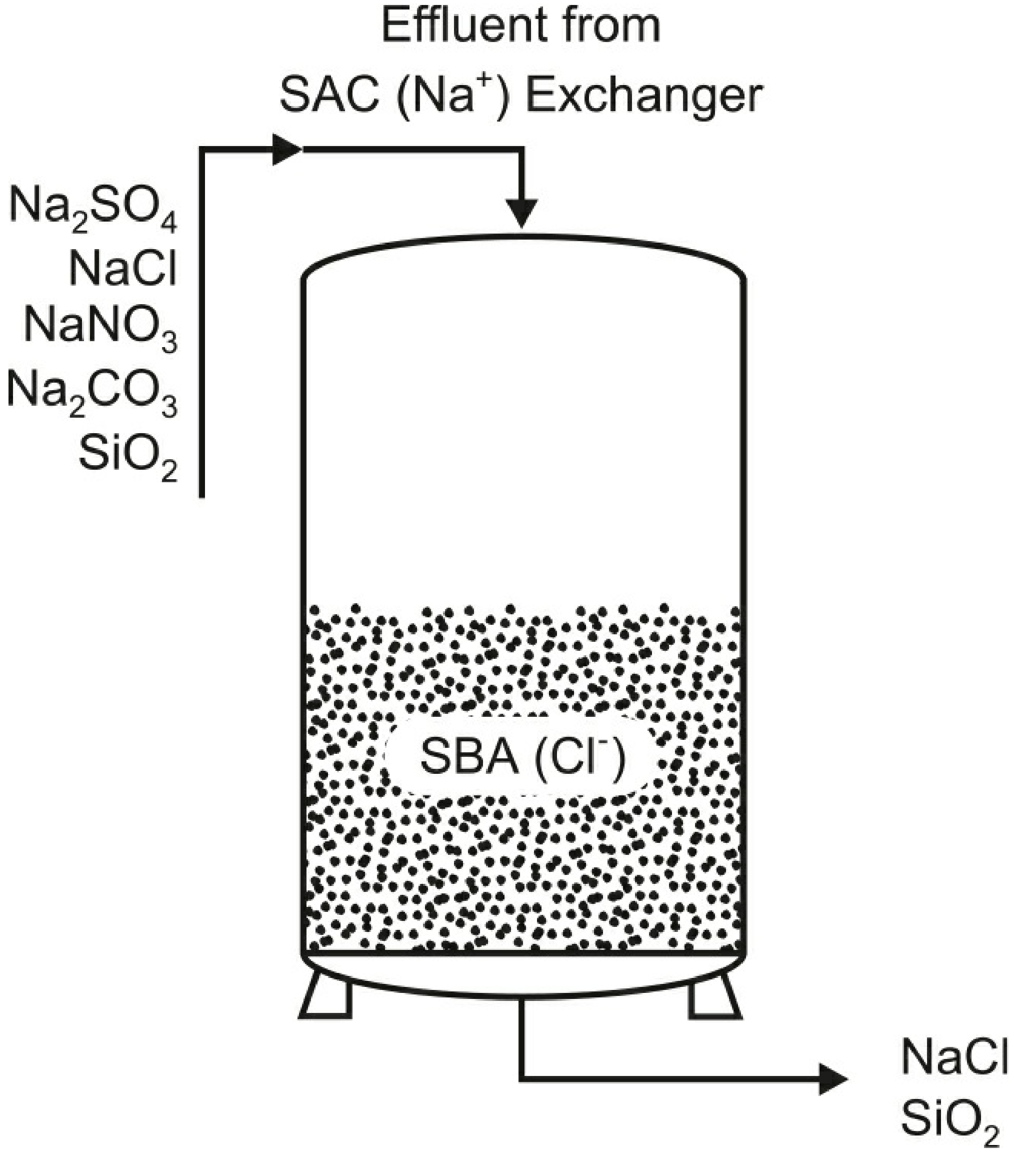


FIGURE 7. 18 SBA exchanger in chloride form.

In addition, sodium chloride used for regeneration must be evaporated grade with very low hardness content, must be dissolved in soft water, and regenerant dilution water must be softened. Type II SBA resin is used to exchange chloride for bicarbonate, carbonate, nitrate, phosphate, and sulfate in the influent.

This process does not reduce TDS. In addition, the effluent is a very weak solution of sodium chloride. As a result, equipment such as unit piping and downstream service piping is likely to corrode and leak. Unit pipe work should be flanged and lined accordingly or be of all plastic construction where pipe size permits. In addition, ion exchange vessels should be lined on all surfaces contacted by the effluent and regenerant chemicals, and all internals should be corrosion resistant.

This process and its ion exchange kinetic characteristics differ considerably from other types of ion exchange, and the process cannot use the much higher cross-sectional flow rates applied to softening and demineralization systems. In addition, low working capacity of the resin usually dictates larger resin volumes to achieve acceptable service run times. Minimum resin bed depth is 3 ft (0.91 m), and the flow rate used is about 5 gpm/ft^2[12 m^3/(h · m^2)].

Alkalinity leakage in the effluent is affected primarily by regenerant dosage, regenerants used, and characteristics of raw water, including TDS and chloride concentration.

Exhaustion chemical reactions are shown in Eqs. (7.29) and (7.30).

$$\mathrm{RCl + NaHCO_3 \rightarrow RHCO_3 + NaCl} \tag{7.29}$$

$$\mathrm{2RCl + Na_2SO_4 \rightarrow R_2SO_4 + 2NaCl} \tag{7.30}$$

One regeneration reaction is shown in Eq. (7.31).

$$\mathrm{RHCO_3 + NaCl \xrightarrow{flow} RCl + NaHCO_3} \tag{7.31}$$

Regeneration efficiency is quite low, particularly when sodium chloride is the sole regenerant. Resin working capacity ranges from 3.3 to 9.3 kgr/ft^3 (7.6–21 g/L) when regenerated at 4 lb/ft^3 (64 kg/m^3) of 100% sodium chloride. Regeneration efficiency ranges from a low of 10% to a high of 28% and is determined by TEA, ratio of M alkalinity to TEA, and concentration of chloride in the influent. Highest capacity is achieved with 90 to 100% M alkalinity:TEA and less than 10 mg/L chloride. Lowest capacity is achieved with less than 80% M alkalinity:TEA and 150 mg/L chloride. Obviously, application of this process is limited to low TDS waters due to economic considerations, as operating cost for regenerant chemicals is very high when compared to other alternatives.

If influent water has less than 100 mg/L chloride, resin working capacity of 10 kgr/ft^3 (23 g/L) can be achieved, if resin is regenerated with 4 lb/ft^3 (64 kg/m^3) of 100% sodium chloride plus 0.4 lb/ft^3 (6.4 kg/m^3) of 100% sodium hydroxide (caustic). This capacity is unaffected by the ratio of M alkalinity:TEA, but carbon dioxide must be included in the TEA calculation when caustic is used.

Effluent characteristics are quite different depending on whether or not caustic is used with sodium chloride (see Fig. 7.19).

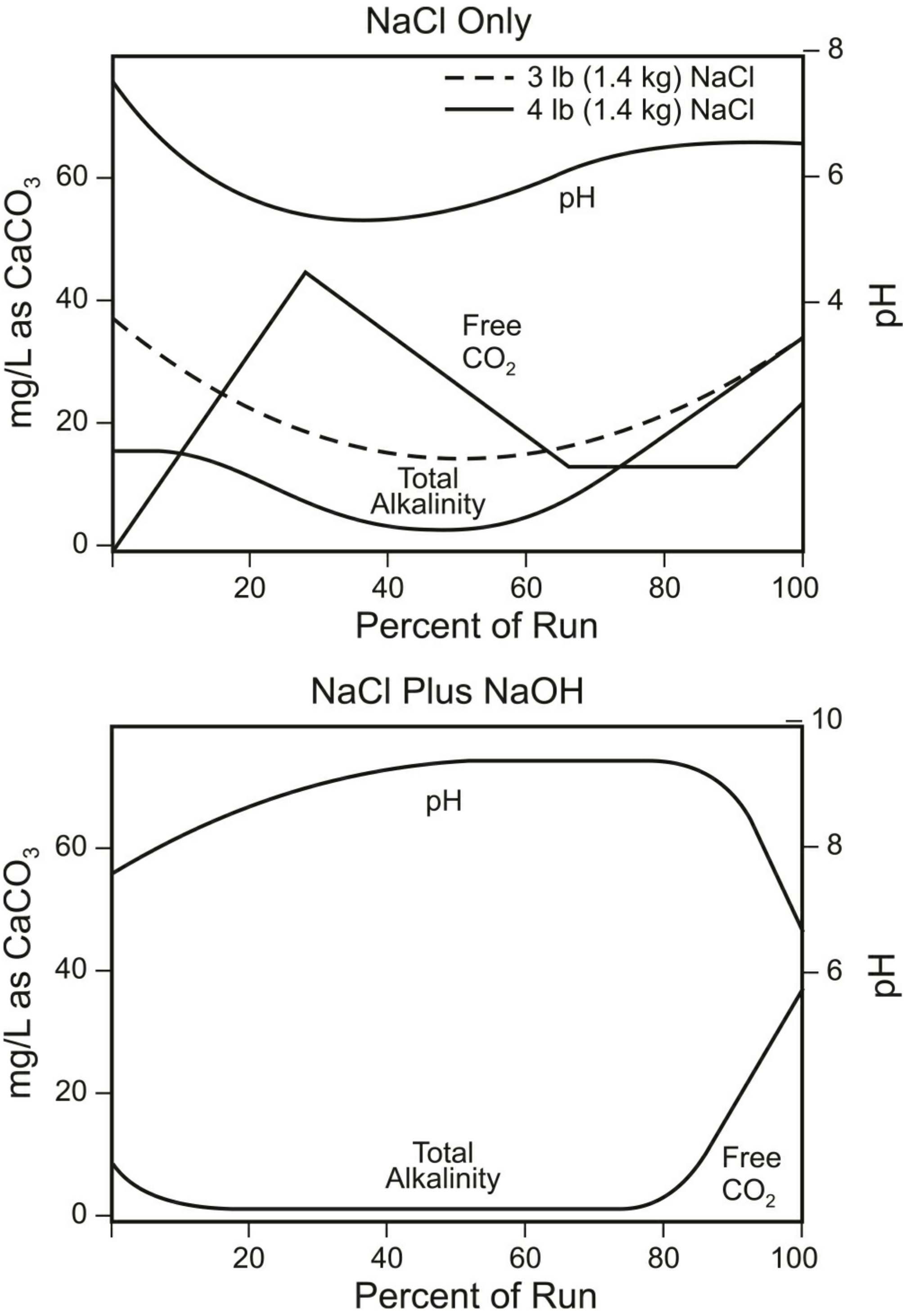


FIGURE 7.19 Dealkalizer performance with and without caustic addition.

The average life span of SBA resins is considerably shorter than that of SAC resins. SBA resins are not as durable and therefore require replacement sooner than corresponding SAC resin. Average life span for anion resins is 3 to 5 years for Type I and III and 2 to 3 years for Type II.

The most common foulant leading to reduced throughput capacity is high molecular weight organic molecules. These are not easily eluted from resin during regeneration, particularly if resin is in the chloride form. Hardness fouls anion resin, and silica is a common foulant in Type II resin. Thermal and osmotic shock play a role in capacity reduction, as does inferior quality regenerants. As SBA resin degrades, strong base sites are converted to weak base sites, which are not capable of exchanging for carbon dioxide or silica, and these tend to leak from the resin earlier.

Weak Base Anion

WBA resins exchange only strong mineral acids and have no capacity for carbon dioxide and silica. They can be regenerated at essentially stoichiometric dosages. Regenerants are sodium hydroxide (NaOH) and on occasion sodium carbonate (Na_2CO_3) or ammonium hydroxide (NH_4OH).

Weak Base Anion—Hydroxide Form

A WBA (OH^-) unit removes only strong mineral acids produced by a SAC (H^+) exchanger, but not weak acids such as carbonic and silicic. Process applications such as mirror silvering, glass manufacture, metal plating, and automotive painting do not require removal of these weak acids. WBA (OH^-) resin is less costly to regenerate and much more efficient than SBA (OH^-). Because effluent still contains silica, effluent is not generally acceptable for boiler feedwater purposes (see Fig. 7.20).

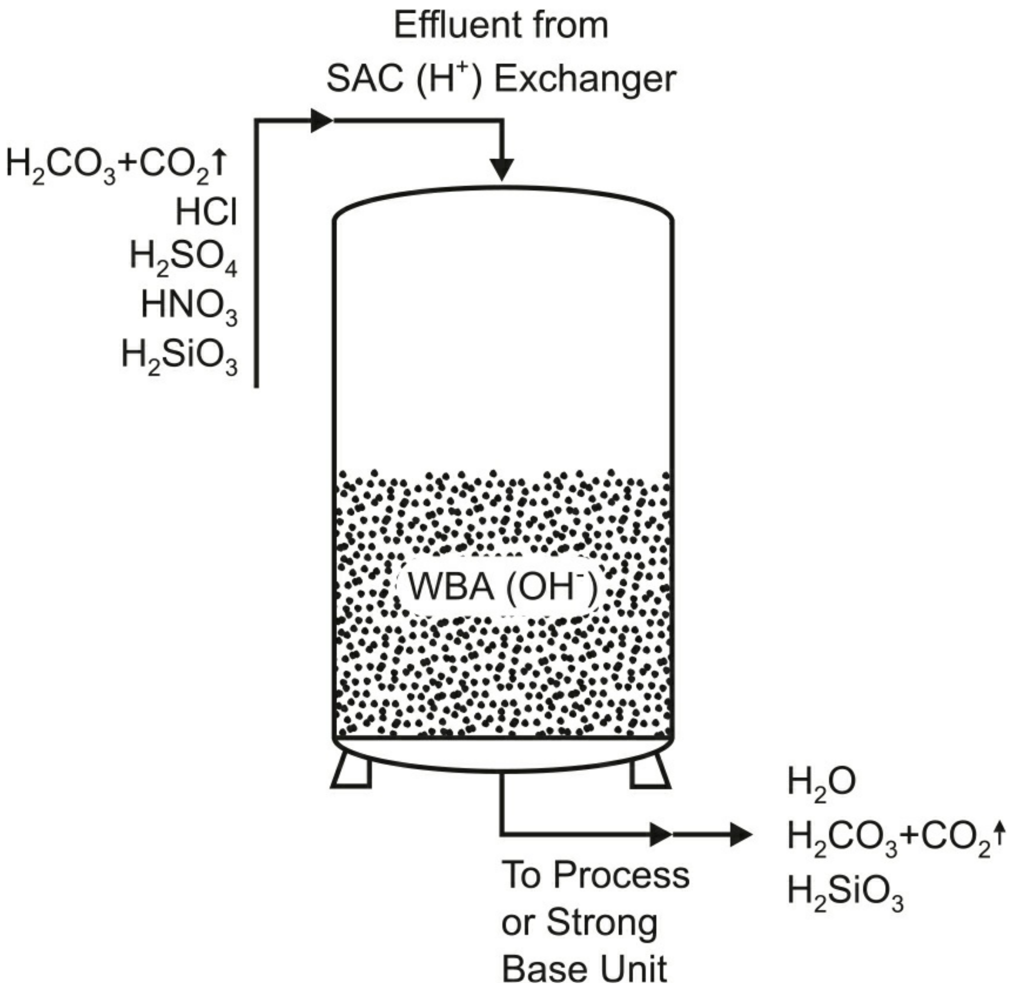


FIGURE 7.20 WBA exchanger in hydroxide form.

Reactions for removal of acids with WBA (OH^-) resin are illustrated below:

$$H_2SO_4 + 2ROH \xrightarrow{\text{flow}} R_2SO_4 + 2H_2O \tag{7.32}$$

$$HCl + ROH \xrightarrow{\text{flow}} RCl + H_2O \tag{7.33}$$

$$HNO_3 + ROH \xrightarrow{\text{flow}} RNO_3 + H_2O \tag{7.34}$$

As the weak base resin adsorbs the whole strong acid molecule, reactions are often shown simply as:

$$H_2SO_4 + 2R \rightarrow R_2H_2SO_4 \tag{7.35}$$

The common regenerant chemical used in WBA (OH^-) demineralization is caustic, but soda ash (Na_2CO_3) or ammonium hydroxide (NH_4OH) can be used. Reactions are shown in Eqs. (7.36) to (7.38).

$$R_2H_2SO_4 + 2NaOH \xrightarrow{\text{flow}} 2RNa_2SO_4 + 2H_2O \qquad (7.36)$$

$$R_2H_2SO_4 + Na_2CO_3 \xrightarrow{\text{flow}} 2RNa_2SO_4 + H_2CO_3 \qquad (7.37)$$

$$R_2H_2SO_4 + 2NH_4OH \xrightarrow{\text{flow}} 2R(NH_4)_2SO_4 + 2H_2O \qquad (7.38)$$

Weak base ion exchange is a very efficient process requiring little more than the stoichiometric amount of regenerant, injected at a 4% as NaOH concentration, which neutralizes mineral acids attached to exchange sites.

When following a SAC (H^+) unit in a two-bed demineralizer system, the WBA (OH^-) unit produces effluent containing free carbon dioxide and silica. As a result, effluent pH is low, primarily due to carbon dioxide. It is usual to employ a decarbonator for mechanical removal of CO_2, but a decarbonator may be placed in two possible locations in a two-bed WBA (OH^-) demineralizer system.

If the decarbonator immediately follows the SAC (H^+) unit, residual carbon dioxide in WBA inlet is normally 5 to 10 mg/L depending on design. In that case, WBA (OH^-) effluent normally is about pH 6.5 to 8.0 for most of the service run. Specific conductance is greater than 20 µS/cm. With this arrangement, decarbonator transfer pumps must be designed to overcome anion unit pressure drop and have full service flow capacity plus anion rinse flow rate, which could equal the service flow rate.

Alternately, the decarbonator may be located immediately downstream of the WBA (OH^-) unit, which reduces pump discharge head and flow rate requirements. However, although WBA (OH^-) resins do not remove carbon dioxide, they do load carbon dioxide in the initial part of the service run and discharge it during the last part of the run. The decarbonator, therefore, must be designed to remove at least double the normal carbon dioxide concentration, which requires a larger unit.

Because the WBA (OH^-) unit does not exchange cations, any cations leaking through the SAC (H^+) unit are present in anion effluent. Leakage through SAC

(H^+) is usually sodium, which WBA (OH^-) converts to NaCl. Each mg/L of NaCl, expressed as $CaCO_3$, in the effluent creates a nominal specific conductance of 2.5 μS/cm, but minimum specific conductance achieved is greater than 20 μS/cm from WBA (OH^-) units.

Weak base resins have very high working capacity, generally greater than 25 kgr/ft^3(57 g/L), but capacity is largely influenced by influent temperature and service flow rate. Working capacity may be 25% higher at 70°F (21°C) than at 40°F (4°C). Working capacity declines when service flow rates exceed 2 gpm/ft^3 (16 $m^3/[h \cdot m^3]$) of resin with a minimum bed depth of 3 ft (0.91 m).

Amines used in manufacturing weak base resins tend to degrade rapidly, which is manifested in development of long rinse times and high rinse water volume to obtain quality specifications following regeneration. Rinse water volume required with new resin can be more than 60 gal/ft^3 (8 m^3/m^3) of resin but might increase to 200 gal/ft^3 (27 m^3/m^3) in a relatively short time.

Average life span of WBA resin is 4 to 7 years. These resins are subject to degradation through thermal and osmotic shock, inferior regenerant quality, and hardness. WBA resin failure is generally seen as reduction of throughput capacity and longer rinse times.

Table 7.5 is a summary of ion exchange resins, regenerants used, and ions removed.

Resin Type	Form	Common Regenerants	Ions Removed
Strong acid cation (SAC)	Na^+	NaCl	Mg^{+2}, Ca^{+2}
Strong acid cation (SAC)	H^+	H_2SO_4, HCl	All cations
Weak acid cation (WAC)	H^+	H_2SO_4, HCl	Mg^{+2}, $Ca^{+2}$of alkalinity
Strong base anion (SBA) Type I	OH^-	NaOH, KOH	All anions
Strong base anion (SBA) Type II	OH^-	NaOH, KOH	All anions, limited on SiO_2 and CO_2
Strong base anion (SBA) Type II	Cl^-	NaCl	All anions, limited on SiO_2 and CO_2
Strong base anion (SBA) Type III	OH^-	NaOH, KOH	All anions
Weak base anion (WBA)	OH^-	NaOH, KOH	Strong mineral acids only
Weak base anion (WBA)	CO_3^{-2}	Na_2CO_3	Strong mineral acids only
Weak base anion (WBA)	NH_2^-	NH_3	Strong mineral acids only

TABLE 7.5 Resin Functionality by Regenerant

Resin Management

Many plants do not put into practice a good resin management program. As such, when resin failure occurs, it can be a shock to the maintenance budget. There are several key components in a resin management program. When taken together, they offer a clear picture of expected resin life, total operating cost, performance expectations, and cleaning cycles. Component pieces of a resin management program are: expected length of service, annual resin analysis, annual regeneration profile, monitoring service performance, chemical cleaning, and resin storage.

Expected Length of Service

Useful life of ion exchange materials is influenced by many factors:

- Influent water characteristics
- Operating environment such as service and regeneration conditions
- Resin chemical structure and stability

- Number of service/regeneration and cleaning cycles
- Exposure to oxidants and foulants
- Thermal and osmotic shock
- Attrition

Influent Water Characteristics

Influent water may contain natural substances or other materials from pretreatment processes or as the result of inefficient pretreatment. This can include suspended matter, turbidity, incompletely reacted precipitation chemicals such as lime, heavy metals such as iron and aluminum, excess polymers, system corrosion products, naturally occurring organics, and contaminants from plant process leaks. Any of these can cause fouling of resin-exchange sites, reducing effectiveness and leading to premature failure.

Operating Environment

Wide and sudden variations in influent water temperature may cause thermal shock and have an impact on useful resin life. This can include backwash water and regenerant solutions. Osmotic shock can occur from inaccurate control of regenerant concentration, leading to rapid changes in resin bead size from one form to another. Quality of regenerant dilution water is a factor in resin life, as internal and external fouling precipitates can be formed.

Resin Chemical Structure and Stability

Ignoring the effects of foulants, oxidants, etc., cation resins are more stable than anion resins, and life expectancy of cation resins is greater than that of anion resins. Type I SBA resins are more stable than Type II, again ignoring effects of fouling, etc. Amines used in anion resin manufacture have finite life spans. As amines degrade, resin loses strong base functionality (salt splitting capacity) and the ability to remove silica and carbon dioxide.

Number of Service/Regeneration and Cleaning Cycles

Each time a resin is exhausted, regenerated, or chemically cleaned, bead size and volume change. This can cause weak beads to crack or break, making them more likely to be washed from the unit during backwash. Bead breakage is called attrition.

Anion resin amine degradation occurs to some degree every regeneration. This results in gradual reduction in total capacity. Regeneration occurs more frequently as influent water TDS increases.

Effects of Oxidants

Residuals of oxidants such as chlorine and chloramines added to water for microorganism control attack the resin skeleton of cation resins. The divinylbenzene crosslink is permanently destroyed, and resin loses total capacity, takes on more water, and expands (Fig. 7.21). This increased bed pressure drop accelerates bead damage, and degraded resin, being less dense, is lost to waste discharge during backwash. Results can be reduced service throughput, inability to meet effluent quality requirements (high leakage), increased regeneration frequency, increased resin replacement frequency, long rinses, increased waste generation, and high operating costs.

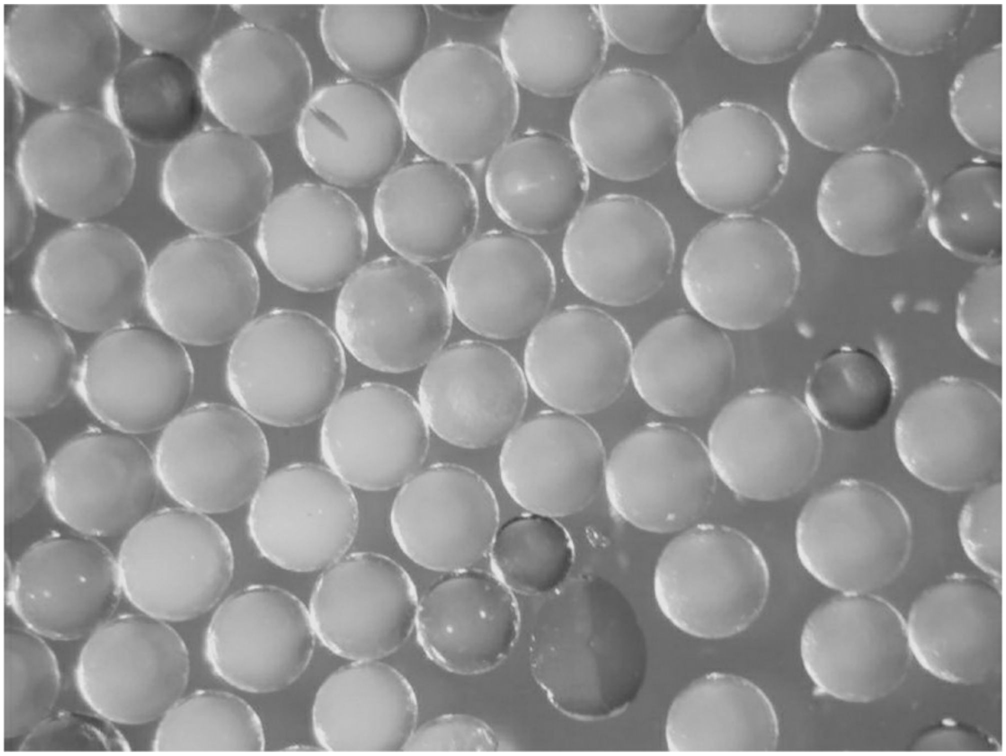


FIGURE 7.21 This cation resin has suffered oxidation and the reduction of divinylbenzene crosslinkage. The current moisture content of this resin is significantly higher than recommended.

Oxygen is released in water by heating, either for energy conservation, system operating requirements, or more efficient regeneration of resins.

Oxygen attacks both cation and anion resins, causing the same effects noted earlier.

Exposure to Foulants

Fouling may be reversible or irreversible, depending on the nature of the foulant and resin. Cation resins, usually being in a primary position in a system, are potentially exposed to suspended matter, turbidity, precipitated compounds from pretreatment, heavy metals, hydrocarbons, microorganisms, etc. In addition, heavy metal concentration and contaminants in regenerant acid may be present due to contaminated shipping containers, bulk trucks or corrosion of storage and handling equipment.

Anion resins are potentially exposed to organic acids, microorganisms of different types, and heavy metals from regenerant chemicals, etc. In addition, degradation products from cation resin oxidation cause irreversible fouling of SBA (OH^-) resins.

All of these foulants can form a film around a resin bead or block surface and internal exchange sites (Fig. 7.22). This impedes ion exchange reactions in both service and regeneration. Results can be reduced service throughput, inability to meet effluent quality requirements (high leakage), increased regeneration frequency, increased cleaning and resin replacement frequency, long rinses, increased waste generation, and high operating costs.

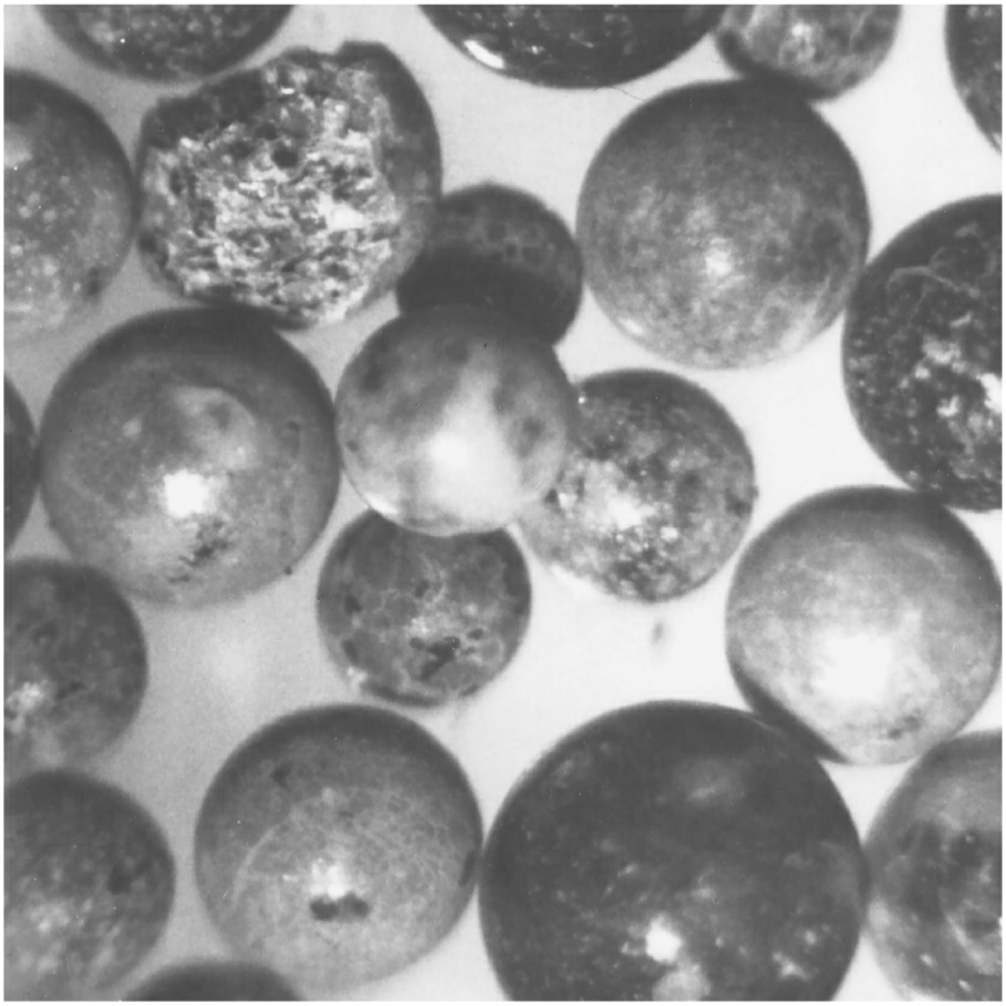


FIGURE 7.22 External organic and inorganic fouling of gel-type resin.

The most common foulant in cation resins is iron, which is normally found in well water as ferrous iron (Fe^{+2}). Ferrous iron exchanges onto resin but is converted to ferric iron (Fe^{+3}) as oxygen in service and backwash water reacts with ferrous iron. Resin holds onto trivalent iron very strongly, which is not eluted completely. Further oxidation forms insoluble iron oxides that foul resin internally and externally. Proper diffusion is prevented, and unit effluent quality decreases while rinse volumes increase. Iron may be introduced to cation resin via contaminated acid or as a result of corrosion of the acid storage and handling system.

Iron is frequently found on anion resin and is the result of contaminated caustic or corrosion of the caustic storage and handling equipment. Iron in influent water reacts with organics that foul anion resin, leading to iron fouling of anion resin.

Aluminum is another common cation resin foulant. It can originate in raw water but more commonly results from overfeed of aluminum sulfate (alum) at the raw water treatment plant. It is very difficult to remove from resin because of its trivalent state.

Table 7.6 summarizes common resin foulants.

Resin Type	Common Foulants
SAC, WAC	Iron (oxidizes on surface and in resin pores) Aluminum Inorganic precipitates Cationic polyelectrolytes Microbiological growths
SBA, WBA	High molecular weight organic acids Iron hydroxide Anionic polyelectrolytes Cation resin degradation products Microbiological growths

TABLE 7.6 Typical Foulants Found on Ion Exchange Resins

Thermal Shock

This occurs with sudden temperature change in water entering a unit, such as in SAC (Na^+) hot water operations following hot lime softening or in condensate polishing. If cold water is introduced suddenly for backwashing or regenerating, resin can crack or shatter. To eliminate this problem, the rate of temperature change must be minimized by introducing cold water at a low-flow rate until resin is cooled sufficiently.

Osmotic Shock

Osmotic shock occurs in resin due to sudden changes in resin bead size or volume. This can be induced by rapid change in solution concentration in contact with resin. For instance, acid regeneration of WAC resin immediately followed by regeneration with caustic can cause this shock, as the increase in resin volume may be 60%. Additionally, osmotic shock may be caused in exhausted resin when contacted by overly concentrated acids or bases.

Attrition

Attrition, or physical breakage, occurs when resin beds are severely compacted by being in service for extended periods without backwashing. Accumulation of dirt or suspended matter increases bed differential pressure and contributes to breakage.

When resin beads break, smaller particles increase differential pressure and can cause further breakage. Similarly, very fine resin particles cause the same condition (Fig. 7.23).

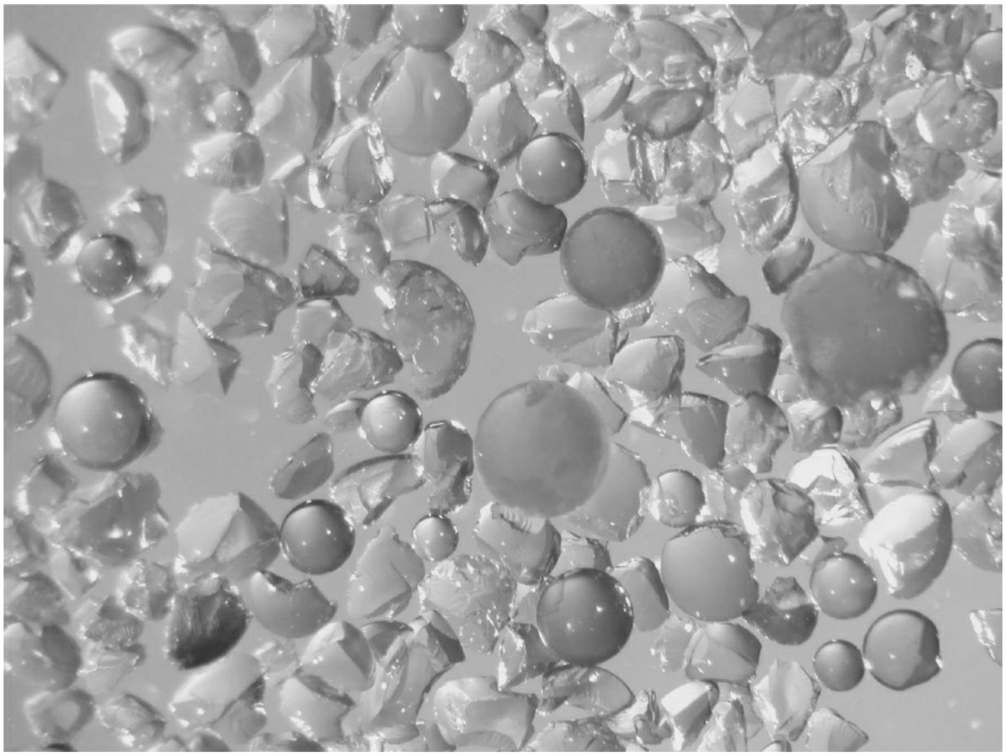


FIGURE 7.23 Badly cracked gel-type resin, which may be caused by internal precipitate or osmotic shock, the latter being common in hot lime softening units if pressure is suddenly released.

Effects of osmotic shock and attrition include:

- Particle fragmentation
- Resin loss during backwash
- Increased bed pressure differential
- Channeling of service and regenerant flows
- Reduced service throughput
- High ionic leakage (slippage)

Annual Resin Analysis

Effects of stresses on resin as mentioned earlier are measured by specific analytical tests, which should be conducted on core resin samples taken from every unit annually. Results should be compared to characteristics of a retained sample of new resin tested at the same time as the first used resin sample is tested.

Proper sampling of resin in an ion exchange unit for analysis is of paramount importance, since results of analysis should lead to positive recommendations for cleaning or replacing resin. The best time to take a sample of resin is after normal regeneration. This is especially important if levels of contaminants are required.

Avoid taking a resin sample scraped quickly from the top of the bed, because resin condition at the top is irrelevant of resin condition of the bed in general (Fig. 7.24). Instead, obtain a core sample of resin, preferably several core samples from each quadrant as seen in Fig. 7.25. These samples are then combined into one container for a composite analysis of the resin bed. Common tests used for resin evaluation include: water retention capacity (WRC), total capacity wet (TCW), salt splitting capacity (SSC), microscopic analysis, metals content, and physical condition.

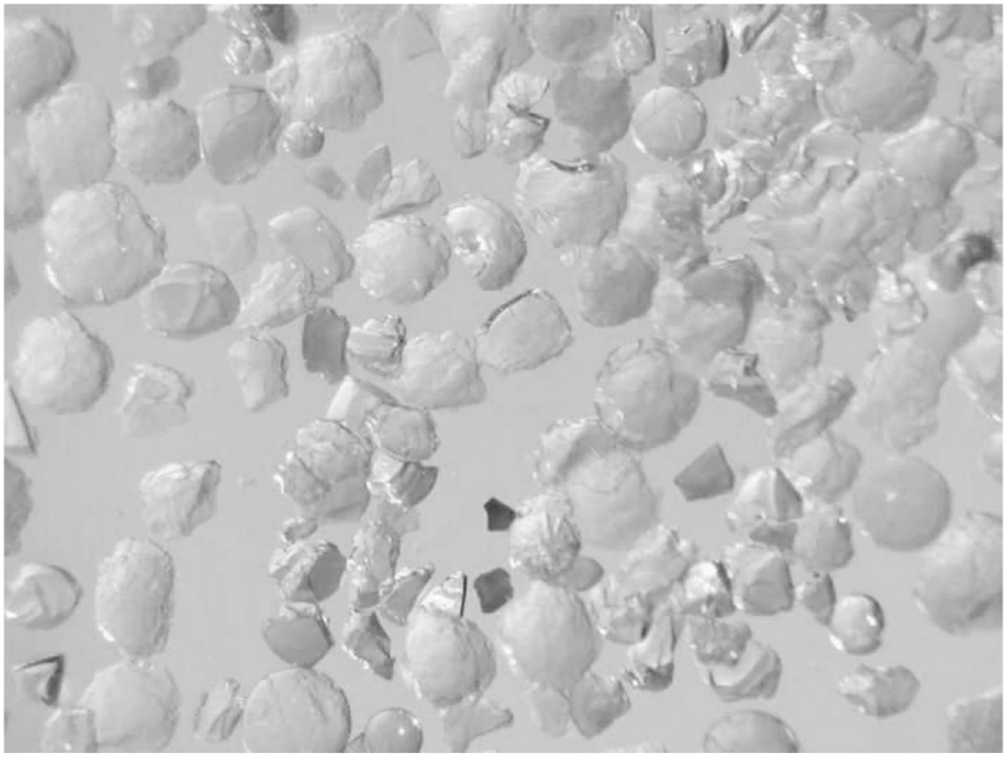


FIGURE 7.24 Picture of a resin sample scraped from the top of the bed. The sample is not at all representative of the core and exhibits mostly broken beads.

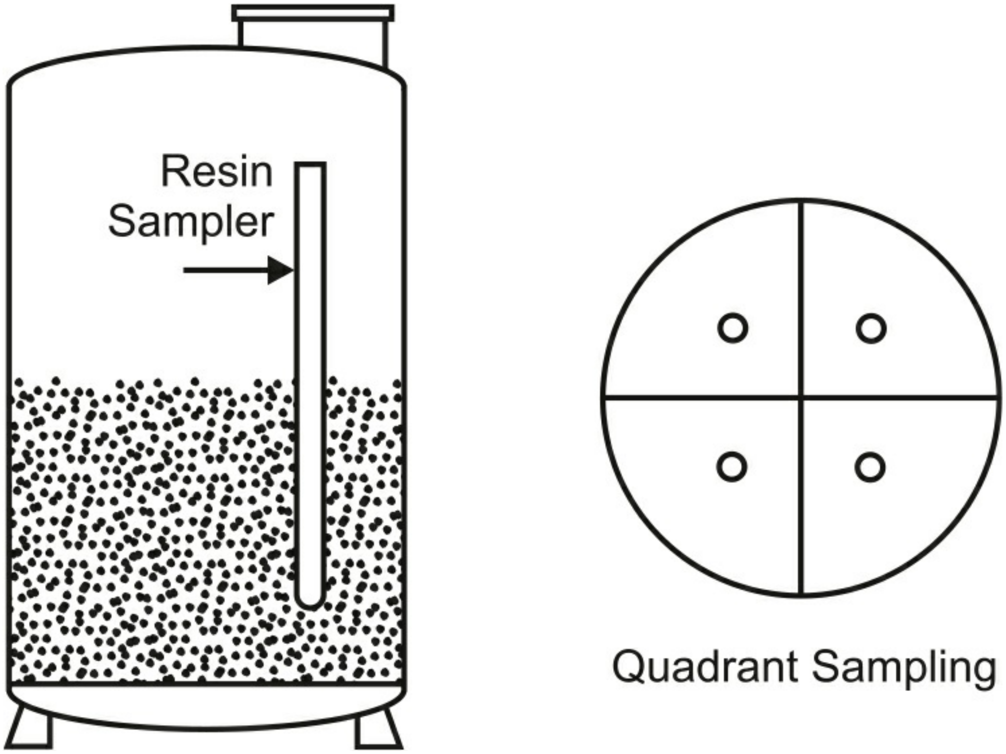
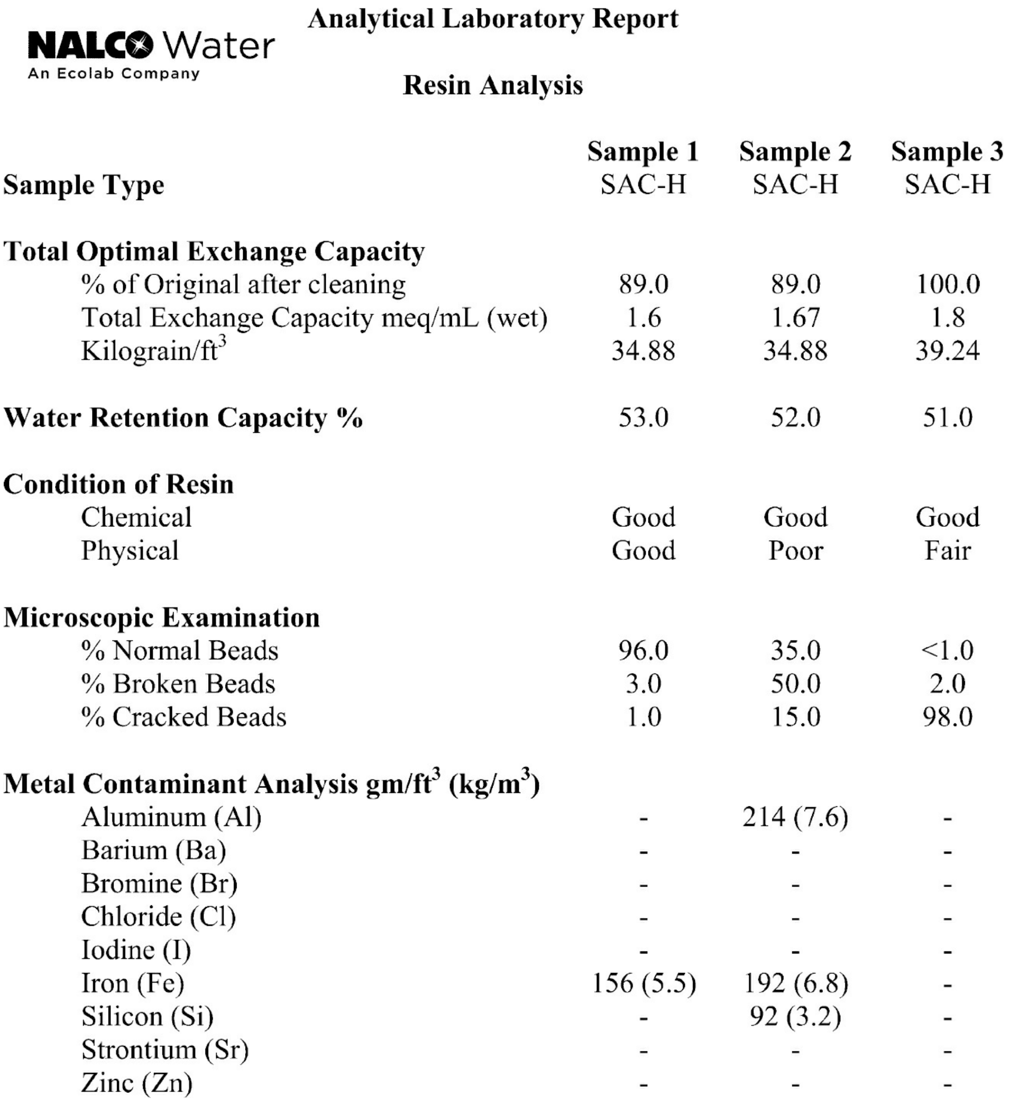


FIGURE 7.25 Obtaining resin core samples.

Contaminant levels considered small, moderate, or high should be provided for guidance. The cause of any contaminant found and reported as high should be investigated and eliminated. Chemical cleaning for removal should be evaluated, taking into account length of service time on the resin. High iron on a resin in service for ten years may not be as significant as the same iron level on a resin that has been in service for only six months.

Figures 7.26 to 7.29 are typical resin analysis examples for SAC resins with the accompanying photographs. Sample 1 indicates that the resin in is good condition both physically and chemically. There is however, a large amount of iron fouling in the resin and inhibiting the exchange capacity. The iron in this case is both on and inside the resin bead. Sample 2 indicates a resin in good condition chemically but in poor condition physically. The exchange capacities are similar to sample 1 but physically the beads have suffered significantly. There is also a significant amount of contaminant on the beads in the form of aluminum and iron that will inhibit ion exchange. Sample 3 indicates a resin that has suffered extreme physical stress. Across all of the samples you can see that even though the beads are in various states of physical decline, chemically they are still functioning reasonably well. This is common with cation resin. They often fail physically prior to failing chemically.



Analytical Laboratory Report

NALCO Water
An Ecolab Company

Resin Analysis

	Sample 1	**Sample 2**	**Sample 3**
Sample Type	SAC-H	SAC-H	SAC-H
Total Optimal Exchange Capacity			
% of Original after cleaning	89.0	89.0	100.0
Total Exchange Capacity meq/mL (wet)	1.6	1.67	1.8
Kilograin/ft^3	34.88	34.88	39.24
Water Retention Capacity %	53.0	52.0	51.0
Condition of Resin			
Chemical	Good	Good	Good
Physical	Good	Poor	Fair
Microscopic Examination			
% Normal Beads	96.0	35.0	<1.0
% Broken Beads	3.0	50.0	2.0
% Cracked Beads	1.0	15.0	98.0
Metal Contaminant Analysis gm/ft^3 (kg/m^3)			
Aluminum (Al)	-	214 (7.6)	-
Barium (Ba)	-	-	-
Bromine (Br)	-	-	-
Chloride (Cl)	-	-	-
Iodine (I)	-	-	-
Iron (Fe)	156 (5.5)	192 (6.8)	-
Silicon (Si)	-	92 (3.2)	-
Strontium (Sr)	-	-	-
Zinc (Zn)	-	-	-

FIGURE 7.26 Typical SAC resin analyses.

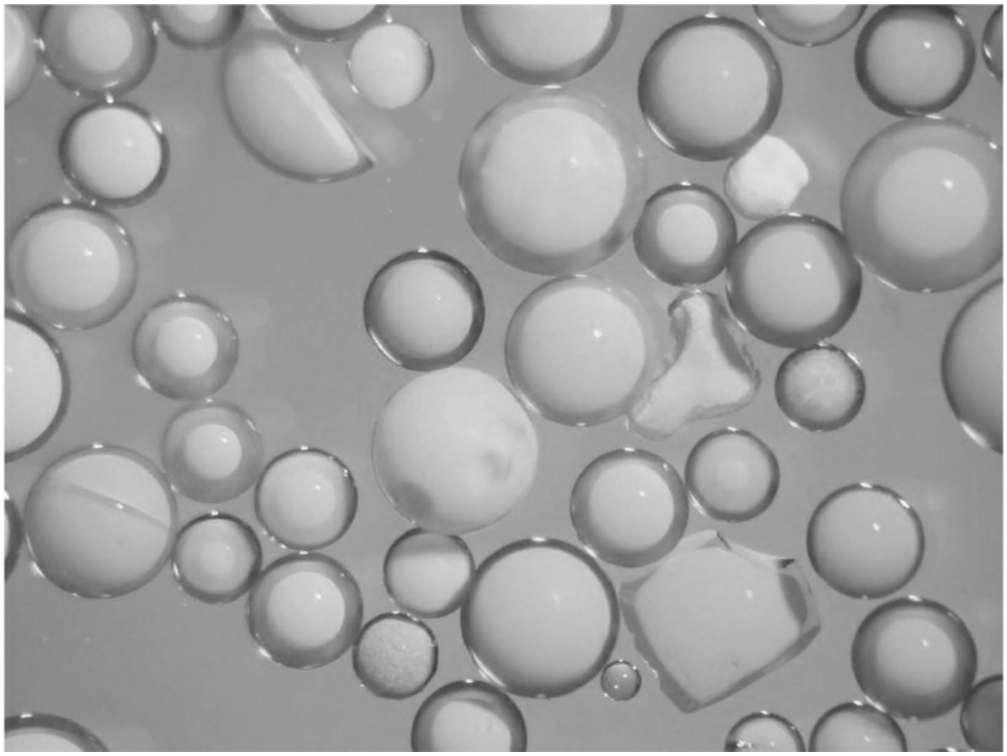


FIGURE 7.27 Sample resin #1 showing significant iron fouling both inside and on the resin bead.

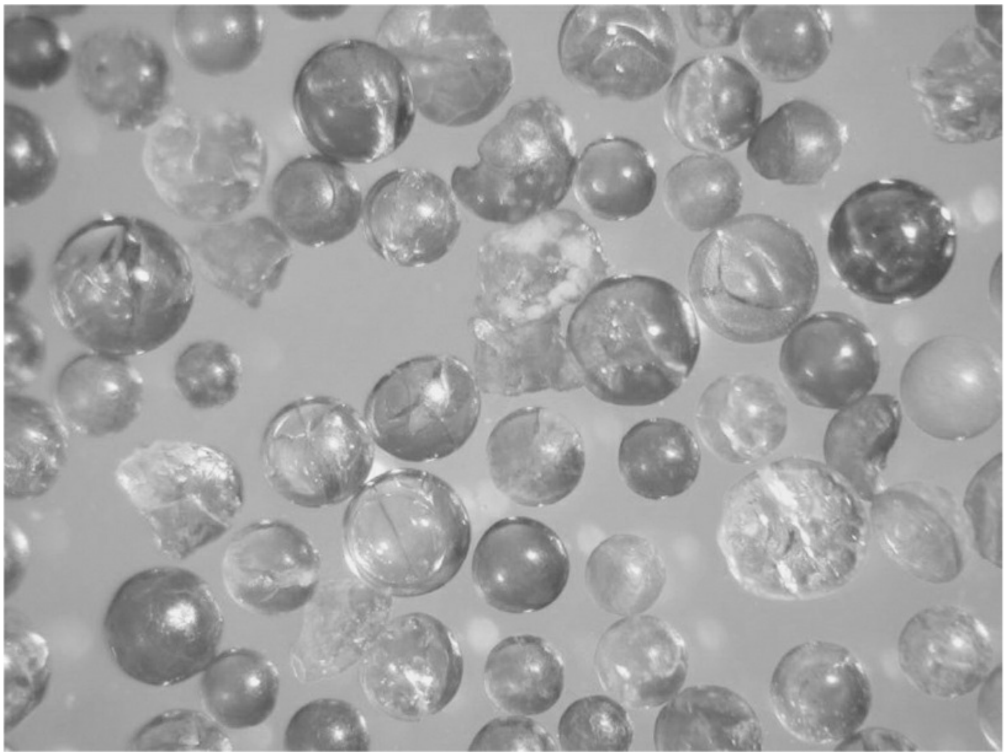


FIGURE 7.28 Sample resin #2 showing stressed beads with iron and aluminum fouling.

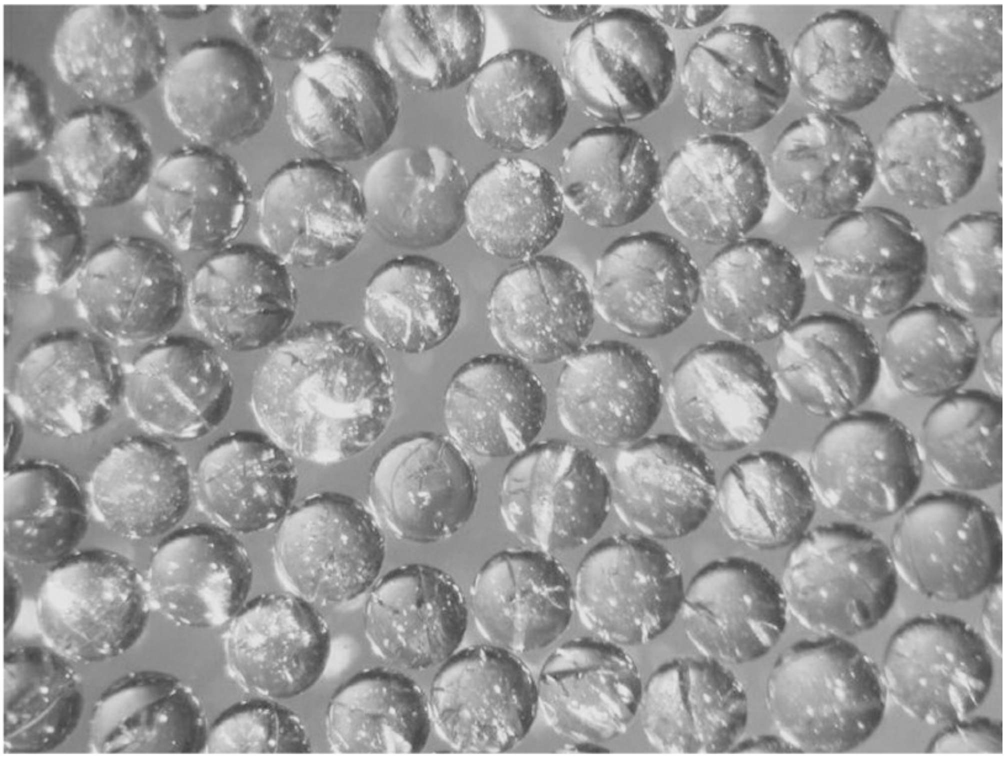
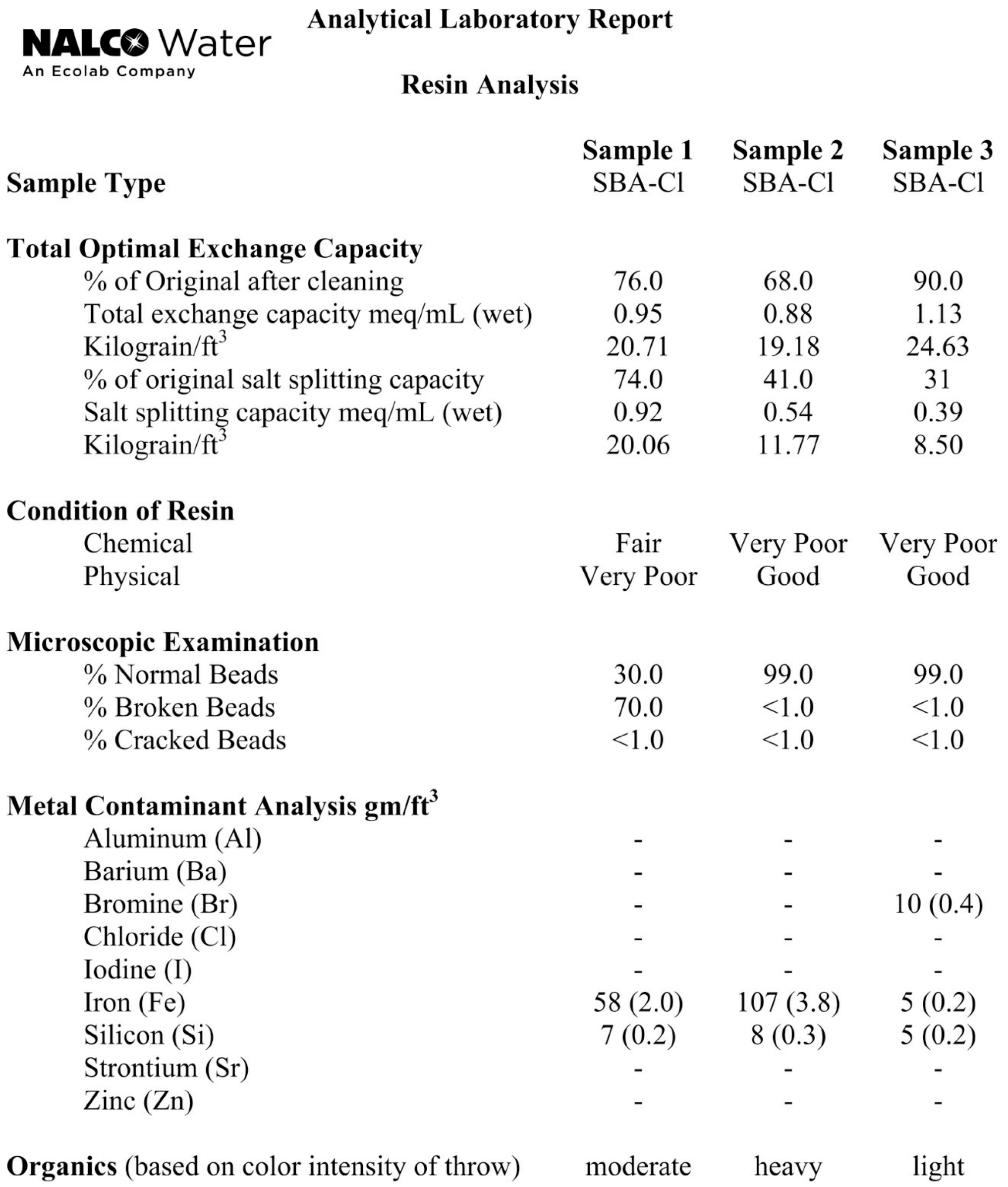


FIGURE 7.29 Sample resin #3 showing extremely stressed beads.

Figures 7.30 to 7.33 are typical resin analysis examples for SBA resins with the accompanying photographs. Sample 1 reveals a resin that still has reasonable salt splitting capacity but is experiencing moderate organic fouling and significant physical stress as seen with the high amount of broken beads. Sample 2 shows a resin with a high level of organic fouling and a low salt splitting capacity. Sample 3 is of a resin that has light organic fouling but has lost a very significant amount of salt splitting capacity. As is typical of anion resins, they often loose salt splitting ability before they fail physically. All of these resins are candidates for replacement.



Analytical Laboratory Report

Resin Analysis

	Sample 1	**Sample 2**	**Sample 3**
Sample Type	SBA-Cl	SBA-Cl	SBA-Cl
Total Optimal Exchange Capacity			
% of Original after cleaning	76.0	68.0	90.0
Total exchange capacity meq/mL (wet)	0.95	0.88	1.13
Kilograin/ft^3	20.71	19.18	24.63
% of original salt splitting capacity	74.0	41.0	31
Salt splitting capacity meq/mL (wet)	0.92	0.54	0.39
Kilograin/ft^3	20.06	11.77	8.50
Condition of Resin			
Chemical	Fair	Very Poor	Very Poor
Physical	Very Poor	Good	Good
Microscopic Examination			
% Normal Beads	30.0	99.0	99.0
% Broken Beads	70.0	<1.0	<1.0
% Cracked Beads	<1.0	<1.0	<1.0
Metal Contaminant Analysis gm/ft^3			
Aluminum (Al)	-	-	-
Barium (Ba)	-	-	-
Bromine (Br)	-	-	10 (0.4)
Chloride (Cl)	-	-	-
Iodine (I)	-	-	-
Iron (Fe)	58 (2.0)	107 (3.8)	5 (0.2)
Silicon (Si)	7 (0.2)	8 (0.3)	5 (0.2)
Strontium (Sr)	-	-	-
Zinc (Zn)	-	-	-
Organics (based on color intensity of throw)	moderate	heavy	light

FIGURE 7.30 Various typical SBA resin analyses illustrating different states of deterioration.

FIGURE 7.31 Sample resin #1 exhibits a moderate fouling with organics with a high percentage of broken beads.

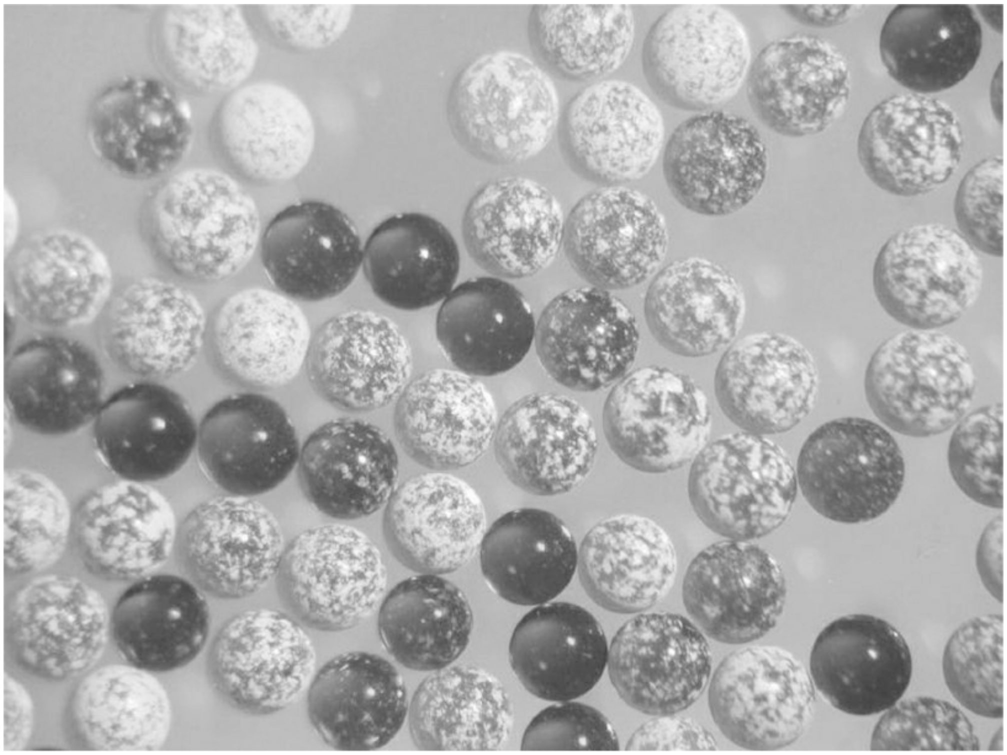


FIGURE 7.32 Sample resin #2 is heavily fouled with organics. Physically the resin looks to be in good

condition but it has lost almost 60% of its salt splitting capacity.

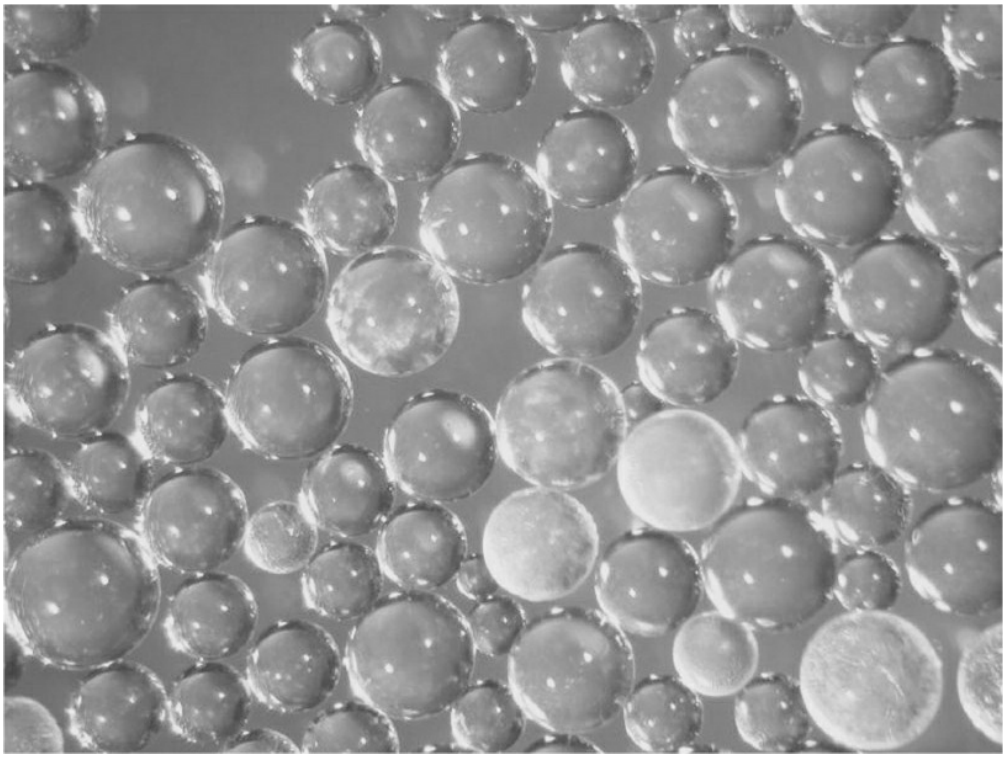


FIGURE 7.33 Sample resin #3. Physically the resin looks to be in good condition but it has lost almost 70% of its salt splitting capacity.

Prediction of Remaining Resin Life

Determining when resin is sufficiently degraded to warrant replacement is a difficult and somewhat complicated process. To a large degree, the decision to replace is based on cost of replacement resin compared to increased labor and regenerant chemical costs resulting from shorter service runs and more frequent regenerations. In addition, degraded resins may cause higher ionic leakage and poor quality water. No hard and fast rules can be stated, and each case must be determined individually based on plant conditions.

Generally, SAC resins can have a substantial service life, provided there is no physical bead breakdown due to conditions outlined earlier. Normal attrition can be expected to be less than 3% per year. However, attack by oxidants causes increased water retention as bead cross-linking is attacked and beads swell. This is detected by the water retention capacity test, and results can be used as a rough rule-of-thumb to predict remaining resin life. Figure 7.34 is only applicable to standard gel-type SAC resins that have an average water retention capacity of 46 to 56% when tested in the hydrogen form.

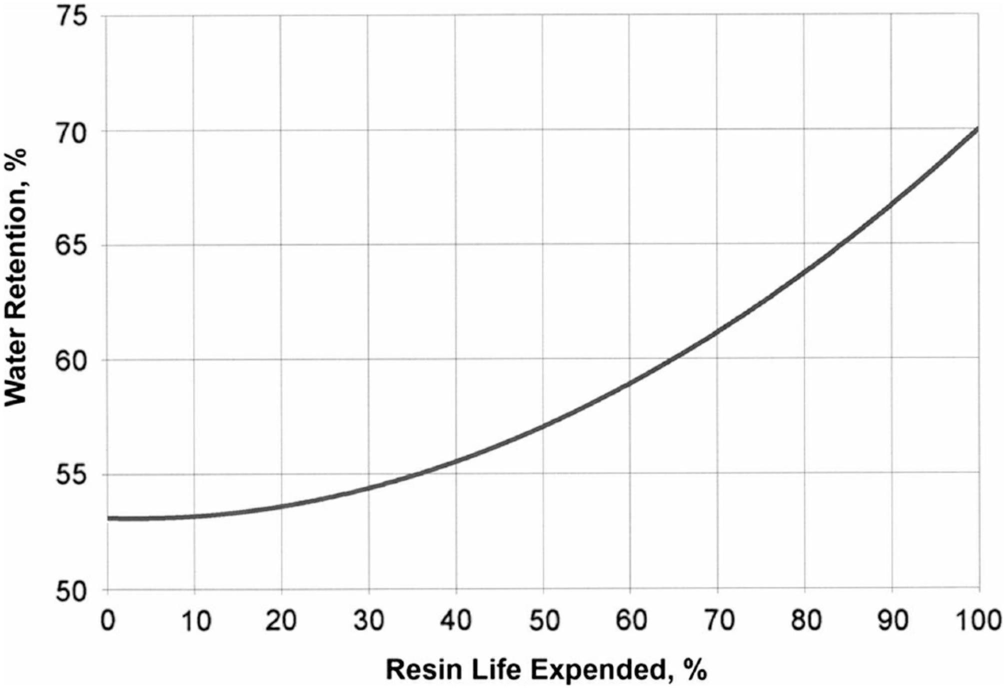


FIGURE 7.34 Useful life expended for SAC resin.

SBA resins, on the other hand, experience continuous and gradual loss of total capacity because of the relatively less stable composition of the active exchange sites. As this normal degradation proceeds, SBA resins lose ability to exchange weak silicic and carbonic acid anions, while retaining ability to exchange strong anions (sulfate, chloride, and nitrate). This is detected by a decrease in salt splitting capacity (development of weak base sites from strong base sites). Under ideal service conditions, Type I resin life is typically less than five years, while Type II resin life is less than three to four years.

In new strong base anion resins, salt splitting capacity should be 100% of total exchange capacity. This determination can be used as a rough rule-of-thumb to predict remaining resin life. Figure 7.35 is only applicable to standard gel-type SBA resins.

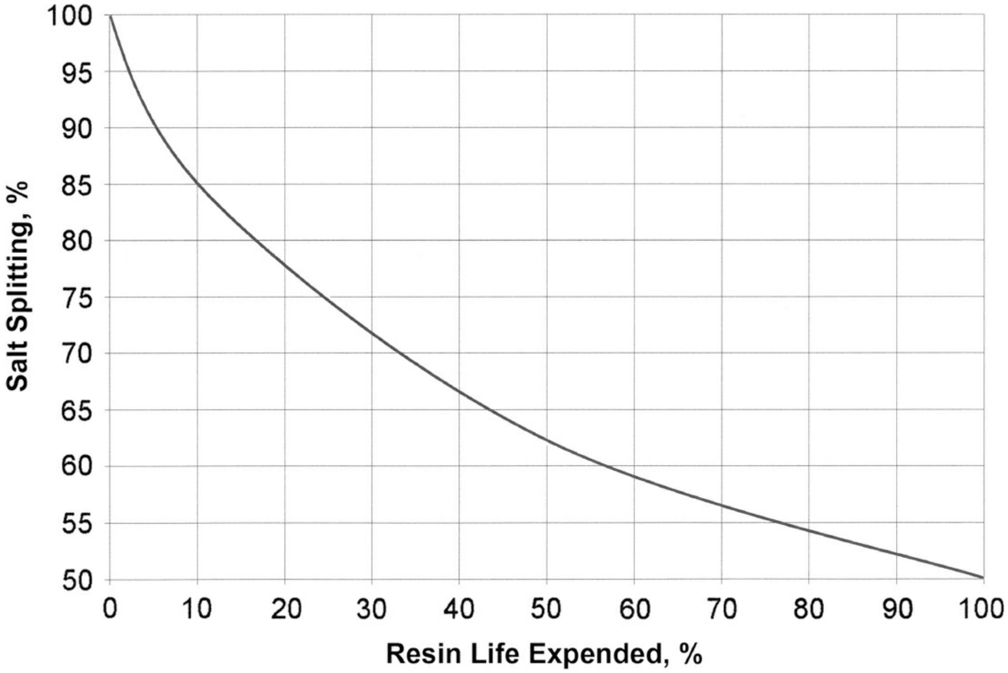


FIGURE 7.35 Useful life expended for SBA resin.

Annual Regeneration Profile

An annual elution study is of particular benefit to SAC (Na^+) and SBA (Cl^-) units. Since both units are regenerated with sodium chloride, an elution study using a salometer to evaluate a set of timed samples provides insight into brine saturation level as well as salt contact time. Adjusting brine intake or rinse flow rates, to manage the salt saturation curve, to that recommended for the resin, helps ensure good quality effluent. Figure 7.36 shows a proper brine plug moving through a SAC (NA^+) bed.

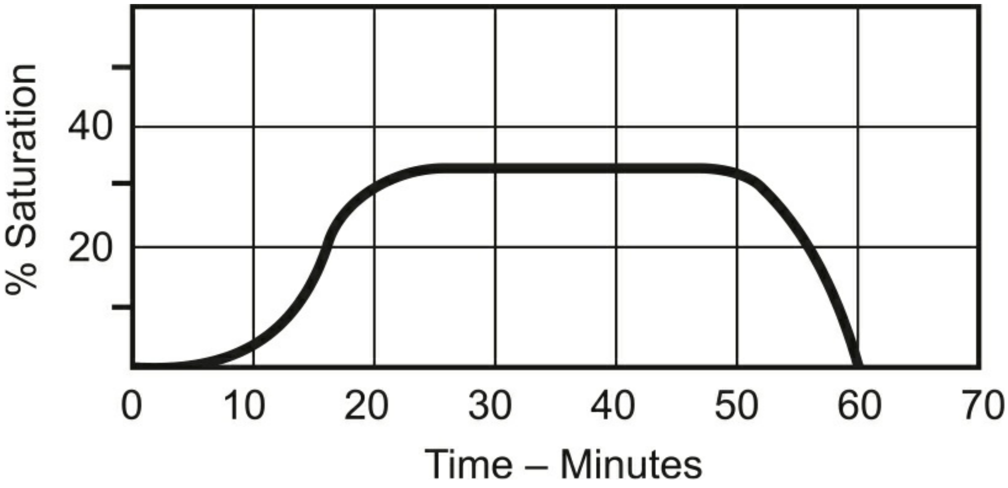


FIGURE 7.36 Ideal SAC (Na^+) elution curve.

While an elution study is generally of most benefit to a sodium chloride regenerated resin, this method can be used on any co-current regenerated vessel with any regenerant. This is of most benefit when looking for early regenerant breakthrough due to channeling. Otherwise, comparing performance of a unit against original specifications for items noted below yields information necessary for regeneration or service adjustments.

- In service cross-sectional and volumetric flow rates
- Regeneration cross-sectional volumetric flow rates
- Comparison of actual service run length to specification
- Regenerant usage per volume of resin
- Regeneration water temperatures
- Backwash turbidity study
- Seasonal water temperature variation

Monitoring Service Performance

Monitoring ion exchange equipment effluent while in service is a task that is done regularly. Breakthrough or leakage of undesirable ions into service water gives an indication of when action needs to be taken and the unit regenerated.

SAC (Na+)

SAC (Na^+) service performance and service endpoint are usually monitored by simple total hardness tests available to most operators. Alternately, online hardness analyzers may be used but are expensive. Figure 7.37 shows the breakthrough profile for a SAC (Na^+) unit.

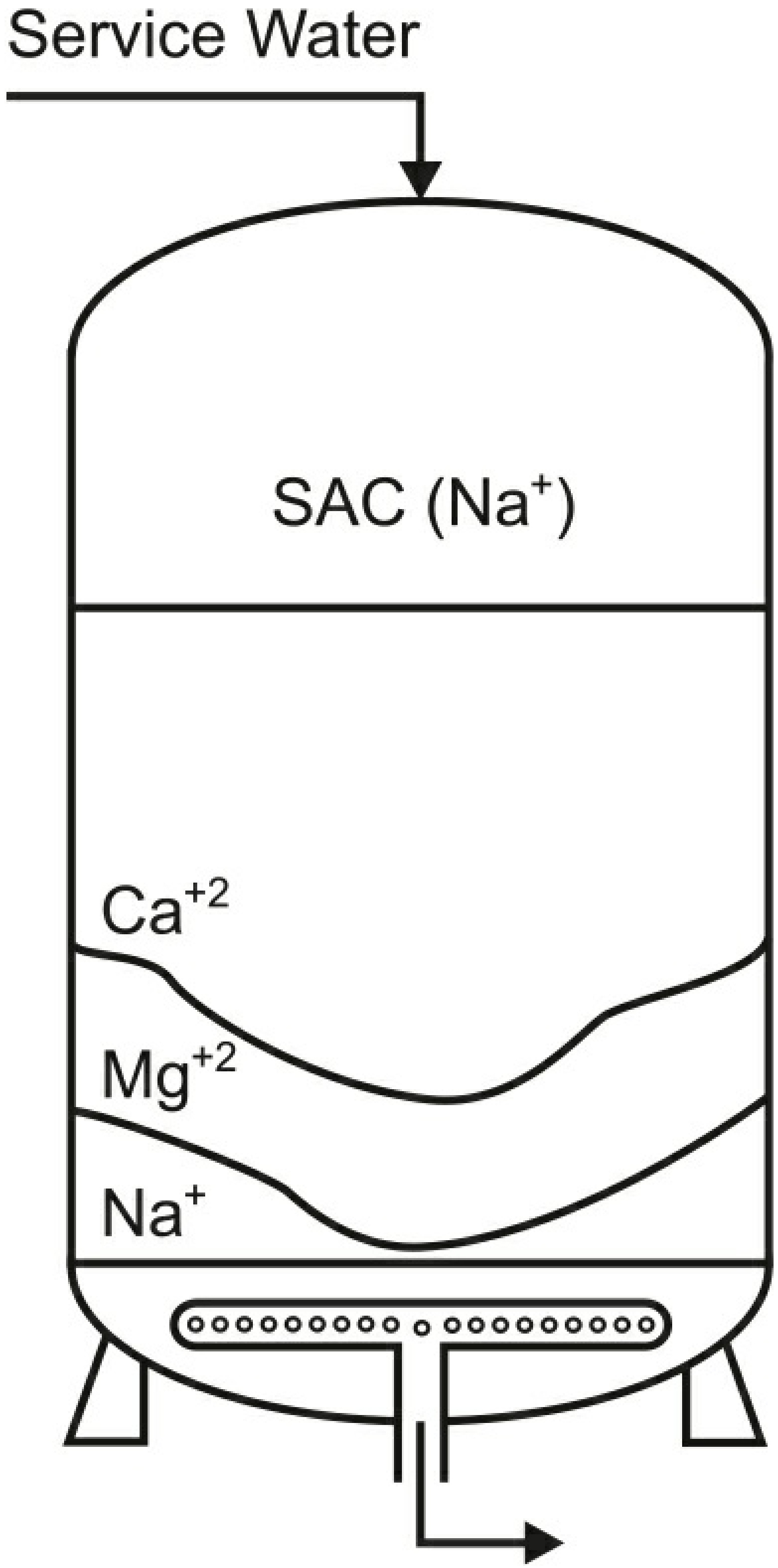


FIGURE 7.37 Breakthrough profile for SAC (Na^+) unit.

SAC (H^+)

SAC (H^+) service performance and service endpoint are not easily monitored by simple chemical tests available to most operators. The only parameters that can be tested dependably are effluent FMA and sodium leakage. Total hardness can be monitored but should not be present at high concentrations (< 0.2–0.5 mg/L as $CaCO_3$), unless the unit is grossly over exhausted or $CaSO_4$ precipitation has occurred. When SAC (H^+) resin begins to exhaust, there is a decrease in effluent FMA with a corresponding increase in sodium leakage. Decreasing FMA can be detected by a decrease in specific conductance of the effluent. However, as this measurement varies considerably with changing sulfate, chloride, and nitrate concentrations in inlet cation water, it is sometimes difficult to monitor accurately. In addition, the change can be very small and difficult to detect being only about 5 µS/cm per mg/L change from H_2SO_4 to Na_2SO_4 (Fig. 7.38). The usual method employed is comparison of FMA titrations or specific conductance values with those of companion cation units still in service producing satisfactory effluent.

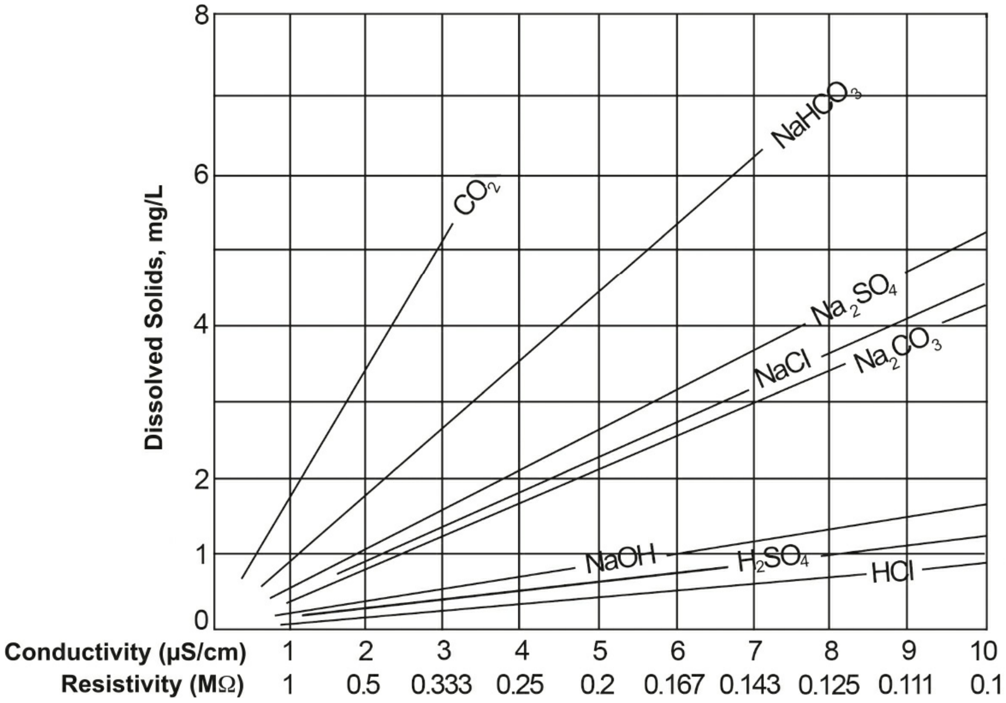


FIGURE 7.38 Conductivity (resistivity) of ionic species to dissolved solids.

Sodium analysis with online analyzers is quite accurate, but such analyzers are expensive and not utilized extensively, except at power generation plants where high-pressure boilers are in use.

Exhaustion may also be checked by measurement of SAC (H^+) outlet pH as compared to companion cation units. The pH rises with a drop in effluent FMA, but the change is quite small and difficult to measure accurately.

As SAC (H^+) sodium leakage increases, sodium ions from the SAC (H^+) combine with an equivalent number of hydroxide ions to form caustic (NaOH) in the anion effluent. Each mg/L of NaOH (expressed as $CaCO_3$) in the SBA (OH^-) effluent results in a specific conductance of 5 µS/cm. Therefore, an increase in sodium leakage of 1 mg/L causes an increase in SBA (OH^-) specific conductance of 5 µS/cm due entirely to cation performance. This can occur if SAC (H^+) and SBA (OH^-) service capacities are mismatched or if resin loss or degradation occurs in one or the other. The SAC (H^+) unit should be suspected first as the cause of service break, unless the system is anion capacity limited. Additionally, silica leakage from SBA (OH^-) increases with rising sodium leakage from the SAC (H^+). Figure 7.39 shows the breakthrough profile for a SAC (H^+) unit.

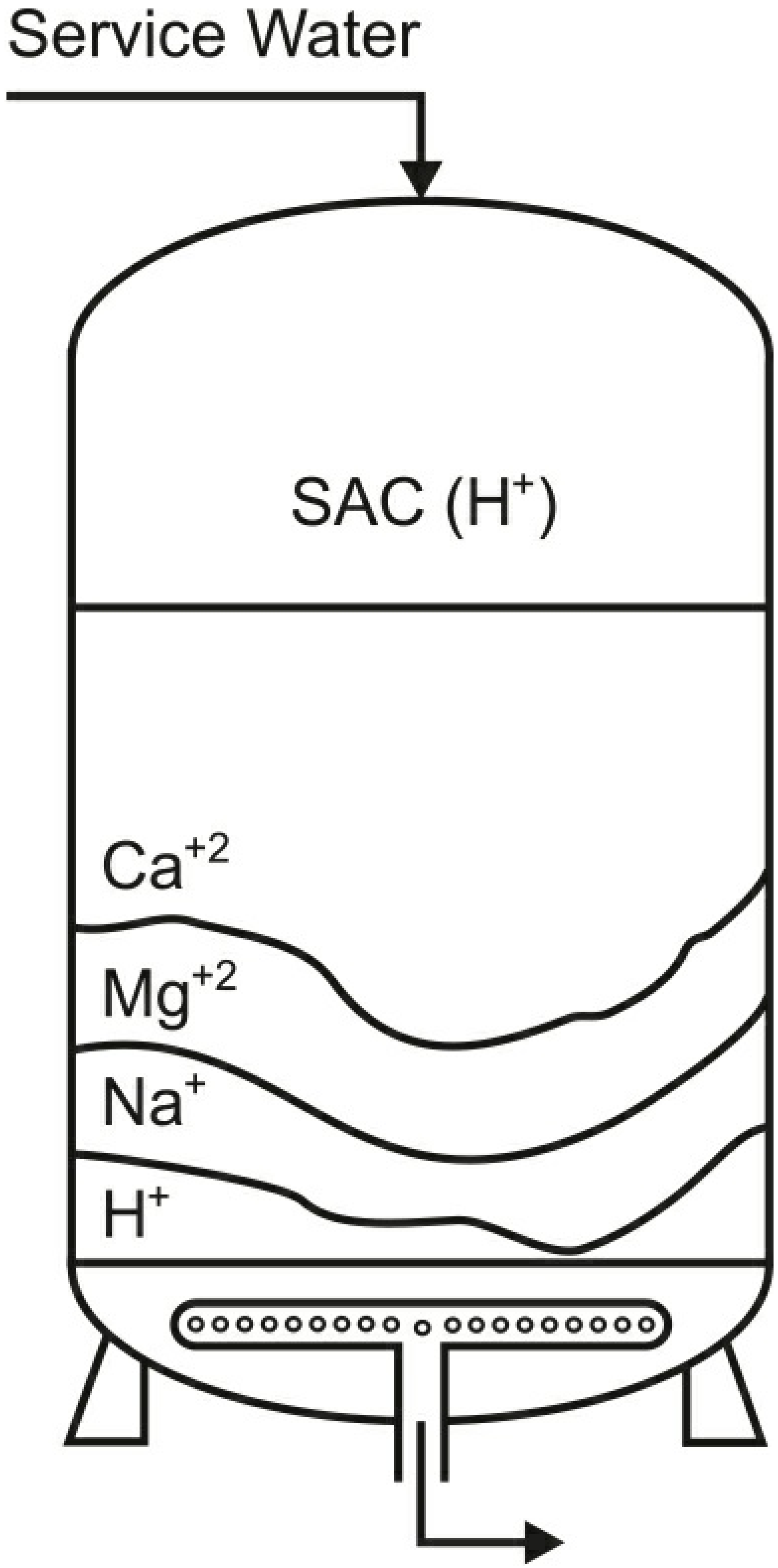


FIGURE 7.39 Breakthrough profile for SAC (H^+) unit.

SBA (OH^-)

SBA (OH^-) units are usually monitored using effluent silica and specific conductance analyses. Both parameters are easily tested by operators but are frequently monitored continuously with online analyzers.

Silica, having lower affinity for SBA resin than other anions, leaks first. Silica does not contribute to effluent conductivity and is not detected by specific conductance instrumentation. Silica break may occur at 85 to 95% of the service run as opposed to specific conductance break at 100%.

pH measurements are not usually recommended as reliable service monitors for demineralizers but can be useful in determining whether the SAC (H^+) or SBA (OH^-) unit is responsible for service break. pH is observed simply and even litmus paper can be used, if a portable pH instrument is unavailable. Figure 7.40 indicates how the exhausted unit may be identified using pH, specific conductance, and silica determinations.

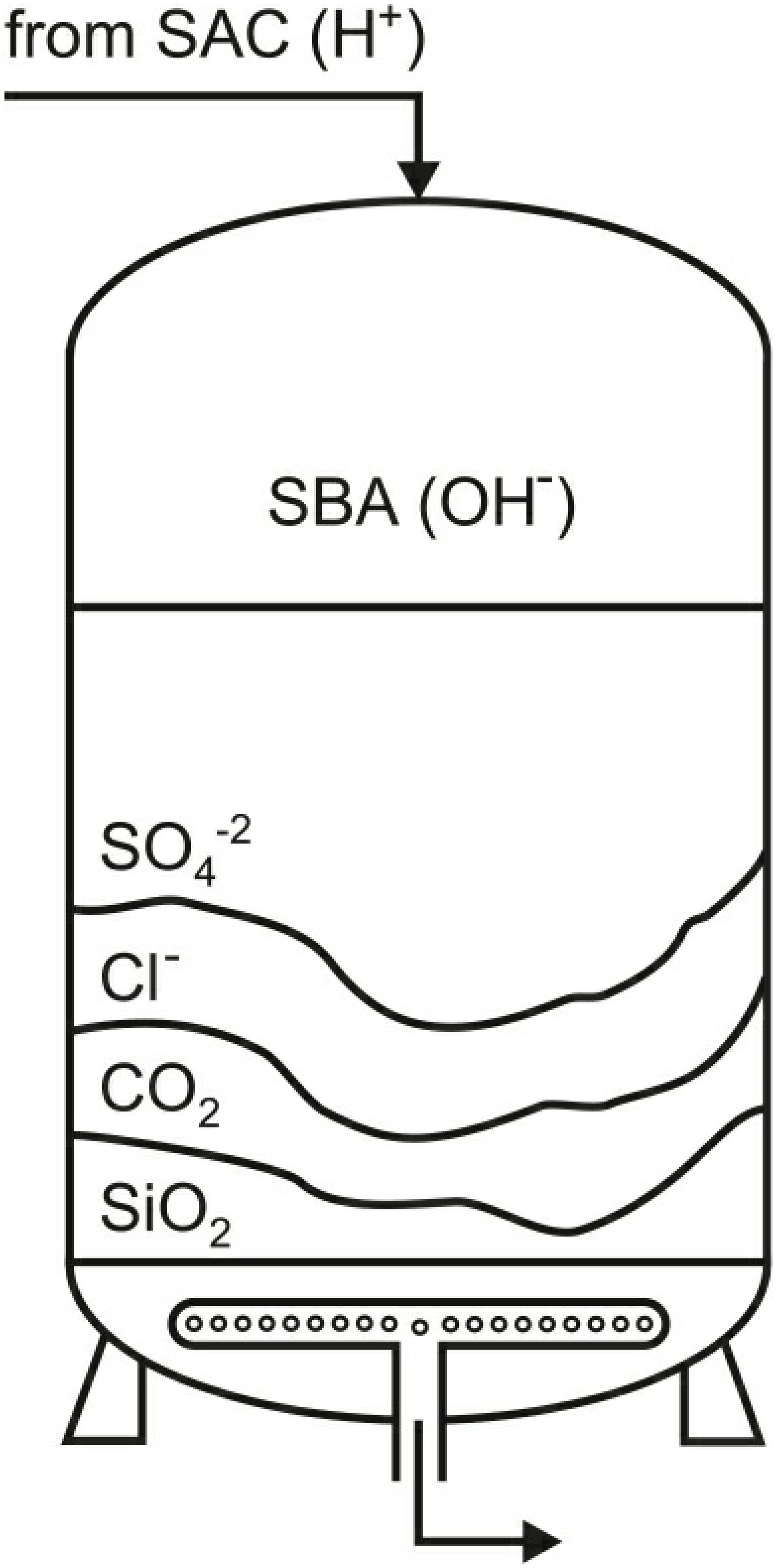


FIGURE 7.40 Breakthrough profile for SBA (OH^-) unit.

Figure 7.41 shows interpretation guidelines for SAC (H^+) and SBA (OH^-) units using the parameters discussed earlier.

Cation Unit Exhaustion

Cation pH	Cation µS/cm	Cation FMA	Anion pH	Anion µS/cm
↑	↓	↓	↑	↑

Anion Unit Exhaustion

Cation pH	Cation µS/cm	Cation FMA	Anion pH	Anion µS/cm
↔	↔	↔	↓	↑

FIGURE 7.41 Demineralizer exhaustion interpretation guidelines (two-bed train operation).

Mixed-Bed Units

In a mixed-bed demineralizer, using both strong acid and strong base resins, similar reactions occur, but it is not possible to sample and test between the two exchange phases to determine which resin is exhausted. Figure 7.42 provides guidelines for correct diagnosis using the parameters discussed earlier.

Exhausted Resin	Effluent pH	Effluent µS/cm	Effluent Silica
Cation	↑	↑	↔
Anion	↓	↑	↑

FIGURE 7.42 Demineralizer exhaustion interpretation guidelines (mixed bed).

Regenerants and Water

Besides breakthrough monitoring, the amount of service water each unit produces during each run, the amount of water needed for a complete regeneration cycle, and the amount of regenerant used should be monitored.

Understanding trends in each of these parameters over time yields useful data and provides additional information as to when a unit needs remedial attention.

Chemical Cleaning

As discussed earlier, various contaminants may be present in waters that contact ion exchange resins. The annual resin analysis reveals contaminants and concentrations present. This information along with reduced quality service water, throughput capacity, or both, indicates whether it is necessary to consider cleaning the resin. Table 7.7 indicates some common foulants and cleaning solutions used to remove them. A proper procedure along with correct concentrations of cleaner is necessary before undertaking cleaning of any resin bed.

Resin Type	Contaminant	Cleaning Solution
Mixed bed	Inorganics	HCl
SBA and WBA	Organics	NaCl with NaOH
SAC and WAC	$CaSO_4$	Sodium citrate
SBA and WBA	$CaSO_4$	HCl
SAC and SBA	Fe^{+3}	HCl

TABLE 7.7 Typical Cleaning Solutions to Remove Various Contaminants

Evaluation of resin age, remaining capacity, expected restored capacity, chemical cleaning cost, and increased regenerant costs due to low throughput are all factors that need to be considered before undertaking resin cleaning. There is a balance point where replacement with new resin is less expensive if remaining capacity of existing resin has deteriorated significantly. Figures 7.43 and 7.44 illustrate the effect of a brine squeeze on an organically fouled anion resin.

FIGURE 7.43 Organically fouled SBA resin before a brine squeeze.

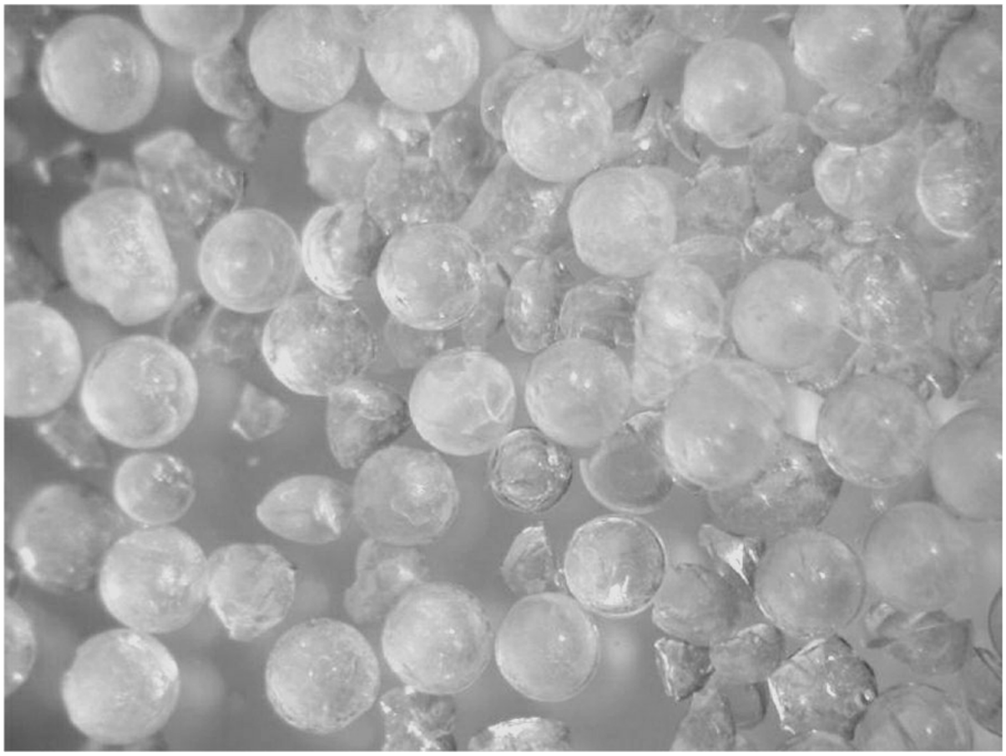


FIGURE 7.44 The same resin as shown in Fig. 7.43 after a successful brine squeeze was used to remove a large portion of the organics.

Resin Storage

Most resin can be safely kept in wet storage for about two years, provided storage conditions are suitable. Resin should be stored in its original packaging between 32 to 86°F (0–30°C) in an interior location protected from container damage. Old resins that can be used to top up existing ion exchange beds require the same consideration.

Resin that undergoes several freeze/thaw cycles or becomes dry loses exchange capacity and even structural integrity. This shortens useful resin life.

Ion Exchange Equipment Configurations

Choosing the right equipment configuration, resin, and regenerant are largely dependent on required service water quality. Equipment is generally classified by the function the resin performs. Typical functions for water treatment are: softening (hardness removal), dealkalization (alkalinity removal), and demineralization (total ion removal). With the exception of simple hardness removal, there are many different equipment configurations and resin choices that can accomplish the task. Some common configurations are discussed below.

Softening

This process involves exchange of the scale forming cations calcium and magnesium for completely soluble sodium. It is most often utilized in treatment of surface and well water supplies for commercial, institutional, and industrial plants for process and boiler feedwater applications. Softening uses SAC (Na^+) resin, and regeneration may be co-current or counter-current in normal or packed bed units. However, when these units are used downstream of lime precipitation processes, only conventional co-current units that allow full backwash every regeneration are used. Producing soft wateris the simplest ion exchange process and is shown in Fig. 7.45. Figure 7.46 shows a typical water analysis for this type of ion exchange unit.

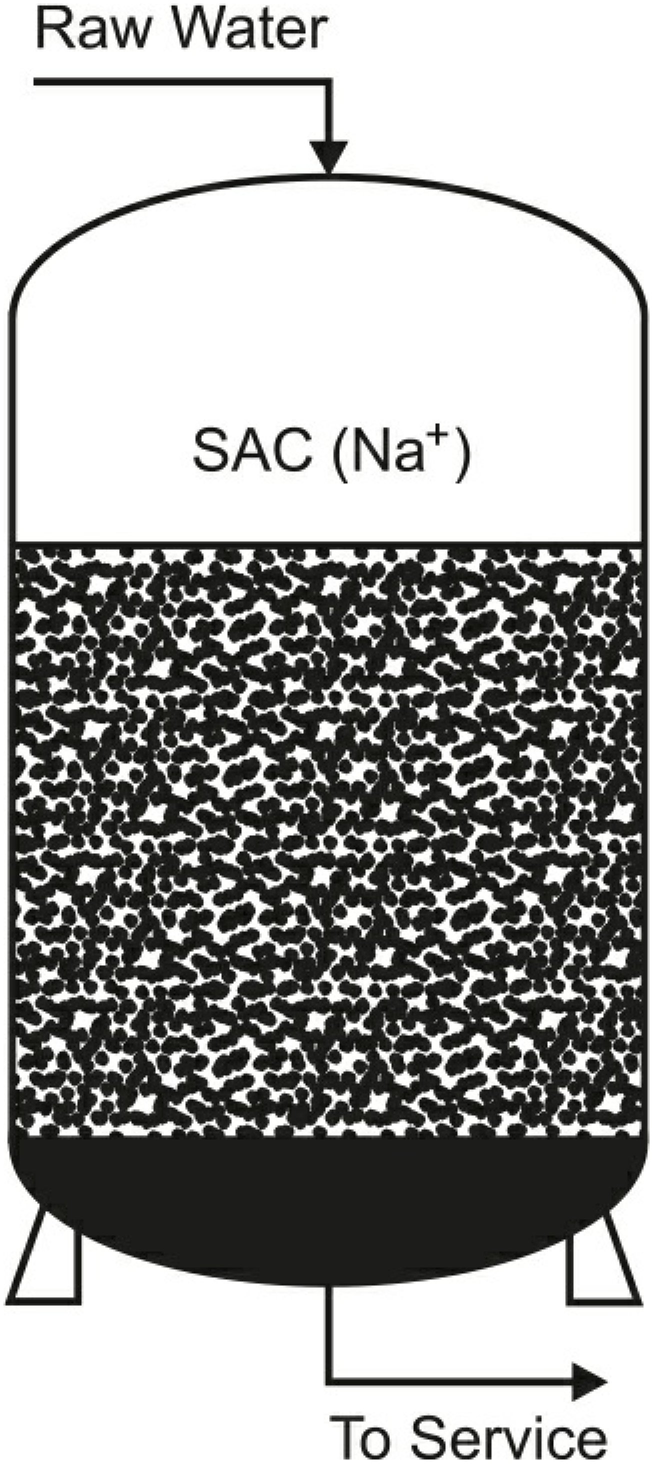
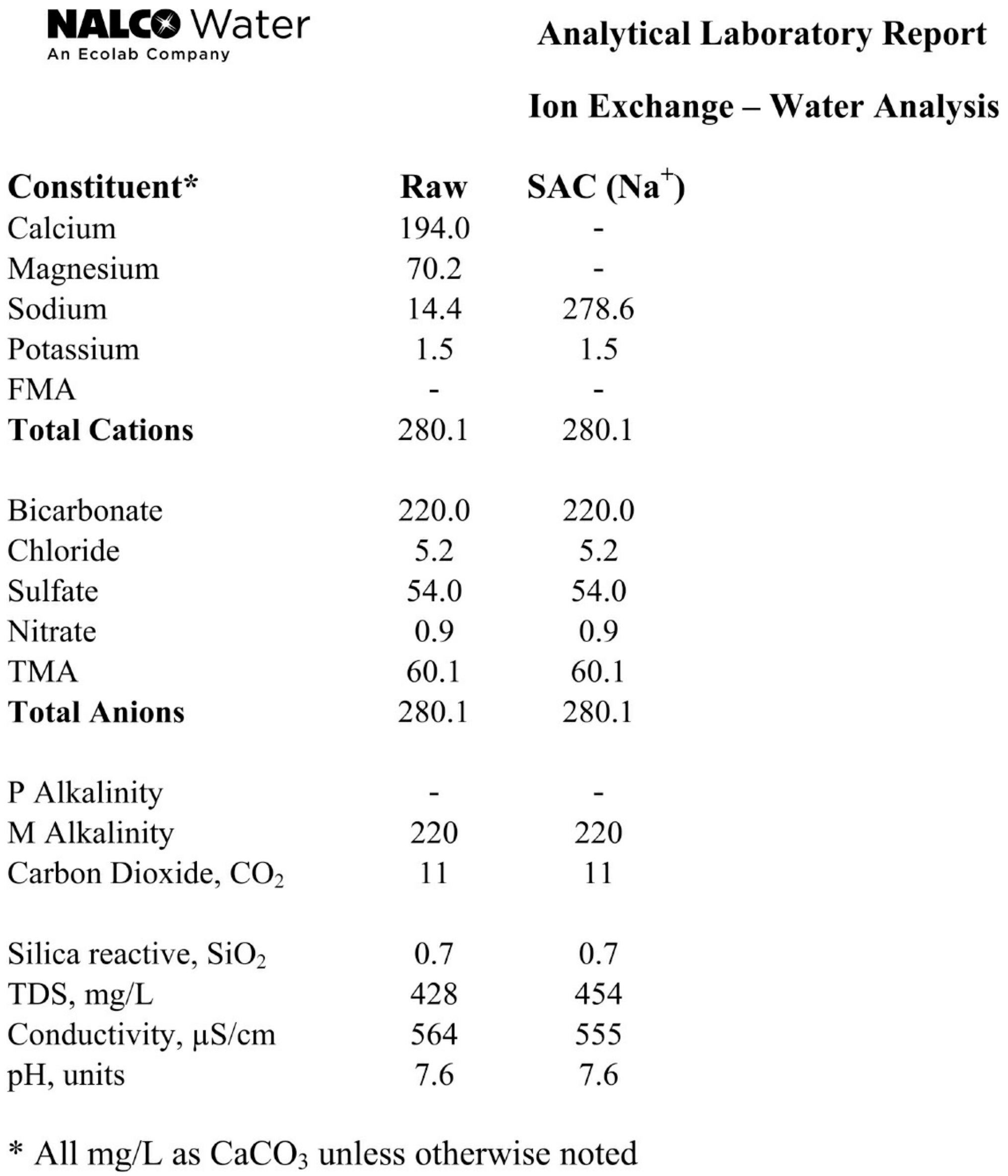


FIGURE 7.45 Typical softener arrangement.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**SAC (Na^+)**
Calcium	194.0	-
Magnesium	70.2	-
Sodium	14.4	278.6
Potassium	1.5	1.5
FMA	-	-
Total Cations	280.1	280.1
Bicarbonate	220.0	220.0
Chloride	5.2	5.2
Sulfate	54.0	54.0
Nitrate	0.9	0.9
TMA	60.1	60.1
Total Anions	280.1	280.1
P Alkalinity	-	-
M Alkalinity	220	220
Carbon Dioxide, CO_2	11	11
Silica reactive, SiO_2	0.7	0.7
TDS, mg/L	428	454
Conductivity, μS/cm	564	555
pH, units	7.6	7.6

* All mg/L as $CaCO_3$ unless otherwise noted

FIGURE 7.46 Example water analyses for SAC (Na^+) softener.

Dealkalizing

Alkalinity in boiler feedwater imposes limits on the number of times bulk boiler water can be concentrated before carryover is caused by foaming and priming. In addition, breakdown of alkalinity in the boiler releases free carbon dioxide that when redissolved in steam condensate forms carbonic acid, which is the cause of extensive return line corrosion. Accordingly, ion exchange systems that remove alkalinity are frequently used to pretreat boiler makeup water, even though boiler pressure does not dictate use of demineralization. Systems commonly used are:

- Chloride anion dealkalization—SBA (Cl^-)
- Weak acid dealkalization—WAC (H^+)
- Layered bed dealkalization—WAC (H^+)/SAC (Na^+)
- Split stream softening/dealkalization—SAC (H^+)/SAC (Na^+)

Chloride Anion Dealkalization

This process is most often used in institutional and light industrial steam plants. Using a Type II SBA resin in chloride form is often seen as more desirable in plants that are not accustomed to handling large volumes of hazardous chemicals such as acids and caustics.

Anion influent must be completely softened to ensure hardness is not precipitated in the anion resin, and sodium chloride used for regeneration must be high purity with minimal hardness content.

While this process exchanges chloride for bicarbonate, carbonate, nitrate, phosphate, and sulfate, it does not exchange for silica. As such, it is unsuitable for use if downstream equipment has silica restrictions. This process does not reduce conductivity of treated effluent, and boiler blowdown is usually not reduced. Figure 7.47 illustrates this type of system. Figure 7.48 shows a typical water analysis.

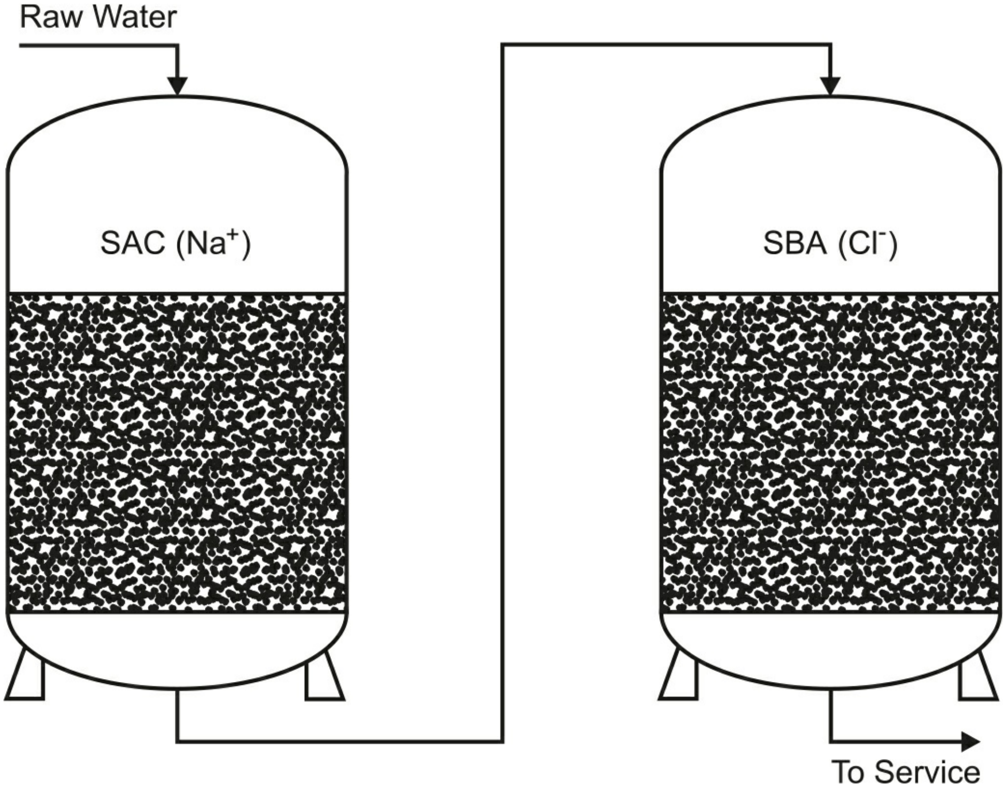
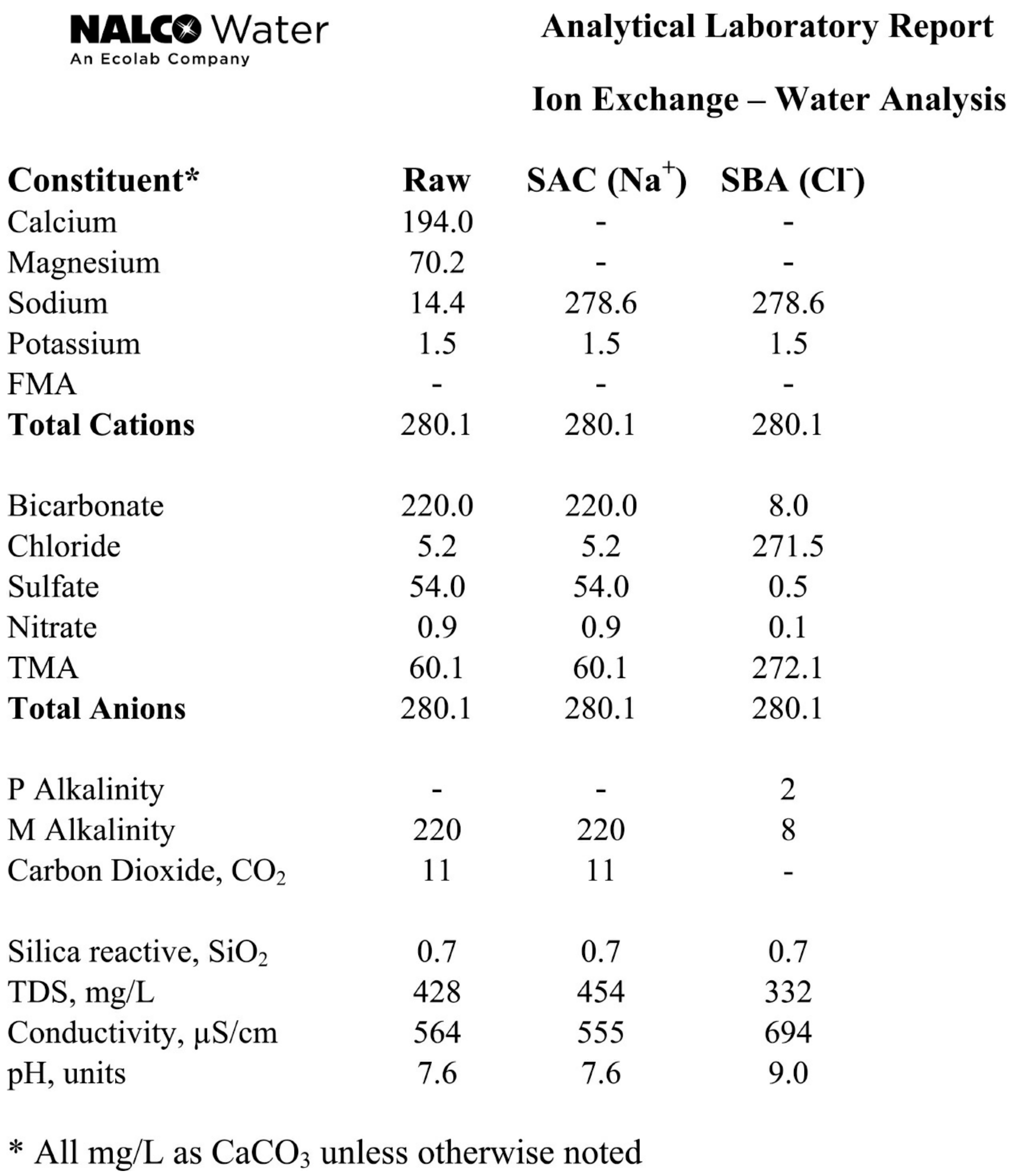


FIGURE 7.47 Typical chloride dealkalizer arrangement.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**SAC (Na$^+$)**	**SBA (Cl$^-$)**
Calcium	194.0	-	-
Magnesium	70.2	-	-
Sodium	14.4	278.6	278.6
Potassium	1.5	1.5	1.5
FMA	-	-	-
Total Cations	280.1	280.1	280.1
Bicarbonate	220.0	220.0	8.0
Chloride	5.2	5.2	271.5
Sulfate	54.0	54.0	0.5
Nitrate	0.9	0.9	0.1
TMA	60.1	60.1	272.1
Total Anions	280.1	280.1	280.1
P Alkalinity	-	-	2
M Alkalinity	220	220	8
Carbon Dioxide, CO_2	11	11	-
Silica reactive, SiO_2	0.7	0.7	0.7
TDS, mg/L	428	454	332
Conductivity, µS/cm	564	555	694
pH, units	7.6	7.6	9.0

* All mg/L as $CaCO_3$ unless otherwise noted

FIGURE 7.48 Example water analyses for chloride dealkalizer.

Weak Acid Dealkalization

When used for dealkalization, WAC exchange and regeneration reactions occur at essentially stoichiometric levels. Since the process removes only hardness associated with alkalinity, some hardness remains in the effluent, and this must be removed by a SAC (Na$^+$) unit installed downstream. All ion exchange processes that use (H$^+$) resins, either SAC or WAC, are regenerated with strong mineral acids that destroy alkalinity, releasing free carbon dioxide, which is generally removed by forced draft atmospheric decarbonation or another process such as vacuum deaeration or gas transfer membranes.

This process reduces TDS and specific conductance of treated water. After reduction of carbon dioxide to 5 to 10 mg/L with a decarbonator (Fig. 7.49), the pH is about 6.0, and the effluent is nonscale forming. The pH is usually adjusted to 8.3 to 10.2 by feeding caustic (NaOH) on a controlled basis to the sump of the decarbonator. Figure 7.50 illustrates this type of system. Figure 7.51 shows a typical water analysis for this type of unit.

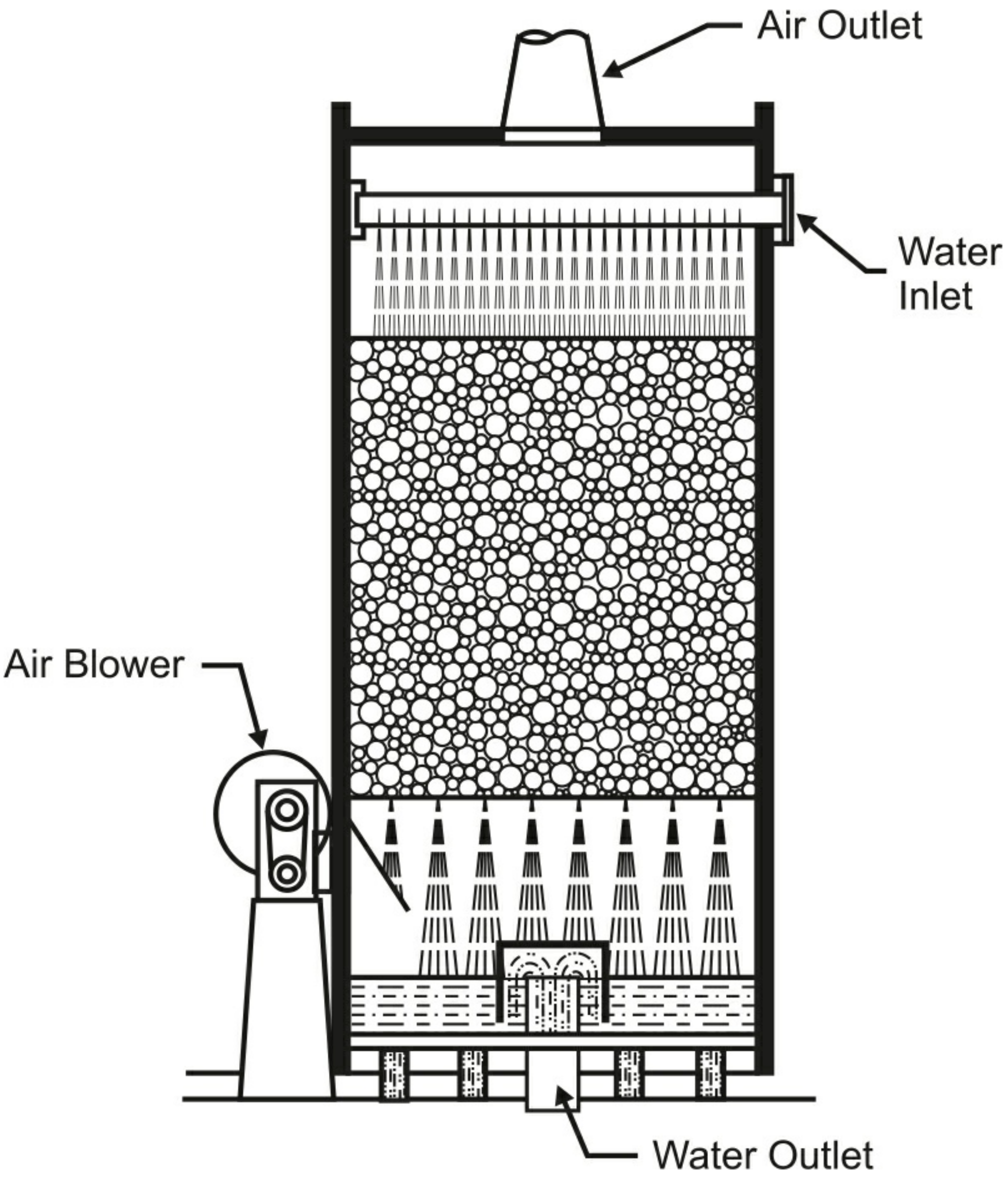


FIGURE 7.49 Typical decarbonator or degassifier.

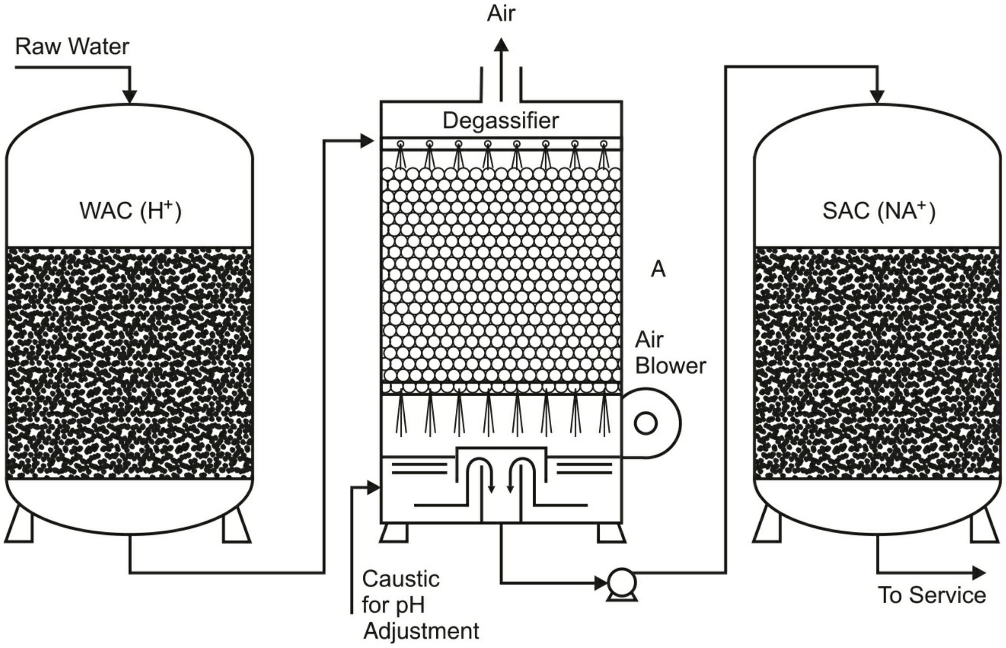
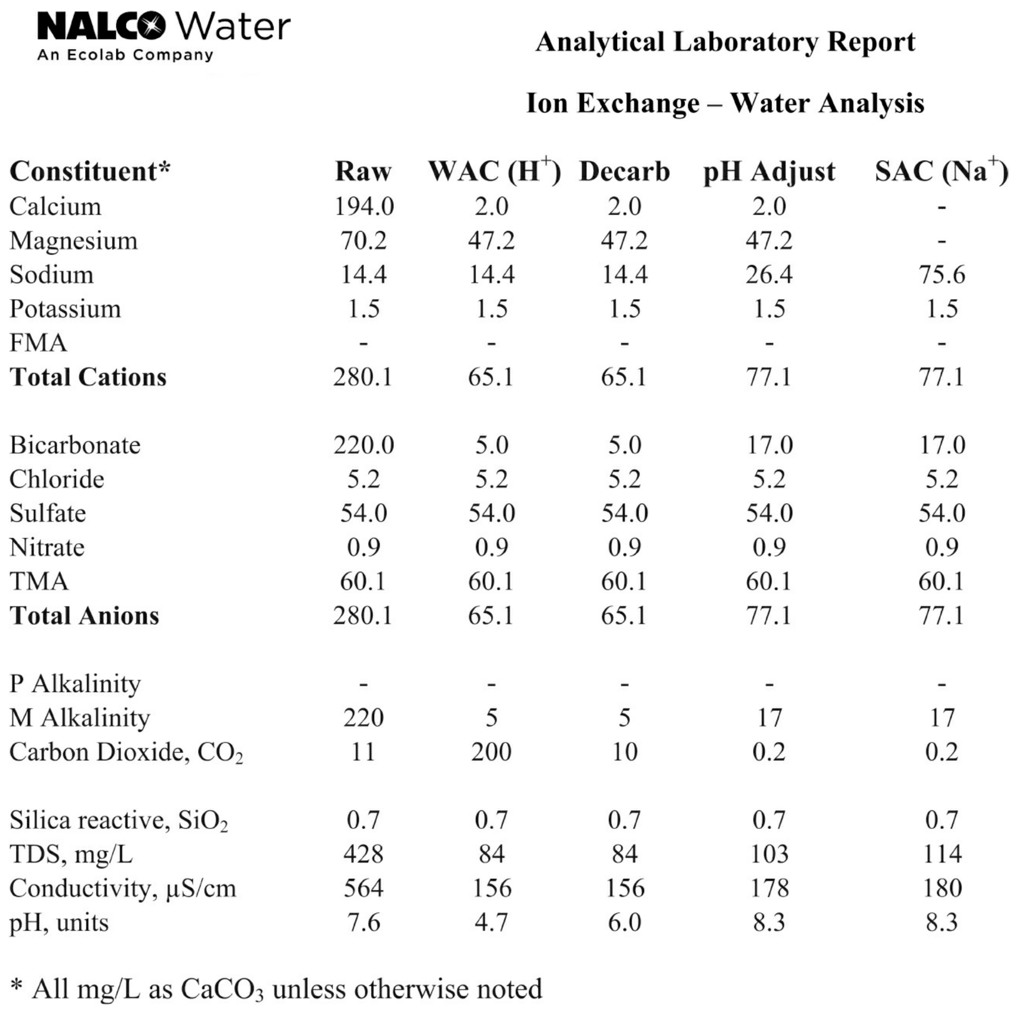


FIGURE 7.50 WAC (H^+) with caustic adjustment.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**WAC (H^+)**	**Decarb**	**pH Adjust**	**SAC (Na^+)**
Calcium	194.0	2.0	2.0	2.0	-
Magnesium	70.2	47.2	47.2	47.2	-
Sodium	14.4	14.4	14.4	26.4	75.6
Potassium	1.5	1.5	1.5	1.5	1.5
FMA	-	-	-	-	-
Total Cations	280.1	65.1	65.1	77.1	77.1
Bicarbonate	220.0	5.0	5.0	17.0	17.0
Chloride	5.2	5.2	5.2	5.2	5.2
Sulfate	54.0	54.0	54.0	54.0	54.0
Nitrate	0.9	0.9	0.9	0.9	0.9
TMA	60.1	60.1	60.1	60.1	60.1
Total Anions	280.1	65.1	65.1	77.1	77.1
P Alkalinity	-	-	-	-	-
M Alkalinity	220	5	5	17	17
Carbon Dioxide, CO_2	11	200	10	0.2	0.2
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	0.7
TDS, mg/L	428	84	84	103	114
Conductivity, µS/cm	564	156	156	178	180
pH, units	7.6	4.7	6.0	8.3	8.3

* All mg/L as $CaCO_3$ unless otherwise noted

FIGURE 7.51 Example water analyses for WAC dealkalization with caustic adjustment.

Layered Bed Dealkalization

A less common type of WAC dealkalizer is a layered unit with WAC (H^+) resin installed on top of SAC (Na^+) resin, so that alkalinity removal and complete softening are accomplished in one vessel. Chemical reactions are the same as previously discussed for both resins. Success of this process depends greatly on the two resins remaining in discrete layers.

Such units are first regenerated with a starvation or small excess acid dosage that is passed downflow through both resins. Hardness ions regenerated from WAC resin contact the SAC resin layer, fully exhausting that layer. A high regeneration dosage of sodium chloride brine is then passed downflow through both resins regenerating only the SAC layer in the bottom of the unit. Figure 7.52 illustrates this type of system. Figure 7.53 shows a typical water analysis for this type of unit.

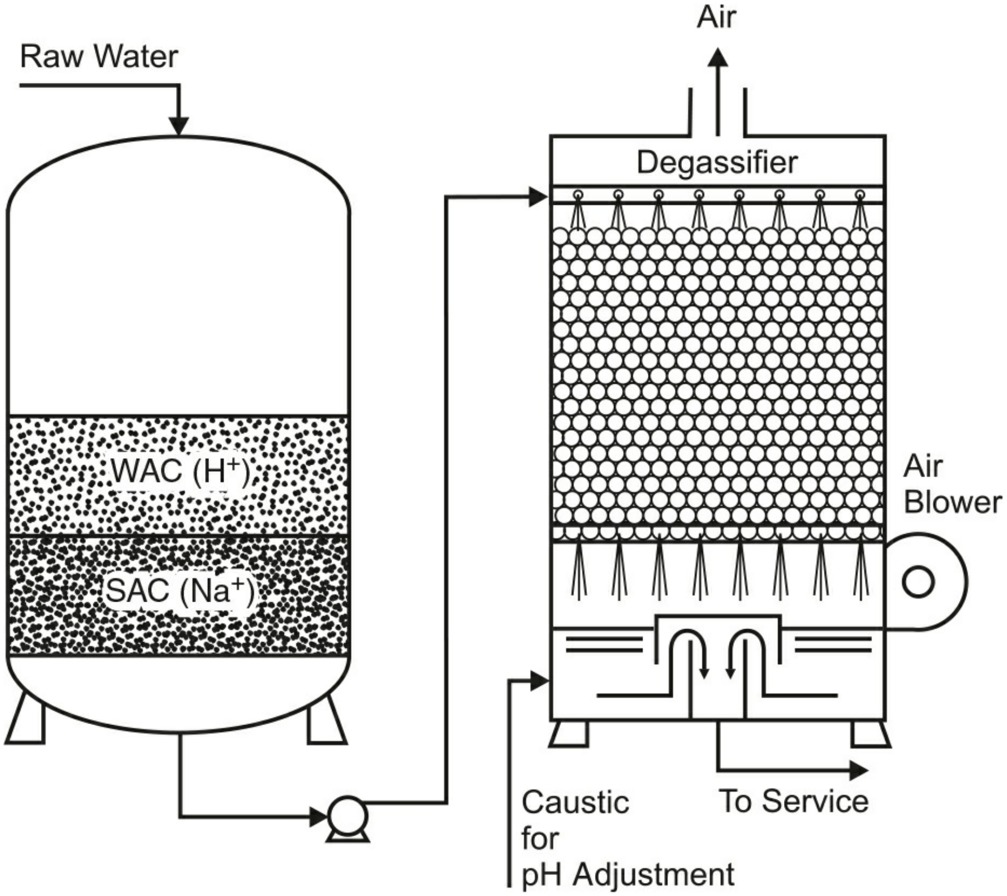
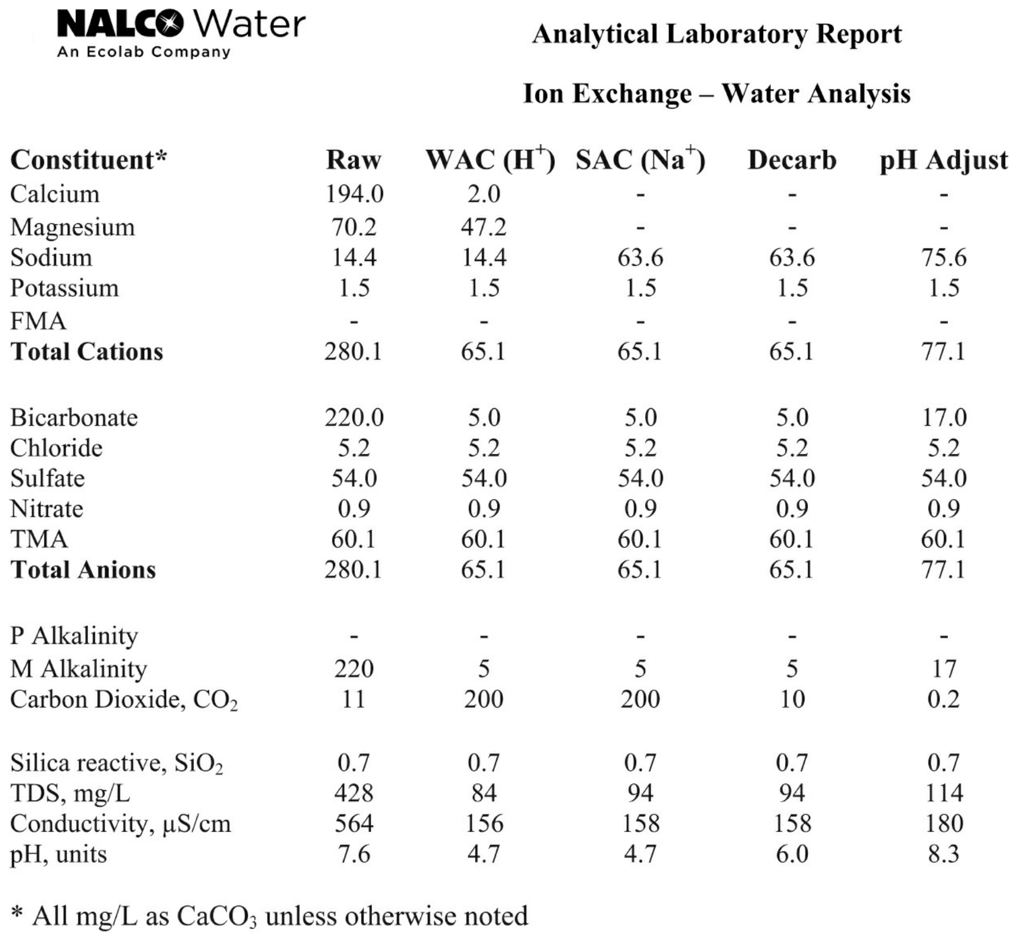


FIGURE 7.52 Layered bed dealkalization arrangement.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**WAC (H^+)**	**SAC (Na^+)**	**Decarb**	**pH Adjust**
Calcium	194.0	2.0	-	-	-
Magnesium	70.2	47.2	-	-	-
Sodium	14.4	14.4	63.6	63.6	75.6
Potassium	1.5	1.5	1.5	1.5	1.5
FMA	-	-	-	-	-
Total Cations	280.1	65.1	65.1	65.1	77.1
Bicarbonate	220.0	5.0	5.0	5.0	17.0
Chloride	5.2	5.2	5.2	5.2	5.2
Sulfate	54.0	54.0	54.0	54.0	54.0
Nitrate	0.9	0.9	0.9	0.9	0.9
TMA	60.1	60.1	60.1	60.1	60.1
Total Anions	280.1	65.1	65.1	65.1	77.1
P Alkalinity	-	-	-	-	-
M Alkalinity	220	5	5	5	17
Carbon Dioxide, CO_2	11	200	200	10	0.2
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	0.7
TDS, mg/L	428	84	94	94	114
Conductivity, µS/cm	564	156	158	158	180
pH, units	7.6	4.7	4.7	6.0	8.3

* All mg/L as $CaCO_3$ unless otherwise noted

FIGURE 7.53 Example water analyses for layered bed dealkalization.

Split Stream Softening/Dealkalization

Split stream dealkalization makes use of both a SAC (H^+) and a SAC (Na^+) unit operating in parallel and then blending the effluents to obtain desired alkalinity. A calculable percentage of the full treatment flow is softened by SAC (Na^+) units, with the effluent containing full M alkalinity. This is blended with the remaining percentage of flow treated in SAC (H^+) units with the effluent containing FMA but essentially free of calcium and magnesium hardness. The blended water M alkalinity in the SAC (Na^+) effluent is reduced to a chosen residual by FMA in the SAC (H^+) effluent, releasing carbon dioxide (see Fig. 7.54).

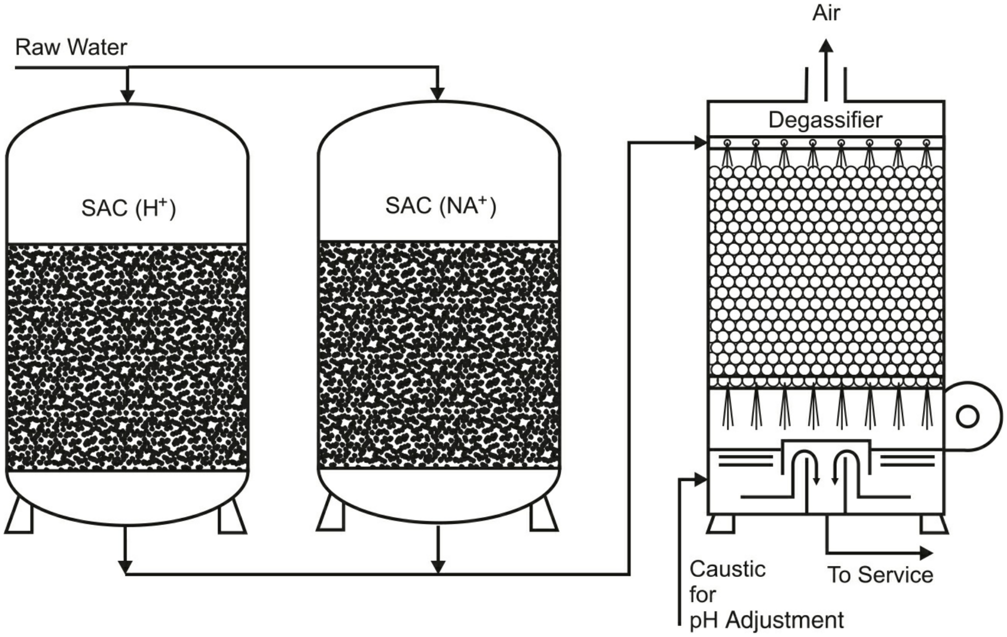


FIGURE 7.54 Split stream softening and dealkalization.

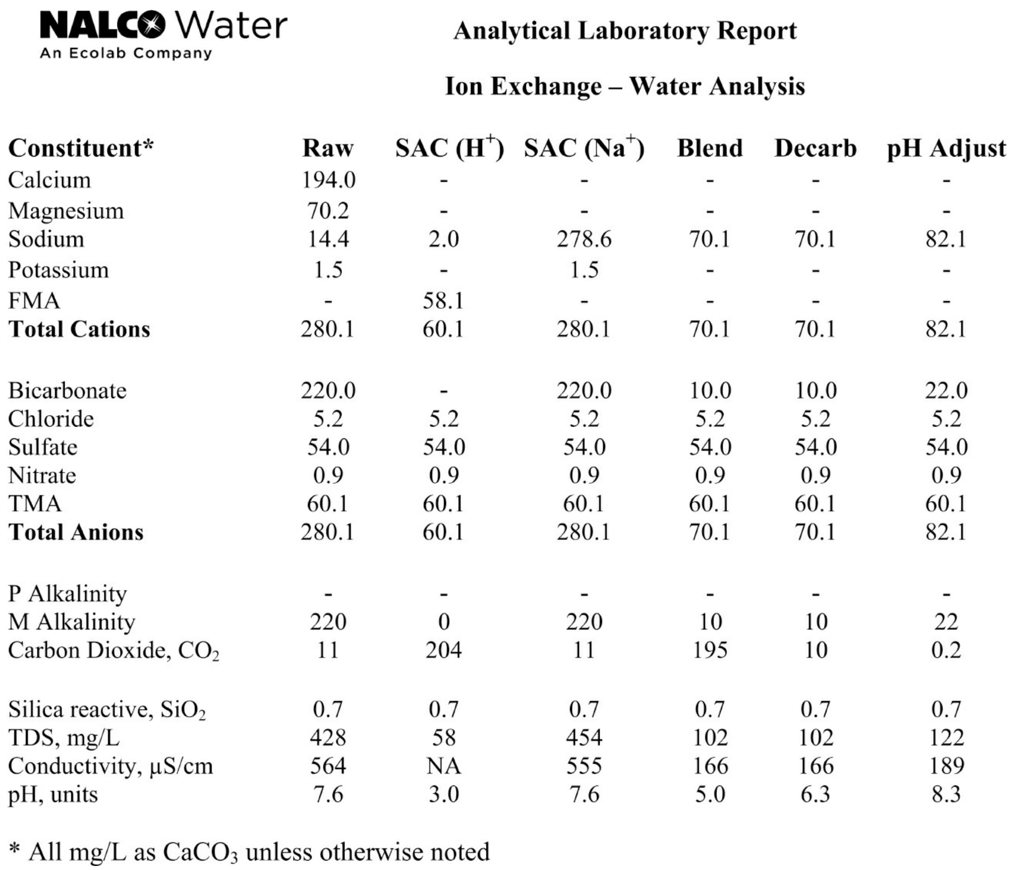
Equation (7.39) is used to calculate the ratio of SAC (H^+) flow to SAC (Na^+) flow.

$$\% \text{ SAC } (H^+) = \frac{100(\text{Alk}_i - \text{Alk}_f)}{\text{Alk}_i + \text{FMA}} \tag{7.39}$$

where % SAC (H^+) = SAC (H^+) flow rate, percent of total flow rate
Alk_i = influent water alkalinity, mg/L as $CaCO_3$
Alk_f = desired alkalinity after blending, mg/L as $CaCO_3$
FMA = free mineral acidity in SAC (H^+) effluent, mg/L as $CaCO_3$

With the split stream process and blending of SAC (H^+) and SAC (Na^+) effluents, sodium leakage is of no consequence. Success of this form of dealkalization is largely dependent on accurate response of the blending system for flow measurement and ratio control. Simple flow control may be inaccurate if the total blended system flow rate varies considerably. For this reason and to ensure that water containing FMA is not discharged to boiler feedwater, it is strongly recommended that positive M alkalinity be maintained at more than 10 mg/L as $CaCO_3$. Following blending of the two streams, free carbon dioxide must be removed to elevate the pH.

This process reduces TDS and specific conductance of treated water. After reduction of carbon dioxide to 5 to 10 mg/L, the decarbonator effluent pH is about 6.3 and is nonscale forming. It is usual to adjust the pH to 8.3 to 10.2 by feeding caustic on a controlled basis to the clearwell of the degassifier. Figure 7.55 shows a typical water analysis from a split stream unit.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**SAC (H^+)**	**SAC (Na^+)**	**Blend**	**Decarb**	**pH Adjust**
Calcium	194.0	-	-	-	-	-
Magnesium	70.2	-	-	-	-	-
Sodium	14.4	2.0	278.6	70.1	70.1	82.1
Potassium	1.5	-	1.5	-	-	-
FMA	-	58.1	-	-	-	-
Total Cations	280.1	60.1	280.1	70.1	70.1	82.1
Bicarbonate	220.0	-	220.0	10.0	10.0	22.0
Chloride	5.2	5.2	5.2	5.2	5.2	5.2
Sulfate	54.0	54.0	54.0	54.0	54.0	54.0
Nitrate	0.9	0.9	0.9	0.9	0.9	0.9
TMA	60.1	60.1	60.1	60.1	60.1	60.1
Total Anions	280.1	60.1	280.1	70.1	70.1	82.1
P Alkalinity	-	-	-	-	-	-
M Alkalinity	220	0	220	10	10	22
Carbon Dioxide, CO_2	11	204	11	195	10	0.2
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	0.7	0.7
TDS, mg/L	428	58	454	102	102	122
Conductivity, µS/cm	564	NA	555	166	166	189
pH, units	7.6	3.0	7.6	5.0	6.3	8.3

* All mg/L as $CaCO_3$ unless otherwise noted

FIGURE 7.55 Example water analysis for split stream softening/dealkalization.

Primary Demineralizing

Demineralization is the process of removing virtually all dissolved solids from water and producing essentially pure water. Demineralized water is used for a variety of purposes:

- Boiler makeup for industrial and utility units of many types with a broad range of operating pressures, even into the supercritical range
- Process water used in a wide variety of diverse manufacturing operations that can include integration of water into a manufactured

product

- High-purity rinse water used to eliminate performance defects, such as in the manufacture of computer chips, where water must have specific conductance less than 0.055 µS/cm or a resistance greater than 18.2 MΩ

Ion exchange units used for demineralization must include both cation and anion exchange processes. Just about any configuration of equipment is possible and is usually determined by raw water characteristics, capital expenditure, and regeneration costs. Following are several common designs.

Conventional Twin-Bed Demineralization

The two component pieces of this type of demineralization are a SAC (H^+) unit that removes all cations followed by a SBA (OH^-) unit that removes all anions. Resulting service water is very close to neutral pH with extremely low conductivity. Although not necessary, there is usually a decarbonator between the cation and anion units. This reduces carbon dioxide loading on the anion bed, and thus, a corresponding reduction in resin and regenerant for the anion unit is possible. In low alkalinity raw waters, a decarbonator is generally omitted, as there is little benefit to offset the capital cost. Anion and cation units are matched so that each exhausts at approximately the same time. This type of sizing allows for a “train” or “set” of exchangers to go into and out of service together. Figure 7.56 illustrates this type of system. Figure 7.57 shows a typical water analysis for this type of ion exchange unit.

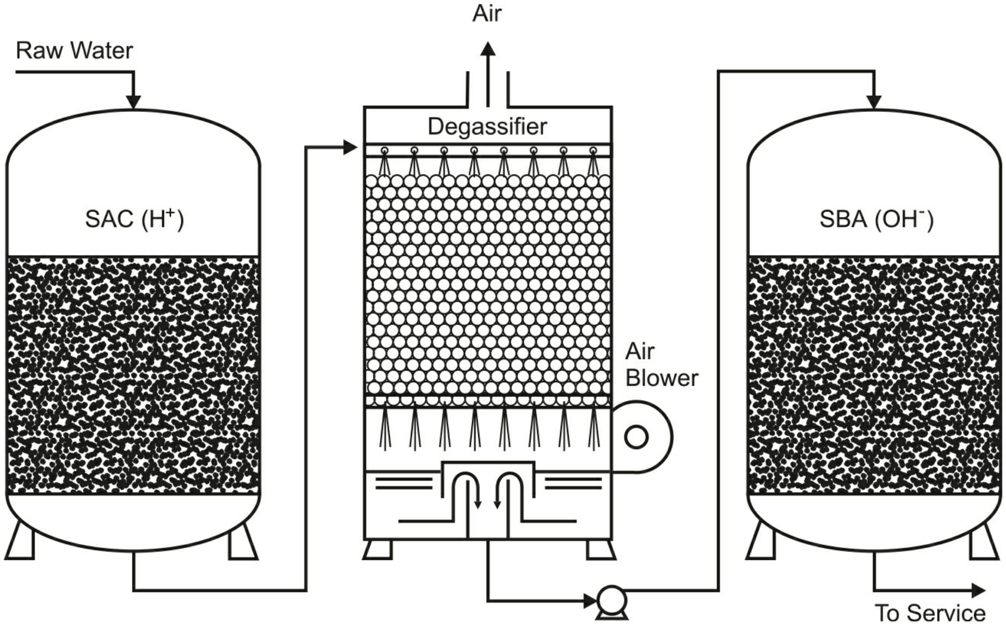
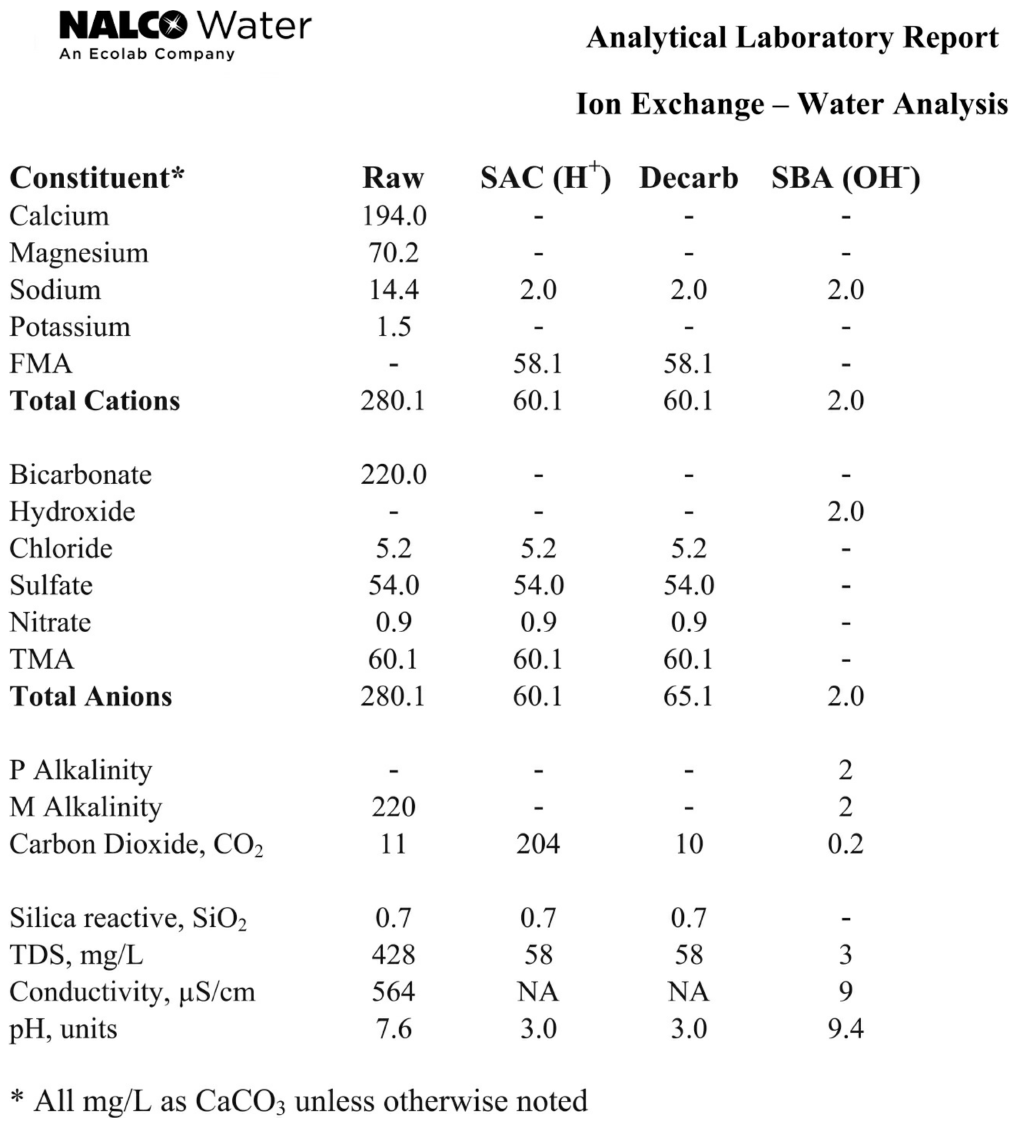


FIGURE 7.56 Twin-bed demineralization with decarbonation.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**SAC (H^+)**	**Decarb**	**SBA (OH^-)**
Calcium	194.0	-	-	-
Magnesium	70.2	-	-	-
Sodium	14.4	2.0	2.0	2.0
Potassium	1.5	-	-	-
FMA	-	58.1	58.1	-
Total Cations	280.1	60.1	60.1	2.0
Bicarbonate	220.0	-	-	-
Hydroxide	-	-	-	2.0
Chloride	5.2	5.2	5.2	-
Sulfate	54.0	54.0	54.0	-
Nitrate	0.9	0.9	0.9	-
TMA	60.1	60.1	60.1	-
Total Anions	280.1	60.1	65.1	2.0
P Alkalinity	-	-	-	2
M Alkalinity	220	-	-	2
Carbon Dioxide, CO_2	11	204	10	0.2
Silica reactive, SiO_2	0.7	0.7	0.7	-
TDS, mg/L	428	58	58	3
Conductivity, µS/cm	564	NA	NA	9
pH, units	7.6	3.0	3.0	9.4

* All mg/L as $CaCO_3$ unless otherwise noted

FIGURE 7.57 Example water analyses for SAC (H^+)-decarbonator-SBA (OH^-).

Twin-Bed Demineralization with WAC (H+)

If raw water contains very high hardness and alkalinity, utilizing a WAC (H^+) unit in front of the SAC (H^+) unit helps reduce load to the strong acid unit. Since the WAC (H^+) unit removes both alkalinity and associated hardness, the SAC (H^+) unit is not taxed with these ions and is thus better equipped to polish the WAC (H^+) effluent. Decarbonation is necessary before effluent passes to the SBA (OH^-) unit. Figure 7.58 illustrates this type of system. Figure 7.59 shows a typical water analysis for this type of ion exchange unit.

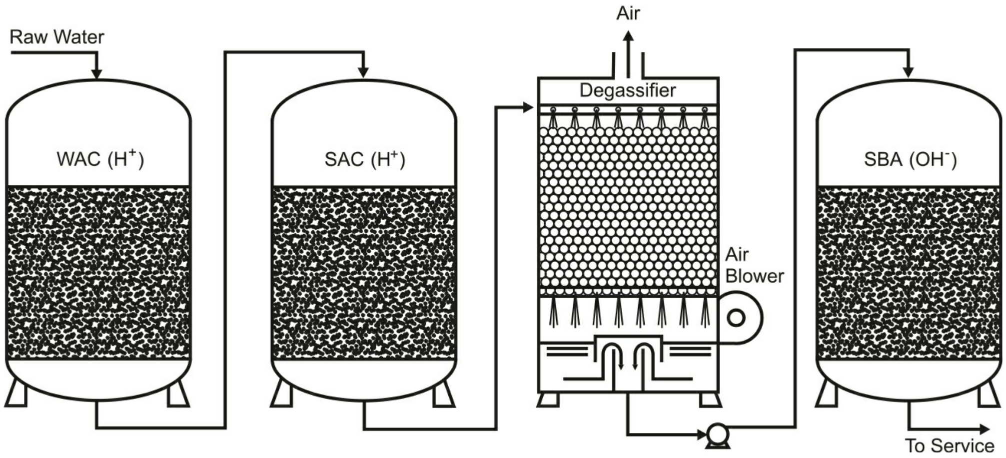

FIGURE 7.58 Twin-bed demineralization with a WAC (H^+) for high hardness and alkalinity waters.

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Ion Exchange – Water Analysis

Constituent*	**Raw**	**WAC (H^+)**	**SAC (H^+)**	**Decarb**	**SBA (OH^-)**
Calcium	194.0	2.0	-	-	-
Magnesium	70.2	47.2	-	-	-
Sodium	14.4	14.4	2.0	2.0	2.0
Potassium	1.5	1.5	-	-	-
FMA	-	-	58.1	58.1	-
Total Cations	280.1	65.1	60.1	60.1	2.0
Bicarbonate	220.0	5.0	-	-	-
Hydroxide	-	-	-	-	2.0
Chloride	5.2	5.2	5.2	5.2	-
Sulfate	54.0	54.0	54.0	54.0	-
Nitrate	0.9	0.9	0.9	0.9	-
TMA	60.1	60.1	60.1	60.1	-
Total Anions	280.1	65.1	60.1	60.1	2.0
P Alkalinity	-	-	-	-	2
M Alkalinity	220	5	-	-	2
Carbon Dioxide, CO_2	11	200	204	10	-
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	-
TDS, mg/L	428	84	58	58	3
Conductivity, µS/cm	564	156	NA	NA	9
pH, units	7.6	4.7	3.0	3.0	9.4

* All mg/L as $CaCO_3$ unless otherwise noted

FIGURE 7.59 Example water analyses for WAC (H^+)-SAC (H^+)-decarbonator-SBA (OH^-).

Twin-Bed Demineralization with WBA (OH-)

Many organics, but not all, detected by methods such as total organic carbon (TOC) in raw surface waters are a problem in demineralizers. Naturally occurring fulvic and humic acids present the greatest threat to continued production of high-purity demineralized water. These are present as the product of decayed vegetation (leaves, grasses, moss, etc.) with which surface waters come into contact. In many cases, these organics can foul SBA resin. Color in water is a good indication that organic fouling potential exists, but color bodies may be absent while organic acid concentrations are sufficient to cause severe fouling of SBA (OH^-) resins. This is particularly true in low TDS waters such as encountered in mountainous coastal regions.

Organic acids poison, or foul, SBA (OH^-) resins but do not cause the same effect when systems use WBA (OH^-) resin. Organic acids are absorbed into the resin skeleton of SBA (OH^-) and block ion exchange sites. This fouling is usually only partially reversible and results in shortened service throughputs, higher operating costs for regeneration, high labor and chemical costs for resin cleaning, high resin replacement costs, lower treated effluent purity, and high wastewater generation.

One approach to remove these organics is to trap them with a WBA unit. The advantage of this approach is that effluent water for this unit does not affect exchange capacity of SBA units that follow. Organics are caught on the WBA and are not passed through to the SBA. Figure 7.60 illustrates this type of system. Figure 7.61 shows a typical water analysis for this type of ion exchange unit.

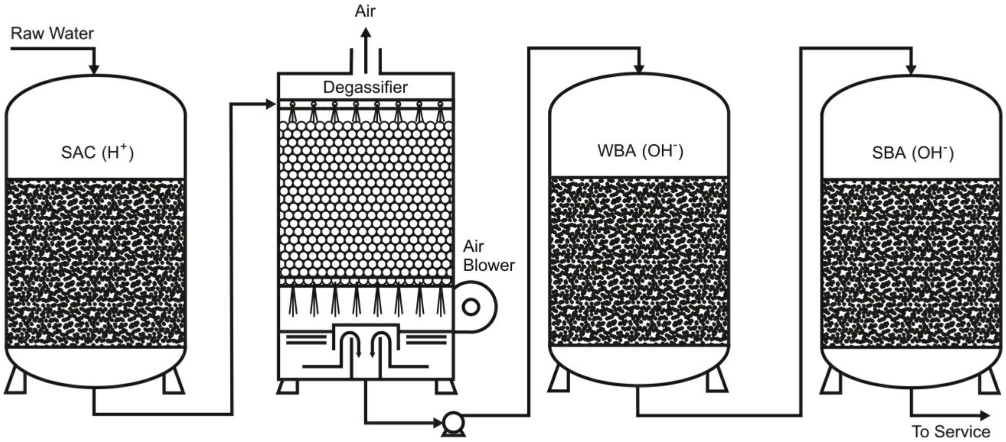
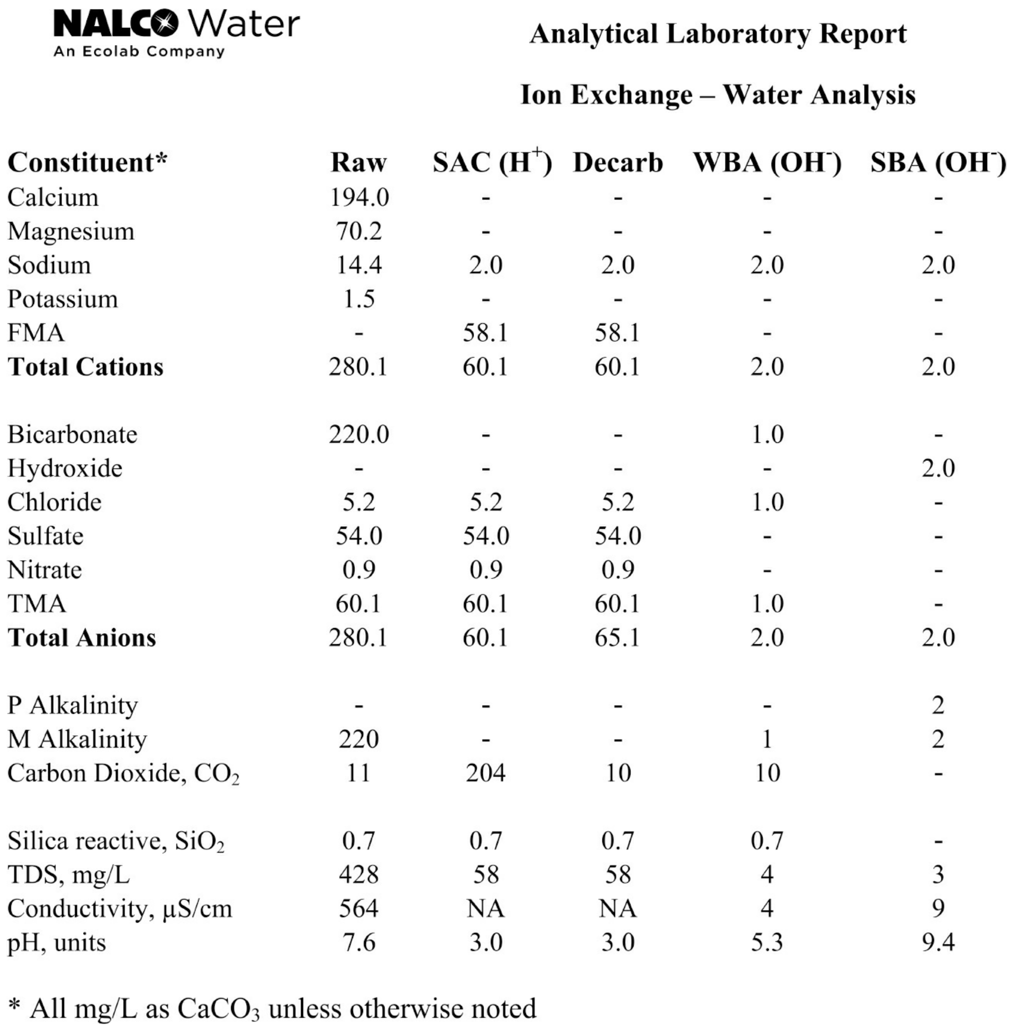


FIGURE 7.60 Organic trap using WBA (OH^-) in a twin bed train.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**SAC (H^+)**	**Decarb**	**WBA (OH^-)**	**SBA (OH^-)**
Calcium	194.0	-	-	-	-
Magnesium	70.2	-	-	-	-
Sodium	14.4	2.0	2.0	2.0	2.0
Potassium	1.5	-	-	-	-
FMA	-	58.1	58.1	-	-
Total Cations	280.1	60.1	60.1	2.0	2.0
Bicarbonate	220.0	-	-	1.0	-
Hydroxide	-	-	-	-	2.0
Chloride	5.2	5.2	5.2	1.0	-
Sulfate	54.0	54.0	54.0	-	-
Nitrate	0.9	0.9	0.9	-	-
TMA	60.1	60.1	60.1	1.0	-
Total Anions	280.1	60.1	65.1	2.0	2.0
P Alkalinity	-	-	-	-	2
M Alkalinity	220	-	-	1	2
Carbon Dioxide, CO_2	11	204	10	10	-
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	-
TDS, mg/L	428	58	58	4	3
Conductivity, µS/cm	564	NA	NA	4	9
pH, units	7.6	3.0	3.0	5.3	9.4

* All mg/L as $CaCO_3$ unless otherwise noted

FIGURE 7.61 Example water analyses for SAC (H^+)-decarbonator-WBA (OH^-)-SBA (OH^-).

Mixed-Bed Demineralizing

Mixed-bed demineralizers contain two resins, SAC (H^+) and SBA (OH^-), which are homogeneously mixed when in service. When exhausted, resin components are separated by backwashing. Due to density difference between the two resins, SAC (H^+) resin remains on the bottom while SBA (OH^-) resin rests on top. Each resin is regenerated separately with appropriate regenerant. After regeneration and rinsing, resins are remixed using air injected through the underdrain. A final rinse returns the unit to service producing very high-purity effluent.

Effectiveness of separation and remixing are crucial to performance in these units. Resin separation is enhanced by the use of resins with special properties such as UPS and particle density. Another option is the use of a narrow inert resin layer that rests between the two active resins after separation. Air mixing is optimized by reducing the head of water over the resin bed to a desired, constant level for all regenerations.

These units operate either as primary treatment when raw water has very low TDS or more commonly as a polishing unit after primary demineralization. Experience shows that only polishing mixed bed demineralizers are consistently capable of producing the purity of water required for microchip manufacturing, provided proper pretreatment is included upstream.

Chemical reactions are the same as previously described for SAC (H^+) and SBA (OH^-) resins in separate units but with very important differences. In separate beds, the SAC (H^+) reaction creates FMA from sulfate, chloride, phosphate, and nitrate ions in the water. These strong mineral acids, even at low concentration, are sufficient to create an acidic environment that elutes sodium ions (leakage) into the effluent. When combined with free hydroxide from the SBA (OH^-) forming NaOH, conductivity of the final effluent is increased.

In a mixed bed, mineral acid created by a SAC (H^+) bead is immediately converted to water by the adjacent SBA (OH^-) bead, maintaining a neutral environment around the bead. The acid environment is eliminated, and sodium leakage is reduced. In addition, in the favorable kinetics of a mixed bed, the SBA (OH^-) leakage is chloride not hydroxide. 1 mg/L of sodium chloride, expressed as $CaCO_3$, contributes 2.5 µS/cm specific conductance to the effluent. As a properly designed and operated mixed bed, even in primary service, can produce water containing 0.2 to 0.5 mg/L sodium as $CaCO_3$, effluent specific conductance may be 0.5 to 1.25 µS/cm. In polishing service, with adequately pretreated influent, mixed beds can produce effluent containing less than 0.022 mg/L sodium and specific conductance below 0.055 µS/cm (Fig. 7.62).

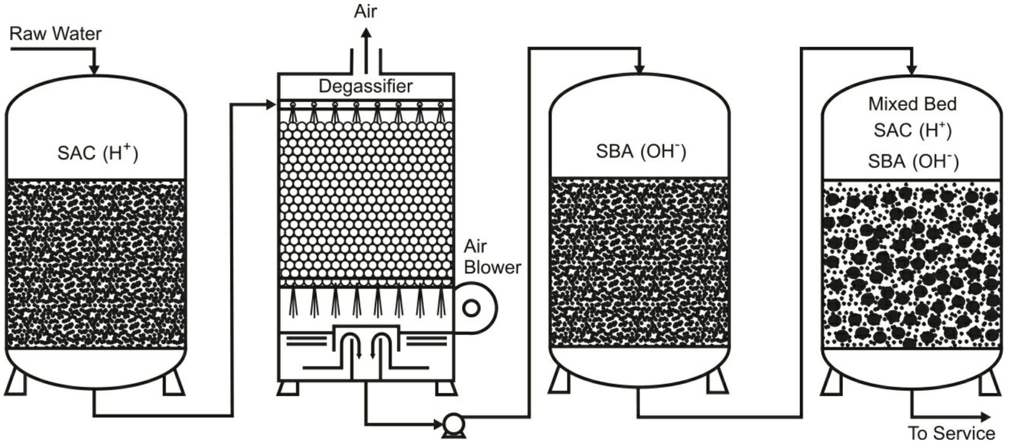


FIGURE 7.62 Mixed-bed polishing demineralizer.

Packed Bed Units

This type of unit operates with the vessel virtually full, or packed, with working resin as opposed to the nearly 50% of the internal vessel volume being open “freeboard” space as it is in a conventionally designed unit. Normally, a layer of inert resin is also used, and the combined bed is sandwiched between upper and lower collector/distributor systems, called nozzle plates, complete with strainers. Total depth of working resin in its maximum swollen state plus inert resin is calculated to leave about 2 inches (51 mm) freeboard. In cases where actual resin swelling does not occur to the extent predicted by the resin manufacturer, excess freeboard and resin fluidization can yield off-specification water.

The concept of such designs is to reduce wastewater generation, and a major feature is to eliminate backwashing and to save rinse water by recirculating within the system. In most of these systems, resin cannot be backwashed in situ and must be transferred to an external tank when backwashing is necessary. In order to achieve this goal, influent, service water, and regenerants must be extremely clean and free of particulates and microorganisms that can cause plugging or fouling and thus create a need to backwash.

Resins used are UPS, and regeneration is counter-current. There are multiple, competitive equipment designs available. Some are downflow service with upflow regeneration, and some are the opposite with upflow service and downflow regeneration.

Some systems are designed so that a single unit contains two distinctly separate resin chambers, each containing a different resin with thoroughfare regeneration of both using a common regenerant. Chamber separation may be a solid diaphragm, called a nozzle plate, through which are installed double ended strainer assemblies with a strainer in either chamber. The water and regenerant solutions pass from one chamber to another through these interconnecting strainers. Alternately, mechanical separation may be a flat panel of perforated alloy well screen (Fig. 7.63).

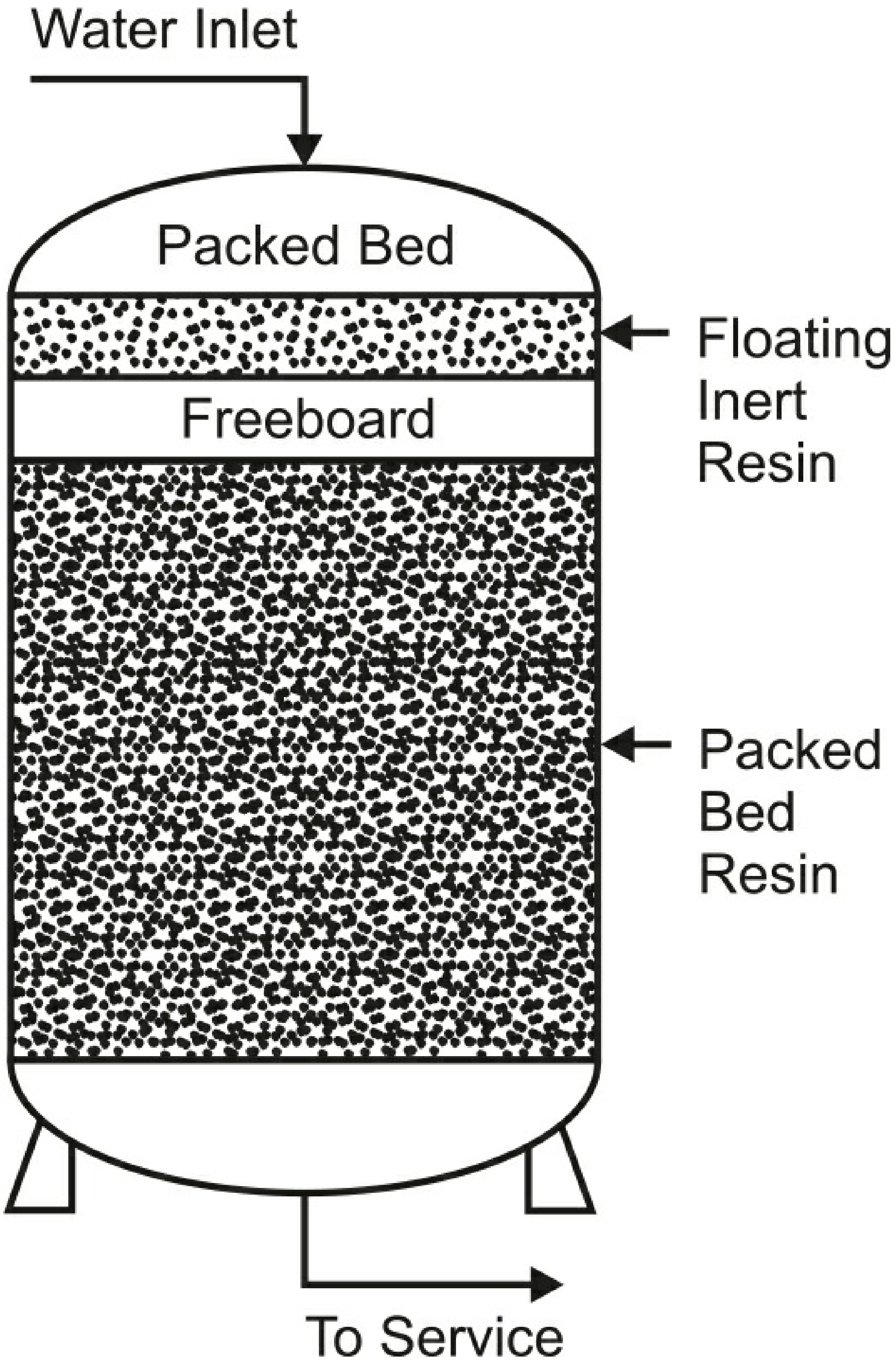


FIGURE 7.63 Typical packed bed arrangement.

Water Use Optimization Strategies

Many industrial plants are located where they are because of the ready access to large volumes of good quality water. Other plants simply tap into city or other municipal water sources. Either way the ion exchange processes in use in these plants are rarely especially larger water consumers. But even so these plants may still seek strategies to minimize water use as a starting point, and wastewater generation more specifically. There are typically two different approaches considered when looking to reduce water in the pretreatment plant:

1. System optimization
2. Water recovery

System Optimization

Regeneration optimization is typically the approach taken when trying to minimizing water utilization in the pretreatment systems. There are four areas where optimization and preventative maintenance can help minimize your water consumption:

1. Regeneration optimization
2. Throughput capacity
3. Regeneration versus throughput
4. Resin quality and quantity

Regeneration optimization is a balance between the amount of regenerant used per ft^3(L) of resin and the tolerable ionic leakage from the vessel. There is a sweet spot for each type of resin and regenerant that provides optimal regeneration. Too little regenerant yields poorer quality water and increased regenerations, too much regenerant starts to flattens the performance curve and doesn't provide the corresponding kgr/ft^3 (g/L) removal capacity. Optimizing the regenerant to provide long throughput capacity minimizes regeneration cycles and improves water quality

Monitoring throughput capacity is an excellent way of determining variability in service run lengths necessity increased regeneration cycles. Utilization of water meters to determine actual service run length is important. There are two comparisons to draw when evaluating service runs. The first is run length against historical run length, while the second is against theoretical or expected length. These comparisons will illuminate the performance of the ion exchange process and can indicate if there are issues that require attention.

Evaluating the amount of water utilized in the regeneration process against throughput capacity is a measure that can be utilized to determine excessive water usage in regeneration. Regeneration water should be in the 3 to 5% of throughput. If above this level, evaluation of the regeneration process will be necessary to determine where the excess water is being utilized.

Many plants do not put into practice a good resin management program. As such, when resin failure occurs, it can be a shock to the maintenance budget. Long before resin failure occurs however, there are indications of shortened throughput, increased regeneration cycles, ionic leakage and the like. All of which increase water utilization in the ion exchange plant. There are several key components in a resin management program. When taken together, they offer a clear picture of expected resin life, total operating cost, performance expectations, and cleaning cycles. Component pieces of a resin management program are: expected length of service, annual resin analysis, annual regeneration profile, monitoring service performance, chemical cleaning, and resin storage. Keeping your resin in good operation condition helps minimize the wastage of water in general.

Water Recovery

The only part of the regeneration process where the water flow could possibly be reused or recycled would be the final or fast rinse of the regeneration process. And even this stream would have a somewhat variable ionic content making its reuse or recovery questionable except under the best controlled circumstances. Using conductivity as a measure of ionic content may be the best way to on-line test a stream to initiate a recovery process. But even so, the economics of these recovery processes are rarely favorable. The piping needed to recovery this water would have to be corrosion resistant in most cases, and therefore quite expensive. Depending on where the recovered water might be used determines the length of the piping run and therefore its cost. Given the intermittent nature of regeneration processes most plants would want to collect the recovered water into a tank and then release it into its point of reuse on a more gradual basis. This makes managing that volume of water in the storage tank to be a considerable challenge, for very little economic benefit. As a result of these concerns and drawbacks water reuse and recovery from the ion exchange process is something rarely seen in industrial systems today.

CHAPTER 8

Membrane Separation

Membrane processes have been around since the early 1900s when Bechhold developed the first ultrafilter cir. 1907.[1] By the 1920s and 1930s, both microfiltration (MF) and ultrafiltration (UF) membranes were popular for laboratory applications. Industrial applications of MF and UF began in the early 1960s and 1970s, about the same time that Loeb and Sourirajan developed the "skinned," cellulose acetate reverse osmosis (RO) membrane (1960) that became the first commercially-viable RO membranes installed in Coalinga, CA (1965).[2] Later, it was the development of the polyamide, thin-film composite (TFC®) RO membrane by Cadotte in 1972 that allowed relatively higher flux and rejection that gave RO membranes broad appeal.[3] Since that time, a host of membrane-based separation technologies have been developed for specific applications. This chapter covers some of the most popular membrane technologies applied today:

- **Microfiltration (MF)**: suspended solids filtration
- **Ultrafiltration (UF)**: finer suspended solids filtration
- **Nanofiltration (NF)**: demineralization of multivalent ions
- **Reverse Osmosis (RO)**: demineralization of monovalent ions
- **Continuous Electrodeionization (CEDI)**: demineralization polishing

These membrane-based separation technologies are categorized here by the nature of the driving force for separation, in this case either pressure or electrochemical.

Pressure-Driven Membrane Separation Technologies: Microfiltration, Ultrafiltration, Nanofiltration, Reverse Osmosis

Pressure-driven membrane separation technologies rely on a difference in pressure, from the feed side of the membrane to the permeate side, which forces water through the membrane. In this manner, water can be recovered from solutions containing both suspended and dissolved solids. MF, UF, NF, and RO are the primary pressure-driven membrane technologies. MF and UF deal with removing suspended solids from the solution, while NF and RO remove dissolved solids. Figure 8.1 shows a filtration spectrum that compares removal capabilities for several types of pressure-driven membrane and conventional filtration techniques.

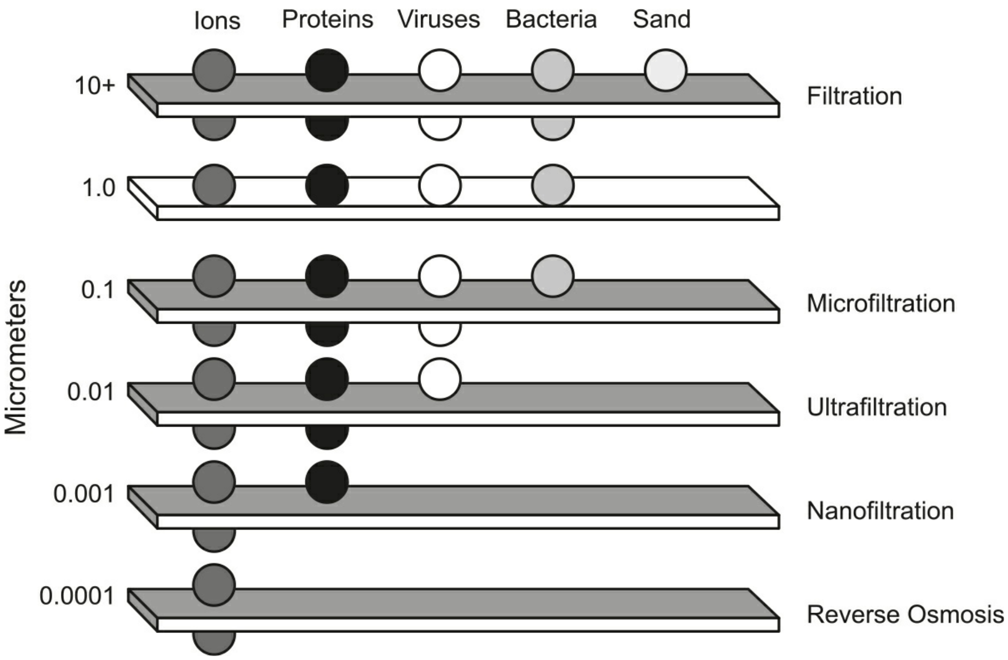


FIGURE 8.1 Removal capability of multimedia filtration and pressure-driven membrane technologies. (*Courtesy of Scrivener Publishing*.)

Filtration

Pressure-driven membrane systems can operate in either dead-end or cross-flow filtration modes.

Dead-End Filtration

Picture a filtration medium, such as a coffee filter, that allows a fluid (water) and some solids (coffee grounds) to pass through but retains the bulk of the coffee grounds.

As shown in Fig. 8.2 dead-end filtration operates with one feed stream and one effluent stream; is it well suited for batch-type operations. In dead end filtration, solids accumulate on the membrane surface relatively quickly, requiring frequent cleaning of the membrane to remove the foulants. Dead-end systems commonly used for MF and UF applications, are cleaned using three techniques: online backwashing, chemical-enhanced backwashing (CEB), and clean-in-place (CIP). Online backwashing involves intermittent backwash with filtered water plus an air pulse to help lift solids off the membrane. Backwashing can occur once every 15 to 60 minutes, depending on the concentration of solids in feedwater (higher concentration results in more frequent backwashing). A CEB using acid or caustic plus hypochlorite is performed occasionally along with the backwash step to remove inorganics (low pH) and organics and biofouling (high pH and chlorine). CIP is performed every few months as needed to remove materials from the membrane that backwashing and CEB do not. (See the section on cleaning for more details about CEB and CIP.) Many, if not most, MF and UF systems operate in dead-end mode.

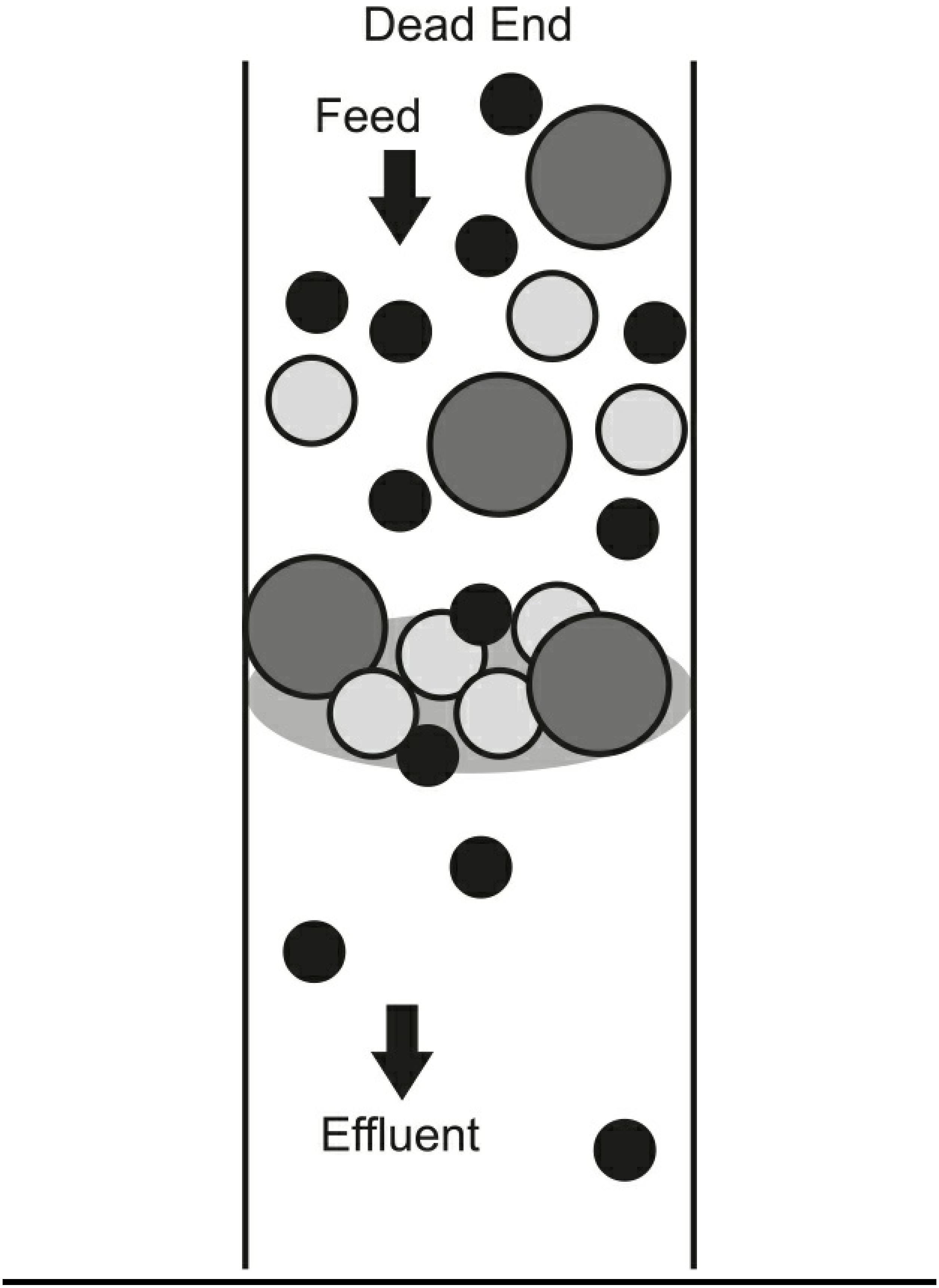

Dead End
Feed
Effluent

FIGURE 8.2 Principle of dead-end filtration.

Cross-Flow Filtration

In cross-flow filtration, feedwater flows tangentially across the surface of the membrane and not all water sent to the membrane actually permeates it. Hence, cross-flow filtration has one influent stream but two effluent streams (versus a single effluent stream for dead-end filtration). The rationale behind cross-flow filtration is that fluid traveling tangentially to the membrane surface essentially scours the membrane surface free of solids that might foul the membrane. Hence, cross-flow filtration is, in theory, a continuous operation, rather than a batch process. In practice, however, the membrane will become fouled enough with time to warrant an occasional cleaning to remove solids from the membrane. Figure 8.3 depicts a cross-flow pattern across a membrane. Virtually all RO/NF systems operate in cross flow. Some MF and UF systems with their feed on the inside of a hollow fiber membrane, also exhibit characteristic cross flow across the membrane, but are usually operated in an overall dead-end mode. Alternately, some MF and UF systems with inside-out feed operate in true cross flow, with the recycle of concentrate back to the front of the system, for streams with consistently high concentrations of suspended solids.

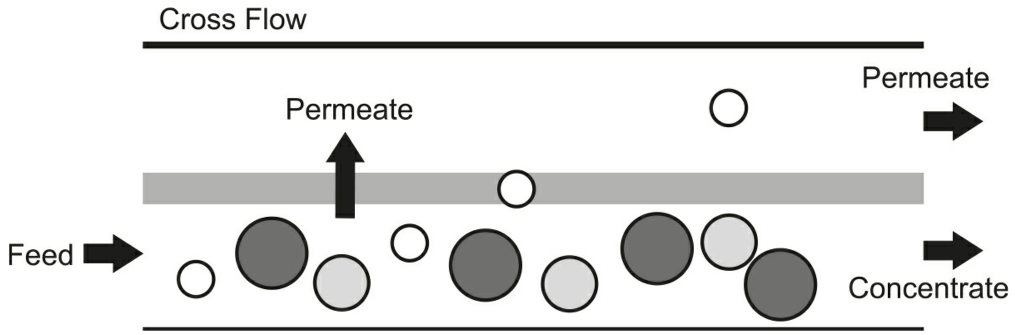


FIGURE 8.3 Principle of cross-flow filtration.

A phenomenon that occurs with cross-flow filtration is concentration polarization; this phenomenon is most pronounced with plate-and-frame, tubular, and spiral wound membrane modules. It involves increased fouling in the diffusion boundary layer next to the membrane surface, and is exacerbated by low cross-flow velocity and high water flux through the membrane. Concentration polarization is discussed in more detail later in this chapter.

Basic Membrane Terminology

Recovery

Recovery is defined as the amount of feedwater that passes through the membrane to become "permeate." It is expressed in terms of percent of feedwater that becomes permeate [Eq. (8.1)].

$$\text{Recovery (\%)} = \left(\frac{\text{Permeate Flow}}{\text{Feed Flow}}\right)(100) \tag{8.1}$$

The higher the recovery of the system, the lower the amount of wastewater generated. Recovery generally ranges from about 50% to as high as 90%, depending on the application. The most common recovery is 75% for most industrial and commercial applications. Recovery is set by the RO system designer and is a balance between the amount of wastewater generated and the degree to which feedwater becomes concentrated as more water is recovered as permeate.

Rejection

Rejection (or salt rejection) is generally a term applied to RO and NF processes. It is defined as the degree to which a given species is retained by the membrane. It is expressed in terms of percent of feed concentration [Eq. (8.2)].

$$\text{Rejection (\%)} = \frac{[(\text{Feed Concentration}) - (\text{Permeate Concentration})]}{(\text{Feed Concentration})}(100) \tag{8.2}$$

The higher the rejection, the more concentrated the permeate *and* concentrate streams become. Rejection is typically dependent on the specific species and the specific membrane. Rejection is a property of the membrane; it is not set by the designer of the RO/NF system. Salt passage is opposite of rejection. A 98% rejection rate corresponds to 2% passage through the membrane of the solute in question.

Concentration Factor

Concentration factor is a term that is again used primarily with RO and NF processes. It is used to determine the relative concentration of the concentrate stream to the feed stream. Concentration factor is calculated by taking the feed flow rate and dividing it by the concentrate flow rate [Eq. (8.3)].

$$\text{Concentration Factor} = \text{Feed Flow}/\text{Concentrate Flow} \tag{8.3}$$

This factor is then used to multiply the feed concentration to determine the approximate concentrate concentration of a species of interest, in a manner similar to cycles of concentration in a cooling tower.

Flux

Water flux is the amount of water that passes through a given membrane area during a given unit of time [Eq. (8.4)]:

$$J_w = A\,(\Delta P - \Delta\pi) \tag{8.4}$$

where J_w = flux of water
A = water permeability coefficient [partition coefficient for water * (diffusivity of water/membrane thickness)]
ΔP = ln mean average of applied driving pressure
$\Delta\pi$ = ln mean average of osmotic pressure

Water flux is expressed in gallons per square foot per day (gfd), liters per square meter per hour (lmh), or cubic meters per square meter per day (M/d).

Water flux is an important design variable, as this flux rate can have a direct impact on the degree and rate of fouling and scaling of the membrane. Flux is a direct measure of the rate at which material is transported to the surface of the membrane. Material that does not pass through the membrane is then trapped in the concentration polarization boundary layer, where the slow rate of diffusion away from the membrane gives solutes and scale sufficient time to foul and scale the membrane (see the following discussion on concentration polarization). The lower the feedwater quality, the greater the potential for fouling and scaling the membrane as water flux increases.

Salt flux is the amount of a solute that passes through a given membrane area during a given unit of time [Eq. (8.5)]:

$$J_S = B\,(C_{A2} - C_{A3}) \qquad (8.5)$$

where J_s = flux of solute
B = salt permeability coefficient [partition coefficient for salt * (diffusivity of salt/membrane thickness)]
C_A = mass concentration of solute A
subscripts:
2 = in the membrane boundary layer
3 = in the permeate

Salt flux is expressed in terms of mass per membranes area per unit time [e.g., grams per square meter per hour (g/m^{2}h)].

Concentration Polarization

Concentration polarization is a phenomenon that occurs in boundary layer next to a surface that forms whenever there is fluid flowing across the surface (Fig. 8.4). Within most membrane modules, the bulk solution experiences turbulent, convective flow, while very near the membrane surface, there is little to no convective flow. Diffusion is then, the primary transport mechanism of material to and from the membrane surface. Diffusion is slower than convection, so there is a tendency for build-up of solids (both suspended and dissolved) in the boundary layer, and hence, on the surface of the membrane. This build up is exacerbated by the flux of water and solids toward the membrane, and when the water flows through, most of the solids are retained on the membrane; higher water flux leads to more rapid buildup of solids on the membrane. This build up leads to membrane fouling and scaling, if the suspended and dissolved solids are given enough residence time to remain in the boundary layer (the residence time is a function of the boundary layer thickness).

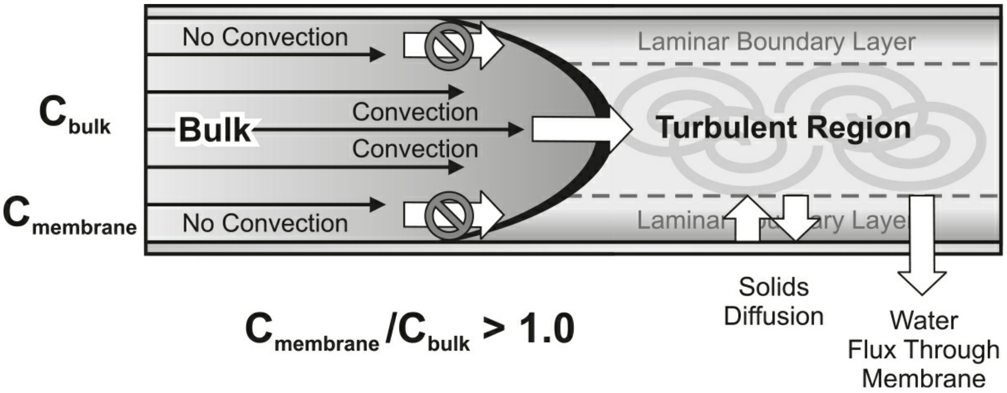


FIGURE 8.4 Boundary layer in cross-flow filtration. (*Courtesy of Scrivener Publishing*.)

Boundary layer thickness is a function of bulk solution velocity along the membrane surface, with higher velocity resulting in a thinner boundary layer. Thinner boundary layer reduces the tendency for the membrane to foul or scale, as the residence time for solids in the layer is reduced as compared to a thicker boundary layer.

Water flux through the membrane also impacts the degree of concentration polarization. Flux brings even more solids into the boundary layer and to the membrane surface. Since the bulk of these solids do no pass through the membrane, but the water does pass, the concentration becomes even higher in the boundary layer. Hence, higher water flux leads to higher concentrations of solids in the membrane boundary layer, increasing the tendency to foul and scale the membrane.

Membrane Modules

Membranes are modularized for practical use. The objective is to pack a relatively large membrane area into a relatively small volume. There are five basic types of membrane modules, as described in Table 8.1.

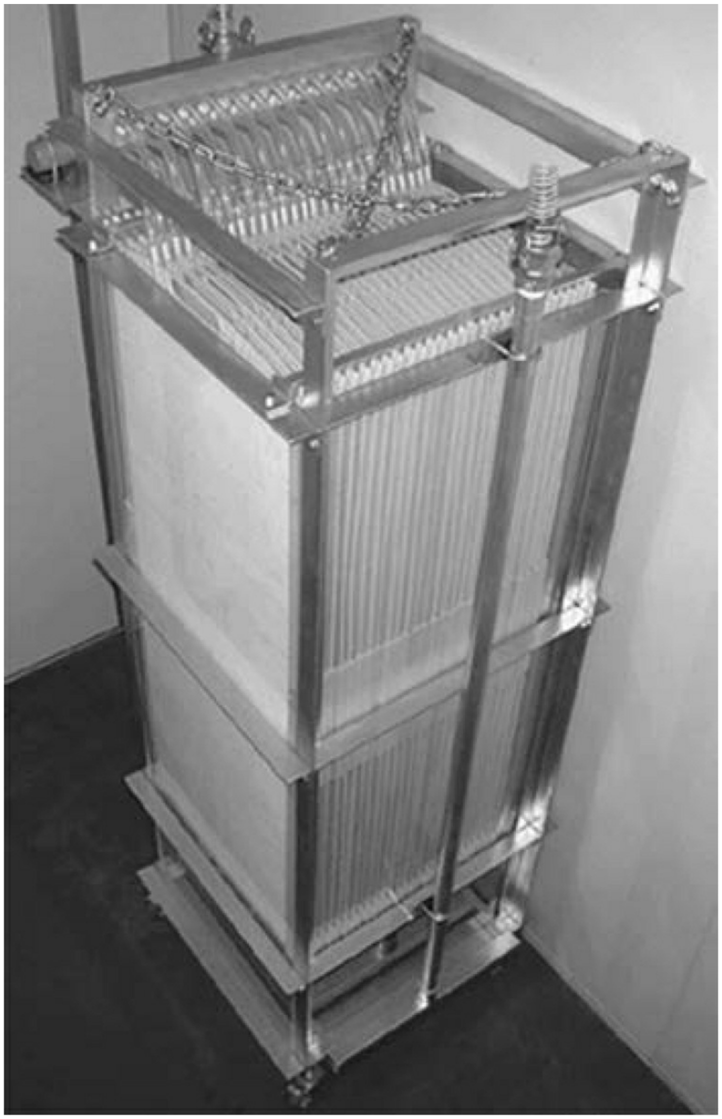
Module Type	Packing Density (Approx. m^2/m^3)	Ability to Clean	Cost/ft^2
Flat sheet (plate-and-frame)	Moderate (150–500)	Moderate	Moderate to high
Tubular	Low (20–275)	Easy	Moderate
Spiral wound	Moderate to high (500–1250)	Difficult	Moderate
Hollow fiber	High (NA)	Moderate	Moderate to low
Hollow fine fiber	Very high (500–4950)	Difficult	Low

TABLE 8.1 Comparison of Five Basic Types of RO Membrane Modules[4]

Flat Sheet—Plate-and-Frame

Flat sheet and plate-and-frame membranes are generally used in membrane bioreactors (MBRs) and specialty, high-solids RO application, respectively.

Plate-and-frame modules are also used in CEDI applications. Figures 8.5 and 8.6 show a flat-sheet arrangement for an MBR application, and an RO plate-and-frame module, respectively.



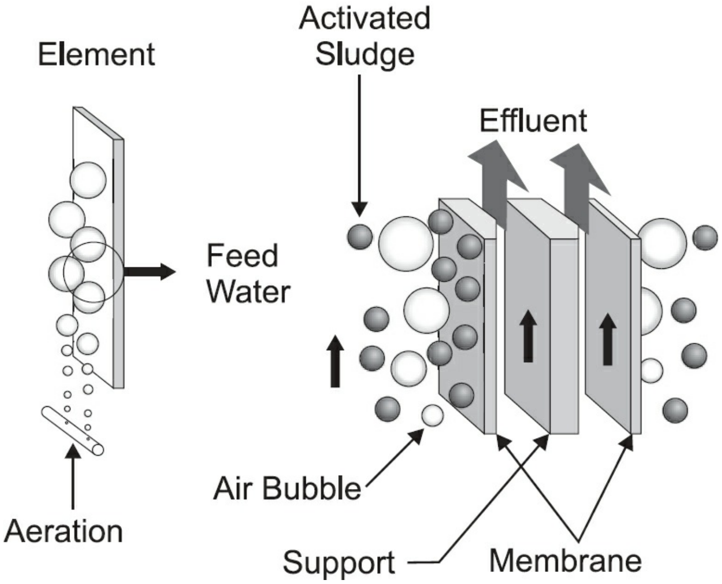

Element
Activated Sludge
Effluent
Feed Water
Air Bubble
Aeration
Support
Membrane

FIGURE 8.5 Flat-sheet membrane as used in a submerged MBR application. (*Courtesy of Toray Industries*.)

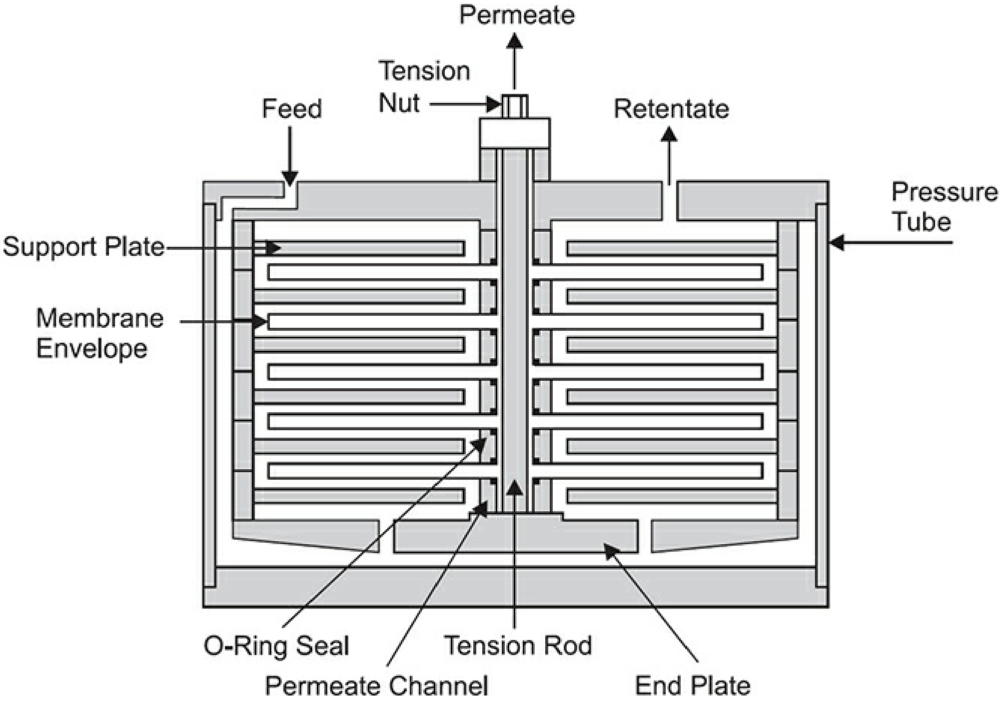


FIGURE 8.6 Plate-and-frame module for RO applications. (*Courtesy of Scrivener Publishing*.)

Tubular

Tubular membrane modules were the first commercially viable RO membranes used in 1965 at the first commercial brackish water RO application at the Raintree facility in Coalinga, California.[5] Today, tubular membranes are typically used for high suspended solids, and oil and grease removal using MF or UF. They are also used in external MBR applications and with ceramic membranes.

Some polymeric tubular modules resemble shell-and-tube heat exchangers. The feed is on the tube side and the permeate exits the module on the shell side. Inner diameters of the membrane tubes can vary from about 5 to 12.5 mm, or even larger, depending on the application. Several membrane tubes can be contained in a single metal, perfluorocarbon (PFC) or fiber-reinforced plastic (FRP) housing.

Some modules are easily cleaned using a sponge ball that is sent down the tube, wiping the surface of the membrane; this technique is generally used for larger diameter tubes. For smaller tubes, frequent cleaning (and backwashing for MF and UF modules) is recommended; cleaning may be as frequent as once a day for applications such as dairy processing.

Tubular modules may also contain several multibore fibers, as shown in Fig. 8.7. These fibers have capillary tubes with smaller diameters.

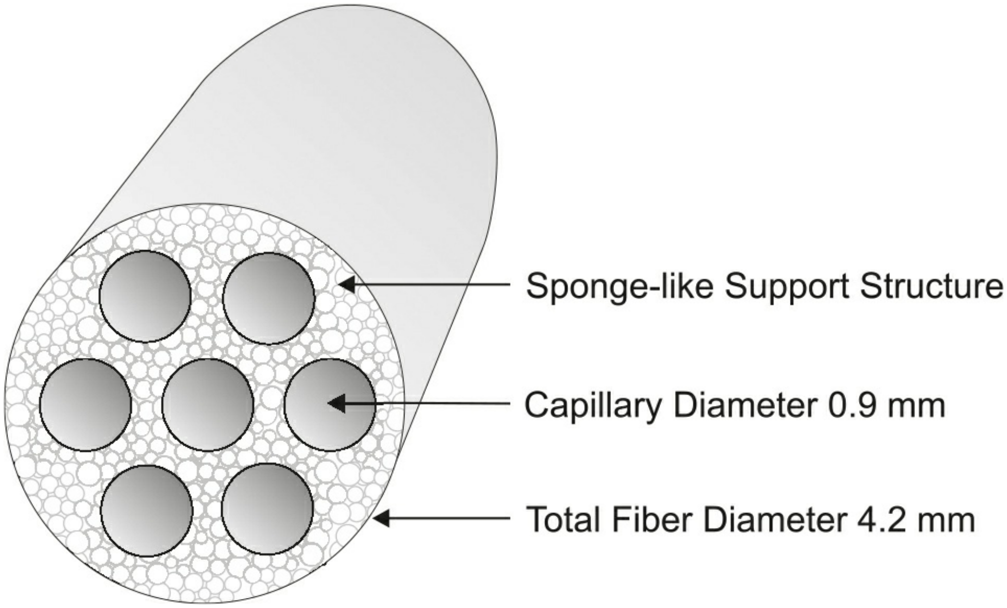


FIGURE 8.7 Multibore, polymeric tubular membrane.

Spiral Wound

Spiral wound modules are predominant for RO and NF applications, but this configuration has also been employed for MF and UF, as well as CEDI applications.

Figure 8.8 is a cross section of a spiral wound module. The module consists of sheets of membranes placed between feed and permeate spacers. Two membranes are placed back-to-back and separated by a spacer. This package is then glued on three sides, so that any permeate that goes through the membranes can only exit at one end of the permeate spacer. Several of these membrane packages or “leaves” are created and then wound around a perforated tube called the permeate tube. The open end of the membrane leaf is toward the permeate tube. Each leaf is separated by a feed channel spacer through which the feed/concentrate stream runs. Feedwater enters the end of the module and travels through the feed channel spacer along the surface of the membrane. Permeate is collected in the permeate spacers and spirals down into the permeate tube and exits the module. Concentrate exits the module at the opposite end to where feedwater enters.

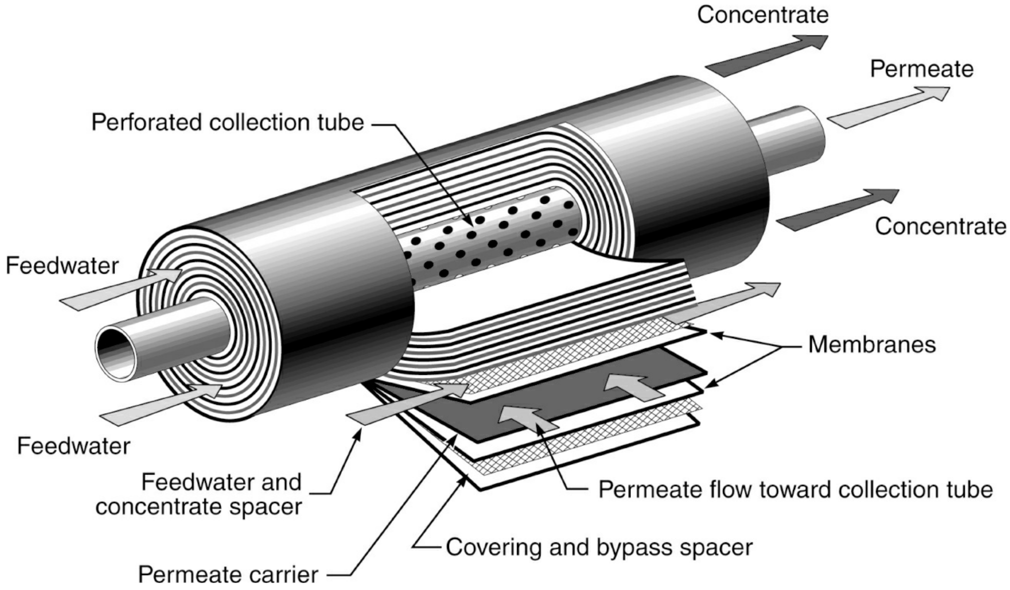


FIGURE 8.8 Spiral wound RO module cross section.

The most common diameters of spiral wound modules are 2.5 inches (63.5 mm), 4 inches (102 mm), 8 inches (203 mm), and 16 inches (406 mm) with lengths of 40 inches (1 m) and 60 inches (1.5 m), and containing up to more than 1000 ft^2 (92.9 m^2) of membrane area.

Hollow Fine Fiber

Hollow fine fibers and modules were first commercially introduced by E.I. DuPont de Nemours and Company in 1970 with the DuPont B-9 (and, in 1974, the B-10) Permeator. The hollow fine fibers are similar to the hollow fibers described later, but are of different polymer composition (linear aromatic polyamide or “aramid”) and are also much finer in construction. The fibers are as flexible as human hair (Fig. 8.9), but are finer. Despite their fine nature, the fibers are self-supporting, with a ratio of outside to inside diameter of at least 2 to 1 (Fig. 8.10), allowing these fibers to withstand pressures up to 69 bar (1000 psi).

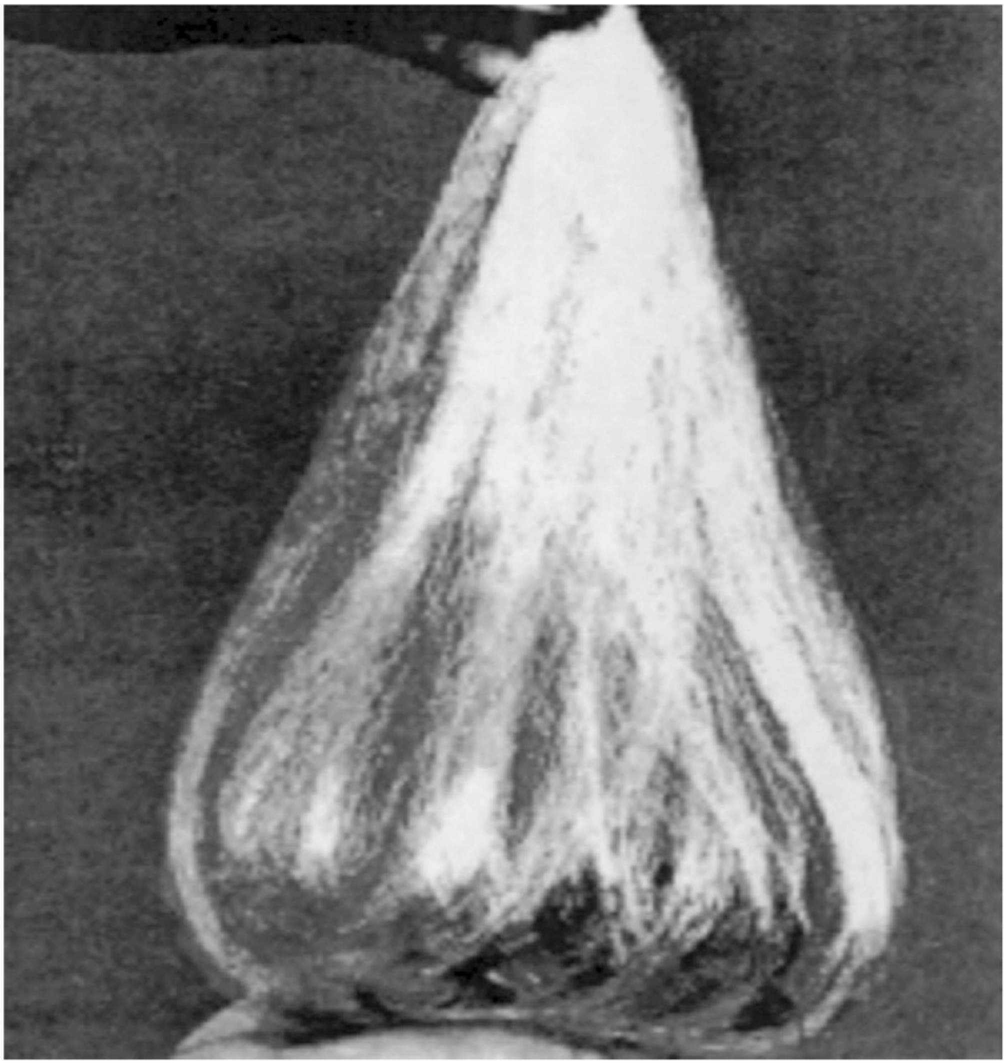


FIGURE 8.9 Hollow fine fibers.

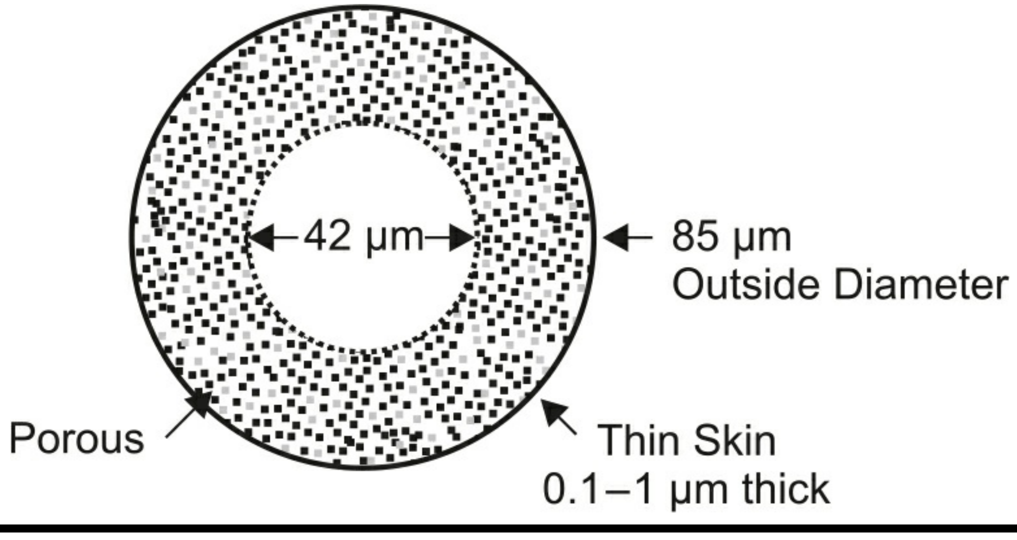


FIGURE 8.10 Cross section of a hollow fine fiber. (*Courtesy of Scrivener Publishing.*)

Hollow fine fiber modules are constructed using fibers that are mounted in a U-fashion in a pressure vessel; fibers are fixed in place with epoxy at both ends, as shown in Fig. 8.11. The configuration resembles a shell-and-tube exchanger, with feedwater entering the shell side of the pressure vessel and permeate exiting through the fiber lumens (known as "outside-in" flow). The DuPont B-9 Permeators could produce up to 94.6 M^3/d (25 000 GPD) for a 254 mm (10 inches) diameter module. The primary disadvantage of this configuration is that the fibers within the modules are prone to fouling with any solids in the feedwater, due to the tight packing of the fibers.

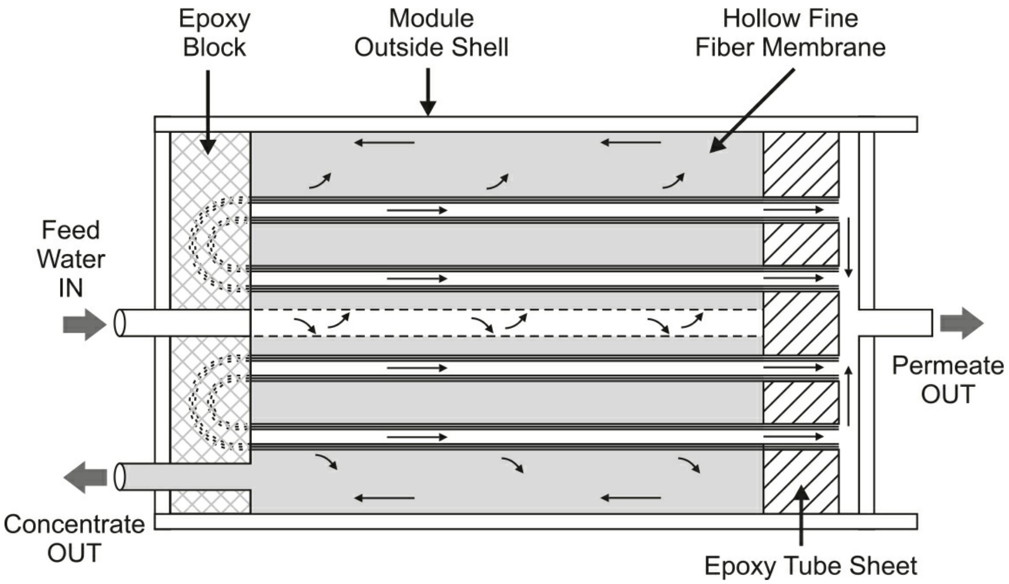


FIGURE 8.11 Hollow fine fiber module. (*Courtesy of Scrivener Publishing.*)

While DuPont no longer manufactures hollow fine fiber RO membranes and modules, hollow fine fiber modules can be found today, most notably the Hollosep membrane modules from Toyobo.

Hollow Fiber

Hollow fiber membranes are used primarily for MF and UF applications, although some have been used in research activities for RO.[6] These fibers differ from hollow fine fibers in that the diameter or the hollow fibers are many times larger than that for hollow fine fibers (Fig. 8.12). Hollow fibers used for UF applications can have an inside dimeter (ID) of up to 1 mm, fully

25 times larger than the ID of the DuPont Permasep hollow fine fiber, RO membranes[7] with a fiber wall thickness of 100 to 200 μm. For RO applications, these fibers can have IDs of 250 to 300 μm, roughly six times that of the DuPont Permasep hollow fine fibers.[8] Fiber wall thickness of 400 to 500 μm has been used for RO applications and did not require an external pressure vessel; the fibers themselves acted as the pressure vessels.[9]

FIGURE 8.12 Hollow fiber membranes for MF and UF applications.

Hollow fiber membranes can operate in outside-in flow or inside-out flow (inside fiber or "lumen" feed) (Fig. 8.13). Inside-out flow more closely resembles cross-flow filtration, in that all portions of the inside surface (feed side) is continuously scoured by the flow of fluid across it, thereby minimizing fouling of the membrane surface. For outside-in flow, the fibers are typically scoured with air bubbles (Fig. 8.14) to try to minimize collection of solids on the outside (feed) of the fibers when used in submerged MF or UF applications, as discussed earlier.

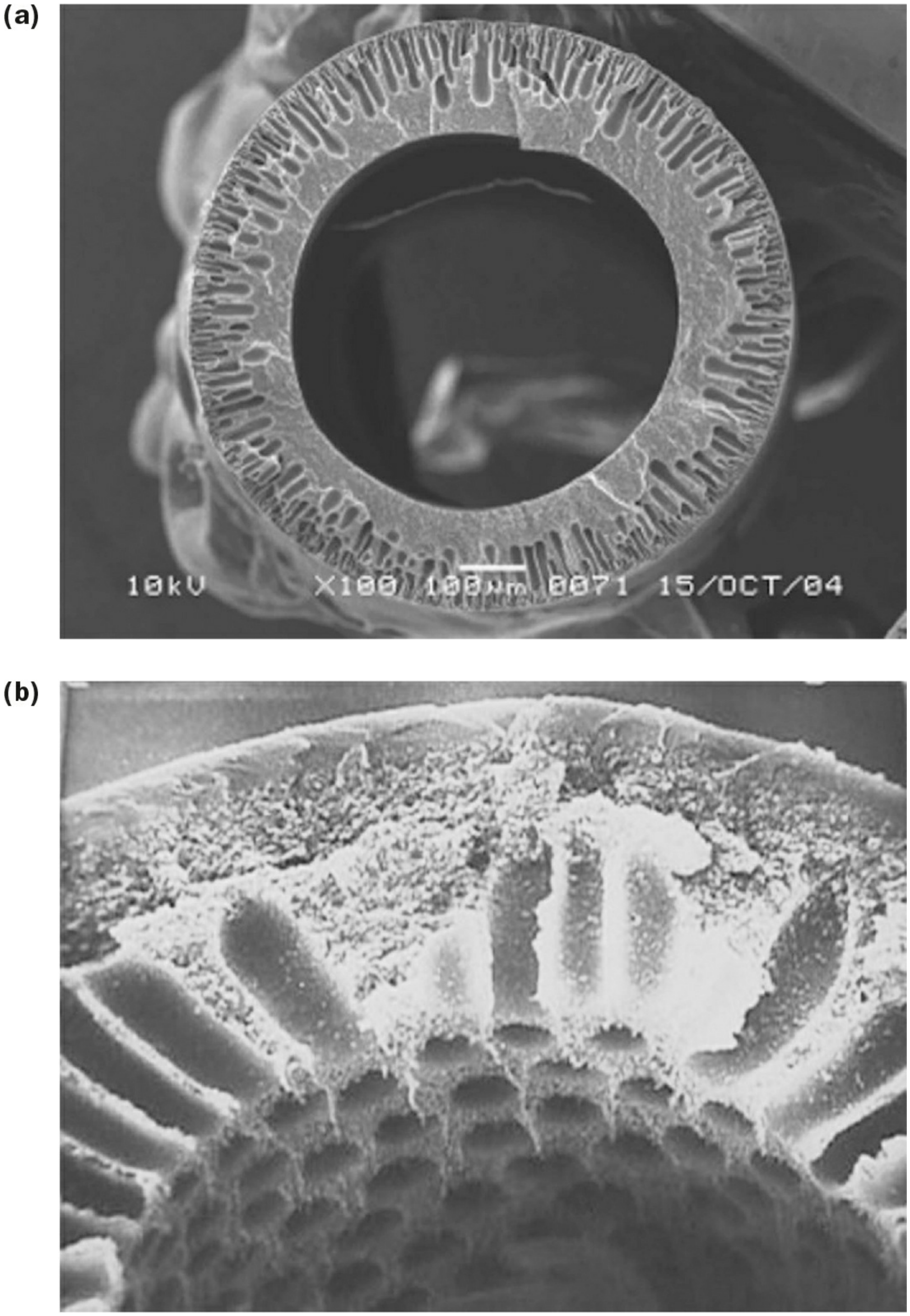


FIGURE 8.13 Cross section of an inside-out feed (“inside skinned”) (a) and outside-in feed (“outside skinned”) (b) hollow fiber membranes.

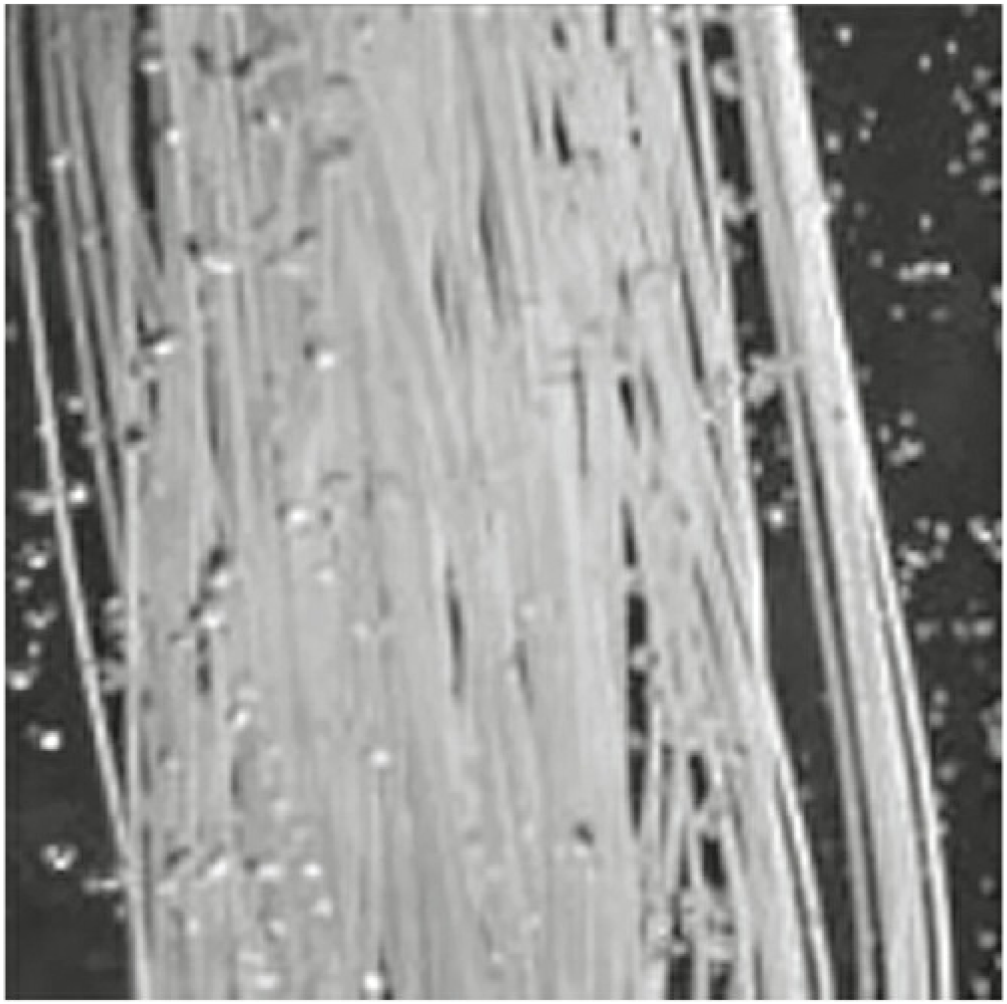


FIGURE 8.14 Air scour of submerged hollow fiber membranes.

Hollow fiber membranes for MF and UF applications are either modularized into cylindrical canisters or cassette (for submerged processes), as shown in Figs. 8.15 and 8.16, respectively. Since the operating pressure of MF and UF applications is less than about 3.5 bar (50 psi) for most pressurized hollow fiber applications, and less than a vacuum 1 bar, the modules do not require pressure vessels. Unlike the hollow fine fiber configuration with the U-shaped fiber bend, which are potted and open at only one end, (as shown in Fig. 8.11), most hollow fiber membranes are potted and open at both ends (the exception is the Koch Puron® submerged fibers, which are potted only at the bottom of the cassette).

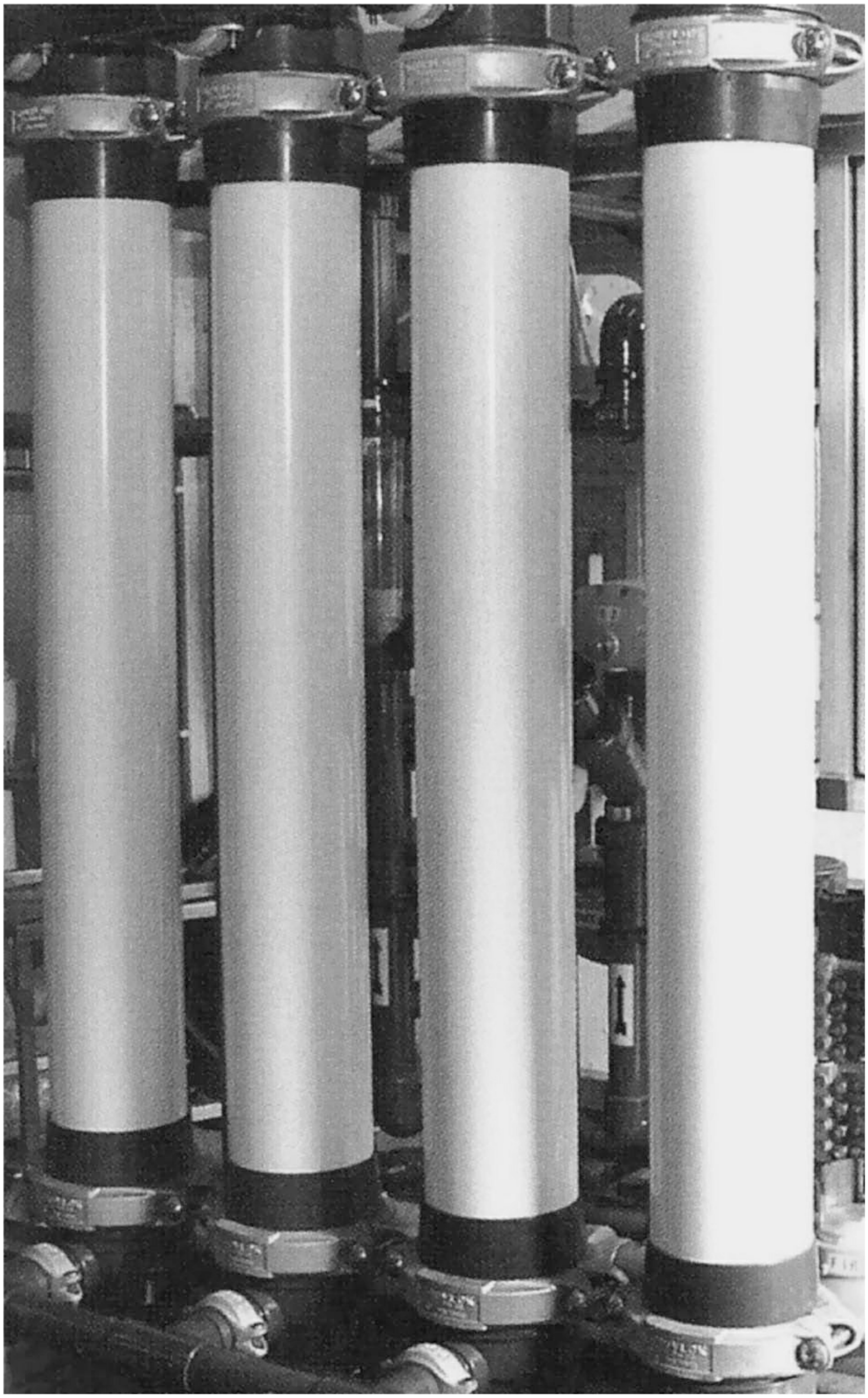


FIGURE 8.15 Canister-type hollow fiber membrane modules for MF and UF applications.

FIGURE 8.16 Cassette-type hollow fiber membrane modules for submerged MF and UF applications.

Microfiltration and Ultrafiltration

Introduction

MF and UF are similar, pressure-driven membrane separation techniques used to separate suspended solids from solution. These membranes have pores, through which the carrier fluid (typically water) and some solids pass. Separation of solids from solution by the membrane is based on size exclusion, where particles larger than the pore size of the membrane are retained, while smaller particles pass through into the permeate. Note that in many cases, solutes can adsorb onto the surface of a pore, thereby reducing pore size and enhancing ability of the membrane system to reject particles smaller than the pore size rating. This phenomenon also contributes to an increase in pressure across the membrane, known as transmembrane pressure (TMP—the pressure from the feed side to the permeate side of the membrane). Transmembrane pressure is a function of the degree of fouling of the membrane surface as well as within the pores. The higher the TMP, the lower the driving force and efficiency of the MF process. Once the TMP reaches a predetermined value, for example, 150 kPag, (22 psig) the membranes must be cleaned (or replaced if unable to clean sufficiently) to restore efficiency.

Membranes

Most MF and UF membranes are made from the same synthetic organic polymers, but are prepared under different conditions to produce different pore sizes. Pore sizes for MF membranes average around 0.1 µm, while UF membrane pore sizes are on the order of 0.02 to 0.03 µm. Typical MF and UF polymers include polyvinylidine fluoride (PVDF), polysulfone (PS), polypropylene (PP), and polyacrylonitrile (PAN). Additionally, polyethersulfone (PES) is used for UF membranes, and polytetrafluoroethylene (PTFE), nylons, cellulose triacetate, and cellulose acetate-cellulose nitrate blends are used for MF membranes.

High strength and good elongation characteristics are important for the integrity of the MF or UF membrane, particularly in the hollow fiber format. Hollow fiber membranes, whether pressurized or submerged, tend to move in the turbulence of the feedwater flow, so the ability of the fiber to flex without breaking is a necessary trait.

Hydrophilicity is also a membrane characteristic of importance. Hydrophilic membranes tend to adsorb water more readily than hydrophobic membranes. Table 8.2 lists the surface tension for some polymeric materials used for MF and UF membranes; the higher the surface tension, the more hydrophilic the material. Hydrophilic membranes are more wettable and require lower operating pressure than hydrophobic membranes. Additionally, since potential foulants in water tend to be hydrophobic, a hydrophilic membrane prefers to bind to water rather than the foulant.

Polymer	Surface Tension (dynes/cm)
Polytetrafluoroethylene	18
Polyvinylidene fluroide	25
Polypropylene	29
Polysulfone	41
Polyacrylonitrile	44
Cellulose	44

TABLE 8.2 Surface Tension of Various MF and UF Polymers

Modules

While MF and UF membranes are modularized into several different configurations, including flat-sheet, spiral wound, and tubular, the most common configuration is the hollow fiber or “capillary.” Hollow fiber modules can be used in submerged applications (such as MBR) and pressurized applications. Figures 8.17 and 8.18 depict submerged and pressurized processes, respectively. In the submerged process, the membranes are submerged in a tank containing the feed solution, and a vacuum is pulled on the lumen side of the fiber to pull through relatively clean permeate. Submerged processes are outside-in flow only. In the pressurized process, the feed solution is pressurized which forces permeate through the membrane. The pressurized process can be outside-in or inside-out flow.

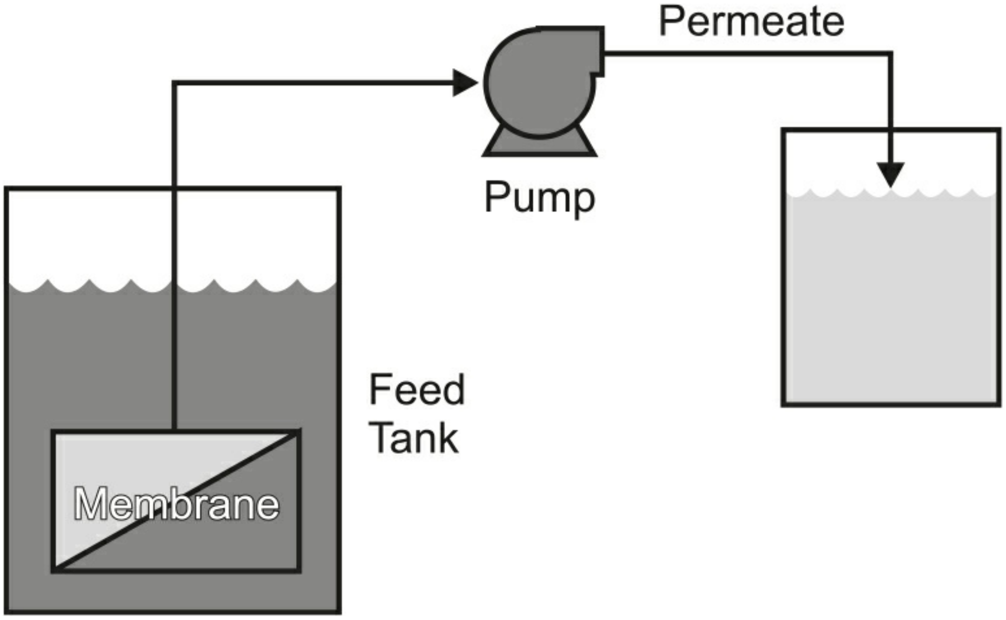


FIGURE 8.17 Submerged MF/UF process.

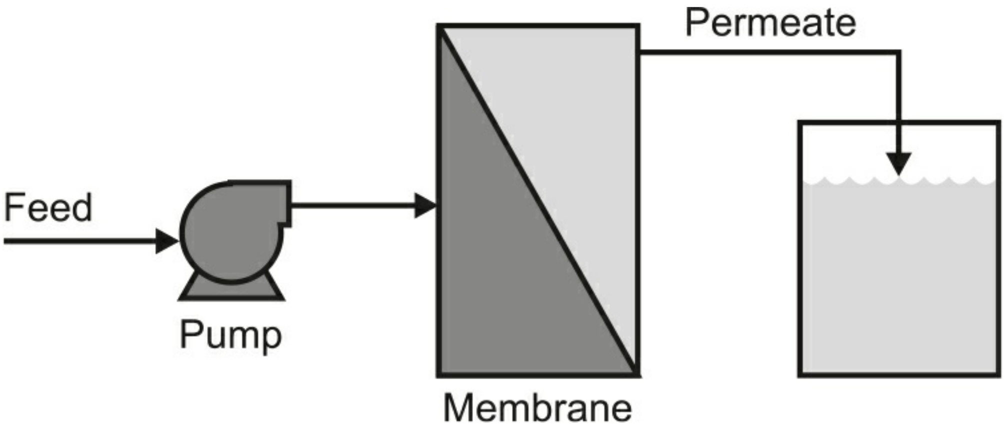
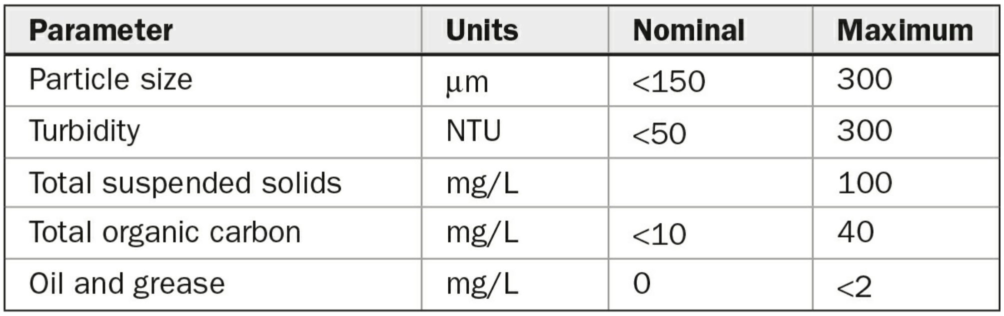


FIGURE 8.18 Pressurized MF/UF process.

Pretreatment

Pretreatment for MF and UF systems is relatively straight forward. Table 8.3 lists generalized feedwater limits for most hollow fiber systems.



Parameter	Units	Nominal	Maximum
Particle size	µm	<150	300
Turbidity	NTU	<50	300
Total suspended solids	mg/L		100
Total organic carbon	mg/L	<10	40
Oil and grease	mg/L	0	<2

TABLE 8.3 General Feedwater Quality Guidelines for MF and UF Hollow Fiber Systems

Pretreatment usually includes a screen filter rated at 100 to 300 µm, to keep large particles out of the membrane modules. In some cases, clarification is also required if the feedwater routinely exceeds the feedwater quality guidelines.

Cleaning

Submerged Hollow Fibers Submerged hollow fiber membranes typically employ a full-time air scour during operations in order to keep membranes clean. Most hollow fiber membranes are potted at both ends of the module (some are only potted at the lower end, as mentioned earlier). Solids tend to accumulate near the potted end(s) since the fibers don't have as much room to move to allow the air to scour the fibers clean.

A back pulse of permeate, from the inside to the outside of the fibers for submerged systems, is used in an attempt to dislodge solids from the feed surface of the membrane fiber. Sometimes, acid, caustic, or chlorine is added to the back pulse to further clean the membrane fiber. Pure water back pulses can occur every 15 to 30 minutes with a duration of 10 to 30 seconds.

Cleaning of submerged membranes involves either evacuating the tank containing the membrane modules and preparing the cleaning solution *in situ*, or removing the rack of modules and placing them in another tank for cleaning. Removing the modules also allows for cleaning by spraying water directly onto the fiber bundles to remove solids.

Pressurized Hollow Fibers Cleaning of a pressurized, hollow fiber system involves several steps: backwash, CEB, and CIP.

Backwash Backwashing is conducted once every 15 to 90 minutes, depending on the degree of membrane fouling that occurs. Backwashing involves sending permeate back through the membrane to the feed side, in an effort to remove solids that have be collected on the feed-side membrane surface. Air scour is sometimes used to assist in sweeping away solids that have been dislodged from the membrane by the backwash. A forward flush to drain is then used to ensure that solids removed during backwash and air scour, are removed from the system prior to bringing the unit back on line. Total backwash/flush time can range from about 90 to 180 seconds.

Chemical Enhanced Backwash A chemical enhanced backwash is a "mini clean," where chemicals are added during the backwash cycle to assist in removing inorganics (such as scale), organics, and bacteria from the membranes. Chemicals used during a CEB include:

- Citric or hydrochloric acid (HCl), for inorganic scale and iron removal; sample concentrations include up to 1000 mg/L of 35% HCl
- Caustic (NaOH) at concentrations up to 500 mg/L of 50% NaOH is used for removal of organic fouling
- Hypochlorite (NaHOCl) at concentrations up to 1000 mg/L is used for biogrowth control.

Frequency of CEB depends on the specific water being processed; caustic and hypochlorite are typically feed together and can be used as often as once every 2 to 12 hours, while acid is generally used less frequently, perhaps once every 12 to 72 hours. Total duration of a CEB is approximately 3 to 5 minutes.

Clean-in-Place A CIP is performed when the backwashes and CEBs can no longer maintain flux or TMP. Chemicals used and concentrations are shown in Table 8.4. A typical CIP requires 2 to 2.5 hours to complete.

Chemical	Hydrochloric Acid HCl	Sodium Hydroxide NaOH*	Hypochlorite NaHOCl*
Addresses	Inorganics	Organics	Bacteria
Percent, %	35	50	10
Concentration, mg/L	2000	1000	2000
pH	2	12	12

*Typically used together.

TABLE 8.4 Clean-in-Place Chemicals Used for MF and UF Pressurized, Hollow Fiber Membranes

Monitoring

There are a few parameters that are monitored with MF and UF systems, including operating pressure, temperature, and flux (or permeability).

Perhaps the most important parameter to determine is transmembrane pressure (TMP) and temperature-corrected TMP (TCTMP). The TMP or TCTMP is a measure of the degree of membrane fouling, and is determined by the pressure difference between the feed side and the permeate side of the membrane. As the resistance to permeation of the fouling and membrane increases, the TMP must increase to maintain flux and/or the flux decreases [see Darcy's law, Eq. (8.6)]. Under constant pressure, some MF and UF membranes operating on particularly challenging waters can lose 50 to 75% of water flux between backwashes due to fouling and the increase in resistance to flow, R_t.

$$J = \mathrm{TMP}/\mu R_t \tag{8.6}$$

where J = flux

μ = viscosity of the solvent (e.g., water)

R_t = resistance of the membrane material + fouling, as a function of temperature

As the resistance to flow, R_t, increases due to fouling, the TMP must increase to maintain flux. At a maximum TMP [usually given by the specific membrane manufacturer, and ranges from 1.5 to 2.0 bar (22–30 psi)], the membranes are backwashed to restore performance. Figure 8.19 shows TMP as a function of time for a UF system operating on Detroit River water.

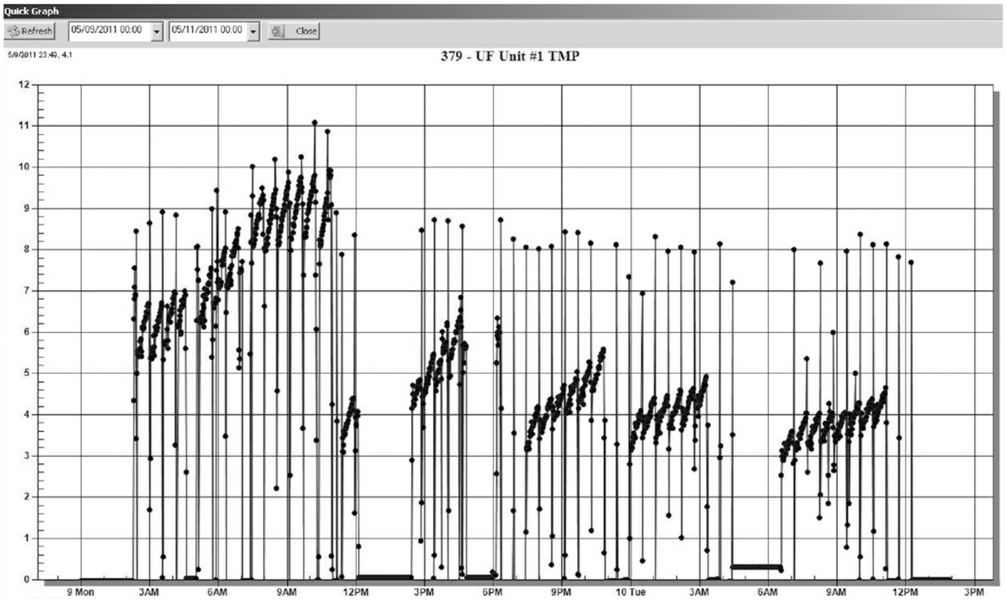


FIGURE 8.19 Transmembrane flux as a function of time for a UF system.

Performance is also measured in terms of permeability, which is productivity divided by feed pressure. Figure 8.20 shows the permeability as a function of time for the same system and time period as the TMP shown in Fig. 8.19. As fouling of the membrane and pressure increases, permeability of the system decreases.

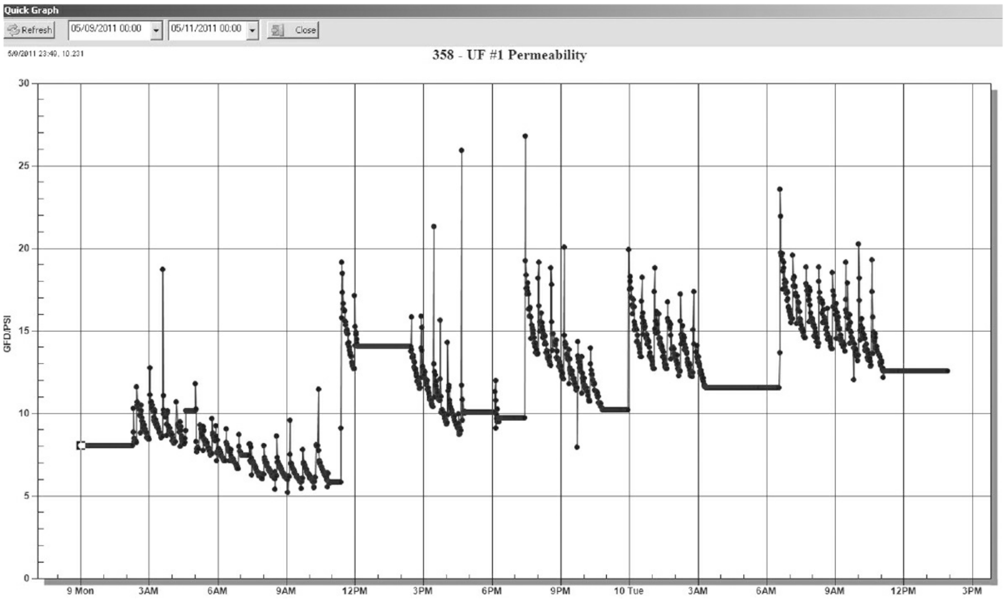


FIGURE 8.20 Permeability as a function of time for a UF system.

Air integrity testing (AIT) is a test used to monitor the integrity of the membrane fibers for hollow fibers configurations. It is uncommon in industrial settings, but a requirement for municipal applications. The test involves pressurizing the feed side of the membrane modules with air at 1.2 to 1.4 bar (18–20 psi), while water is still on the permeate side of the fibers. The pressure should hold for 10 minutes. If the pressure decays during the 10 minutes, this is indicative of leaks in the modules, either through the fibers or around O-rings. If the system is built with clear piping for the permeate stream (Fig. 8.21), bubbles can be seen during the test if integrity is compromised. Fibers that are compromised will pass suspended solids into the system permeate stream, increasing the likelihood of fouling of any RO equipment downstream. Fibers can be removed from service by inserting a pin into the fiber of interest, as shown in Fig. 8.22.

FIGURE 8.21 Ultrafiltration skid showing clear permeate piping.

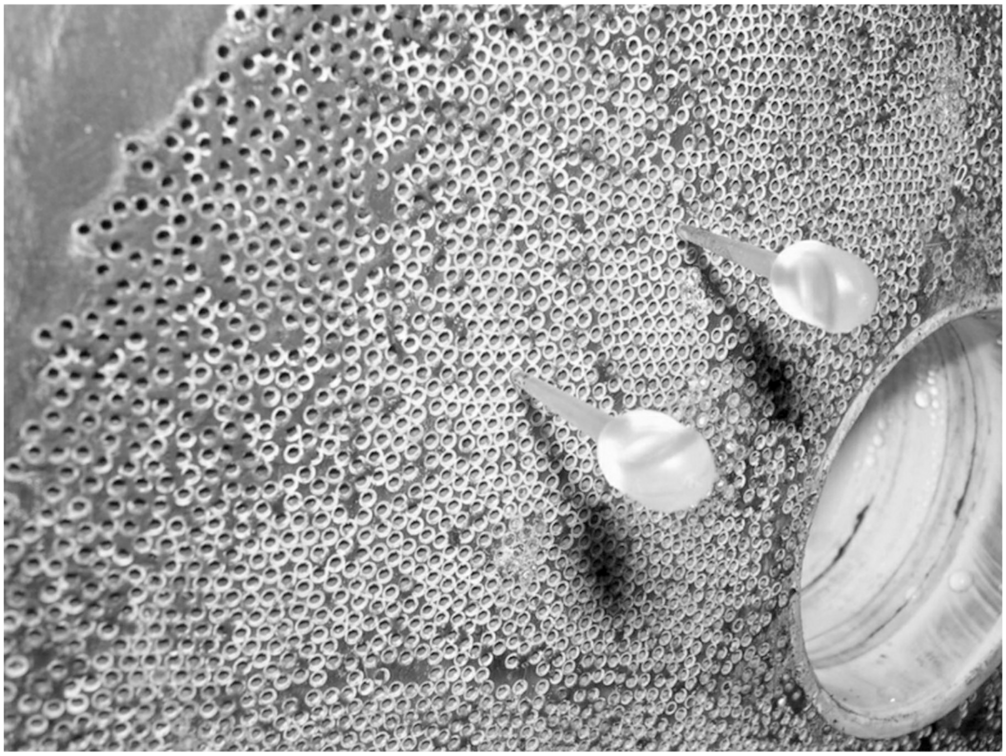


FIGURE 8.22 Pinning broken fibers identified during air integrity testing.

Other parameters to monitor and trend directly from instrumentation:

- Conductivity—membrane feed
- Temperature—membrane feed
- Turbidity—membrane feed and permeate
- Pressure—membrane feed (both top and bottom of module is inside-out or cross flow feed) and permeate
- Flow—membrane permeate, backwash, waste, and recycle (if cross flow)

Calculated performance data to trend include:

- Pressure—average feed side
- TMP and TCTMP
- Flux—permeate and backwash
- Specific flux and temperature-corrected specific flux—permeate flux

divided by average feed side pressure

Microfiltration

MF is a pressure-driven membrane separation technique used for separating particles, including some bacteria, from liquid streams. As shown in Fig. 8.1, MF can remove particles about 0.1 µm in size. Specifically, MF membranes can be prepared with definite pore sizes, ranging from about 0.05 to 2 µm, such that particles of interest can be removed from solution by selecting the MF membrane with the proper pore size.

Microfilters are used to remove or reduce suspended solids, including turbidity and some algae and bacteria, from water (bacteria removal is 4-log, or 99.99%). As such, applications range from treatment of municipal drinking water to RO pretreatment of secondary and tertiary effluent and industrial systems. When MF is used for RO pretreatment, higher RO fluxes can be used, resulting in smaller RO systems to treat a given volume of feed (as shown in Table 8.9, higher RO flux rates can be used of feedwater treated with MF than with conventional pretreatment; higher flux means less membrane area is required to treat a given volume of water).

The use of MF for bioreactors has become very popular. MF membranes reduce the need for biomass sedimentation, allowing for smaller treatment tanks. MBRs can be used to treat wastewater for surface water discharge, urban reuse, groundwater recharge, industrial reuse, and irrigation.

Ultrafiltration

UF is a pressure-driven membrane separation technique used for separating particles such as colloidal silica and some higher-molecular weight soluble species, such as organics, from solution. UF relies on size exclusion, where species larger than the pore size or the molecular weight cut off (MWCO) are retained by the membrane, and smaller species pass through. Molecular weight cut off is a measure of the pore size of the membrane, from 0.1 to 0.001 µm for UF, in that it describes the ability of a UF membrane to retain 90% of a challenge macrosolute (typically polyethylene glycol, dextran, or protein). However, it should be noted that there is no international standard for MWCO, and MWCO ratings for membranes from different manufacturers cannot be directly compared. Molecular weight cut off does not refer to 100% retention because other factors, such as the shape of the species (spherical, linear, etc.)

and operating conditions, contribute to the ability of the membrane to retain a specific species. In general, however, the pore size of a UF membrane is approximately an order of magnitude smaller than an MF membrane pore size. In contrast to MF, UF membrane can claim 6-log (99.9999%) removal of bacteria, and some jurisdictions allow for 4-log (99.99%) reduction of viruses with UF.

UF is used for a wide variety of applications, including concentration of proteins, recovery of electrodeposition paint, purification of bottled water, treatment of oily wastes, purification of blood, and RO pretreatment. When UF is used for RO pretreatment, higher RO fluxes can be used, resulting in smaller RO systems to treat a given volume of feed.

Reverse Osmosis and Nanofiltration

RO and NF are similar, pressure-driven membrane separation techniques used to separate dissolved solids from solution. RO and NF are used for a wide variety of applications, from seawater desalting for drinking water and electric power generation to makeup pretreatment for boilers and cooling tower systems. Typical uses include replacing sodium softening to increase boiler cycles in steam production, and replacing traditional cation/anion ion exchange to eliminate the need to store and handle acid, caustic, and regeneration waste.

Both RO and NF rely on a combination of charge exclusion and solution/diffusion permeation to affect separation (NF membranes also rely on size exclusion via pore structures, as discussed earlier). The solution/diffusion model (nonporous model) of transport through a membrane involves three important steps:[10]

1. Sorption of solute into the membrane
2. Diffusion of solute through the membrane
3. Desorption of solute out of the membrane

The solution/diffusion, or nonporous model of membrane transport assumes an ideal, defect-free, nonporous membrane. Although developed in the 1960s, it is still a valid transport model that is empirically well-approximated.

The ability of a solute to essentially dissolve and diffuse through a membrane polymer is a function of several variables, including temperature, pressure, concentration of solute, and membrane polymer selected. For example, NF membranes, by design, are created to pass more salts than RO membranes. NF membranes typically reject only up to about 75% of sodium chloride (although the range of rejection for various membranes is quite broad), while RO membranes typically reject more than 96%.

Ionic charge, polarity, and size of an ion play roles in the ability of an RO or NF membrane to reject or pass the ion. In general, NF and RO membranes are negatively charged. Negatively charged ions are repulsed (rejected) by the Donnan effect. This leads to the rejection of positively charged ions to maintain electrical neutrality in both the feed and permeate streams. The higher the valance, the greater the repulsion forces.[11] For example, the passage of sodium (+1 charge) is about double that of calcium (+2 charge) for a typical RO membrane, with passages of about 4% and 2%, respectively (rejections of 96% and 98%, respectively). The presence of polar functional groups within the membrane polymer serves to favor solubility of polar compounds, such as water, over nonpolar compounds, thus enhancing the flux of polar species over nonpolar species.[12] Larger species would be less soluble and also exhibit lower diffusivities through the membrane, essentially leading to high rejections of these species.[13]

Table 8.5 lists typical rejection for various species as functions of charge for two common RO membrane types, as well as the range of rejection for NF membranes. As the table shows, rejection of all species is higher for RO membranes than for NF membranes. This is by design, as NF membranes, also called softening membranes, are used primarily to reduce hardness from feedwater sources. NF membranes are often used in place of sodium softening to produce drinking water or boiler feedwater for low to medium pressure steam systems. Gases permeate very well through both NF and RO membranes because they are uncharged, polar, and small.[14]

Species	RO Membranes	NF Membranes
Divalent ions (Ca, Mg)	98–99%	90–98%
Monovalent ions (Na, Cl)	96–99%	50–95%
Gases (O_2, Cl_2, CO_2)	0%	0%

TABLE 8.5 Rejection of Various Species by RO and NF Membranes

Osmosis and Reverse Osmosis

Osmosis should be understood first, in order to understand the basic principal behind RO and NF. Consider Fig. 8.23, where a container is separated into two compartments by a semipermeable membrane. This membrane allows water and some dissolved solids to pass through, but retains the majority of dissolved solids. One compartment has a relatively high concentration of dissolved solids, while the other compartment has a relatively low concentration of dissolved solids. Osmosis is the natural process by which water diffuses from the low concentration compartment, through the membrane, and into the high concentration compartment, in essence diluting the one solution. Water continues to diffuse in this direction until equilibrium is achieved, when the concentration of dissolved solids is the same in both compartments.

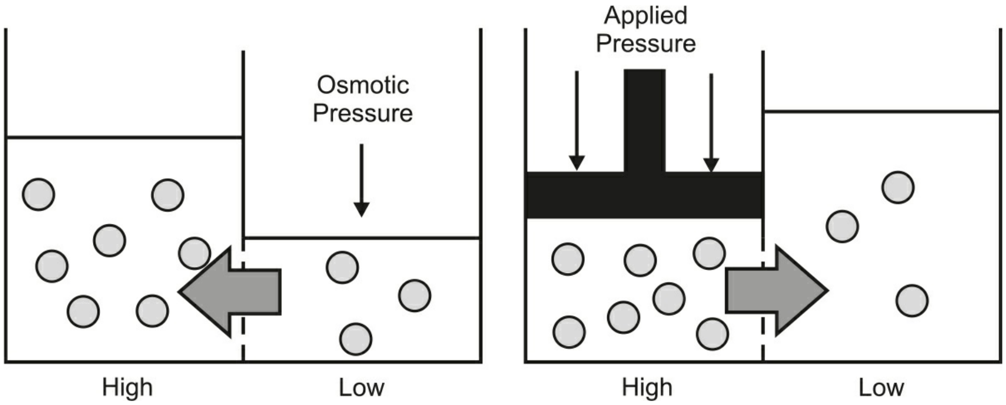


FIGURE 8.23 Concept of osmosis and reverse osmosis.

At equilibrium, there is a difference in height between the two compartments, and the difference corresponds to the osmotic pressure of the solution. The higher the concentration of dissolved solids, the greater the difference in height, and the greater the osmotic pressure of the solution. Approximately 4 kPa (0.6–1.1 psi) corresponds to 100 mg/L total dissolved solids (TDS). Therefore, for seawater at a concentration of 35 000 mg/L TDS, osmotic pressure is roughly 2.4 MPa (~350 psi). For brackish water with a concentration of about 1500 mg/L TDS, osmotic pressure is roughly 103 kPa (~15 psi).

If pressure is applied to the compartment containing that originally contained the higher concentration of dissolved solids, and that pressure is greater than the osmotic pressure of the solution, water is forced to move in the reverse direction. Water moves from the compartment being pressurized to the other compartment, leaving behind a more concentrated solution in the pressurized compartment, while generating relatively pure water in the other. This is RO.

While the description above depicts a batch, dead-end process, RO and NF systems rely on cross-flow filtration to affect separation of solutes from liquid. Figure 8.24 shows simplistically, how NF and RO systems functions. The concentration control valve is the key to operating the system, in that this valve is used to set the operating pressure and recovery of the system. Without this valve, RO and NF would be simply flow through the concentrate side of the membrane, with no resistance in terms of backpressure to force water from the high concentration feed, through the membrane, to the low concentration permeate.

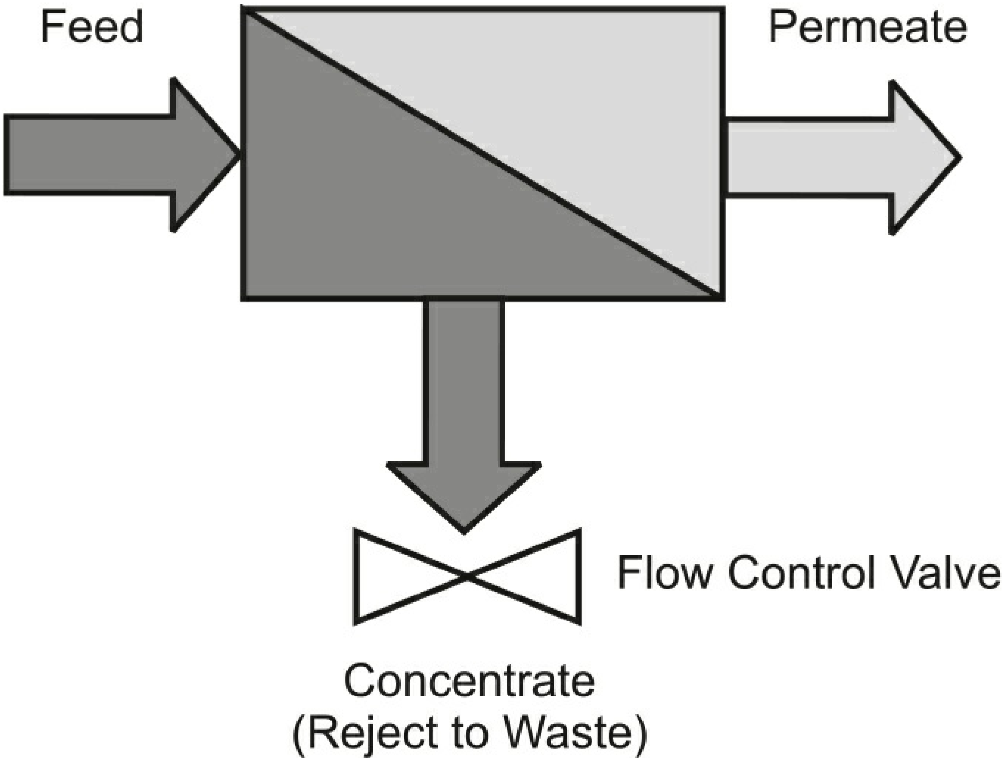


FIGURE 8.24 Conventional depiction of NF and RO operations.

RO and NF Membrane Materials

The most common RO membranes are either homogeneous, asymmetric cellulose acetate (CA) or a version of polyamide (PA) composite. Cellulose acetate membranes were the first commercially viable RO membranes developed and are still used today for some highly fouling and niche applications. These membranes consist entirely of the cellulosic material. Polyamide composite membranes, on the other hand, consist of a thin skin (typically 0.2 µm thick) of polyamide that is interfacially polymerized on top of a polysulfone support. The composite of the polyamide thin film and polysulfone microporous support, is supported on a non-woven fabric backing that plays no role in the performance (rejection and flux) of the membrane. Figure 8.25 shows a cross section of a composite membrane. Because of the composite nature, PA membranes are sometimes referred to as thin-film composites (TFC®). (Note that all PA membranes are TFC®, but not all TFC® membranes are composed of polyamide.) PA membranes exhibit higher rejection of silica and other solutes than CA membranes, and therefore, are used for most industrial (medium to high pressure boiler feed) and high-purity applications. Cellulosic membranes are used in bottled water processes where high rejection is not as critical and chlorine tolerance is essential, as well as some other niche applications. Table 8.6 compares characteristics of CA and PA membranes.

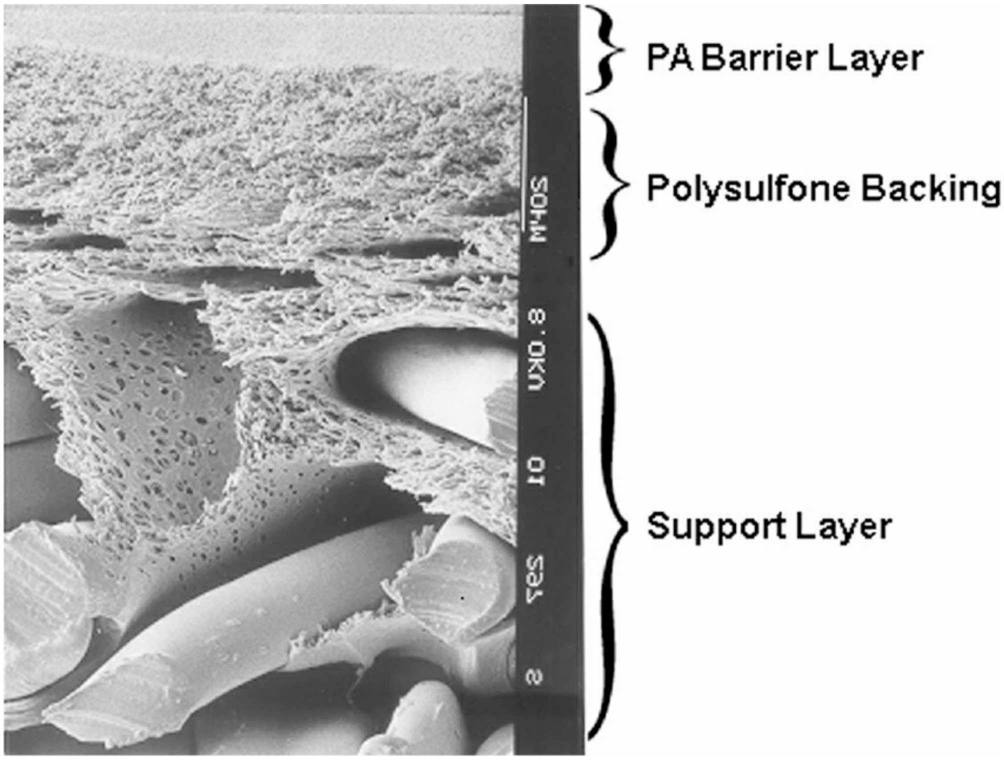


FIGURE 8.25 Composite membrane cross section.

Item	PA Membranes	CA Membranes
Membrane surface charge	Negative	Neutral
Membrane surface morphology	Rough	Smooth
pH range, continuous	3–10	4–6
pH range, cleaning	1–13*	3–7*
Operating pressure, psig (MPag)	150–400 (1–2.8)	200–600 (1.4–4.1)
Temperature, °F (°C)	113 (45)	95 (35)
Chlorine tolerance (continuous), mg/L	0 (<0.02)†	1.0

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*Check with membrane supplier for actual limits
†Practical limit

TABLE 8.6 Comparison of PA and CA RO Membranes

RO and NF membranes are very similar in that most NF membranes are based on polyamide chemistry.[15] However, some manufacturers use polypiperazine or polyethersulfone chemistries to adjust the performance of the membrane.[16] The performance of NF membranes spans a great range (Table 8.5), such that researchers have used the terms "loose" and "tight" to describe the various NF membranes. Tight NF membranes resemble low-pressure RO membranes in that the separation is based on the solution/diffusion model and charge exclusion, while loose NF membranes rely primarily on charge exclusion, and preferentially pass lower valence ions over ions with higher valence.[17]

There is debate in the membrane community whether RO and NF membranes have defined pore structures that contribute to mass transfer through the membrane.[18] While RO membrane performance can be described very well by the solution/diffusion model (nonporous model), NF can be adequately described by both porous (size exclusion) and nonporous modeling. Hence, most researchers now consider NF to span the gap between RO and UF membranes in terms of performance and mechanism of transport.

Modules

The first commercial RO membranes were tubular CA membranes installed in

1965 in Coalinga, CA. These membranes were easy to prepare. Figure 8.26 shows a schematic of the casting equipment used by Sidney Loeb in preparing these tubular membranes. But, the modules were more complicated to assemble. Figure 8.27 shows a cross section of a tubular RO module.

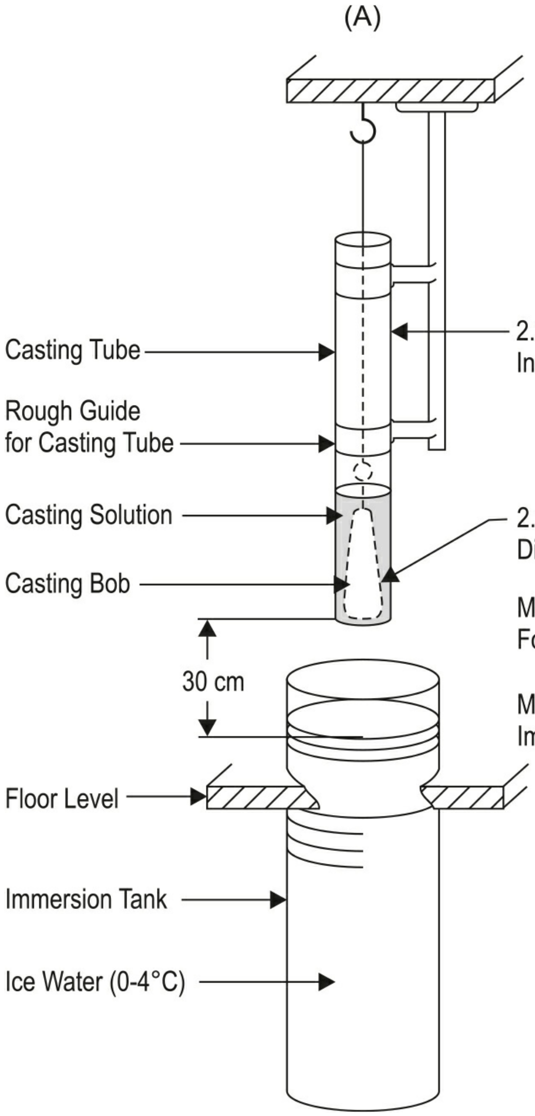

FIGURE 8.26 Schematic of tubular casting equipment used by Sidney Loeb to prepare the first commercially-viable RO membranes. (*Courtesy of Julius Glater, UCLA.*)

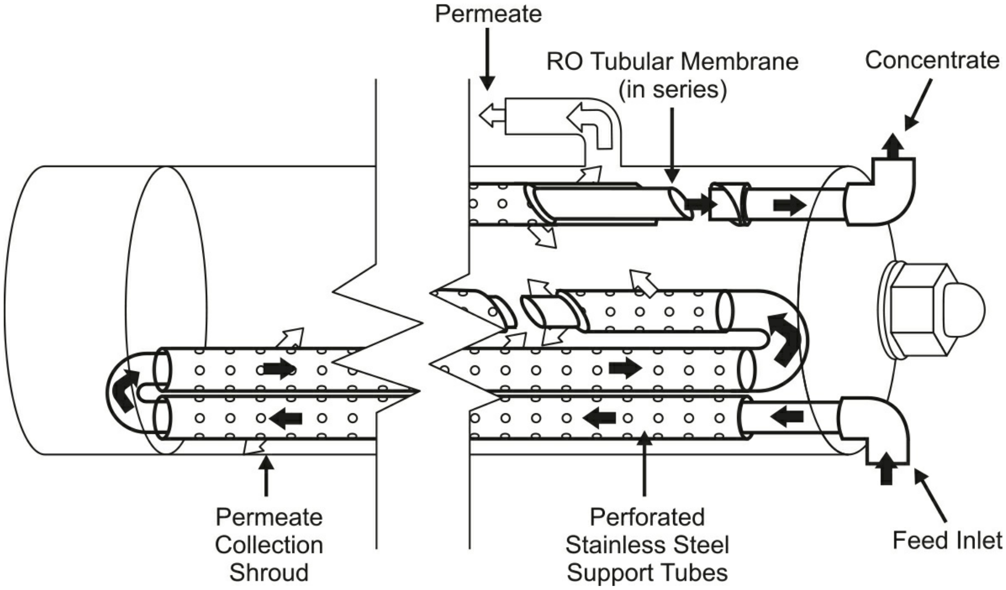

FIGURE 8.27 Tubular RO membrane module. (*Courtesy of Scrivener Publishing*.)

DuPont then developed the hollow fine fiber RO membranes and modules in 1967. While DuPont no longer makes RO membranes, some manufacturers (Toyobo) still make the hollow fine fiber membranes and modules.

Typical commercial RO/NF modules today are the spiral wound configuration. These modules are relatively easy to assemble using automated equipment. They can be manufactured in a wide range of sizes, with a broad range of membrane area per module, and various feed spacer thicknesses and configurations. For example, a standard 203 mm (8 inches) diameter, 1 m (40 inches) long module can contain anywhere from 32 to 41 m^2 (345–440 ft^2) of membrane area. The greater the membrane area per module, the thinner the feed spacer tends to be to allow for the additional membrane area. Feed spacer thicknesses for RO and NF applications range from about 28 to 34 mil. A thicker feed spacer provides a wider channel for feedwater, thereby reducing the tendency to foul the spacer, slowing the increase in feed-side pressure drop. This also allows for a more effective cleaning of the membrane. Research work has also improved the flow characteristics of feed spacers, to promote more turbulence in an effort to minimize concentration polarization and minimize “dead” zones on the membrane where fouling and scaling can occur.

Industrial spiral wound modules have an outer casing of fiberglass. There are also “sanitary,” or “full fit,” with a net that wraps around the module, without the outer casing. They are operated with a feed bypass to eliminate dead-zone hideouts for bacteria that typically occur under the fiberglass casing. These modules are used in applications such as pharmaceuticals, and food and beverage, where hideout must be avoided.

High-temperature modules are available. These modules are typically full-fit, and are assembled using different materials, (e.g., glues) so that the membranes can be operated at higher temperatures. Some modules can be heat sanitized at up to 90°C (194°F), but must be chemically cleaned at 40°C (104°F) or below to prevent damage to the membrane itself. Pressure plays a role in how hot the modules can be operated, with higher pressure necessitating lower temperature. For example, some seawater membranes operating at 8.3 MPa (1200 psi) can only operate at 15°C (77°F) to minimize damage, while at 2.6 MPa (400 psi), a temperature of 70°C (158°F) is possible. Also, note that as the operating temperature increases, the rejection decreases, dropping to as low as 95% at temperatures greater than 70°C (158°F).

System Design

Figure 8.28 shows a typical cross-flow RO or NF configuration. This particular configuration is a 2:1 or "2 by 1" array. The first number in the array refers to the number of parallel pressure vessels and is called the first stage. The second number in the array refers to the number of parallel pressure vessels in what is known as the second stage. RO configurations may have just one, or as many as five or six stages.

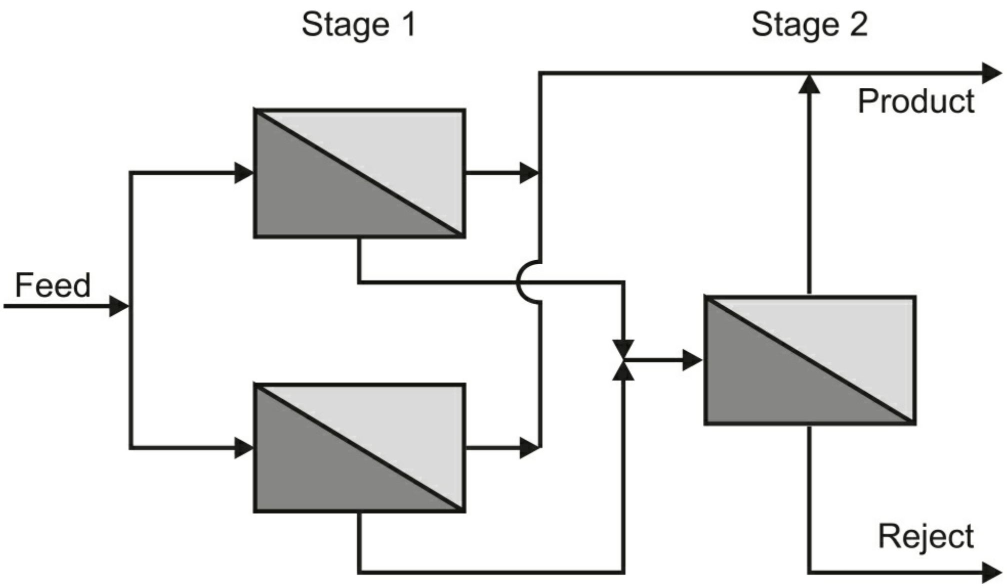

FIGURE 8.28 2:1 vessel array RO or NF system.

Feedwater is divided more or less equally among pressure vessels in the first stage. The feed flows in a cross-flow manner across the surface of the membranes. Permeate from each membrane module in the first-stage pressure vessels is combined to become overall permeate from the first stage. Concentrate from each of the pressure vessels in the first stage is combined and becomes feed to the second stage. Permeate from each membrane modules in the second-stage pressure vessels is combined with the permeate from the first stage to become overall permeate from the system for this two-stage configuration. Concentrate from the second stage becomes overall concentrate from the system for a two-stage configuration. If there were a third stage, concentrate from the second stage would become feed to the third stage, and so on. The permeate from each successive stage is combined with the permeates from all the previous stages to become the overall permeate form the system.

The number of stages in an NF or RO system is determined by the overall recovery. In general, a stage containing six, 40-inches modules will recovery about 50% of the feedwater as permeate. Each additional stage serves to generate more total permeate from the system, resulting in less wastewater from the system. However, higher recovery means that the feedwater becomes more concentrated through each successive stage. And, as feedwater becomes more concentrated through each successive stage, the permeate also becomes successively more concentrated. Hence, higher recovery results in lower quality permeate. This is demonstrated for an RO system in Figure 8.29.

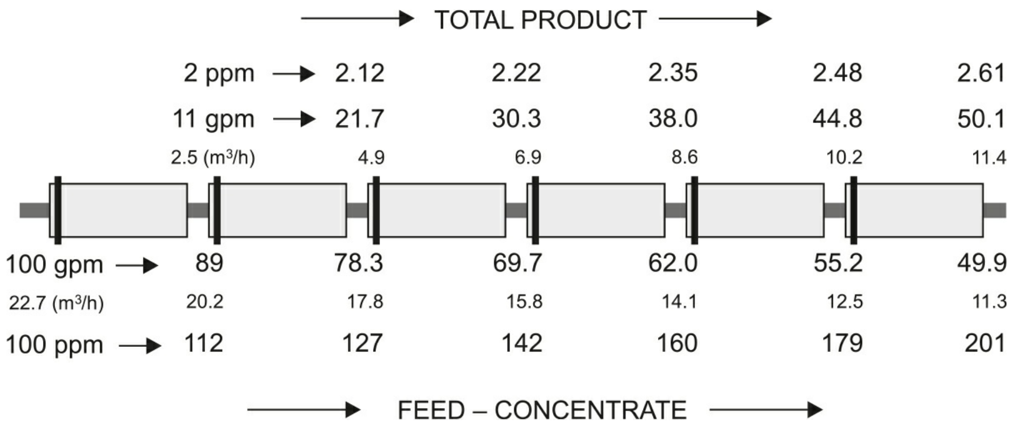

FIGURE 8.29 Water and mass balance through an RO pressure vessel illustrating the rising concentration of solids in both the feedwater and permeate as water is recovered (removed) from the feed. (*Courtesy of Scrivener Publishing*.)

Figure 8.30 shows the flows and concentrations that would be expected given an RO system with 22.7 m^3/h (100 gpm) feed containing 100 mg/L TDS (this assumes the typical ~50% recovery per stage). Table 8.7 summarizes the conditions.

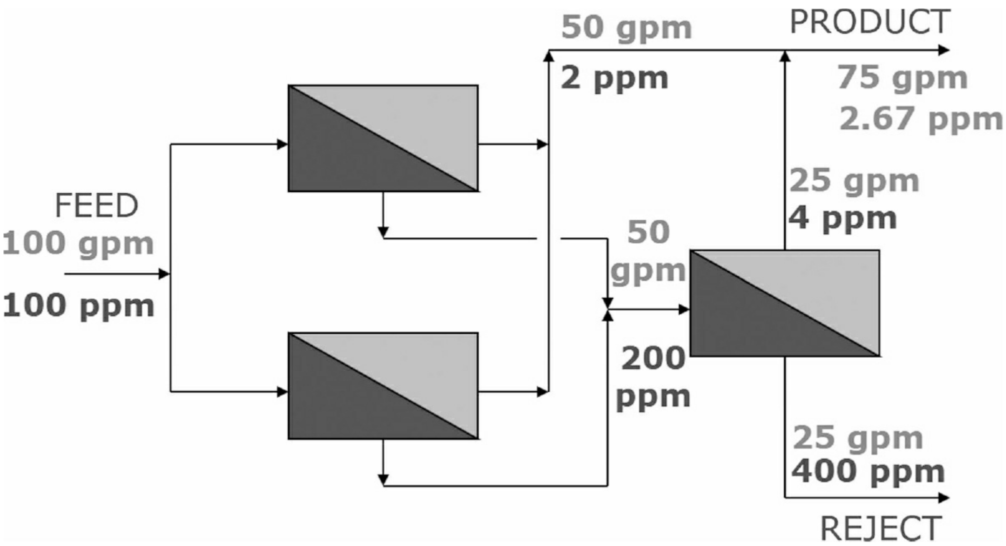

FIGURE 8.30 Water and ion balance in 2:1 RO array with 50% recovery per stage and 98% solute rejection.

The number of pressure vessels in each stage is determined by velocity (typically measured using flow rate) through each pressure vessel. Table 8.8 lists the recommended concentrate flow rate out of a single pressure vessel as a function of feedwater quality for RO and NF systems. Since a higher velocity yields a thinner boundary layer and, hence, less concentration plarization, a high velocity is recommended for lower-quality feedwater, as shown in the table.

Location	Flow Rate, gpm (m^3/h)	Concentration, mg/L
Feed	100 (22.7)	100
Interstage permeate	50 (11.4)	2
Interstage concentrate	50 (11.4)	200
Second-stage permeate	25 (5.7)	4
Second-stage concentrate	25 (5.7)	400
Overall permeate	75 (17)	2.67

TABLE 8.7 Flow Rates and Concentrations through a 2:1 Array at 50% Recovery per Stage and 98% Solute Rejection

TABLE 8.8 Recommended Minimum Concentrate Flow Rate versus Feedwater Quality for 8 Inches (203 mm) Diameter Spiral Wound Membrane Modules to Minimize Fouling and Scaling

A third factor in determining the array for a given application is the overall water flux through the membranes. Table 8.9 lists the recommended water flux rates for feedwater as a function of the feedwater quality for RO and NF systems. Recall that higher flux leads to higher fouling and scaling due to concentration polarization effects. Hence, lower feedwater quality feed streams (e.g., higher concentration of suspended solids and scale forming minerals) require lower flux to minimize fouling and scaling, as shown in Table 8.9. The advantage of higher flux rates is that less membrane area, hence smaller footprint and, more importantly, lower capital cost, are required.

Feedwater Quality	**Recommended Flux, gfd* (L/[m^2•h])**
RO permeate	21–25 (36–42)
Well water	16–20 (27–34)
Surface water, SDI[†] < 3	13–17 (22–29)
Surface water, SDI[†] < 5	12–16 (20–27)
Municipal wastewater, MF pretreatment	10–14 (17–24)
Municipal wastewater, conventional pretreatment	8–12 (14–20)

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*Gallons per square foot per day

[†] Silt density index

TABLE 8.9 Recommended Flux versus Feedwater Quality to Minimize Membrane Fouling and Scaling Due to Concentration Polarization Effects

Reverse Osmosis Permeate Polishing

For some applications, the permeate from an RO skid is not high enough to meet quality specifications. In these cases, RO permeate is polished, typically using either mixed-bed ion exchange polishers, second-pass RO, or CEDI. The second-pass RO skid takes the permeate from the first-pass skid and further removes dissolved solids to reduce the concentration of species, such as silica. Figure 8.31 shows a two-pass RO system. Note that concentrate from the second-pass RO skid is virtually always recycled to the front of the first-pass RO skid. This is because quality of the second-pass concentrate is significantly better than feed to the first pass. This concentrate stream serves to dilute the system feedwater and to keep cross-flow velocity high. Both of these are measures that minimize fouling of first-pass membranes. Diluting the feedwater also improves overall permeate quality from the two-pass RO system.

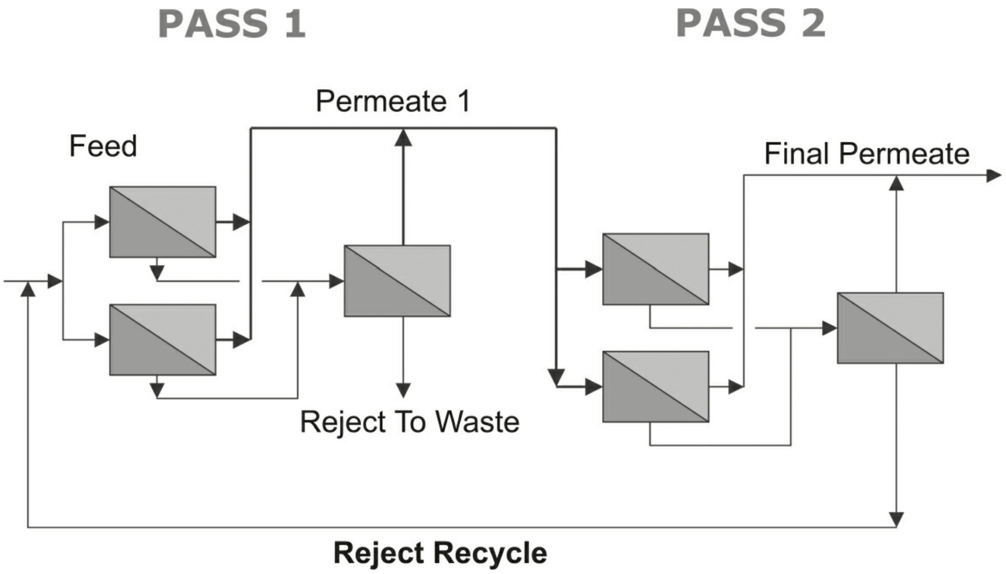


FIGURE 8.31 Two-pass RO system.

Performance, Data Collection, and Analysis

The key to keeping an NF or RO system operating well is to measure the proper parameters and use appropriate analytical techniques to interpret the data. Table 8.10 lists data that should be collected from an NF or RO system at a minimum. Of these data points, perhaps interstage data are most critical, because these allow determination of where in the system performance has declined. For example, if pressure drop is higher over the first stage, one could surmise that issues that affect the first stage, such as fouling, are occurring. Likewise, decline over the second stage could imply membrane scaling. It should be noted, however, that many NF and RO skids do not come equipped with interstage monitoring capability, making troubleshooting more difficult. In these cases, other data, such as water quality and mass balances, are required to determine what issues are affecting the membranes.

	Feed	Interstage	Permeate	Concentrate
Pressure	X	X	X	X
Flow	X	*	X	
Conductivity	X	*	X	X
Temperature	X			
pH	X			*
Chlorine	X			

*Not necessary for non-critical applications.

TABLE 8.10 Minimum Data to Be Collected from an NF or RO System

Data Normalization Once data have been collected, it should be normalized to allow comparison with previous data and to allow trending. Comparison of actual data, such as permeate flow rates and rejection, is difficult because these parameters are functions of temperature, solute concentration, and pressure, as well as degree of membrane fouling, scaling, and degradation. Since these conditions vary constantly, it is virtually impossible to accurately compare data collected at different times. To address this issue, data is "normalized" or standardized to common temperature, pressure, and concentration, typically those at startup of new membranes (see ASTM D4516-00 for normalization calculations). Without the variables of temperature, pressure, and concentration affecting normalized permeate flow rate, changes in normalized permeate flow rate are due to membrane fouling, scaling, and degradation.

Normalized permeate flow is calculated using Eq. (8.7):

$$\text{Normalized Flow} = \frac{[(\text{AAP}_S - \Delta\Pi_S)]\text{TCF}_S}{[(\text{AAP}_a - \Delta\Pi_a)]\text{TCF}_a}(\text{Actual Flow}) \tag{8.7}$$

where AAP = the average applied transmembrane pressure

$$\text{AAP} = P_{\text{feed}} - \frac{\Delta P}{2} - P_{\text{perm}} \tag{8.7a}$$

where P_{feed} = applied feed pressure
ΔP = pressure *drop* from feed inlet to concentrate effluent
P_{perm} = permeate pressure
$\Delta\Pi$ = difference between the osmotic pressure on the membrane feed and permeate sides
TCF = temperature correction factor (membrane and manufacturer dependent)
Subscripts s = subscript for "standard" conditions
a = subscript for "actual" conditions

Figure 8.32 shows the slopes of normalized permeate flow curves for membrane degradation, fouling, and scaling, and no net change in normalized performance. Note that a flat curve may mean all is well with the system, or that membranes degradation and fouling/scaling are occurring simultaneously, and cancelling each other out. In this case, further investigative work is required to determine the status of the system.

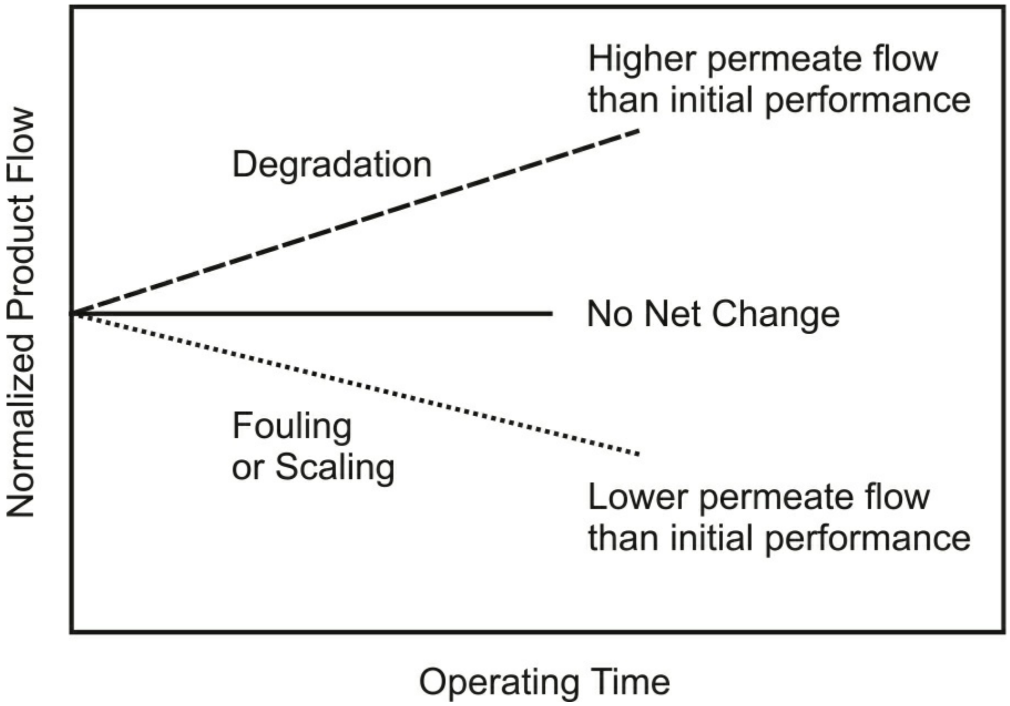


FIGURE 8.32 Normalized permeate flow slopes versus time and membrane fouling, scaling, and degradation.

Figures 8.33 and 8.34 show observed and normalized permeate flow rates for an actual RO system operating on a combination of Delaware River water and cooling tower blowdown. Figure 8.33 shows the observed permeate flow rate from this RO system. Operators did an excellent job of maintaining design productivity. However, in order to maintain the permeate flow rate of 77 M/h (340 gpm), operators had to gradually, but significantly, increase operating pressure of the system. Figure 8.34 shows normalized permeate flow rate for the same system. Normalized permeate flow rate does detect increased operating pressure to maintain productivity and reflects this as a decrease in normalized permeate flow.

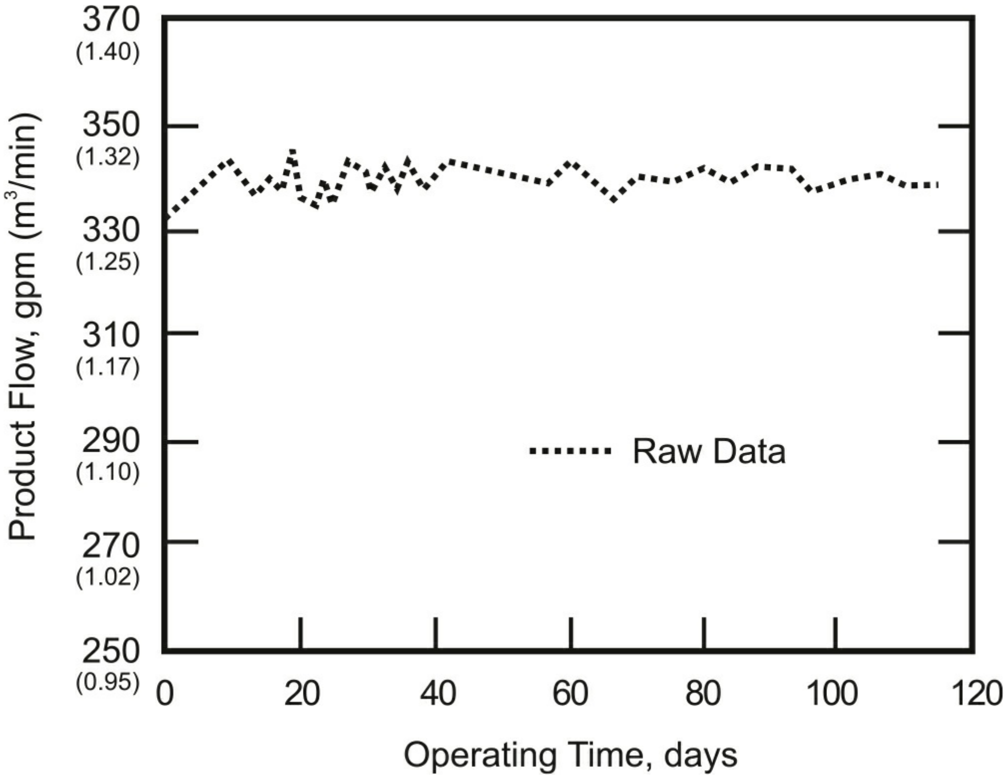


FIGURE 8.33 Observed permeate flow rate for actual RO system.

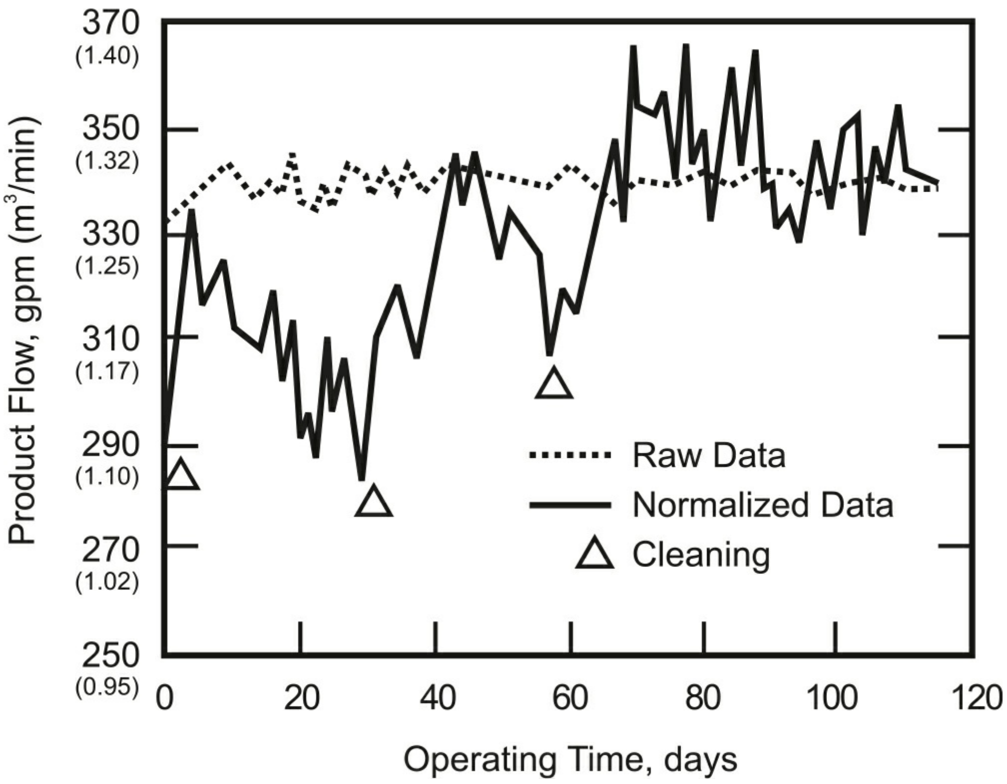


FIGURE 8.34 Observed and normalized permeate flow rate for same RO system as in Fig. 8.33.

Membranes in this example were periodically cleaned to restore performance. In addition, the pretreatment system to the membranes was upgraded to minimize membrane fouling that was occurring. As Fig. 8.34 shows, normalized permeate flow rate and observed permeate flow rate began to track at about day 90, indicating fouling issues were resolved.

Other Parameters of Interest Other parameters to monitor include pressure drop from the feed to the concentrate streams and normalized salt passage.

Nominal pressure drop should be about 21 to 28 kPa (3–4 psi) per membrane module, such that the first-stage pressure vessel with six membranes elements should have a pressure drop of about 124 to 165 kPa (18–24 psi) (note that the pressure drop per module is a function of the specific type of membrane employed and can vary from type to type). Pressure drops higher than this could be indicative of membrane fouling or scaling. Pressure drops approaching 345 kPa (50 psi) over a six-element single stage can lead to catastrophic failure of the membrane module via telescoping or cracking of the outer fiberglass shell.

Pressure drop can be normalized using Eq. (8.8):

$$\text{Normalized Differential Pressure} = \frac{\Delta P_{\text{actual}} \times (2 \times \text{CF}_{su} + \text{PF}_{su})^{1.5}}{(2 \times \text{CF}_{\text{actual}} + \text{PF}_{\text{actual}})^{1.5}} \qquad (8.8)$$

where ΔP_{acutal} = actual differential pressure
CF = concentrate flow
PF = permeate flow
su = subscript for start up

Finally, salt passage can be normalized using Eq. 8.9:

$$\text{Percent Normalized Salt Passage} = \left[\frac{\text{EPF}_a}{\text{EPF}_s} \times \frac{\text{CFC}_s}{\text{CFC}_a} \times \frac{\text{STCF}_a}{\text{STCF}_s} \times \frac{C_{fa}}{C_{fs}}\right] \times \%\ \text{SP}_a \qquad (8.9)$$

where EPF = average permeate flow divided by the number of membrane modules
STCF = salt transport temperature correction factor (from membrane manufacturer)
C_f = feed salt concentration
%SP = percent salt passage
CFC = concentration of the feed concentrate:

$$\text{CFC} = C_f \times \frac{\ln \frac{1}{1-Y}}{Y} \qquad (8.9a)$$

where Y = product flow/feed flow
subscripts:
s = subscript for "standard" conditions
a = subscript for "actual" conditions

Common Causes of Reduced Efficiency: Fouling, Scaling, and Degradation

Primary concerns for NF and RO users are fourfold:

1. Quantity

2. Quality
3. Reliability
4. Safety

If water quantity requirements are not met, plant efficiency and operating costs are affected. In severe cases, plant shutdowns may be required. If water quality drops, downstream treatment equipment such as ion exchange polishers requires additional maintenance and expense. And, it is important to have a system that operates reliably and safely.

Keeping an NF or RO system running at optimum efficiency requires: scale and deposit control, fouling prevention, timely membrane cleaning, routine membrane replacement, and membrane integrity testing. All of these factors represent system costs (chemical, labor, energy, and maintenance). As membranes foul or scale, total operating cost for water production increases.

Membrane Fouling Membrane fouling is caused by particles and microbes that stick to feed channel spacers and to the surface of the membrane. Table 8.11 lists species that commonly foul NF and RO membranes. The table also lists generally accepted guidelines established to minimize the effect of these species.

Species	Measure	Generally Accepted Guidelines
Suspended solids	Turbidity	<1 NTU*
Colloids	Silt density index (SDI)	<5* (best practice, <3)
Organics	Total organic carbon (TOC), mg/L	<3
Color	Color units	<3 APHA†
Metals: Fe, Mn, Al	mg/L	<0.05
Hydrogen sulfide (H_2S)	mg/L	<0.1
Microbes	Dip slides	<1000 colony forming units/mL‡

*Membrane manufacturer's warranty condition
†American Public Health Association
‡In RO concentrate

TABLE 8.11 Species That Commonly Foul NF and RO Membranes and Generally Accepted Guidelines to Minimize Fouling

Fouled membranes exhibit two key performance problems: high operating pressure (or low permeate flow) and high pressure drop. Foulants form essentially a second layer through which feedwater must travel before reaching the membrane. Higher feed pressure is required to force water through this layer of foulants. Higher feed pressure naturally results in higher pressure drop. The foulant layer increases resistance to flow of water across the membrane, which is measured as additional pressure drop. Finally, foulants that 'stick' to the feed channel spacer greatly contribute to pressure drop through the system.

The phenomenon of fouling occurs primarily in the lead stage of an NF and RO system. This is because the lead membranes act as barrier filters to particulates that cannot pass through them. The lead membranes in the system are exposed to the particulates first in the process, so these membranes tend to foul more than the membranes that follow.

Colloids Fouling of membranes with colloidal silica and clays is a serious problem for NF and RO membranes, particularly those operating on surface water sources, where colloidal silica and clays are commonly found.

Colloidal fouling is typically controlled by using pretreatment steps to remove particles to a silt density index (SDI) of less than five [see ASTM D4189-07 (reapproved 2014) for the SDI testing method]. Silt density index measures the fouling potential of the membranes with particulates larger than 0.45 μm.

It should be noted that when metals, such as iron, aluminum, or even calcium, coexist with silica, the respective silicates can form, even when the concentration of silica is below saturation. In the case where silicates can form, it is necessary to reduce the concentration of metals and/or silica via pretreatment so minimize this potential.

Organics Organic compounds, natural as well as synthetic, present in feedwater can cause NF/RO membrane fouling by various means. They can adsorb directly onto the membrane surface (adsorptive fouling), interact with other constituents of feedwater to produce gelatinous foulants on the membrane surface (organic deposit fouling), or promote growth of biofilm on the membrane (biofouling). The term organic fouling is used broadly here to include all types of fouling caused by organics, which is a frequent cause of NF and RO performance deterioration, and can account for 50% of membrane failures as shown in Fig. 8.35.

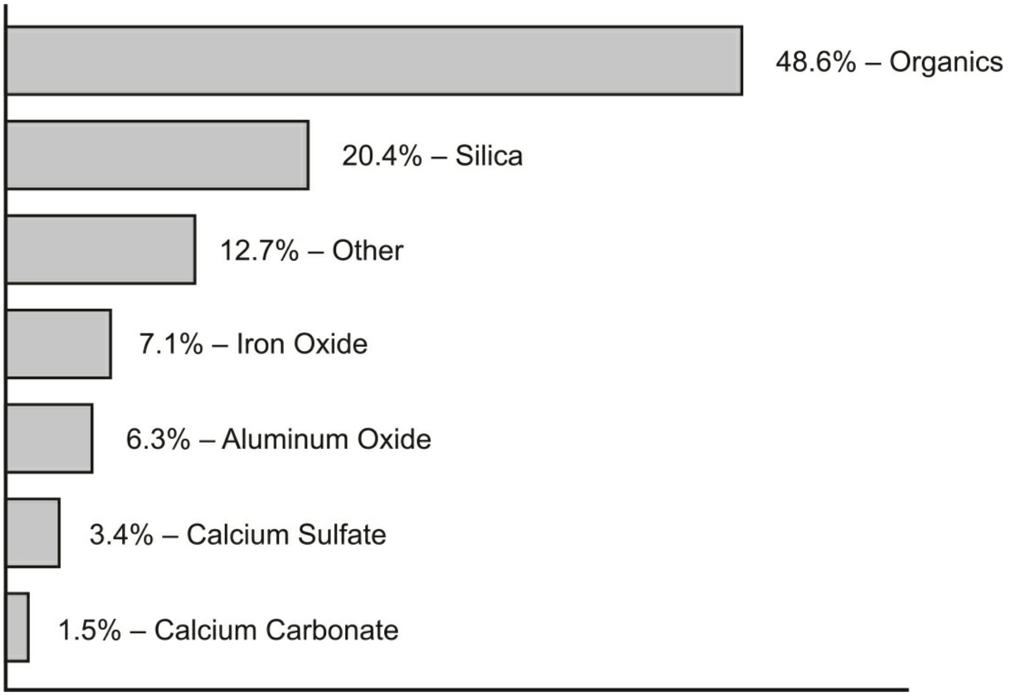


FIGURE 8.35 Typical causes of RO fouling, as gathered from 150 membrane autopsies, as presented at the 62nd Annual International Water Conference. (*Courtesy of IWC.*)

Potential sources of organics include natural organic matter (NOM such as humic and fulvic acids), synthetic chemical contaminants (especially in wastewater reclamation applications), and water treatment chemicals added to feedwater. Due to electrostatic interaction of cationic polymers with the anionic membrane surface, cationic polymer coagulants used in clarifiers or as filter aids can cause NF and RO membrane fouling when overdosed. Polymeric NF and RO antiscalants, if excessively overdosed, can deposit on membrane surfaces and cause fouling. Acid addition, while sometimes used for scale control, has been reported to increase propensity for NOM to cause membrane fouling.

Potential for water treatment organic chemicals to promote biofouling is often overlooked but has been studied. Organic chemicals provide organic carbon that can be metabolized by microbes as energy and carbon sources. Assimilable organic carbon (AOC) is generally accepted by the scientific community as the best indicator of biofouling potential of an organic compound.

Levels of AOC of various commercial antiscalants have been measured and found to vary as much as tenfold. To achieve highest RO system reliability in critical applications such as ultrapure water (UPW) production, it is desirable to minimize AOC contribution of water treatment chemicals.

True Color True color fouling due to lignins and tannins is irreversible; they adsorb onto the membrane polymer and foul the surface of the membrane. This leads to permanent flux decline and lost productivity of the system. True color is typically removed from NF and RO feedwater via clarification and sedimentation.

Metals Several metals and metallic compounds are of interest. Metal oxides, such as those of iron and manganese, can precipitate on membranes. Further, soluble forms of these metals can catalyze the oxidization of the membranes if an oxidant were present. Hydrogen sulfide is important in that it can release elemental sulfur, a very sticky element that is virtually impossible to remove from the membrane. These compounds are best reduced in feedwater using filtration through manganese dioxide media, such as pyrolusite, or sand coated by manganese dioxide (Greensand).

Biofouling Biofouling is the bane of existence for operators of NF and RO systems. Poorly operated pretreatment equipment, especially filters such as carbon filters, can promote biofouling by providing a large surface area as a breeding ground for microorganisms. The presence of organics can promote biogrowth on the membranes, as discussed earlier. The combination of organics within a carbon filter can create an incubator-type environment to foster proliferation of bacteria, and then can easily slough out of the filter into the NF or RO system.

Membrane biofouling is exceptionally difficult to control, because no oxidants can be used on the membranes to kill the organisms. Hence, the efforts to control biofouling are confined to pretreatment and on-time cleaning of the membranes. Pretreatment with oxidizers is typically used to control biogrowth in the feed system, with the hopes of minimizing the proliferation of microorganisms in the pretreatment system and on the membranes. Once biofouling has developed on the membrane, it is imperative that the membranes are cleaned on a regular schedule, as determined by the normalized performance of the system.

Membrane Scaling Scaling occurs as selective permeation of water through the membrane causes supersaturation and precipitation of sparingly soluble mineral salts, such as calcium carbonate and calcium sulfate. A method to avoid scale formation is to keep water recovery low. However, this means inefficient use of water and is not practical for industrial NF and RO plants, which must use water resources efficiently and avoid excessive concentrate waste.

Sodium regenerated ion exchange softeners technically offer a good method for scale control. However, using a softener can involve significant capital and operational expense. In addition, chlorides in brine regenerant discharge are becoming more regulated.

Other approaches to NF/RO scale control include acid and antiscalant dosing. Antiscalants are often the most attractive than acid due to the following advantages:

- Lower capital costs
- No handling of hazardous chemicals
- Applicable to a broad range of scales
- Better permeate quality

Antiscalants generally fall into one of two classes of compounds:

1. Threshold inhibitors (including crystal modifiers)
2. Dispersants

Threshold inhibitors prevent scaling by interfering with the crystal formation process. Dispersants, on the other hand, allow scale to form, but keep crystals small and interfere with ability of the crystal to deposit on a surface.

Polyphosphates such as sodium hexametaphosphate (SHMP) were used widely in the past, but their use has declined due in part to their tendency to hydrolyze and form orthophosphate that can lead to calcium phosphate scale problems. In addition, more effective antiscalant chemistries are available.

Polymeric dispersants are popular antiscalants; however, they are not compatible with many coagulant chemistries. Polymeric dispersants have limited calcium tolerance and can contribute to organic/biofouling due to their AOC content.

Phosphonates have proven to be significantly more effective scale control agents with higher tolerance to system variation. A wide variety of commodity and specialty phosphonates is available for scale control. Differences in performance, stability, and calcium tolerance are observed, depending on the phosphonate. System modelling helps determine which phosphonate is more appropriate for a given application.

Non-phosphonate chemistries that function through chelation are also used. This method of scale control is well documented, but effectiveness at substoichiometric levels can be limited.

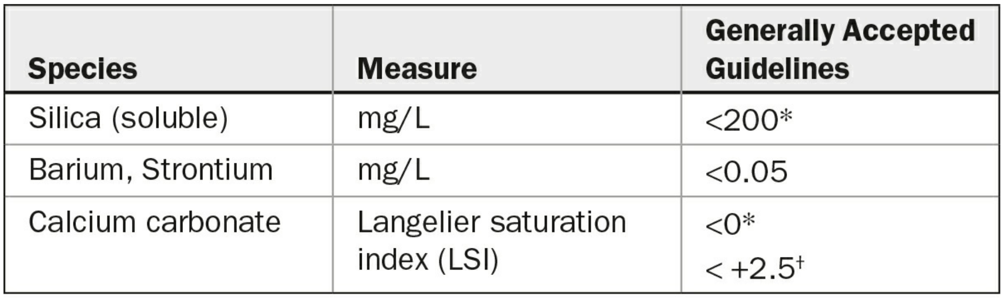
Regardless of the type of antiscalant chosen for use in an NF or RO system, it is generally accepted that both underfeed and overfeed of antiscalant chemical can be detrimental to both the performance, and total cost of operating the system. Underfeed means not enough chemical is present to prevent fouling or scale formation. Overfeed can lead to membrane fouling, which can result in severe operating problems and increased operating costs. Often, antiscalant dosed to prevent fouling is the actual cause of it. Consequences of antiscalant underfeed and overfeed suggest that dosage control is critical to good and cost-effective operation of NF and RO systems.

Unfortunately, traditional methods for monitoring antiscalant feed such as timed draw down are inherently inaccurate, do not give a rapid response, and are not easily monitored. In fact, it is primarily due to limitations on antiscalant dosage control that costlier methods such as softening or pH control are used.

Chemical suppliers, plant operators, and NF/RO experts generally assume chemical dosage (such as antiscalant) to an NF or RO unit is constant. Field studies using fluorescent tracing of antiscalants demonstrates this assumption is often false. Fluorescence technology can reveal previously unseen variations in chemical antiscalant dosing.

While antiscalants perform well as the only means or controlling most scales, in some cases such as calcium phosphate and calcium fluoride scales, acid may need to be feed in addition to, or instead of the antiscalant, due to the relative inefficiency of antiscalants for these types of scale.

Membrane scaling is caused by precipitation of saturated salts onto the membrane surface and feed channel spacers. Table 8.12 shows species that commonly scale RO membranes. The table lists generally accepted guidelines established to minimize the effect of these species.



Species	Measure	Generally Accepted Guidelines
Silica (soluble)	mg/L	<200*
Barium, Strontium	mg/L	<0.05
Calcium carbonate	Langelier saturation index (LSI)	<0* < +2.5†

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*In RO concentrate without antiscalant feed

†In RO concentrate with antiscalant feed

TABLE 8.12 Species That Commonly Scale RO Membranes and Generally Accepted Guidelines to Minimize Scaling

Scaled membranes exhibit three key performance problems:

1. High operating pressure (or low permeate flow)
2. High pressure drop
3. Low salt rejection

High pressure is required to force water through the additional scaling layer on the membranes in a manner similar to that described for fouled membranes (above). The effect of scaling on pressure drop is also similar to that of foulants, which may deposit on the feed channel spacer. The most interesting feature of scaled membranes is that apparent rejection by membranes decreases. This is because the concentration of the scaled species can be significantly higher at the membrane surface than in bulk solution. Since the membrane rejects based on what is contacting the membrane, intrinsic rejection is still the same, but rejection of the higher surface concentration means more of that species passes through the membrane than if the membrane were rejecting based on bulk concentration.

Since scale is a concentration phenomenon, it follows that it would form at the back end of the NF or RO system where feed concentration is the highest.

Calcium-Based Scales Calcium carbonate ($CaCO_3$) is the most common scale to affect NF and RO membranes. Potential for forming calcium carbonate scale is measured using the Langelier saturation index (LSI). A positive LSI favors formation of this scale. LSI can be reduced using acid. Antiscalants are also effective in minimizing formation of calcium carbonate scale. Membrane manufacturers recommend that the LSI be limited to +2.5 or less when antiscalants are used to minimize formation of calcium carbonate scale; if antiscalants are not used, the LSI should be 0.0 or less.

Calcium phosphate ($Ca_3(PO_4)_2$) and calcium fluoride (CaF_2) scales can be more difficult to control than calcium carbonate, as their solubility constants are lower (10^{-33} and 10^{-11}, respectively, compared to 10^{-9} for calcium carbonate). Most antiscalants are not very effective for these scales, so acid is typically used either alone or with an antiscalant for control.

Sulfate-Based Scale Sulfate scales of calcium and trace metals such as barium and strontium will also scale NF and RO membranes. Such scales are also sparingly soluble, for example, solubility constants of barium sulfate and strontium sulfate are 1.1×10^{-10} and 3.2×10^{-7}, respectively. It should be noted that sulfuric acid, which is commonly used for reducing LSI or to address calcium phosphate or calcium fluoride scales, increases potential for forming sulfate-based scale. This is due to the additional sulfate to the solution this type of acid introduces. Care should be exercised when sulfuric acid is used for reducing the scaling potential of calcium-based scales.

Silica Formation of silica scale is dependent upon the temperature and pH of the water as well as the concentration of silica present. Silica decreases in solubility at lower temperatures and is least soluble between pH 6 and 9. Hence, operation at higher temperature and slightly acidic or highly alkaline conditions is preferred to minimize formation of silica scale. Another method of prevention is operating the system at a recovery that does not concentrate the silica to the point of saturation. In general, a concentration of about 160 to 180 mg/L is feasible at typical temperature and pH conditions for RO/NF systems. Silica scale is extremely difficult to remove from membrane surfaces, so prevention is the key method of control.

Note that at pH greater than 8, silica exists as the silicate anion (SiO_3^{-2}), which readily reacts with metals such as aluminum and iron to from insoluble silicates. These particles can foul an NF or RO membrane as discussed earlier.

Membrane Degradation Membrane damage or integrity loss, resulting in lower salt rejection and higher total dissolved solids (TDS) in NF or RO permeate, can be caused by:

- Chemical attack (e.g., oxidation by residual chlorine, frequent membrane cleaning
- Exposure to hydrocarbon solvents which dissolve the polyamide membrane layer)
- Physical stress (e.g., water hammer or excessive pressure drop due to excessive membrane fouling or scaling)

Methods to minimize membrane damage include complete feedwater dechlorination, proper mechanical design and operating conditions, and adequate pretreatment to reduce cleaning frequency.

Membrane degradation occurs when membranes are operated outside limits that have been established for safe RO operation. Table 8.13 lists conditions under which most RO/NF membranes will degrade.

Item	Measure	Value
Chlorine, free	mg/L	<0.02
Temperature	°C	45*
pH, normal operations	Units	3–10
pH, cleaning operations	Units	1–13*
Metals catalysts: Iron, manganese, cobalt	mg/L	<0.05
Hydrocarbon solvents	mg/L	0.0

*Check with membrane manufacturer; maximum pH and maximum temperature are related

TABLE 8.13 Conditions That Lead to RO Membrane Degradation

Degraded membranes exhibit higher permeate flow and lower salt rejection than intact membranes. Operating pressure may also be lower.

Chlorine and other oxidizers attack (oxidize) most NF and RO membranes. With exposure to 1 mg/L free chlorine noticeable degradation can occur in as little as 200 hours. Most NF and RO membranes can tolerate from 200 to 1000 mg/L.h of exposure to chlorine; by this time, salt will have doubled. (Cellulose acetate membranes can tolerate up to 1 mg/L free chlorine continuously.)

Chloramines are generally less damaging to NF and RO membranes, typically up to 300 000 mg/L.h exposure to pure chloramine, by the time salt passage doubles. But since they are typically in equilibrium with free chlorine, degradation can occur much sooner. Additionally, free ammonia can also be present, which will swell the membrane, leading to a *reversible* increase in salt passage. This phenomenon is a function of ammonia gas, and, therefore, occurs when the pH of the solution is greater than about 7.5. Most membrane manufacturers recommend keeping the pH at 7.2 or below minimize membrane swelling with ammonia gas.

Metals such as iron, manganese, and cobalt catalyze oxidation of NF and RO membranes if any oxidizers are present (chlorine, chloramine, ozone, hydrogen peroxide, etc.). This will significantly reduce the exposure time until salt passage doubles. Thus, the concentration of transition metals should be limited to avoid this catalytic degradation.

Most NF and RO membranes are safe to operate at pH between 2 and 10, depending on temperature. Outside of this range, membranes can begin to hydrolyze, which results in destruction of polymer chains that make up the membrane. The effect is enhanced at higher temperatures. The maximum pH a membrane can tolerate is lower at higher temperatures (Table 8.15). This is particularly important during membrane cleaning, where high temperature and high pH are beneficial for cleaning organics from the membranes.

Pretreatment

Pretreatment for NF and RO membranes, particularly for spiral wound modules, is much more involved than pretreatment for MF and UF membranes. Table 8.14 lists pretreatment guidelines and typical treatments for a number of potential foulants, scale formers, and degradation promotors.

Item	F,S,D[a]	Units	Guideline	Pretreatment Techniques
Suspended solids	F	NTU	<1[b]	Multimedia filtration
Colloids	F	SDI	<5[b]	Multimedia filtration + coagulant Membrane filtration (MF, UF)
Hydrogen sulfide	F	mg/L	<0.1	Oxidation + pyrolusite filtration
Organics (TOC)	F	mg/L	<3	Clarification Carbon filtration
True color	F	APHA or Pt-Co	<3	Clarification
Transition metals (iron, manganese)	F, D	mg/L	<0.05	Oxidation + pyrolusite filtration
Aluminum	F	mg/L	<0.05	UF + acidification to pH 6.5
Microbes	F	CFU	<1000[c]	Membrane filtration (MF, UF) Oxidizers
Calcium carbonate	S	LSI	<0.0[d] < +2.5[e]	Acid
Metals (barium, strontium)	S	mg/L	<0.05	Sodium softening Antiscalants
Silica (soluble)	S	mg/L	140–200[f]	Antiscalants Acid (< pH 5) or caustic (> pH 9) Heat Reduced system recovery High efficiency RO (HERO) process
pH	D	-	CA: 4–6 PA: 2–12	Acid or caustic
Temperature	D	°C	CA: < 35 PA: < 45[g]	Heat exchanger
Oxidizers	D	mg/L	0	Carbon filtration Sodium bisulfite

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[a] F = fouling, S = Scaling, D = Degradation
[b] Meets membrane manufacturer's warranty
[c] In the RO/NF concentrate stream
[d] Without antiscalant
[e] With antiscalant
[f] In RO/NF concentrate stream, function of pH and temperature
[g] Standard spiral wound membrane modules

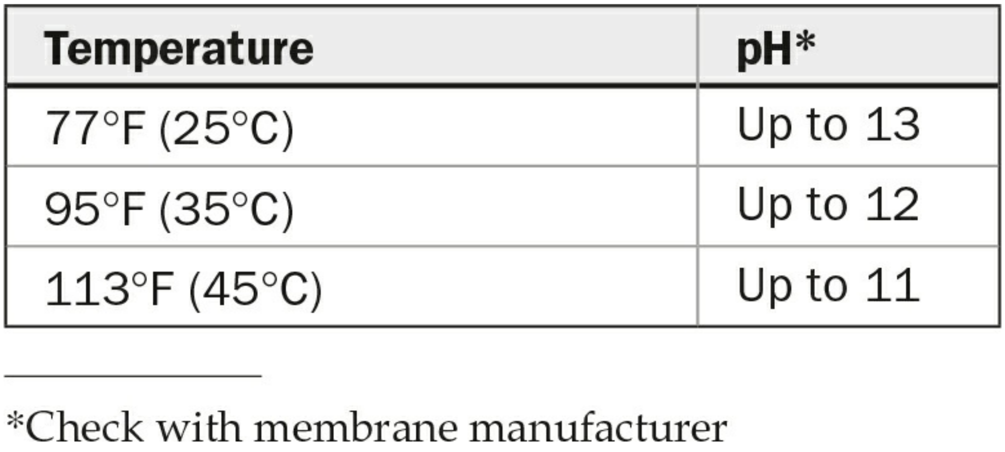
TABLE 8.14 Pretreatment Guidelines for Spiral Wound RO/NF Membranes

Membrane Cleaning

Proper membrane cleaning is integral to keeping the membrane system operating well. Membranes should not be cleaned on a predetermined timetable but rather cleaned when needed. Cleaning on a timetable can result is either too frequent cleaning, resulting in premature degradation, or to infrequent cleaning, resulting in more permanent fouling and scaling. The proper time to clean is when normalized permeate flow drops 15% or pressure drop increases 15% from start-up conditions with new membranes. A good rule-of-thumb for cleaning membranes is that they are cleaned about four times per year or twelve times in the lifetime of the membrane. More frequent cleaning implies that the pretreatment system may be inadequate, and can lead to shorter membrane life.

Membranes are cleaned at pH extremes, ranging from 2 to 13. Many times, additives such as surfactants or chelants, like ethylenediaminetetraacetic acid (EDTA), are included to aid in cleaning membranes. In general, high pH cleaning serves to remove organics, microbes, and sulfate-based scales. Low pH cleaning removes iron oxide and calcium carbonate scales. It is typically recommended that the high pH cleaning be conducted first, as low pH cleaning has been shown to "set" or harden organic and biological materials, which makes it more difficult to remove them from NF and RO membranes.[19]

Membranes should be cleaned at elevated temperatures. Table 8.15 lists the temperatures and pH combinations that are used to clean membranes. Cleaning outside these ranges can accelerate hydrolysis of the membranes.



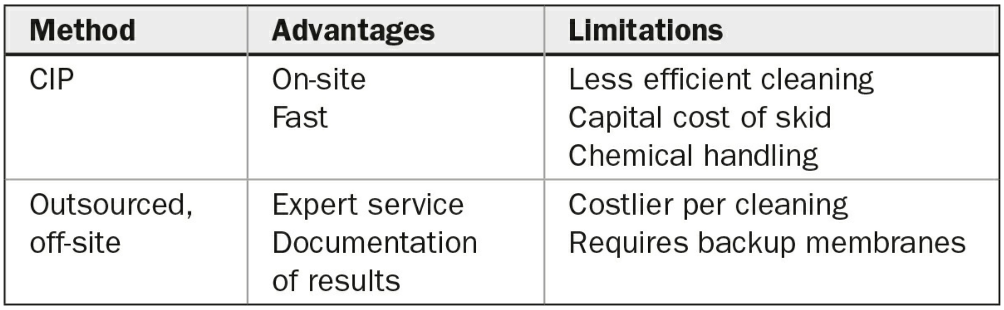
Temperature	pH*
77°F (25°C)	Up to 13
95°F (35°C)	Up to 12
113°F (45°C)	Up to 11

*Check with membrane manufacturer

TABLE 8.15 Temperature and pH Allowed During Membrane Cleaning

An NF or RO skid should be cleaned one stage at a time using a separate cleaning skid and pump. This will make sure that all the membranes are cleaned at the appropriate flow rate and pressure for optimal results. A typical protocol for a 203 mm (8 inches) diameter pressure vessel is to recirculate fresh cleaning solution through each stage individually at about 7.9 to 9.1 m^3/h (35–40 gpm). The first couple of minutes of recirculation should be discarded. If the entire cleaning solution volume turns dark immediately as it is recirculated, it should be discarded and a new batch should be prepared. After recirculation of 45 to 60 minutes, the solution is then left to soak for up to 12 hours for stubborn fouling or scaling. Final recirculation for a 203 mm (8 inches) diameter pressure vessel should be 10 m^3/h (45 gpm). It is important that the cleaning pump be sized to handle 10 m^3/h (45 gpm), while producing no more than about 414 kPag (60 psig) as no permeate should be made during cleaning. Any permeate that is generated should be sent back to the cleaning tank. The membranes should then be rinsed with permeate or higher quality water at ambient temperature, in preparation for the next cleaning solution or for return to service. Note that a high pH cleaning solution tends to “loosen” the membranes, resulting in temporary high flux and high salt passage. A low pH cleaning solution “tightens” the membrane, resulting in a temporary low flux and higher rejection. The cleaning solution should be discarded after each stage.

Membranes can be cleaned in place (CIP) or sent out for cleaning. Table 8.16 lists the advantages and limitations for each option. In general, the larger the NF or RO system, the more likely the membranes are cleaned on-site.



Method	Advantages	Limitations
CIP	On-site Fast	Less efficient cleaning Capital cost of skid Chemical handling
Outsourced, off-site	Expert service Documentation of results	Costlier per cleaning Requires backup membranes

TABLE 8.16 Advantages and Limitations of CIP Versus Outsourced Off-Site Membrane Cleaning

Troubleshooting

Virtually all NF and RO systems eventually experience problems. Low permeate quality and quantity and high operating pressures seem to be the most common ailments afflicting these systems. There are several techniques available to troubleshoot NF and RO systems:

- Mechanical inspection
- Water analyses and mass balance
- Data monitoring and normalization
- Comparison of actual performance with performance projections
- Profiling and probing
- Membrane integrity testing
- Membrane autopsy

Mechanical Inspection Mechanical inspection involves checking all instruments and probes as well as valves and fittings to make sure they are all calibrated and working properly. Checking pretreatment equipment is also important, to make sure these are operating as designed, and that the design is appropriate for the application. Channeling of water through pressure vessels can occur when the feed flow rate is too high or too low, or the media inside the vessel is dirty. Channeling results in poor removal of contaminants from the feed, which then travel on into the membrane system.

Checking to make sure the vessel was designed properly for the application is also important. For example, a carbon filter designed for chloramine removal should be sized significantly larger than one designed for chlorine removal.

Water Analyses and Mass Balance Water samples should be collected and analyzed for membrane feed, concentrate, and permeate streams. Mass balances can then be calculated for species of interest. If the amount of a species in the sum of the concentrate plus permeate, is less than that in the feed, there could be some deposition of this species within the membrane module. That this is a mass balance so the amount of a species in the feed, permeate, or concentrate is determined by multiplying the concentration by the solution flow rate.

Also, checking the water analysis periodically to make sure no new contaminants have appeared, or that the concentrations of contaminants have not changed is critical. Recall that rejection is a percentage, so that if the concentration of a species increases in the feed, its concentration will also increase in the permeate.

Data Monitoring and Normalization Data should be collected and normalized as described earlier. Using normalized data is the only true way of comparing performance over time and determining condition of the membranes. Pressure drop should be monitored as another means of determining whether membranes are fouled or scaled. Pressure drop should average about 4 to 6 psi (~27–41 kPa) per element, so that a six-element pressure vessel should have a pressure drop of about 24 to 30 psi (~165–207 kPa). Maximum pressure drop per six-element vessel is 50 psi (~345 kPa); higher pressure drop can lead to physical damage of the module and membranes within. High pressure drop over the first stage is usually indicative of membrane fouling, while high pressure drop over the last stage is usually indicative of scaling.

Comparison of Actual Performance with Projected Performance Comparison of projected performance and actual performance can be very useful. The projections give an indication of what the operating pressure should be, as well as pressure drop, and permeate quality. Most membrane manufacturers indicate that the actual operating pressure and permeate flows should be within ±15% of the projections; permeate concentration should agree with the projection. It should be noted that projection and actual performance should be compared at the same temperature, as temperature affects performance. For example, higher temperature means lower pressure is required to pump the same amount of water through the membrane. Higher pressure also results in lower permeate concentrations, (better quality).

Profiling and Probing Profiling and probing techniques are used to identify leaks in the RO system due to breaches in the membrane from degradation, or damaged O-rings on inter-connectors or end caps. These techniques can also be used to detect membrane scaling.

If an RO skid is exhibiting low permeate quality, it should be subjected to profiling. Profiling involves measuring conductivity out of each individual pressure vessel permeate sample port. The pressure vessels exhibiting high conductivity should then be probed. Probing requires that a 6.4 mm (0.25 inch) diameter tubing be snaked down through the permeate channels in all the membranes loaded in the pressure vessel of interest. While the RO is running, a sample of water running through the tubing from the other end of the pressure vessel is measured for conductivity. The tubing is then extracted about 0.5 m

(20 inches) and conductivity is measured again. This is repeated until the tubing reaches the end of the pressure vessel. These data are then graphed, an example of which is shown in Fig. 8.36.

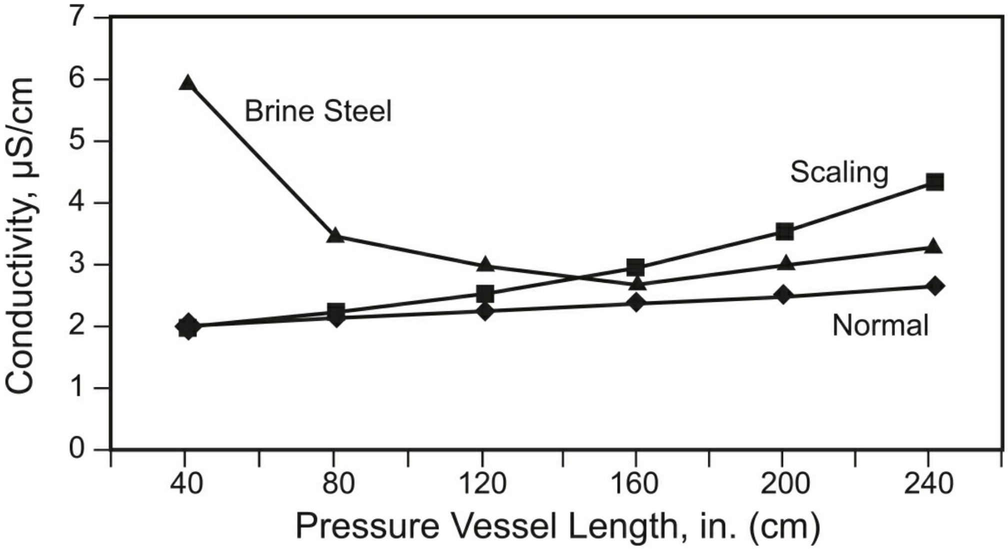


FIGURE 8.36 Data results from RO vessel profiling.

A well-operated system will show a gradual increase in concentration over the length of the pressure vessel. Spikes in the graph correspond to locations where there is higher salt passage. This can be due to O-rings failure if the spike occurs at the multiples of 1 m (40 inches), which corresponds to the space between membrane modules. Or, it can be due to damaged membranes, if the spike occurs within the length of a module. A smooth curve that is steeper than that for nominal operations is indicative of membrane scaling.

Membrane Integrity Testing Two in-situ tests can be conducted to determine if membranes have been damaged or degraded:

Vacuum Decay Test This test identifies leaky membrane modules. The test requires isolation of an entire pressure vessel. A vacuum is applied to the pressure vessel and to modules within, and the rate of decay in pressure is measured. A decay rate faster than about 10 kPa/min (1.5 psi/min) is indicative of damage. Refer to American Society of Testing and Materials (ASTM) Standards D3923 and D6908 for a complete review of this technique.

Rhodamine B Test This test also identifies damaged membranes. Rhodamine B dye is fed to pressurized RO feedwater and should be rejected 100% if the membrane is intact. If permeate turns pink, dye is leaking through damaged membranes.

Membrane Autopsy Membrane autopsy is a destructive test, and therefore, it should be considered a last resort in determining the cause of membrane failure. Several tests are involved to determine the nature of degradation, fouling, or scaling:

Fujiwara Test This test measures the degree of halogenated organics in a membrane sample. A positive test is indicative of halogen attack on the membrane polymer.

Methylene Blue Die Test This test is used to determine if there is any damage or leaks to the membrane, whether from chlorine (oxidative) or other causes. The die is rejected 100% by an intact RO membrane, so any membrane showing blue die on the permeate side has been damaged. However, some NF membranes do pass the methylene blue die, so interpreting the results for this test for NF membranes can be difficult.

Microbial Analysis Deposits on the membrane are analyzed for microorganisms. The organisms may be further analyzed into their specific types.

Spectroscopy Several different methods are available for membrane autopsy evaluation utilizing spectroscopy.

- Standard light microscopy is used to determine morphology of materials on the surface of the membrane.
- Scanning electron microscopy (SEM) is used to determine morphology of deposits on the membrane.
- Energy dispersive X-ray fluorescence (EDXRF) is used to determine compounds or elements present in membrane deposits.
- Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is used to determine the amount of metals and silica in a membrane deposit.

- Electron spectroscopy for chemical analysis (ESCA) is used to identify organically bound materials on the membrane surface.

Electrochemically-Driven Membrane Separation Process: Electrodeionization/Continuous Electrodeionization

Electrodeionization (EDI), is a family of processes which includes electrochemical ion exchange, capacitive deionization, and continuous electrodeionization (CEDI), also known as continuous deionization (CDI). While EDI processes have been researched since the 1950s, CEDI is a relatively recent addition to the field of membrane separations, having been first commercialized in the late 1980s. CEDI is an electrochemically-driven membrane separation technique used for removing trace ionizable dissolved solids from water. Separation is affected with ion exchange membranes and resins via an electrical current.

CEDI systems were developed to replace conventional ion exchange, specifically mixed bed polishers following RO. Mixed-bed water quality can be achieved with CEDI without the need for regeneration chemicals and waste neutralization.

Since the early 1990s, the power industry has been a leader in employing RO/CEDI technology for boiler makeup water. Other industries currently employing CEDI technology include pharmaceuticals and semiconductors, laboratories, food and beverage, and chemical. There have been also some inroads into wastewater treatment and recycling applications. The use of CEDI eliminates the need for storing and frequent handling of relatively large volumes of acid, caustic, and regeneration waste that would be required if traditional ion exchange were used.

Theory of Operation

Figure 8.37 shows an expanded view of a CEDI stack, which consists of layers of cation- and anion-exchange membranes separated by spacers that act as alternating product and reject compartments. Traditionally, every other compartment is filled with ion exchange resin (the diluting compartment). However, with the newer “all-fill” configurations, all compartments are filled with resin. The resin is used primarily to enhance the transport of ions through the compartments, and as a substrate for splitting water into hydrogen (H^+) and hydroxyl ions (OH^-) used for the continuous regeneration of the resins. At one end of the stack is the cathode, and the other end of the stack has the anode. An electrical potential is applied to the stack, typically 100–600 volts DC at 3 to 20 amp. This electrical field drives cations toward the cathode and anions toward the anode.

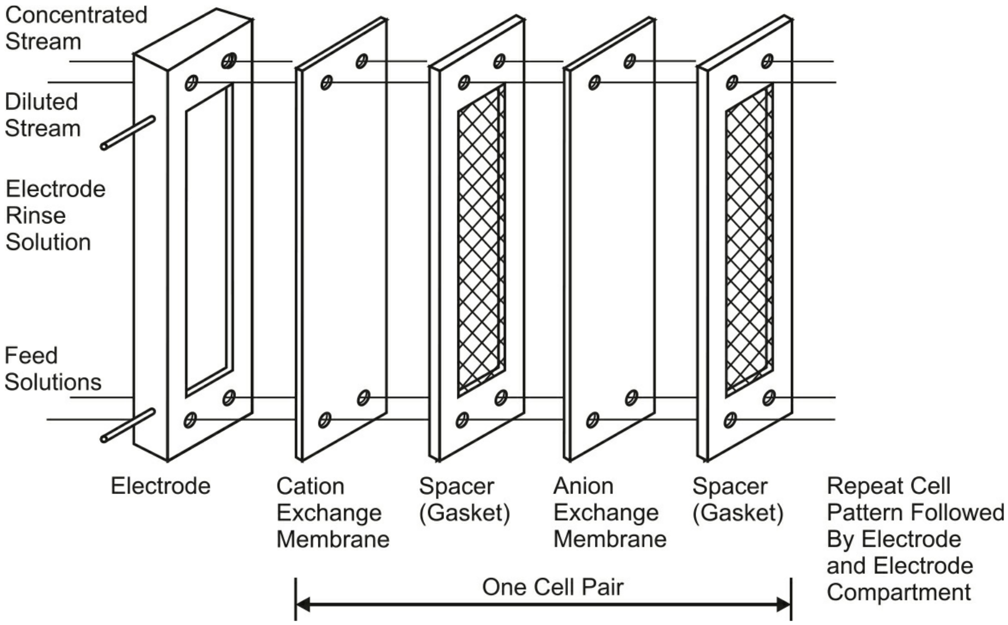


FIGURE 8.37 Expanded view of CEDI stack.

Cations readily pass through cation-exchange membranes but not through anion-exchange membranes. Likewise, anions pass through anion-exchange membranes but not through cation-exchange membranes. In this manner, every other compartment becomes dilute in ions, while the other compartments become concentrated in ions (Fig. 8.38). The resin serves to facilitate the transfer in low ionic strength solutions. Additionally, at the low salinity or outlet portion of the resin bed, the current dissociates water in the diluting compartment into hydrogen and hydroxyl ions, which serve to regenerate resin at the outlet of the resin bed. This allows for production of multi-mega-ohm water from a CEDI system. Specifically, CEDI can produce 18 MΩ water at up to 99% water recovery, with 95% rejection of boron and silica and 99% rejection of sodium and chloride.

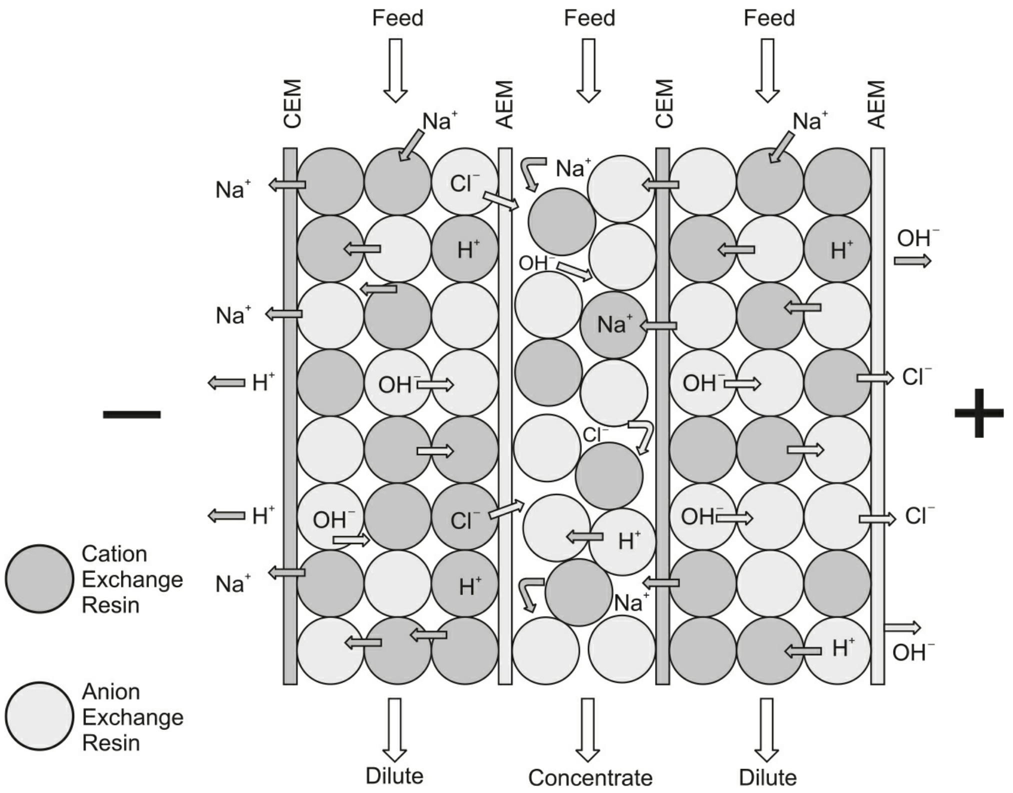


FIGURE 8.38 Cross section of an “all-filled” CEDI cell. (*Courtesy of Jonathan Wood.*)

Advantages of the newer, all-fill configuration are several. First, recycle of concentrated solution is not required. Recycle increases the mass transfer rate and minimizes the potential for fouling and scaling of the membranes. However, utilizing water dissociation to regenerate resin with the all-fill configuration, mass transfer rates are significantly improved, and weakly ionized species such as carbon dioxide and silica are more readily removed from solution. Additionally, all-fill configurations are much less complex in design, as the recirculation mode requires additional hardware, including motor starters, controls to balance pressure in all streams, and controls to prevent pump cavitation.

Membrane modules

Continuous electrodeionization modules are available in plate-and-frame [stacked-disk (see Fig. 8.37), and rectangular-plate configurations], as well as in the spiral wound configuration (Fig. 8.39). Plate-and-frame devices resemble plate-and-frame heat exchangers, with alternating compartments of cation/anion-exchange membranes, and product and reject compartments located between end plates and electrodes. Spiral wound devices resemble the

RO spiral wound configuration, but with the center permeate tube replaced with an electrode (Fig. 8.40). Commercial modules are available in sizes from 0.2 m^3/h (1 gpm) up to about 18 m^3/h (80 gpm). Typical module life is up to five years.

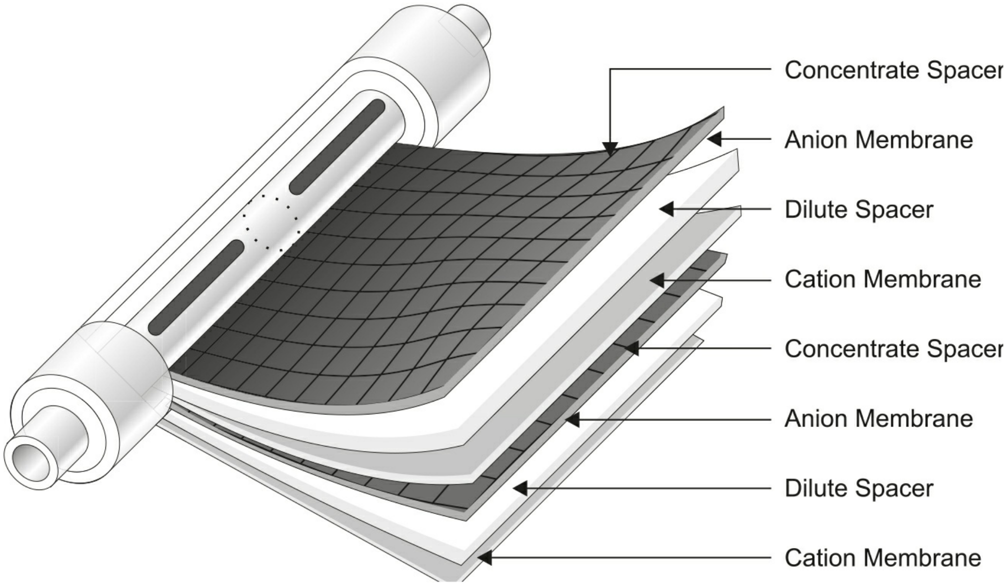


FIGURE 8.39 Spiral wound CEDI module. (*Courtesy of Dow Water and Process Solutions*.)

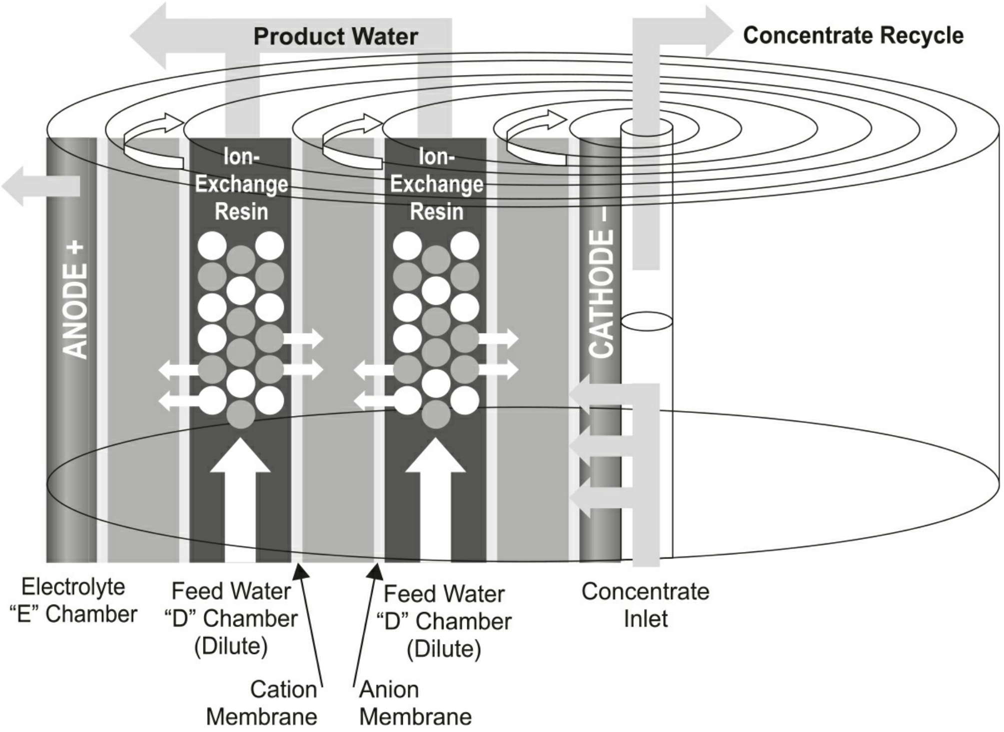


FIGURE 8.40 Spiral wound CEDI cross section. (*Courtesy of Dow Water and Process Solutions*.)

Cell Spacing

Spacing of the diluting (product) compartment between ion-exchange membranes can be either thin-cell or thick-cell[20], with thick-cell devices exhibiting a spacing of 8 to 10 mm, and thin-cell spacing of about 1.5 to 3.5 mm. The thin-cell devices typically contain mixed-bed resin in the product compartments, while thick-cell devices are more suited to lower TDS waters where cation and anion resins are located in separate regions of the compartment.

Resins

Typical ion exchange processes rely on the capacity of the resin. The CEDI resins are optimized for their ability to rapidly transport ions to the ion exchange membrane, not selectivity. The combination of the membrane and resin must be chosen so that the electrochemical splitting of water can occur within the device, so that regeneration can happen.

Pretreatment

CEDI requires a significant amount of pretreatment to prevent damage to the module, and fouling and scaling of membranes. Table 8.17 lists general feedwater quality requirements for CEDI systems. As always, one should follow the requirements for the specific device being used. To achieve these requirements, virtually all CEDI systems are preceded by RO. In some cases, double-pass RO, sodium softening followed by RO, or RO followed by sodium softening is necessary to meet the feedwater quality requirements.

Parameter	General Requirement
Feedwater type	RO permeate quality
Conductivity	<40 µS/cm
Carbon dioxide	<5 mg/L
Silica	<0.5 mg/L
Fe, Mn, H_2S	<0.01 mg/L
Total chlorine	<0.05 mg/L
Free chlorine	<0.05 mg/L
Total hardness	<1.0 mg/L $CaCO_3$ (<0.5 for some applications)
Total organic carbon (TOC)	<0.5 mg/L
pH	4–11
Temperature	5–45°C (41–113°F)
Pressure	172–689 kPag (25–100 psig)

TABLE 8.17 General Feedwater Quality Requirements for CEDI Systems

Select Conditions That Can Influence CEDI Performance

Carbon Dioxide Just as with ion exchange systems, carbon dioxide (CO_2) in CEDI feedwater imparts an ionic load on the system. In some cases, a concentration of 10 mg/L may be enough to prevent the system from meeting boiler feedwater requirements. Typically, carbon dioxide removal systems, including gas separation membranes, are employed to remove CO_2 from CEDI feedwater.

Temperature CEDI systems operate best within a temperature range of 5 to 45°C (41–113°F). At lower temperatures, kinetics and diffusion rates are slower, and electrical resistance increases. This results in an increase in voltage along with a decline in performance. Materials of construction limit the upper end of the temperature range. Many materials used to construct CEDI cells cannot tolerate high temperatures and degrade, resulting in leaks, poor performance, and higher energy requirements.

Total Organic Carbon Organics foul ion exchange resin, particularly anion resin. This results in poor performance and an increase in electrical requirements.

Cleaning

Chemical cleaning of CEDI membranes is generally undertaken when the electrical resistance of the unit increases or the product quality decreases. Some of the substances that cleaning helps to remove include, scale, organics and biological material. Common cleaners include sodium chloride, sodium hydroxide, and hydrochloric acid. The CEDI modules can tolerate pH ranging from 1 to 14, so aggressive cleaning is possible, as is overnight soaking at pH extremes to remove stubborn foulants. As with RO membranes, the high pH cleaning should be conducted prior to the acidic cleaning to minimize the setting of organics and biological material on the membrane.

Monitoring and Troubleshooting

Unlike RO/NF, there is no data normalization of CEDI data. Rather, online instrumentation is used to check performance of the system. Conditions that should be regularly monitored for troubleshooting include:

Feed Pressure—Should not exceed maximum rating for the device, typically around 4.0 to 6.9 bar (60–100 psig).

Product Pressure—The pressure of the product stream should be maintained at about 0.14 to 0.34 bar (2–5 psi) higher than the reject stream to minimize the negative effects on the product quality should a cross-leak occur.

Recovery—The recovery of the CEDI system should be monitored to make sure that no hardness deposits are occurring in the system. Typical recovery for CEDI ranges for 80 to 95% and is generally limited by feedwater hardness.

Temperature—Feedwater temperature will affect the performance of the system, as discussed previously.

Voltage—An increase in voltage required by the system can be indicative of fouling of the membranes. As discussed previously, temperature can affect voltage, so any changes in voltage should be compared against temperature to determine if fouling or a temperature decrease is responsible for the voltage increase. If temperature has not decreased, the increase in voltage indicates that fouling or scaling has occurred, and a chemical cleaning is required to restore performance.

Feedwater Analysis—Analyses of the feedwater quality to the CEDI unit should be conducted frequently. Species to test for include free and total chlorine, TOC, and total hardness. The values for these species should all meet the requirements for feedwater as set forth by the device manufacturer.

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SECTION 3.2

Applications—Steam Generation

CHAPTER 9

Boiler Systems

Water, when sufficiently heated, is converted to its vapor form, steam. Because of its heat or energy content and because it is an easily transportable fluid, steam is an efficient means of moving energy from one point (the source or boiler) to its intended end use (heating, electric power generation, etc.). Here, the energy contained in the steam is transferred to an operation requiring heat such as a chemical reaction or heating of a fluid, or is converted into work such as in driving a piston or turbine. Steam finds use in a wide variety of applications: comfort heating in buildings; process heating in many industries such as food, petroleum, chemical processing, and pulp and paper; and electric power generation.

Many things can happen to the water and steam en route to the final destination. Steam may be lost; some is condensed and returned to its liquid state. Some of the highly concentrated boiler water must be removed to limit scale deposition and corrosion. Water may be added to compensate for these losses or to replace water removed deliberately.

Steam Generation

Steam is produced in a steam generator or boiler, which is usually heated by the burning of coal, oil, gas, wood waste, or organic by-products of a plant process. Steam is also produced at some electric utility plants by nuclear reaction. Water is boiled, and the vapor is discharged at a controlled temperature and pressure. As vapor leaves the boiling water, the dissolved solids originally in the water are left behind. A simple conceptual diagram of the steam generation section of a boiler system is shown in Fig. 9.1.

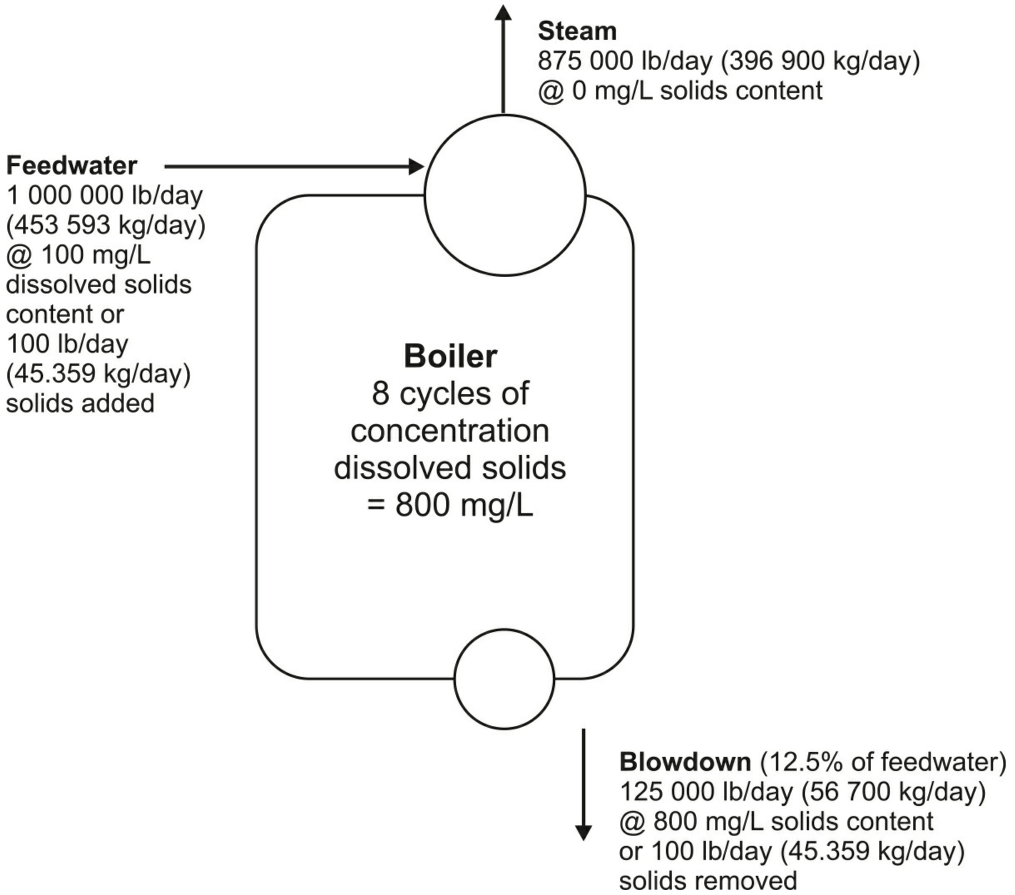

FIGURE 9.1 Simple boiler material balance.

The boiler water left behind becomes increasingly concentrated, and eventually reaches a level where further concentration could cause scale or deposits to form or result in problems with steam quality or steam purity. This highly concentrated water must be removed to prevent scale deposition or corrosion. This removal process is known as blowdown. Additional water (makeup) must be added to the system to replace any steam or condensate not returned to the boiler, as well as the blowdown withdrawn from the boiler.

In the steam generator, water circulates in a pattern produced by the path of heat from the fuel through a network of boiler tubes, as illustrated in Figs. 9.2, 9.3, and 9.4.

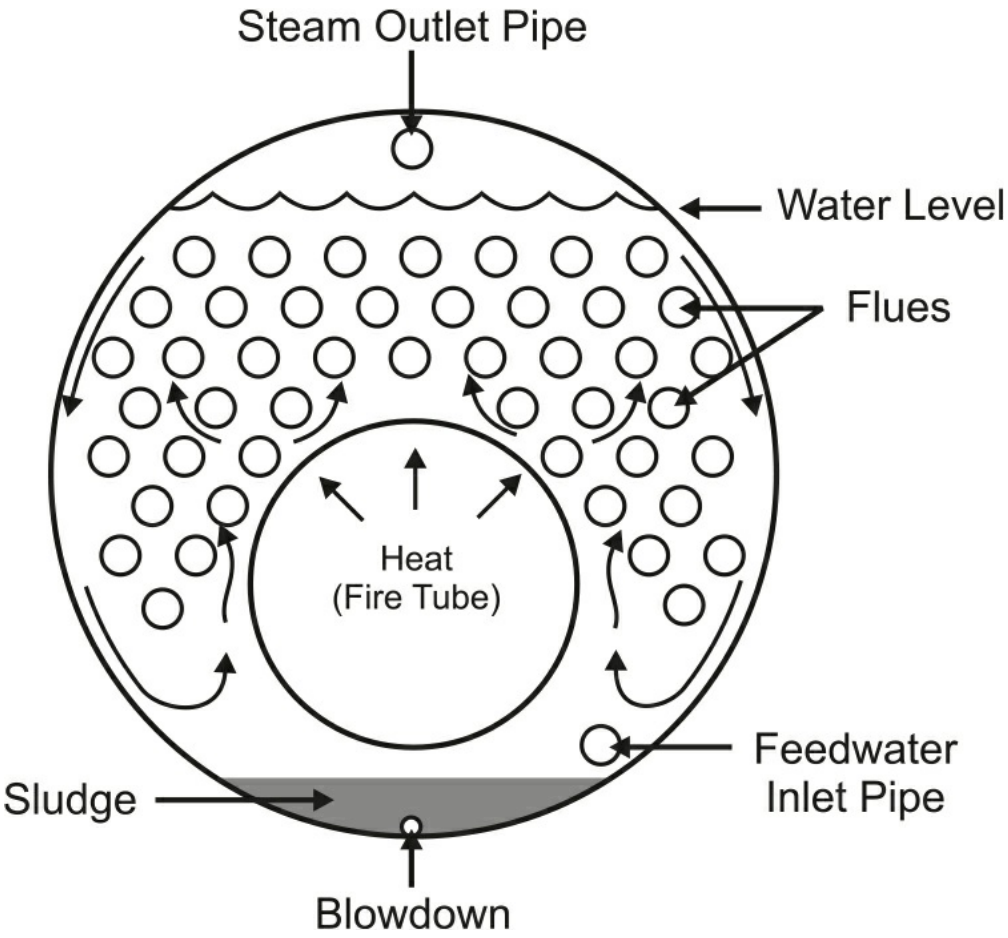

FIGURE 9.2 Water circulation in a firetube boiler.

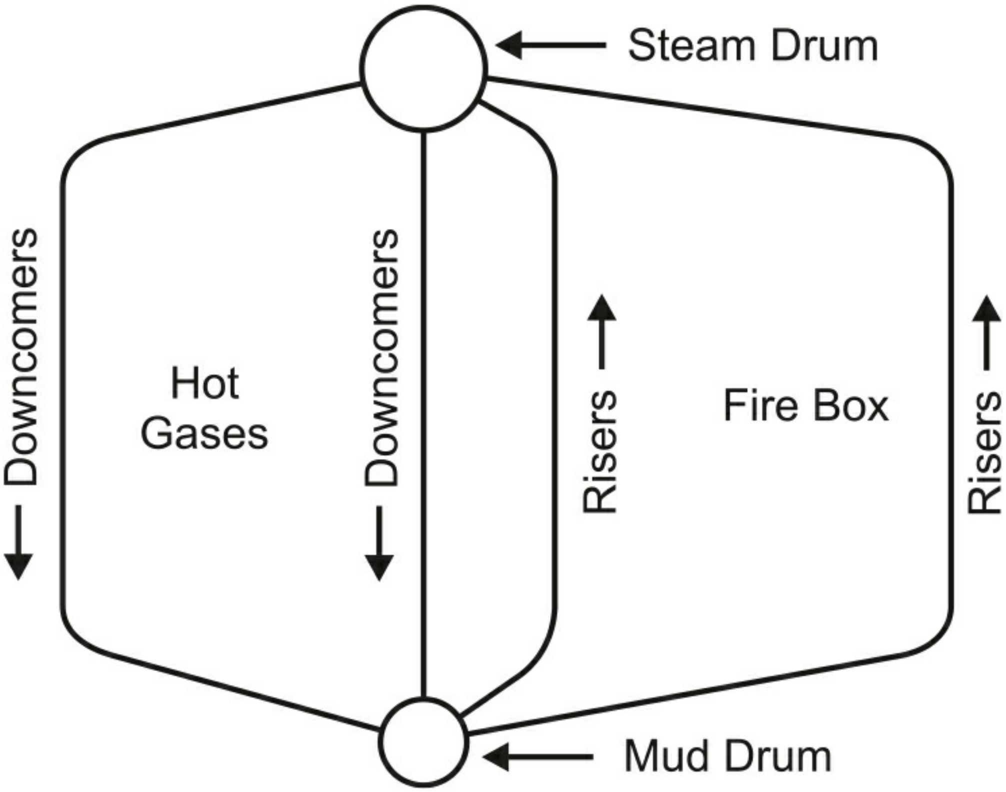

FIGURE 9.3 Circulation in a two-drum watertube boiler.

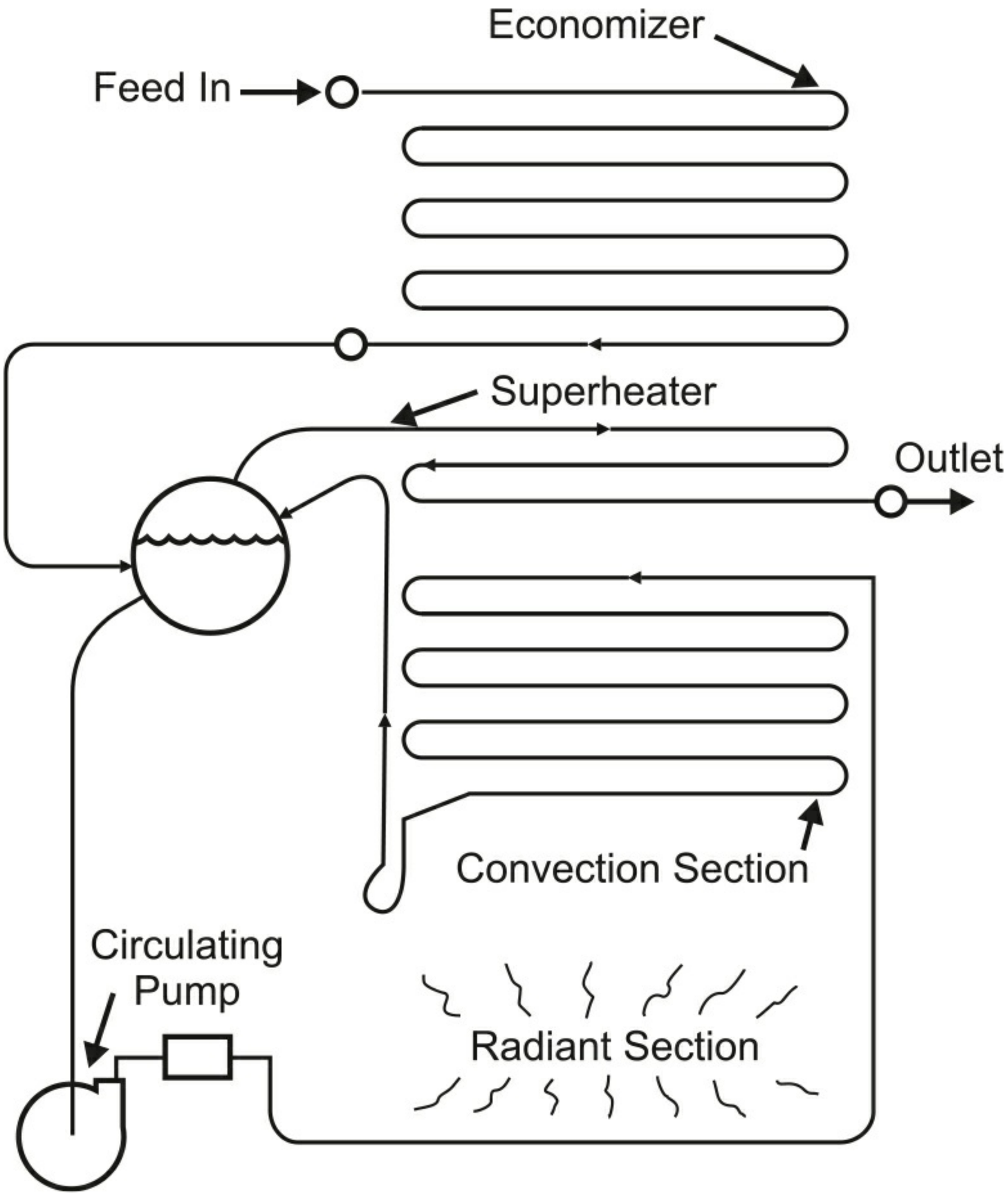

FIGURE 9.4 Pumps assist in circulating water through a boiler when natural circulation is restricted by limited density difference because of pressure or elevation.

Condensate

When the steam delivers its heat to the point of use, depending upon pressure, it gives up between 210 to 1100 Btu/lb (488–2560 kJ/kg) as it condenses at the prevailing temperature, and returns to the lower energy level state of a liquid. Condensate is usually free of mineral contamination and contains heat, so it is a very valuable source of water. As much condensate as possible is collected and returned to the boiler because of its heat value.

As condensate forms, it must be drained to a reservoir (receiver) for return to the feedwater stream, usually at the deaerator. The drainage system, which is usually separate for each major steam user and condensate producer, consists of the following components:

- Steam traps to maintain backpressure and to permit condensate flow but not steam flow
- Collection tanks, which are usually vented to a low-pressure steam line or to the atmosphere
- Pumps to deliver the condensate to the deaerator or another point in the system

Steam or Condensate Losses

Very little steam or condensate is lost in a large electric utility station, except in a few operations that are usually intermittent such as soot blowing. In an industrial plant, however, it is quite common to lose 30 to 80% of steam, condensate, or both. Major causes of steam and condensate loss include consumption in the process, contamination of condensate through product inleakage, and pipe leaks. Other losses might result from erratic demands for steam by different operating departments, which can upset the heat balance and cause a loss of low-pressure steam because of a momentary or seasonal inability to use it.

Economics also play a role; the cost of installing condensate collection systems with piping, especially for minor use, is often not justified by the value of recovered condensate, particularly in plants where piping installation is difficult or fuel costs are low.

Makeup

Fresh water of acceptable quality must be added to compensate for losses. Hence, this fresh water is called makeup. Scale-forming minerals are generally removed from makeup by precipitation softening, ion exchange, or reverse osmosis before it is added to the boiler system. Waste heat streams, such as blowdown, may also heat makeup before it is added to the boiler system. Figure 9.5 shows a simple but typical boiler makeup water system.

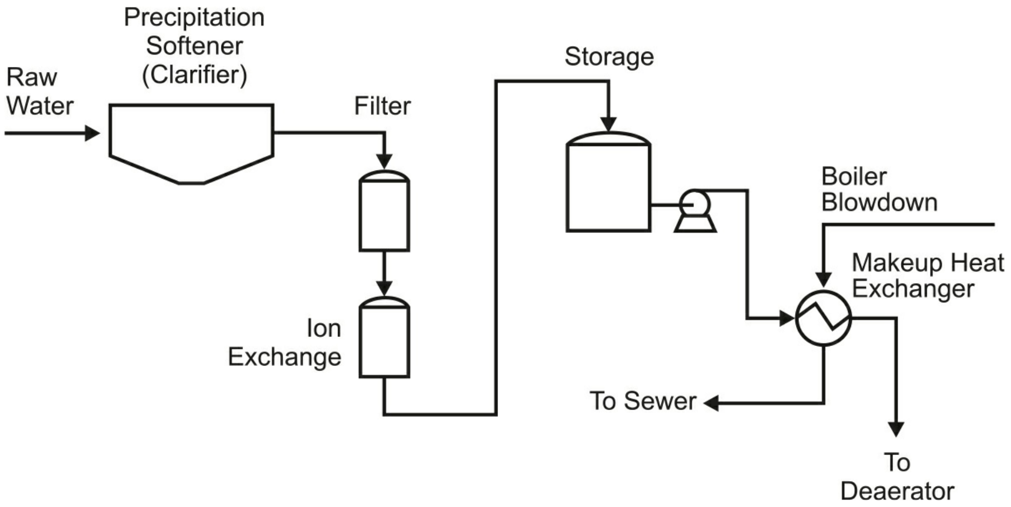

FIGURE 9.5 Typical boiler makeup water system.

Concentration by Evaporation

Even after primary treatment, makeup still contains dissolved solids, such as traces of hardness, and variable amounts of sodium, alkalinity, and silica. Makeup must be treated to reduce this dissolved matter to acceptable levels (depending on the pressure of the boiler and the uses of the steam); the choice of pretreatment technology is based principally on economics.

As relatively pure steam is withdrawn from the boiler, the solids left behind concentrate in the boiler water. Based upon pressure and steam purity, there is a limit to the maximum concentration levels the boiler can tolerate. Exact limits are impossible to determine; however, several consensus guidelines have been gathered based upon operating experience, laboratory data, etc., and have been published by various organizations including the American Society of Mechanical Engineers (ASME), the American Boiler Manufacturing Association (ABMA), and Nalco. In addition to the above, there are other references such as the Electric Power Research Institute (EPRI), the VGB (a German organization of large power station operators), the Association of German Technical Inspectorates (VdTÜV), the British Standards Institute (BSI), and the Japanese Industrial Standard (JIS). Each of these may approach the problem of defining feedwater and boiler water concentrations from a different perspective; therefore, the recommended values may differ, depending on the source. Remember that the values provided are suggested guidelines and that actual boiler specification limits must be established on an individual basis, depending on the desired steam purity and end use requirements.

Blowdown

Blowdown is a deliberate loss of boiler water intended to keep the critical components dissolved in the boiler water from over-concentrating. Blowdown must also be replaced by makeup, so that the following relationship applies:

$$\mathrm{TM} = \mathrm{SL} + \mathrm{CL} + \mathrm{BL} \tag{9.1}$$

where TM = total makeup
SL = steam losses
CL = condensate losses
BL = boiler water losses

In low-pressure units or in boiler systems that do not produce large quantities of steam, blowdown is often sewered. In larger systems, considerable amounts of blowdown contain valuable heat, which can be recovered in flash tanks and heat exchangers. Flash tanks extract low-pressure steam and send it to various users, which may include the deaerator or lower-pressure processes. Water from the flash tank still has considerable heat value and may be used further to preheat incoming makeup water. Figure 9.6 shows a blowdown system and possible schemes. Calculations showing the relationship between blowdown and feedwater are presented later in this chapter.

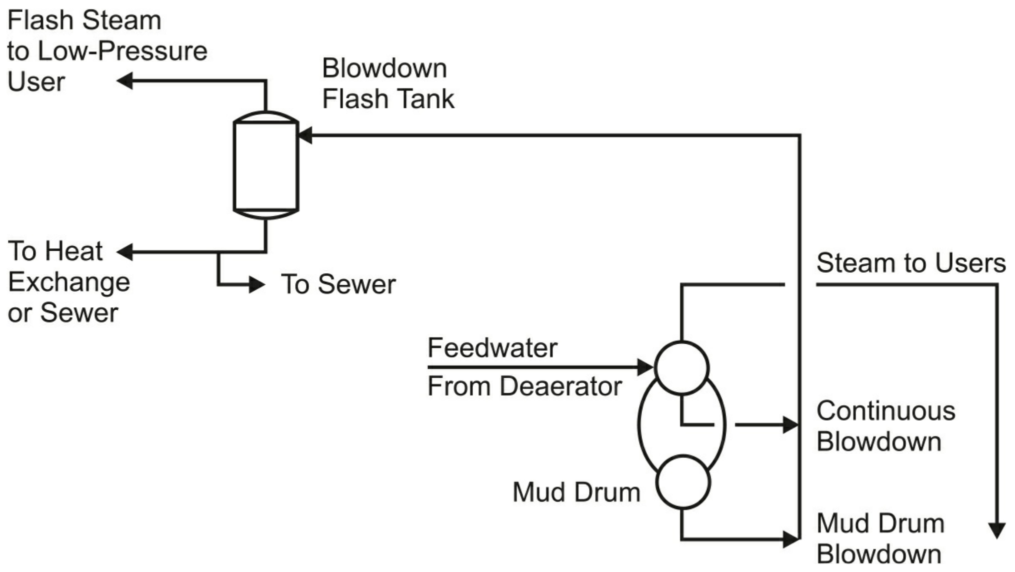

FIGURE 9.6 Typical boiler blowdown system.

Feedwater

Makeup and return condensate combine with deaerator steam to become boiler feedwater. A simple diagram showing a typical feedwater system is presented in Fig. 9.7. ASME has established guidelines for feedwater quality, and the reader is referred to these guidelines for details.

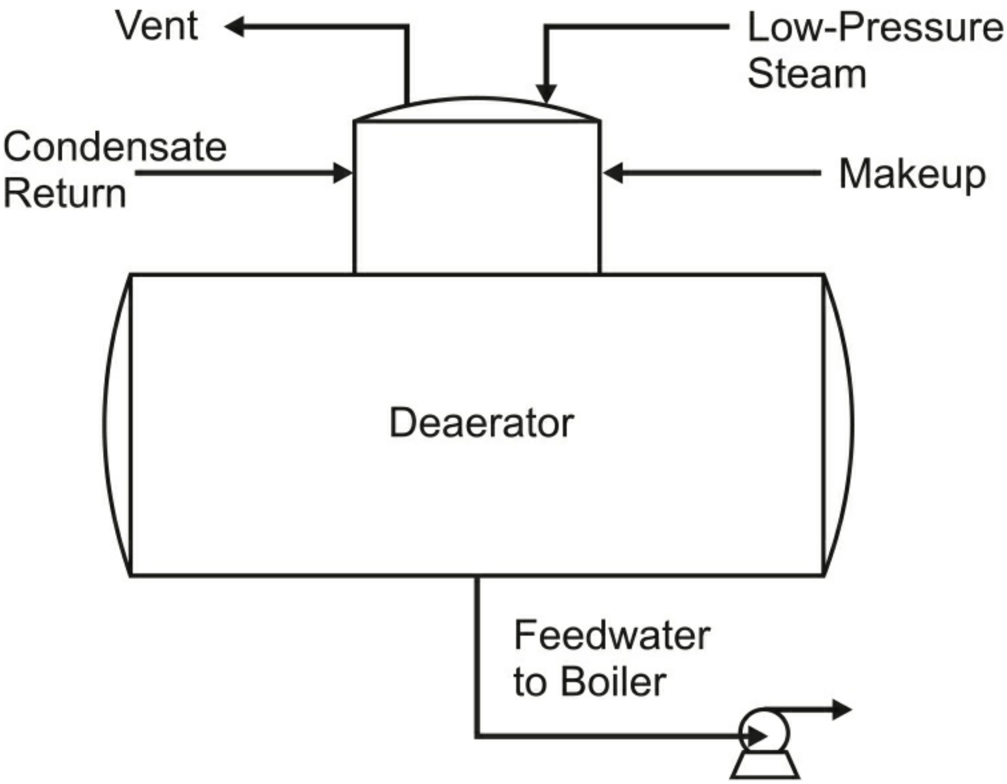

FIGURE 9.7 Typical boiler feedwater system.

Mathematical Relationships

All of the flows, input and output, in a typical industrial boiler system are shown schematically in Fig. 9.8. In the system illustrated, steam discharges from a boiler to a turbine and other users. All or part of the steam may be condensed in the condenser; some may be extracted for process use. Other steam may go directly to a process, where it may be lost or may become contaminated and must be discarded. Still other steam may go directly to a process and then be condensed and returned to the boiler. The relationships among blowdown, makeup, and feedwater are discussed in detail here and are illustrated in the materials balance diagram in Fig. 9.1.

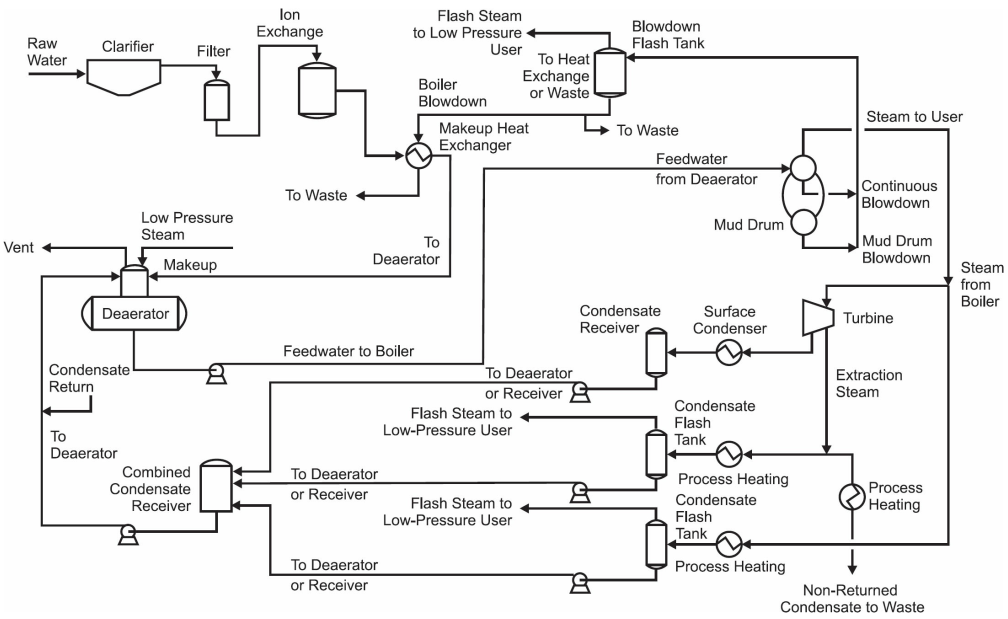

FIGURE 9.8 Typical industrial boiler system.

Blowdown and Makeup

Blowdown and makeup are usually expressed as a percentage of feedwater. (They can also be calculated as a percentage of steam flow; however, this book will use the feedwater calculation convention.) When the flow rates of these streams are known, the following equations can be used to describe their relationship:

$$\%BD = (100)(BD)/FW \qquad (9.2)$$

$$\%MU = (100)(MU)/FW \qquad (9.3)$$

where BD = blowdown mass flow, lb/h (kg/h)
MU = makeup mass flow, lb/h (kg/h)
FW = feedwater mass flow, lb/h (kg/h)

Many times, actual quantities of blowdown, feedwater, and makeup are not known. In such cases, percentages of blowdown and makeup can be calculated based upon the concentration of a particular dissolved solid or total dissolved solids (TDS) in the various streams.

$$\%BD = (100)(TDS_{FW})/TDS_{BD} \qquad (9.4)$$

where TDS_{FW} = TDS in feedwater, mg/L
TDS_{BD} = TDS in blowdown, mg/L

It is very important that when dissolved solids are used to measure the percent blowdown, the feedwater sample must be taken after all chemicals have been added to the system. If conductivity is used for the measurement of dissolved solids, the boiler water sample must first be neutralized before measuring the conductivity, because any hydrate (O) alkalinity will greatly increase the conductivity of the sample, leading to a low percent blowdown. Ideally, both the feedwater and boiler water samples should be neutralized, but this is rarely done.

The percent makeup can be calculated using the TDS in the feedwater, makeup, and condensate.

$$\%MU = (100)(TDS_{FW} - TDS_C)/(TDS_{MU} - TDS_C) \qquad (9.5)$$

where TDS_C = TDS in recovered steam condensate, mg/L
TDS_{MU} = TDS in makeup, mg/L

Note that the above calculations do not apply to boilers using high-purity feedwater, because the TDS in the feedwater is too low to measure accurately. Chapter 33 on the Power Industry discusses alternate methods for these applications.

Cycles of Concentration

As discussed earlier, when steam (devoid of solids) is generated, dissolved solids remain behind and concentrate in the boiler water. Figure 9.9 shows that as water evaporates, remaining dissolved solids increase in concentration. The ratio of the quantity of dissolved solids in the boiler water to those in the feedwater is defined as the concentration ratio (CR) or cycles of concentration (COC). Expressed another way, the number of COC in a boiler system is simply the reciprocal of the percent blowdown.

$$COC = 100/\%BD \qquad (9.6)$$

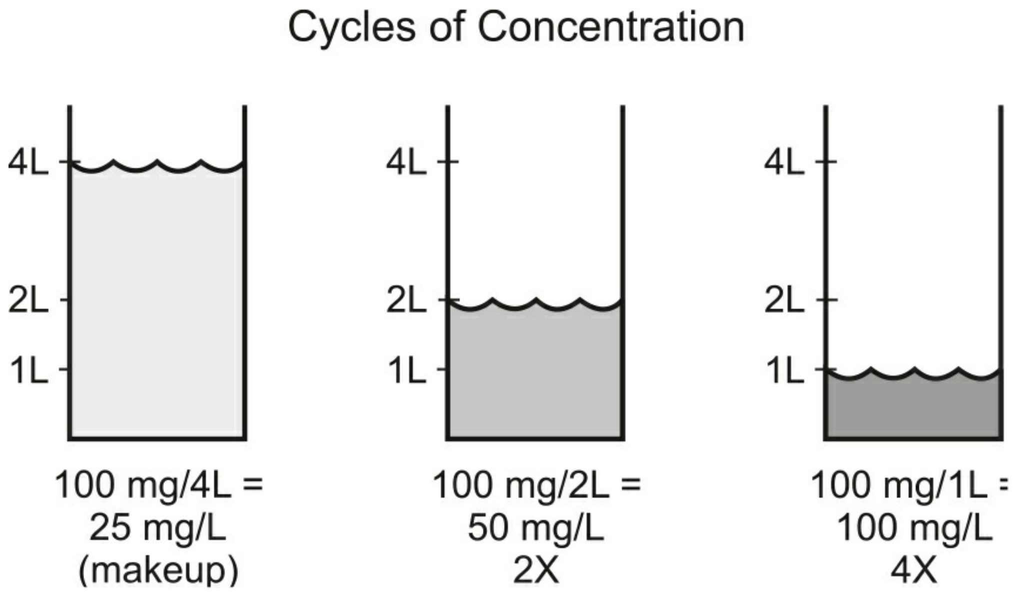

FIGURE 9.9 An illustration of increasing dissolved solids as water evaporates.

There are times, such as when the makeup water is demineralized and contains little to no dissolved solids, when conductivity cannot be used to measure the COC. In these cases, some other method must be used to measure the COC. This can be done by injecting into the feedwater a tracer that is nonvolatile, nonreacting, and nonprecipitating. By measuring the concentration of traced fluorescence chemistry in the feedwater and in the boiler water, the ratio of the boiler water concentration of the tracer chemistry to the concentration of tracer chemistry in the feedwater represents the COC.

$$\text{COC} = \text{BW concentration}/\text{FW concentration} \tag{9.7a}$$

If the boiler continuous blowdown and the steam flows are measured, the COC can be calculated using Eq. (9.7*b*).

$$\text{COC} = (S + \text{BD})/\text{BD} \tag{9.7b}$$

where S = steam mass flow, lb/h (kg/h)

Once the COC is known, the blowdown flow can be calculated from the following:

$$\text{BD} = S/(\text{COC} - 1) \tag{9.7c}$$

Likewise, the feedwater flow can be calculated using Eqs. 7*d* and 7*e*.

$$\mathrm{FW} = S + \mathrm{BD} \tag{9.7d}$$

$$\mathrm{FW} = (S)(\mathrm{COC})/(\mathrm{COC} - 1) \tag{9.7e}$$

The blowdown flow can also be calculated from measurements of the steam flow and the feedwater flow, although this calculation will result in a higher error, because a relatively small number is calculated from the difference between two larger numbers, and these numbers are taken from two separate meters, both of which may be out of calibration.

$$\mathrm{BD} = \mathrm{FW} - S \tag{9.7f}$$

Mass Balance Equations

Figure 9.8 shows the boiler plus the three support systems: pretreatment, feedwater, and condensate systems. Simple mass balances describing these systems and their relationships are defined by the following equations.

$$\mathrm{FW} = \mathrm{MU} + \mathrm{RC} + \mathrm{DA} - V \tag{9.8}$$

$$S = \mathrm{RC} + \mathrm{NRC} \tag{9.9}$$

where RC = returned steam condensate mass flow, lb/h (kg/h)
DA = deaerator heating steam mass flow, lb/h (kg/h)
V = deaerator vent mass flow, lb/h (kg/h)
NRC = nonreturned steam condensate mass flow, lb/h (kg/h)
S = steam

An accurate water analysis plus one or two measured flow rates can be used to determine most other system flow rates. These, in turn, can be used to calculate chemical dosages, size equipment properly, and estimate the heat and energy content of various streams.

Many times, feedwater and makeup flow rates are not metered but steaming rate is. Knowing boiler water and feedwater chemical compositions will allow feedwater, makeup, and blowdown flow rates to be calculated.

Optimizing the Water Balance

Because boiler systems are energy intensive and the fuel needed to produce energy is expensive, it is in a plant's best interest to maximize steam production and minimize fuel consumption.

The first step in optimizing the system is to take every practical measure to eliminate steam and condensate losses, in addition to working within the economic constraints of the cost of revisions, new equipment, piping, and installation. For example, it might be practical to install piping to return condensate from a tank farm in a refinery or petrochemical plant, but if the condensate is badly contaminated with oil, the extra cost of installing and operating condensate filters may not be justified.

The next major step is to minimize blowdown, or to get the most mileage from the makeup for the control limits required by the boiler. Because the makeup treatment system is in place, a plant usually must do its best with the system at hand; in some cases, however, a new system may be required to optimize makeup use. Major unit operations of makeup treatment are discussed in Chap. 6 on Raw Water Clarification and Filtration, Chap. 7 on Ion Exchange, and Chap. 8 on Membrane Separation; all found in Sec. 3.1.

As shown in the ASME guidelines, the limits on such controls as total dissolved solids, silica, and alkalinity are related to the amount of these materials coming in with the makeup water. These concentrations are usually adjusted by blowdown, but some manipulation of the makeup treatment system might be possible, depending on system flexibility. Other constituents such as phosphate, organics, and sulfite are introduced as internal treatment chemicals, and their concentration can be adjusted by changing their rate of application.

Table 9.1 illustrates how minimizing boiler blowdown can optimize a boiler system. Consider a 600 psig (4.1 MPag) boiler system in a paper mill. The makeup is treated by hot lime softening followed by ion exchange softening, and after treatment has a total dissolved solids concentration of 150 mg/L and a silica concentration of 3 mg/L. The makeup rate is 50% based on the feedwater flow.

Factor	Makeup	Feedwater	Limit	Maximum Boiler Concentration Ratio
TDS, mg/L	150	75	2000	26.7
SiO_2, mg/L	3	1.5	30	20.0
SiO_2, mg/L (after reduction)	2	1.0	30	30

TABLE 9.1 Maximum Concentration Ratio

Using 50% condensate return, this example will yield a feedwater TDS and silica of 75 mg/L and 1.5 mg/L, respectively. With an allowable limit of only 30 mg/L silica in the boiler, silica is the controlling factor that sets the maximum CR at 20 (5% blowdown). The water could be concentrated by a factor of 26.7, however, based on total dissolved solids, so there is incentive for additional silica reduction in the treatment unit. The addition of dolomitic lime (rather than hydrated lime) or the addition of magnesium oxide in the hot lime softener, might permit a reduction from 3 mg/L to less than 2 mg/L silica in the makeup. With lower silica in the makeup, silica in the feedwater will be reduced accordingly.

Reducing silica in the makeup from 3 to 2 mg/L will reduce it equivalently in the feedwater. Therefore, the feedwater would then contain only 1 mg/L silica, and blowdown based on silica could potentially be reduced to 1/30 or 3.3%. Now, the limiting factor would no longer be silica but total dissolved solids. The boiler may now be cycled up to its maximum for conductivity at 26.7 cycles or 3.75% blowdown. Depending upon steam production, the availability of blowdown heat recovery equipment, and fuel costs, the additional 25% blowdown reduction (5–3.75% blowdown) could result in sizeable fuel savings for fired boilers. There will be additional savings in reduced makeup water costs and blowdown sewer costs.

This example shows that the CRs are determined easily by chemical analysis. Blowdown rate is rarely metered, although most plants meter makeup, and some meter feedwater as well. Steam flow is usually metered in most plants, and the feedwater flow can be calculated based on the CR and the steam production by using the mathematical relationships discussed previously.

Thermodynamic Properties of Steam

Steam and water at different pressures and temperatures contain different amounts of energy. The difference between the energy content of steam and water at the same pressure and temperature is significant and represents the driving force of the steam. The thermodynamic properties of saturated steam and water are shown in saturated steam tables, which are available in numerous reference books and on the internet.

Terminology

The concepts of work and energy are important to understand how steam can be utilized in a wide variety of applications. Following are terms commonly used for defining energy, work, and power.

Work: The product of a force (F) applied uniformly along or through a distance (d) is defined as work. For example, the work expended in lifting a weight requiring an applied force (F) where the distance (d) in transit is upward is calculated as follows:

$$\text{Work} = (\text{force})(\text{distance})$$

Work is expressed in ft · lb or kg · m

Heat: The amount of energy given up or absorbed by a substance is equal to the product of the mass of a substance (m) heated uniformly, its temperature change (ΔT), and its specific heat (C_p), which is a function of the nature of the substance heated (for water, C_p = 1 Btu/lb, 1 kcal/kg, or 4.184 kJ/kg).

$$\text{Heat} = mC_p\Delta T$$

Heat is expressed in Btu, kcal, or kJ

Heat equivalent of work: A Btu is defined as the amount of heat necessary to raise the temperature of 1 lb of water 1°F. Also, 1 Btu = 777.6487 ft · lb. A kilocalorie is defined as the amount of heat necessary to raise the temperature of 1 kg of water 1°C, and 1 kcal equals 4.184 kJ.

Also, 1 J = 0.102 kg · m.

Electrical equivalent of work: The unit of electrical energy is the kilowatt-hour (kWh). The mechanical energy of an engine driving an electrical generator is converted to electrical energy. Common units of energy include Btu, ft · lb, kg · m, kWh, kcal, and kJ.

1 kWh =3414.426 Btu = 2 655 224 ft · lb

1 kWh = 860.42 kcal = 3600 kJ = 367 098 kg · m

This is the most commonly misunderstood energy relationship, because kilowatts are often erroneously considered an energy term rather than a power term.

Power: This is the rate or speed of doing work, generating heat, or producing electricity. For example, a person weighing 150 lb (68 kg) and climbing a 100 ft (30.5 m) hill would expend 15 000 ft · lb (2074 kg · m) of energy. If this climb requires 10 minutes (600 seconds), the energy expended would be 25 ft · lb/s (3.46 kg · m/s). The power applied is defined as:

25 ft · lb/s/[550 (ft · lb/s)/hp] = 0.045 hp

3.46 kg · m/s/[76 (kg · m/s)/hp] = 0.045 hp

If the hill is climbed in five minutes, 15 000 ft · lb (2074 kg · m) of energy are still used, but the power exerted is doubled.

15 000 ft · lb/300 s/(550 [ft · lb/s]/hp) = 0.09 hp

2074 kg · m/300 s/(76 [kg · m/s]/hp) = 0.09 hp

Common units of power include hp, kW, Btu/h, kcal/h, and kJ/h.

1 hp = 550 ft · lb/s = 0.7457 kW = 2546.137 Btu/h

1 hp = 76 kg · m/s = 641.62 kcal/h = 2684.52 kJ/h

Boilers

The primary purpose of chemical treatment is to protect the generating system from such problems as scale, corrosion, and carryover. When these problems occur, production efficiency decreases, maintenance requirements and costs increase, and overall plant productivity decreases.

The proper application of chemical technology requires a thorough understanding of the systems to be treated. Each piece of equipment, be it a boiler, a turbine, a superheater, or a condenser, has its own requirements. Special care must be taken that each piece of equipment in a system be compatible with the overall system and with the treatment program selected.

It is not enough that each element of the heat-generating unit be efficient and well-constructed. In today's economy, the unit must provide the anticipated maximum overall efficiency and reliability at minimum cost. To achieve this goal, the unit and all auxiliary components must comprise a balanced, well-designed system.

The following requirements must be considered when selecting equipment:

- Adequate strength of all components
- Satisfactory service life
- Adequate expansion capabilities
- Accessibility of all parts for inspection
- Readily available replacement parts
- Safety and reliability
- Overall energy integration and utilization

Plants frequently sacrifice one or more of these considerations in favor of low cost. This sacrifice may eventually result in operational and control problems after the unit is installed.

Plants and engineering companies often call upon water treatment chemical suppliers to work with them in the design stages and recommend the best treatment program for the new system. Such input can help the plant avoid costly mistakes that could result in serious operating problems once the boiler is online. Careful input, based on a strong knowledge and understanding of the equipment and of the equipment selection process, will mean fewer problems once the boiler is operational.

Boiler Classifications

Boilers today may be classified on the basis of any number of the following characteristics:

- Use
- Pressure
- Orientation
- Materials of construction
- Size
- Tube contents
- Firing
- Heat source
- Circulation

A general understanding of these classifications will promote better owner-supplier understanding and communication.

Use: Boilers are normally classified by the particular service they are to perform. Customarily, boilers are classified as either stationary or mobile (mainly marine) units. Stationary boilers may be used for building heat, plant process steam, power generation, or waste heat removal. Mobile boilers can serve all of the purposes that stationary boilers serve; however, their location will not be permanently fixed.

Pressure: The ASME boiler code differentiates boilers based on the following pressure differences:

- Low-pressure units are all steam boilers that do not exceed pressures of 15 psig (103 kPag), and all hot water boilers that do not exceed 160 psig (1.1 MPag) and 250ºF (121°C).
- Power boilers are all boilers that exceed the low-pressure limits.

Orientation: Looking at the boiler from the burner side, the front of the boiler is the side of the boiler where the burner(s) is/are located; the back of the boiler is the side opposite the burner(s); the left side of the boiler is to the left, and the right side of the boiler is to the right. Some boilers, such as opposed-wall fired and tangentially fired, do not adhere to this typical convention.

Materials of construction: Boilers are normally constructed of steel or cast iron. Steel boilers are more common, consisting of steel plates and tubes joined together by riveting, welding, or rolling. Cast iron boilers are constructed of gray iron casting connected by push-in nipples.

Size: Boilers are rated in heating surface available and heat input per hour that they can tolerate. Industrial boilers are normally considered to have a heating surface greater than 294 ft^2 (27.3 m^2); residential units have heating surfaces of 16 to 294 ft^2 (1.5–27.3 m^2).

Tube contents: Boilers classified by tube contents consist of two types: watertube boilers and firetube boilers. Firetube boilers are those in which the tubes are surrounded by water, and the hot gases pass through the tubes. Watertube boilers are those in which water flows through the inside of the tube, and the hot gases are on the outside.

Firing: Boilers may be classified as either fired or unfired. In fired boilers, the heat supplied to generate steam is a direct result of burning fuel. Unfired boilers are units that use waste heat to generate steam; there is no direct burning of fuel.

Heat source: The heat to warm the water and generate steam may be derived from the following sources:

- Combustion of solid, liquid, or gaseous fuels
- Hot gases from chemical reactions
- Electrical energy
- Nuclear energy

Circulation: Boilers classified by circulation patterns include natural, positive (or forced), and once-through. Each of these classes will be discussed under Boiler Circulation later.

Boiler Types

Steel boilers are by far the most common type of boiler constructed today. These boilers are constructed as either firetube or watertube units.

Firetube Boilers

The original shell boiler (tea-kettle type) was first improved upon by passing the hot gases through the inside of tubes located within a shell filled with water. This modification marked the beginning of the firetube boiler as we know it today.

Firetube boilers are used principally for heating systems, for industrial process steam, and as portable steam-generating units. These boilers operate at pressures up to 600 psig (4.1 MPag) and steam flows up to 40 000 lb/h (18 000 kg/h). The firetube unit is best suited for a plant where steam demands are relatively small, and no turbine applications require superheated steam.

The firetube units have the advantage of large water storage capacity and the ability to partially dampen the effect of wide and sudden load swings in steam demand. Because of their large water volume, however, the time required to arrive at operating pressure from a cold start is considerably longer than for a watertube boiler.

The shells of firetube boilers are normally cylindrical, with the tubes set into tube sheets. This type of construction is particularly adaptable to boilers operating at 250 psig (1.7 MPag) or less. The steam boiler water line is normally more than 2.5 inches (63.5 mm) above the top of the upper rows of tubes or crown sheet. The space above the water line is called the steam space.

Tubes normally measure 2 to 4 inches (51–102 mm) in diameter. The boiler may have one, two, three, and occasionally four gas passes, a pass being a group of tubes through which the combustion products flow in essentially one direction. Three-dimensional cutaway views of firetube boilers are shown in Figs. 9.10 to 9.12.

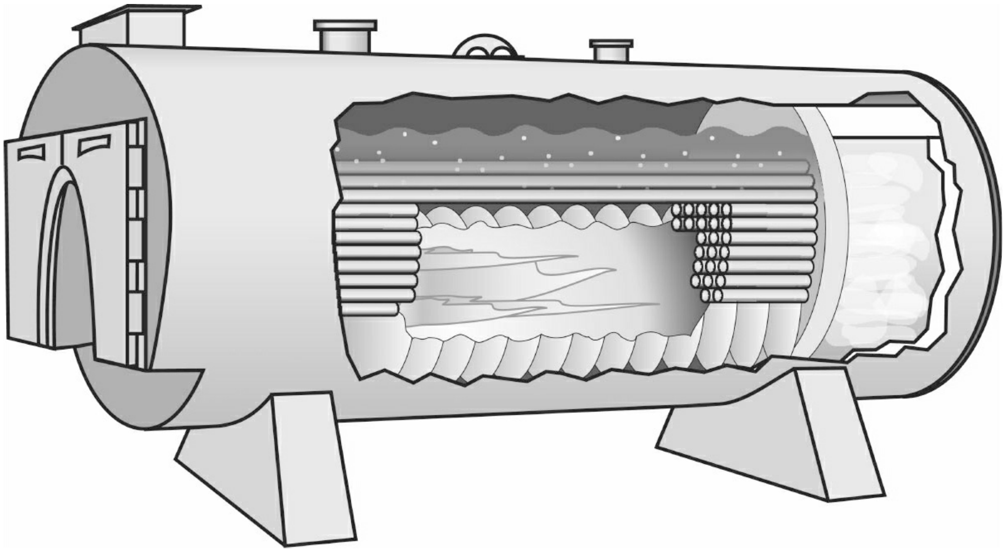

FIGURE 9.10 Scotch-type boiler. Combustion occurs in the corrugated internal furnace; refractory-lined rear chamber reverses flow and directs gas forward through tubes to outlet at front.

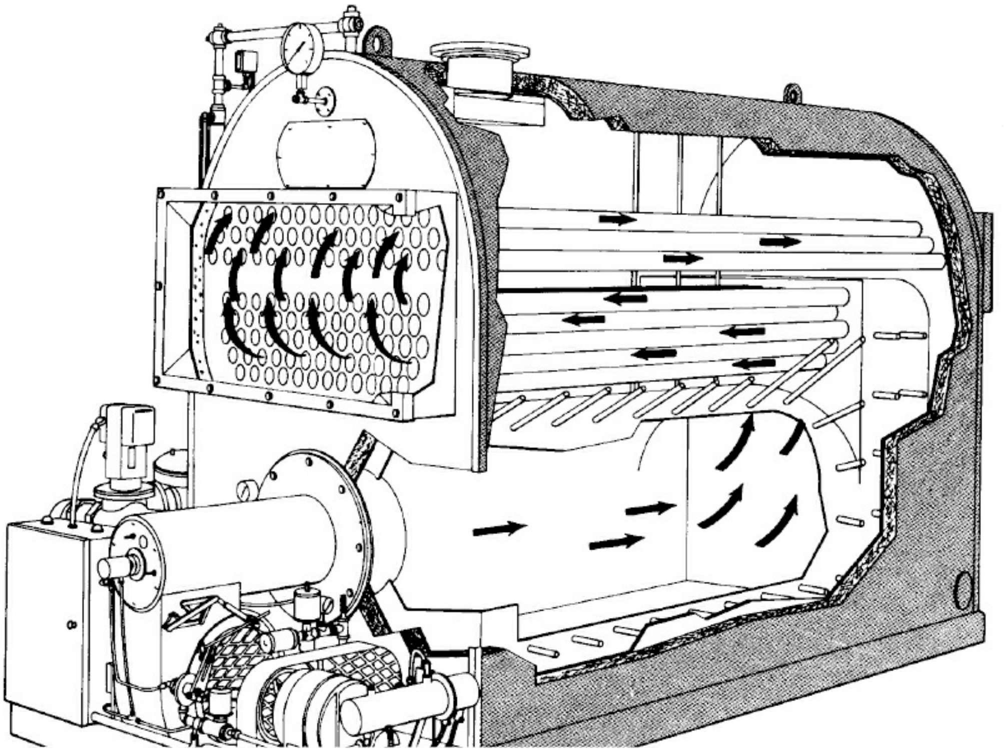

FIGURE 9.11 Large firebox-type unit. Direction of gas flow is forward in the short second-pass tubes and to the rear in the longer third-pass tubes.

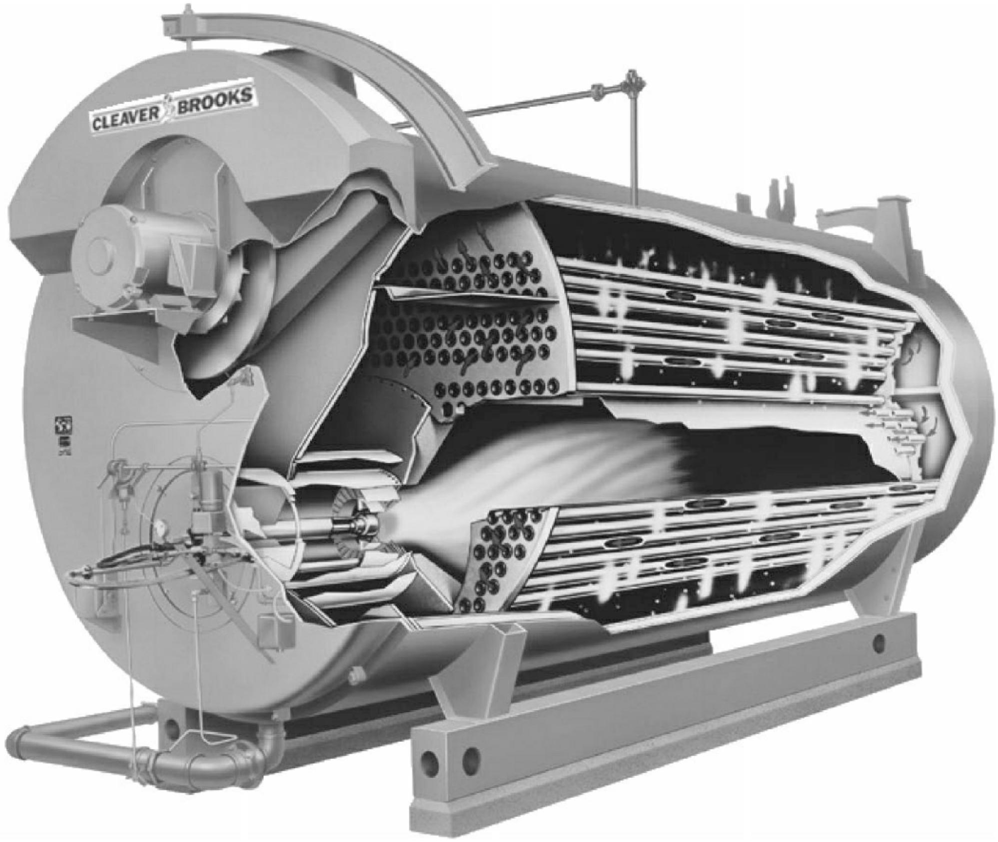

FIGURE 9.12 For maximum travel of hot gas and high efficiency, the four-pass design is used. In this boiler, gas velocity is maintained by a decrease in the number of tubes to give each succeeding pass a smaller cross-sectional area. (*Courtesy of Cleaver Brooks, Inc.*)

In most firetube boilers, the burner is located at the front end of the boiler in the combustion chamber, which is a large diameter tube running the length of the unit. The hot gases from combustion travel down the combustion chamber to the back end of the boiler where the gases are directed, by baffles, toward the front of the unit through the smaller diameter tubes. In multipass units, the hot gases are redirected back toward the rear of the unit, again with the use of baffles.

Watertube Boilers

A watertube boiler is composed of drums, headers, and tubes. The water and steam are contained within the tubes, while the heat is applied outside the tubes. The tubes, through which the water circulates and in which steam is generated, are outside the drums. Because the water drums are used for storage of water and steam, they are not required to contain any tubular heating surface. Most watertube boilers have natural circulation; however, some forced (positive) circulating units are in use.

Watertube boilers may be of the straight-tube or bent-tube type. The various bent-tube boilers, with higher pressures and temperatures, have gradually replaced the horizontal straight-tube units.

The initial cost of a watertube boiler is higher than that of an equivalent firetube boiler. The cost of a firetube boiler is commonly said to be half of the cost of an equal steaming rate watertube boiler. The higher efficiency of watertube boilers will, however, eventually offset higher initial capital cost. Additions of economizers, superheaters, and reheaters will permit recovery of initial capital cost even more quickly.

Horizontal Straight-Tube Boilers Modern, more efficient boilers are largely replacing the horizontal straight-tube boilers of the early 1900s. Some of these older units, however, are still operational, and a brief discussion is appropriate. Horizontal straight-tube boilers cover a wide range of capacities and pressures. They are used primarily to generate process steam and occasionally to generate building heat and power.

The horizontal units are limited to an hourly production of 10 000 lb of steam per foot of boiler width (14 900 kg/m). The unit is usually field erected. These boilers had early and persistent popularity because of favorable manufacturing and erection costs plus their adaptability to many uses.

These units are not without their drawbacks, however:

- Access into these units involves considerable downtime.
- Limited steam separating ability makes adequate separation at higher steaming rates difficult, if not impossible.
- Steaming rates are sharply limited by relatively low circulation rates and poor water distribution.

The straight-tube boiler is made up of a bank of tubes that are inclined and staggered. The tubes are inclined at an angle of 5 to 15° to promote circulation.

The header provides a flat surface for tube connections. It may be connected to the drum by means of circulation tubes (risers and downcomers) or by sheet steel saddles. The drum may be either longitudinal (parallel to the tubes), or it may be across (perpendicular to the tubes).

Boiler manufacturers varied the heating surface area (corresponding boiler capacity) by changing the tube length and number of tube rows in both height and width. For higher pressures, the header design was changed and required greater tube spacing and tubes of a smaller diameter.

Superheaters may be installed on straight-tube units with a maximum temperature rise of about 100°F (38°C). They are normally called over deck or inter deck, depending upon where they are installed.

The steam and water move along the inclined tubes to the front. The water then flows through the headers and into the steam drum. The cooler water flows down the downcomer to the rear header and finally into the generating tubes to complete the circulation cycle.

Bent-Tube Boilers The common bent-tube boiler offers many advantages over the straight-tube units, such as:

- Great economies in fabrication and operation because of the use of welding, improved steels, water-wall construction, and new manufacturing techniques
- Greater accessibility for cleaning and maintenance
- Ability to operate at higher steaming rates and produce a better quality of steam

The main elements of the bent-tube boiler are essentially drums connected by bent tubes (Fig. 9.13). With a water-cooled furnace, bent tubes are arranged to form the furnace enclosure. Most modern boilers, from small packaged boilers to large utility stations, are of this general design.

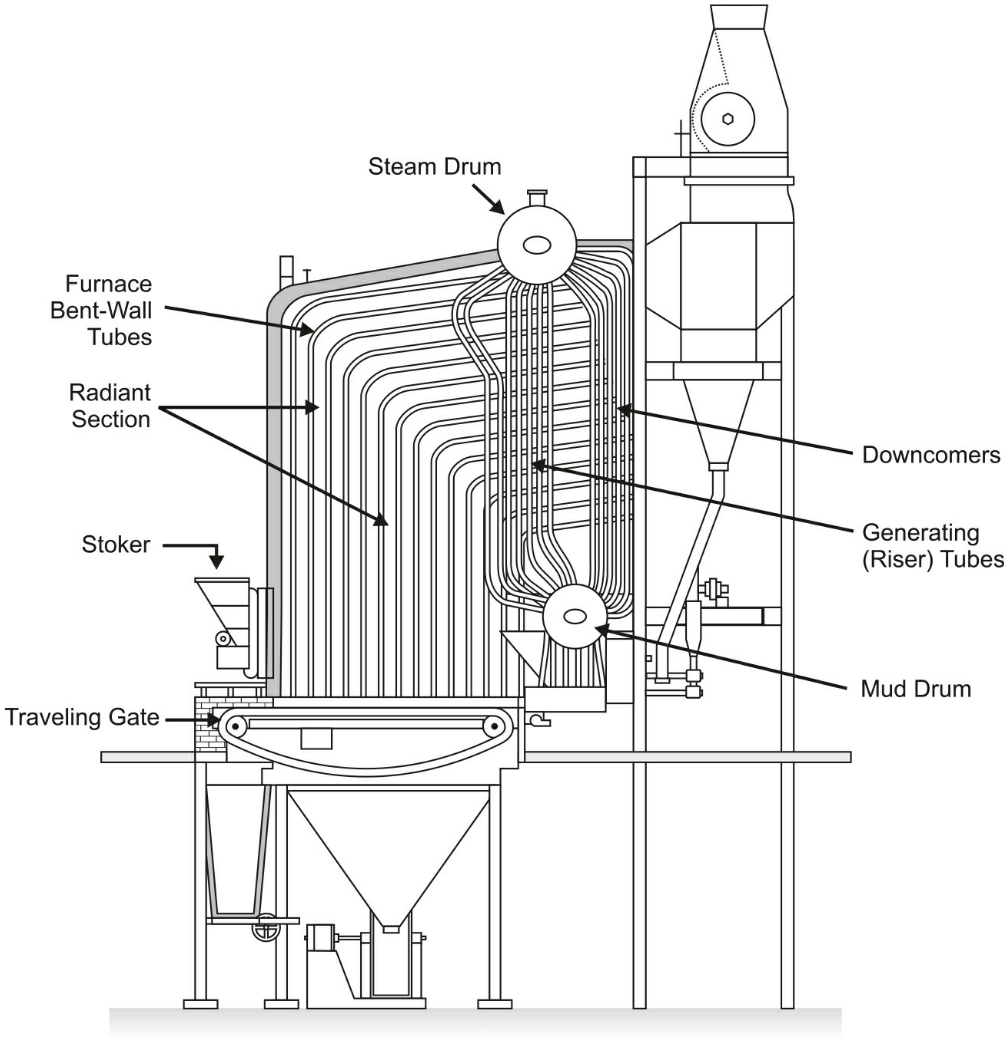

FIGURE 9.13 Bent watertube boiler.

The early bent-tube units were of the four-drum design. Although the four-drum design is sound, improvements permitted the trending toward three- and later two-drum units. The smaller bent-tube units (packaged boilers) of today have been standardized to three basic designs. Popular packaged boiler designs are the two-drum "O" type and "D" type units as well as the three-drum "A" frame unit (see Figs. 9.14–9.16).

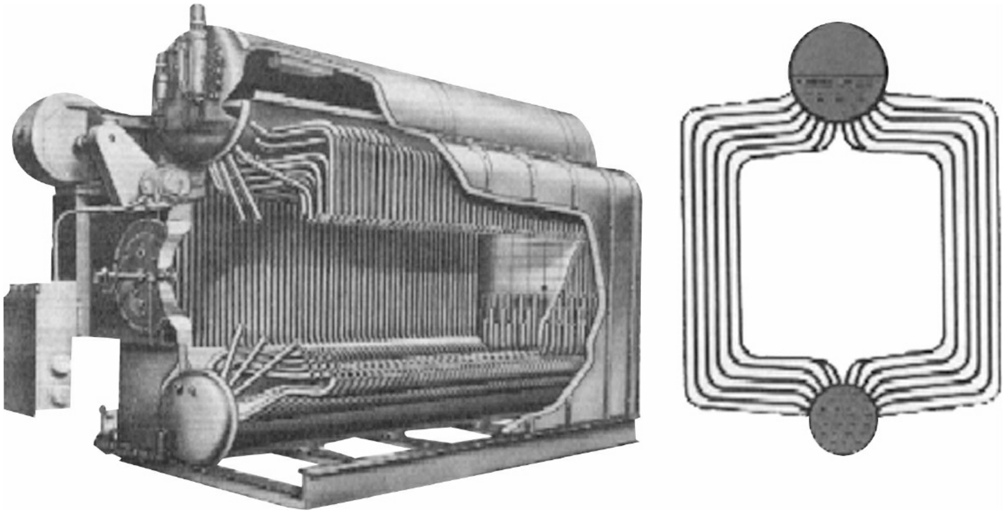

FIGURE 9.14 O-type packaged watertube boiler. Transportation limits the height of the furnace; for higher capacity, a longer boiler is required.

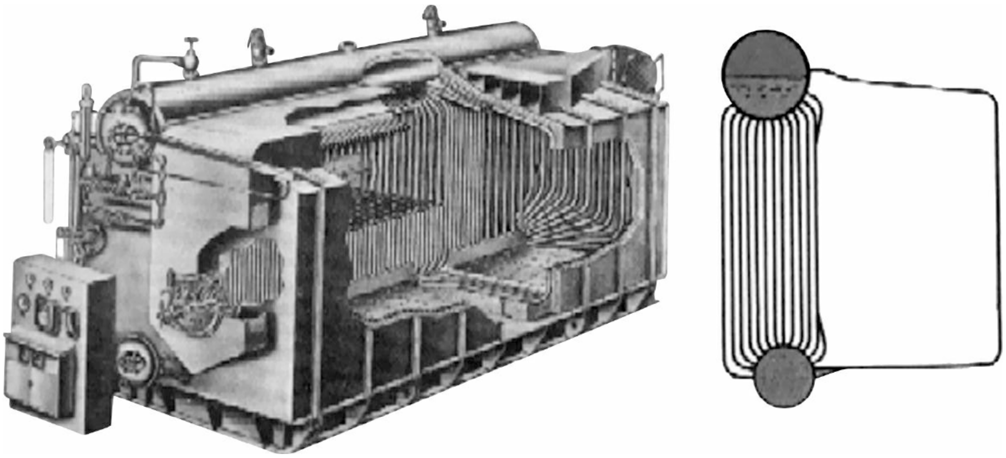

FIGURE 9.15 D-type packaged watertube boiler. Burners may be located in one-end wall.

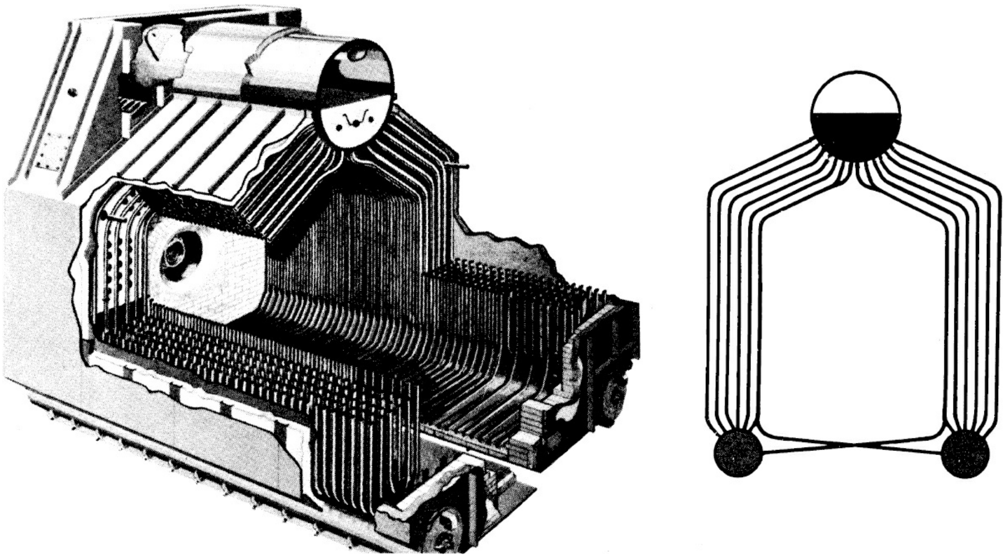

FIGURE 9.16 A-type packaged watertube boiler. The upper drum is larger to permit separation of steam and water.

As furnace size and temperatures increased, refractory maintenance became excessive, particularly when firing with coal in field-erected units. The higher gas temperatures caused increased slagging of the boiler surfaces. Furnaces today are normally completely water cooled (water-wall tubes) to overcome short refractory life and excessive fireside temperatures due to slagging. An additional advantage of water-wall tubes is that they are also steam generators, an aid in obtaining higher steaming capacity.

In Figs. 9.14 to 9.16, water enters the main steam drum and flows down the downcomers to the mud drum, then up the steamer or riser tubes and back to the steam drum. For a more detailed explanation of boiler circulation, see Boiler Circulation later in this chapter.

Cast Iron Boilers

Cast iron boilers are used primarily for low-pressure heating system applications. They generate 15 psig (103 kPag) steam or 30 psig (207 kPag) hot water. Cast iron boilers are usually designed in sections. These sectional castings are connected together by push-in nipples, and the whole unit is held together by tie rods or bolts.

Waste Heat Boilers

Heat recovery from industrial waste products or gases is often necessary from an economic, process requirement, or pollution standpoint. All or part of the steam requirements of a plant may be supplied by waste heat boilers. This section presents only a brief overview of the many types of waste heat boilers in use today.

Heat may be recovered from any number of sources, such as:

- Heat that originated as a necessary part of the process and would otherwise be discarded, for example, ammonia reformer, open-hearth furnaces, basic oxygen furnaces, gas turbine exhaust, etc.
- Heat that is a by-product of a chemical reaction process, for example, black liquor recovery boilers.
- Heat that is available from burning wastes, for example, waste wood, organic waste, garbage, or carbon monoxide (CO) gas in a refinery. In one respect, these could be considered fired boilers, but in another respect, they could be considered waste heat boilers. For example, the main purpose of a garbage incinerator is to burn garbage, and the heat generated can be considered waste heat.

Wherever a process waste product or gas is discharged at a temperature of 1000°F (538°C) or higher, heat recovery should be considered. Table 9.2 illustrates the temperature of various waste heat gases that can be used to heat boilers.

Source of Gas	Temperature	
	°F	°C
Ammonia oxidation process	1350–1475	730–800
Annealing furnace	1100–2000	590–1090
Black liquor recovery furnace	1800–2000	980–1090
Cement kiln (dry process)	1150–1350	620–730
Cement kiln (wet process)	800–1100	430–590
Coke oven beehive	1950–2300	1070–1260
Coke oven by–product	Up to 750	Up to 400
Copper refining furnace	2700–2800	1480–1540
Copper reverberatory furnace	2000–2500	1090–1370
Diesel engine exhaust	550–1200	290–650
Forge and billet heating furnace	1700–2200	930–1200
Garbage incinerator	1550–2000	840–1090
Gas benches	1050–1150	570–620
Glass tanks	800–1000	430–540
Heating furnace	1700–1900	930–1040
Malleable iron air furnace	2600	1430
Nickel refining furnace	2500–3000	1370–1650
Open hearth steel furnace		
• Producer gas-fire	1200–1300	650–700
• Oil, tar, or natural gas	800–1100	430–590
Petroleum refinery still	1000–1100	540–590
Sulfur ore processing	1600–1900	870–1040
Zinc fuming furnace	1800–2000	928–1090

TABLE 9.2 Temperature of Waste Heat Gases

The selection of a waste heat boiler is based upon many of the following considerations:

- Chemical nature, temperature, and corrosivity of the gases
- Quantity, amount, and nature of the dust contamination
- Available draft
- Desirable location for the flue outlet

- Whether the gases are under pressure or suction
- Available space
- Requirements for supplemental firing for start-up, preheating, emergency use, stabilizing furnace conditions, or added capacity
- Other special requirements of the individual process

In general, to offset the lower gas temperatures available in a waste heat system, design considerations are made to provide for a relatively high gas velocity over a small number of tubes to increase the convection heat transfer. Mass flows of 6000 to 8000 lb/[h · ft^2] [29 000–39 000 kg/(h · m^2)] of gas are common today. An average gas velocity of 40 to 50 ft/s (12–15 m/s) is used at gas temperatures of 1300°F (704°C).

Boiler capacity is limited by the maximum allowable draft loss; heat efficiencies of 60 to 70% can still be obtained by using economizers.

Specific process requirements in the production of steel, paper, ammonia, and other products have resulted in the design of various types of waste heat boilers. Two common designs today are the gas-tube unit for gas streams containing contaminants that could cause fouling, and the watertube unit for clean gases.

Gas-Tube Waste Heat Boilers A direct-fired, firetube boiler that has part of its shell exposed to the furnace absorbs heat by both radiation and convection, thus making more efficient use of its surfaces. Gas-tube waste heat boilers, however, usually have just a single-pass arrangement that absorbs only convection heat from the gases. These gas-tube units have a high weight-to-heat output ratio because the exterior shell is not used as a heating surface. Gas-tube boilers of this type are most suitable for pressures around 400 to 500 psig (2.8–3.4 MPag) and gas temperatures as high as 1800°F (982°C).

Tubes of these units are of smaller diameter and more closely spaced than tubes in watertube waste heat units. The tubes are kept clean of deposits by a rotating arm soot blower with nozzles directed toward the tube ends. These boilers are designed to handle only light dust loading (gas particulates) and should not be used where dust loading of the gas is greater than 0.5 g/ft^3 (17.7 g/m^3).

Gas-tube units may be either horizontal or vertical in design. In horizontal units, practically the entire space within the shell is filled with tubes (Fig. 9.17). The steam space is minimized; instead, a separate steam drum may be used. The boiler may be set at an angle of 15° to improve circulation, provide for steam collection at the highest point, and permit suspended matter to move to the lowest point. Vertical units are very similar to horizontal units except the gas tubes are vertical.

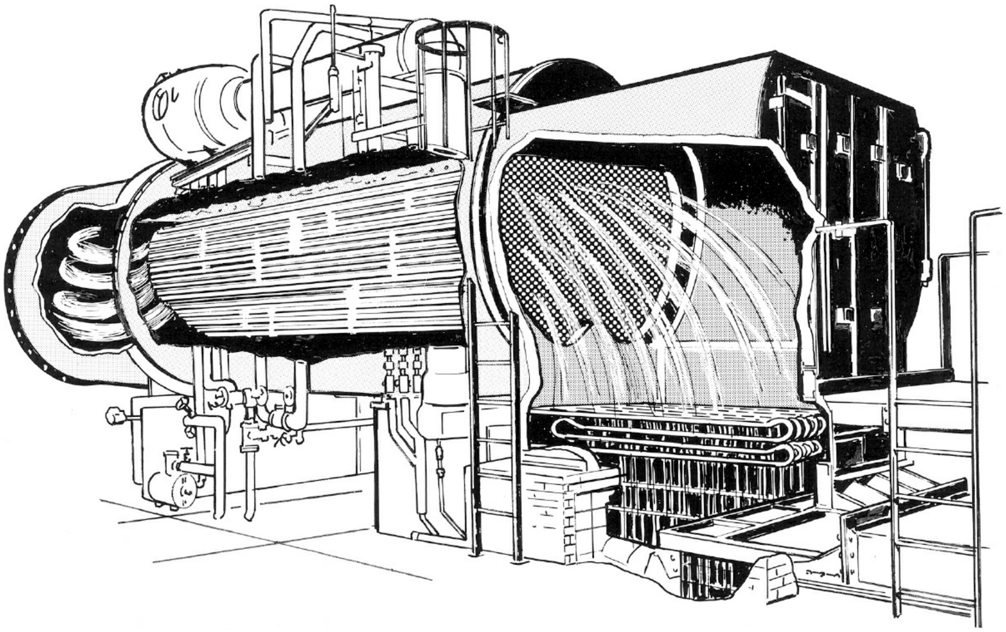

FIGURE 9.17 Gas-tube waste heat boiler.

Watertube Waste Heat Units The major considerations in the design of a watertube unit are the cooling of sticky particles before their entry into the convection section and the problems caused by high dust loading.

Watertube waste heat units are more widely used than gas-tube waste heat boilers for the following reasons:

- Dust may be recovered and collected.
- Tube sizing and spacing may be varied to prevent slagging.
- Damage due to gas temperature fluctuations is minimized.
- The waterside is easier to treat and keep clean.
- More economical design arrangements are possible.

Applications of Waste Heat Boilers Open hearth, forge, and continuous heating furnaces in steel mills are usually equipped with waste heat boilers. Coke oven gas and blast furnace gases are normally used as the heat source for the waste heat units. Much of the steam generated in refineries and petrochemical and chemical plants is of the waste heat type. Ammonia plants, for example, generate steam via waste heat units by cooling the synthesis gas from the reforming furnaces. In the case of ammonia plants, approximately 95% of the steam on-site is generated by waste heat. In the Kellogg-type ammonia plants, the main waste heat boilers are bayonet tube/scabbard design, where other ammonia plant designs might use vertical shell-and-tube designs. Waste heat units such as bayonet, TLX (transfer line exchanger), and numerous other types are found more often in plants where process temperature control and energy conservation are of prime concern.

Ore roasters and cement kilns: A three-drum, low-head, watertube, waste heat boiler is used to recover heat from the ore roasters and kilns.

Lead and zinc smelters: After the lead and zinc are boiled out from the slag, they are reoxidized in a fuming furnace. Gaseous products from the fuming furnace have temperatures of 2200°F (1200°C) and are passed through a watertube waste heat boiler to cool them down to 1400°F (760°C).

Papermaking: In the manufacture of paper, wood is cooked in digesters with live steam, sodium hydroxide, and sodium sulfite. The liquid waste from these cookers contains lignin and reacted chemicals. A recovery unit (black liquor boiler) is used to recover the chemicals (salt cake), generate process steam by burning the waste liquor, and eliminate waste to meet pollution requirements. During the burning of black liquor, the recovered salts are molten, and this smelt accumulates in the bottom of the boiler, where it is decanted into the dissolving tank. The recovered green liquor is then reused in the process. If a tube leak should occur in these boilers, the water from the leak will react with the molten salt, potentially resulting in a violent explosion.

Petroleum industry: In the petroleum industry, the efficient operation of a fluid catalytic cracking unit produces gases rich in carbon monoxide (CO). To reclaim the thermal energy represented by these gases, the cracking units are designed to include a CO boiler that uses this carbon monoxide as the fuel source to generate steam.

The operation of the CO boiler (Fig. 9.18) is coordinated with that of the catalytic cracker. Normally, the boiler is required to supply steam for the operation of the cracking unit and is started using supplementary fuel, for example, natural gas. Once the furnace temperature reaches approximately 1800°F (982°C), the CO gas is admitted to the furnace, and the supplemental fuel is reduced.

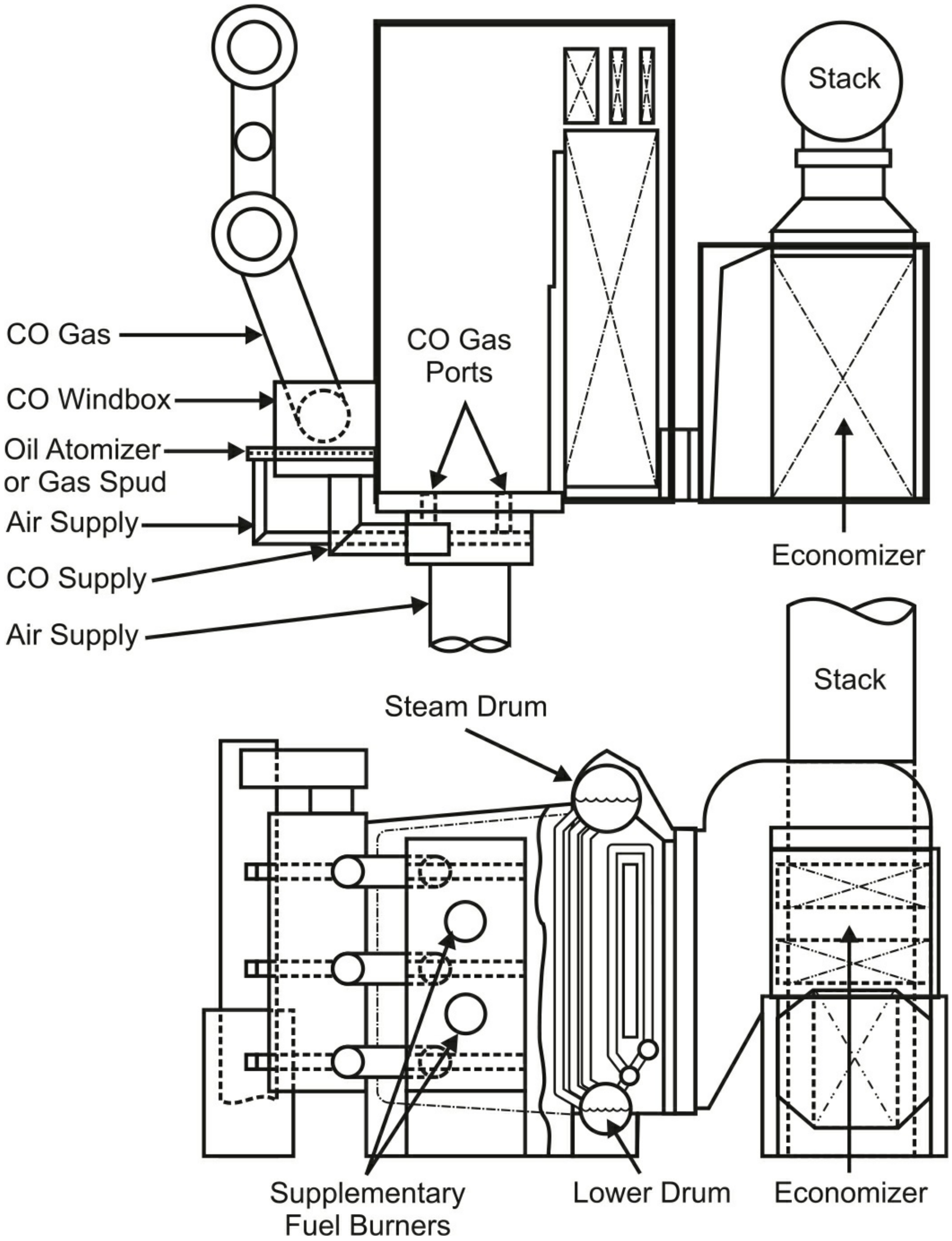

FIGURE 9.18 CO boiler illustration.

Coil Boilers

Coil boilers, or steam generators as they are commonly called, have become popular since the 1980s in medium industrial and institutional accounts for several reasons:

- Low water volume to boiler output
- Small footprint
- Quick steaming capability
- Skilled operators not required

While these boilers provide customers with the advantages presented above, they pose some interesting and unique treatment challenges.

There are two main design differences between boilers that fall into this category. The differences are in how steam and water are separated. One design (Fig. 9.19) utilizes a conventional steam drum to allow for the separation of steam and water, while the other design (Fig. 9.20) utilizes a steam separator and a trap to allow for steam/water separation. The coil orientation in the conventional design is horizontal, while the orientation in the steam separator system is vertical.

FIGURE 9.19 Photograph of a typical coil tube boiler with a conventional steam drum for steam/water separation. (*Courtesy of Thermogenics Inc*.)

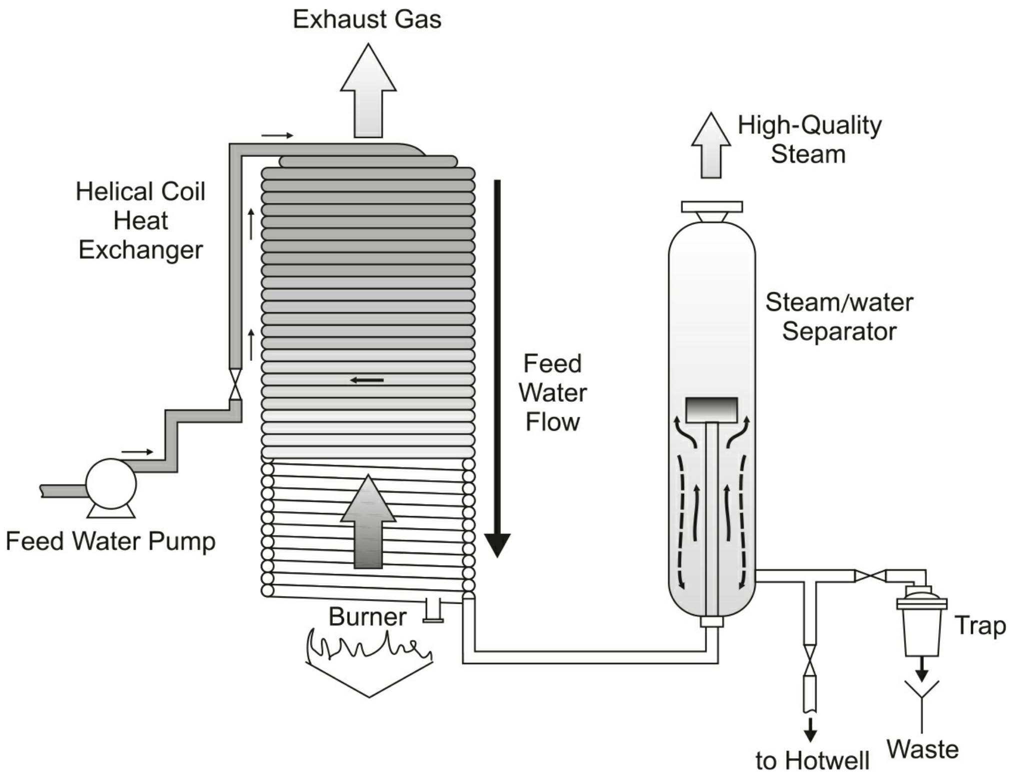

FIGURE 9.20 Schematic of a typical coil design boiler with a steam separator and trap system for steam/water separation.

Design differences notwithstanding, there are a few characteristics that are common in all coil steam generators:

- Maximum operating pressure of 250 psig (1.7 MPag)
- Boiler power range from 20 to 600 hp (14.9–447 kW)
- Water holding capacity range is 0.12 to 0.25 gal/hp (0.61–1.3 L/kW)
- Feedwater to steaming rate ratio of 1.1 to 1.25

Operation Despite the common characteristics, the ways water and steam are separated govern how these steam generators work. The steam generators with conventional steam drum operation (Fig. 9.19) operate on conventional methods of feedwater supply. That is, the feedwater demand is controlled by the steam drum water level. These units are, therefore, suitable to be integrated into a conventional firetube or watertube steam plant.

The steam generators that have a steam separator and trap system for steam/water separation (Fig. 9.20) recycle a portion of the boiler water back to the feedwater system and, therefore, are generally considered unsuitable for integration into an existing steam plant that has conventional firetube or watertube boilers. These steam generators need a stand-alone feedwater system.

Steam Separation with Drum In a coil boiler with steam drum separation (Fig. 9.19), there is a forced recirculation pump that pulls boiler water from the steam drum and sends it to a manifold that feeds several horizontal coils. These coils are designed in such a manner that they remain flooded at all times, with a steam/water mixture suitable for coil cooling. Each coil has a thermocouple to provide coil temperature data. The temperature on each coil should be closely monitored and is typically within 30 to 40°F (17–22°C) of the steam saturation temperature. Coils that exhibit a trend toward higher temperatures are typically not being cooled sufficiently and generally indicate deposition is occurring on the coil.

The steam/water mixture exits each coil and is gathered in a manifold and returned to the steam drum through a steam lance that is the primary steam separation vehicle. Secondary separation may be accomplished through baffling or screens. Blowdown is accomplished via a surface skimmer and conductivity control. Clean feedwater is fed into the steam drum to maintain a consistent water level in the drum from a conventional deaeration or atmospheric hotwell system.

Steam Separation with Separator and Trap In a coil boiler that utilizes a steam separator and trap system (Fig. 9.20), a feedwater pump feeds from an atmospheric hotwell or deaerator to the top of a vertical coil. This coil has three distinct sections:

1. Economizer pancake coil
2. Intermediate heating coil
3. Water-wall coil

The feedwater enters the economizer pancake coil at the top of the generator and travels counter-current to the flue gas. This coil is small in diameter with many winds. It transitions to the intermediate heating coil that has fewer winds and is larger in diameter. The final water-wall coil is single wound and larger again in diameter. A thermocouple is located in the water-wall coil. The steam/water mixture exits the base of the water-wall coil and is directed to a steam separator. The separated boiler water accumulates in the bottom of the separator and is trapped via an inverted bucket trap and directed back to the feedwater system for recycle. A proportioning valve is installed on the trap discharge that allows for some system blowdown each time the trap discharges.

The inverted bucket-trapping rate is governed by feedwater temperature. The trapping rate is usually set at 4 to 6 times per hour for systems where feedwater temperature is between 180 to 190°F (82–88°C). Systems with higher feedwater temperatures, such as those expected from a deaerated system at 250 to 350°F (121–177°C), have trapping rates of 10 to 15 times per hour. Since the discharge from the trap is recycled back to the deaerator or atmospheric hotwell, the calculation for cycles of concentration in this type of system must take into account the contribution of dissolved solids from this source. Hence, this type of system is designed to run between 4 to 5 COC of this less pure feedwater.

System Challenges While there are advantages in using a coil boiler, there are also challenges in keeping them running. Both of these systems are prone to specific difficulties that are treated a bit differently than a conventional watertube or firetube boiler. The common problem areas on these systems come from design, operation, and chemistry perspectives. Approaching system issue evaluation from the mechanical, operational, and chemical perspective generally yields good troubleshooting results. While each system is unique in design and operation, a number of the common problems are discussed below.

Oxygen Attack Coil boilers are very prone to failure from oxygen corrosion. They are usually treated with higher levels of oxygen scavenger to minimize this failure mechanism. The typical sulfite levels carried are at least 50 to 100 mg/L at the coil. While sulfite is the recommended oxygen scavenger, others can be utilized but must be carried at sufficiently high levels to ensure complete oxygen removal from the system before water enters the coils. Since these boilers are prone to failure from oxygen attack, storing idle equipment can be very challenging. It is highly recommended that the plant follow the manufacturer’s procedures for lay-up.

Oxygen corrosion typically occurs either during a short-term outage or during lay-up. It can occur in operation, if the system chemistry is insufficient to protect against attack. Oxygen pitting at the upper pancake economizer sections of a vertical coil indicates wet lay-up failure. Pitting in the upper section of a vertical coil also indicates wet lay-up failure. Pitting in the lower sections of either type of system generally indicates dry lay-up failure.

Deposition Coil boilers are very prone to deposition in the form of scale. The temperature profiles generated by the thermocouples over time can indicate if deposition is occurring in the system. In addition to the temperature profiles of the coils, the recirculation pump pressure can be used as an indication of deposition. The pressure rises over time as deposition occurs. Since they are prone to scaling, a polishing softener on the makeup line is common to ensure minimal hardness ingress. Precipitating programs, such as a phosphate program, are typically not recommended for these systems.

Boiler Water Carryover This can be a result of high alkalinity or dissolved solids levels but is often operational in nature. Due to the small steam separating spaces and low steam-to-water ratios (steam reserve capacity) in these boilers, systems with a rapid increase in steam demand can cause carryover. Other areas of investigation for carryover include:

- Operation beyond design capacity
- Water contamination by organics such as hydrocarbons
- Steam separator trap failure
- Erratic operation

Coil Failure from Thermal Stress While the typical overheating failures caused from deposition are common in these boilers, these coils can also fail from other thermal stresses:

- The more the boiler is cycled on and off, the more thermal stress is imparted to the coil. If the mode of operation causes frequent start and stop operation, the boilers are prone to failure.
- Starvation of the coils by partial plugging from chip scale or any other cause quickly results in an overheating failure.
- Feedwater pump failure causes starvation of the coil.

Electric Boilers

The electric or water resistance steam generator has been in existence since 1905. However, the number of these units currently in operation is small. The electric boiler provides some advantages and tangible savings over the more conventional boilers, such as:

- No handling and storage of fuel
- No need for fans, breeching, and chimneys
- No ash handling
- Limited floor space requirements
- Low costs of installation and operation help offset higher electricity costs

Typically, electric boiler designs are limited to less than 600 kWh [2100 lb/h (953 kg/h)] output. However, in some countries where electricity is of particularly low cost, for example, where power is supplied by hydroelectric generation, electric boiler designs of up to 12 000 to 24 000 kWh [42 000–85 000 lb/h (19 000–39 000 kg/h)] or more are commonly used in large process industry applications. The maximum continuous rated (MCR) output is about 220 000 lb/h (100 000 kg/h).

The electric steam generator produces steam rapidly and can be taken off line very quickly. Some units are said to need only five seconds to raise the steam production from 0 to 100%. Roughly, 35 kWh of electricity are required to produce the same heat as one gallon (3.8 L) of No. 6 fuel oil.

Electric boilers are classified as immersion type and electrode type, depending on their method of operation. The immersion-type electric boiler is basically a pressure vessel in which a number of resistance-type heating elements are submerged in water. This type of boiler is generally restricted to the lower capacity applications where steam production is less than 10 000 lb/h (4500 kg/h). The electrode-type boiler, however, uses the conductive and resistive properties of the water itself. A three-phase alternating current passes among three electrodes, with water as the conductor. This is accomplished either by immersing charged electrodes into the water or by spraying water onto the electrodes. Because water has electrical resistance, the current flow generates heat directly in the water. Steam production is a function of the amount of water exposed to the electrodes.

Nuclear Reactor Boilers

Very basically, nuclear energy for steam generation is obtained by the fission (splitting) of the heavy atoms of uranium. The fission process releases tremendous amounts of thermal energy, which can be used to heat water and generate steam.

A nuclear reactor is the equipment used for initiating, maintaining, and controlling a fission chain reaction to gradually release the resultant energy. In a Pressurized Water Reactor (PWR) design, the heat is removed by a closed water system primary loop (Fig. 9.21). The temperature limit of the primary loop is controlled by the rate of fission. This water is sent to a subsequent heat exchanger, where it controls the temperature and pressure of the steam in the boiler (intermediate loop). Special metallurgy limits corrosion and the creation of radioactive isotopes. For more information on nuclear steam generators, refer to Chapter 33 on Power Industry.

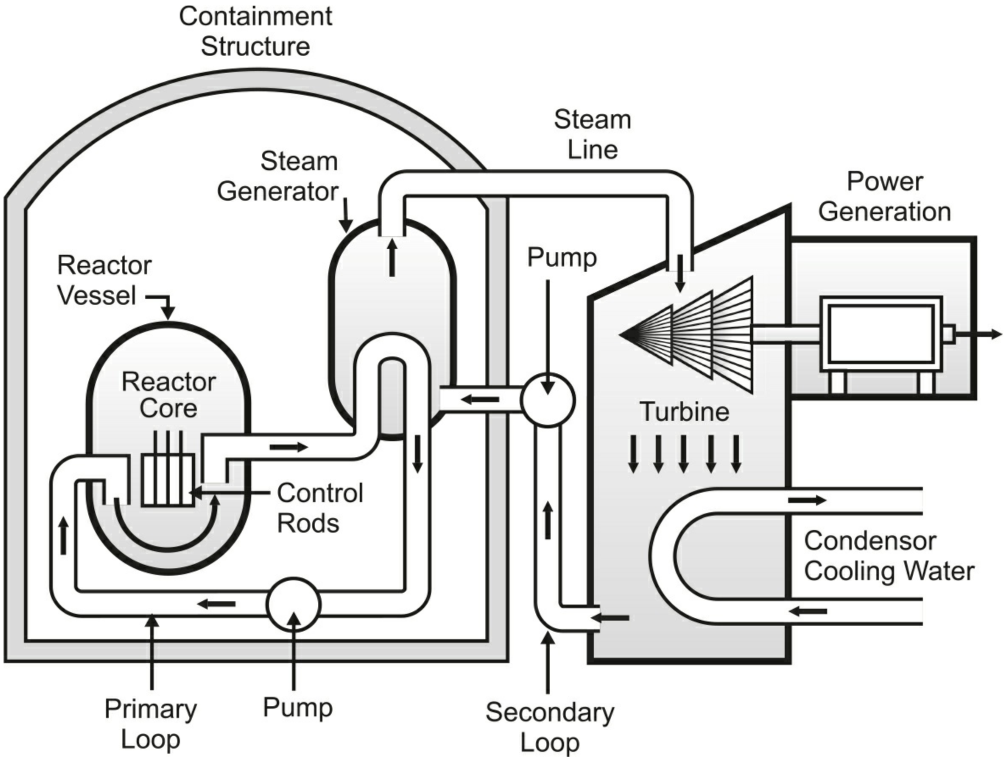

FIGURE 9.21 Nuclear reactor boiler.

Once-Through Boilers

Natural circulation boilers have been designed up to 2850 psig (19.7 MPag). They depend on the circulation of an excess amount of water and the separation of steam from water in some type of drum. This separation is possible because of the difference in density between water and steam. At 2700 psig (18.6 MPag), for example, water weighs 32.9 lb/ft^3 (0.527 g/cm^3) and steam weighs 9.0 lb/ft^3 (0.14 g/cm^3). As the pressure increases beyond 2700 psig (18.6 MPag), the differences in the steam-water densities become less and less, until at 3200 psig (22.1 MPag), the densities of steam and water are the same.

In a once-through boiler, there is no recirculation of water and no steam drum. As Figs. 9.22 and 9.23 illustrate, water is forced through pipes, where all of it is turned into steam.

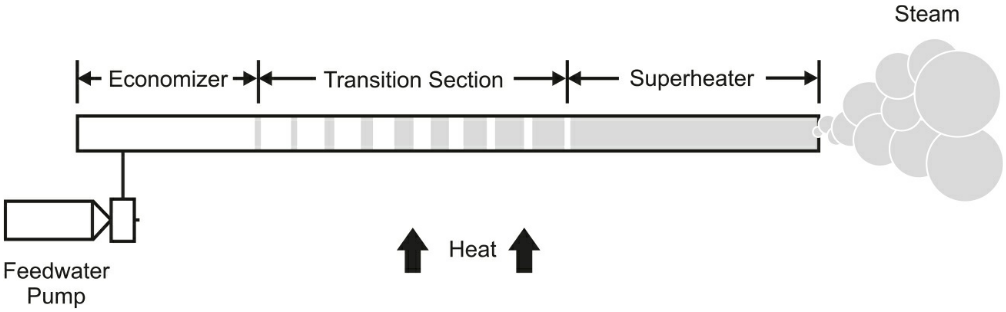

FIGURE 9.22 Once-through boiler principle.

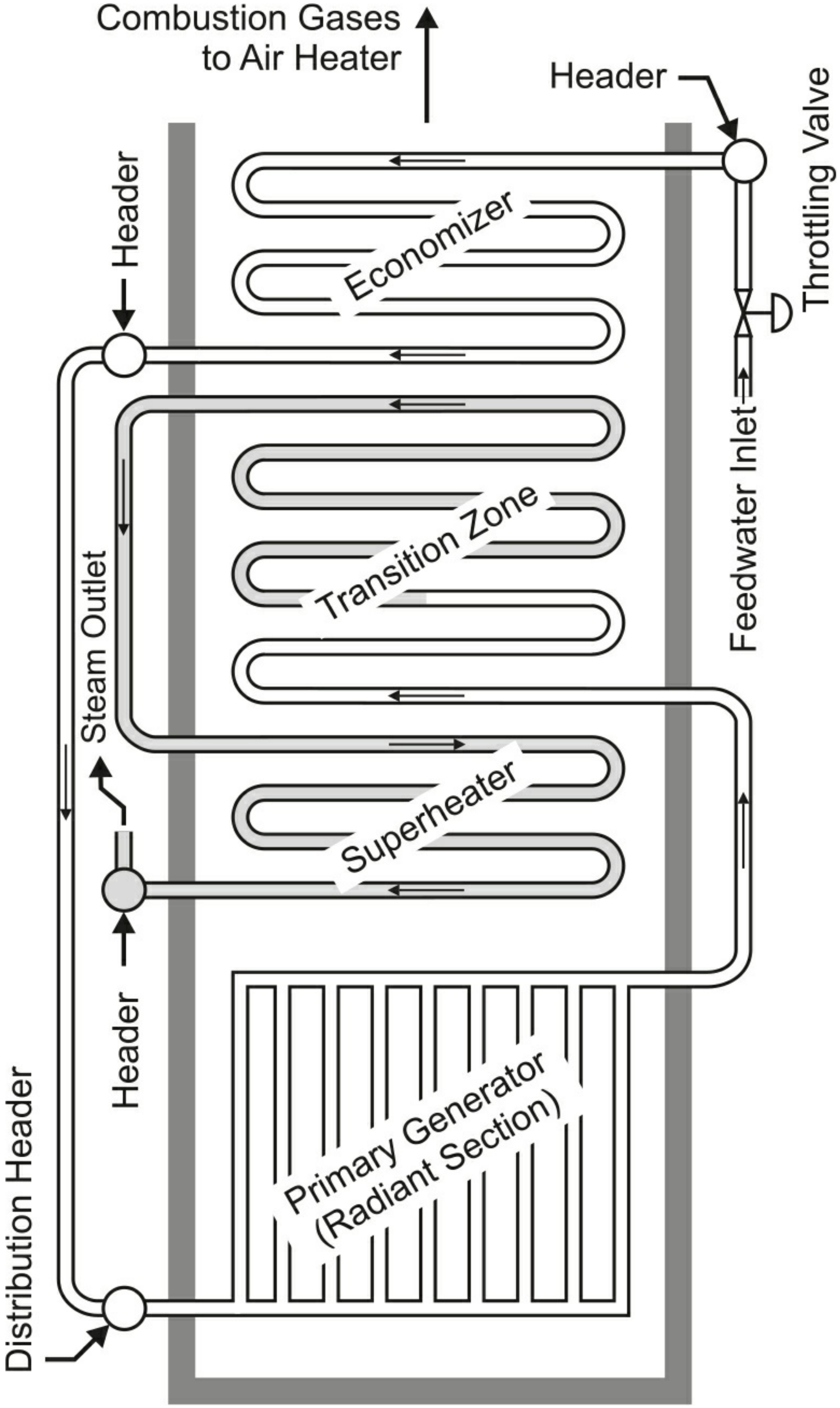
Combustion Gases
to Air Heater
Header
Throttling Valve
Header
Economizer
Feedwater Inlet
Transition Zone
Steam Outlet
Superheater
Header
Distribution Header
Primary Generator
(Radiant Section)

FIGURE 9.23 Once-through boiler forced flow principle.

Once-through boilers offer some advantages over the more common water-recirculatory units in that once-through boilers are not limited by pressure, there are no drum costs, no recirculatory and downcomer costs, and they have high thermal efficiency.

Once-through boiler design complexities and feedwater purity requirements limit their usefulness in most industrial applications. Once-through boilers are most commonly found in electric utility plants.

Boiler Ratings

There is no standard means for expressing the capacity or rating of modern steam generation equipment. The capacity of boilers may be stated in terms of area of heating surface, rated boiler horsepower, or maximum steam generating capacity. The boiler horsepower is used only when expressing the capacity of small, simple boilers such as firetube boilers. The capacity of medium and large modern boilers is expressed in maximum mass of steam per hour at a specified feedwater temperature and outlet steam pressure and temperature.

The heating surface of a boiler consists of those areas that are in contact with heated gases on one side and water on the other. The ASME boiler code specifies that the gas side is to be used when calculating heating surfaces. It follows that in determining the heating surface for flue and firetube boilers, the inside diameter of the tubes must be used; for watertube boilers, the outside diameter is used.

The boiler horsepower (rarely used today) is defined as the equivalent evaporation of 34.5 lb/h (15.6 kg/h) of water from and at 212°F (100°C). The energy equivalent is 33 476.73 Btu/h (8436.0 kcal/h, 35 296.2 kJ/h, or 9.8 kW). This expression was derived from an original rating for steam engines stating that for one horsepower of work, approximately 30 lb (13.6 kg) of steam would have to be supplied per hour.

It was further determined that a steel boiler supplying steam for an engine had 10 ft^2 (0.929 m^2) of heating surface for each horsepower. This meant that it had a heat absorption rate of 3347.673 Btu/[h · ft^2] (10.5 kW/m^2) of heating surface. As time passed, more and more boilers were rated in boiler horsepower based on heating surface, that is, one boiler horsepower for every 10 ft^2 (0.929 m^2) of heating surface.

Boilers improved and so did fuel burning equipment and methods. It became apparent that boilers could develop several times the capacity based on former rating methods. Today, boiler horsepower has little correlation to boiler performance. The historical evaporation rate of 34.5 lb steam per hour per 10 ft^2 [16.8 $kg/(h \cdot m^2)$] of boiler heating surface has long since become obsolete. Because of engineering advances, improvements in radiant heat utilization, and better circulation (of both water and gas), the present evaporation rate is greater than 250 lb steam per hour per 10 ft^2 [122 $kg/(h \cdot m^2)$] of heating surface in large utility plant steam generators.

More commonly, the quantity of water evaporated into steam per hour is known as the evaporation rate. The unit evaporation rate is expressed in pounds steam per hour (kg/h), pounds steam per hour per square foot [$kg/(h \cdot m^2)$] of heating surface, or pounds steam per hour per cubic foot [$kg/(h \cdot m^3)$] of furnace volume.

When capacity is expressed in pounds (kilograms) of steam per hour, further information is required, including feedwater temperature; quality (moisture content); steam pressure; steam temperature or degrees of superheat; and specified conditions of fuel, burner, firing method, and draft.

Today, there is a fair degree of standardization for low-pressure heating boilers. Smaller power boilers can be compared based on total heating surface. Some ratings (for packaged units especially) are determined by actual test, accompanied by manufacturer's certification. Large power boilers and utility plant equipment are sold based on performance test after installation.

The purposes of the testing and rating codes adopted by the industry are twofold:

1. To assure the purchaser and specifier that the boiler will actually deliver the output claimed by the manufacturer
2. To provide a basis for comparison between different boilers

Today in the United States, most industrial boilers are built according to the ASME specifications for steam generating units. ASME codes are universally applied; other codes take into consideration specialized designs or pieces of equipment. In Great Britain and Europe, the British Standards Institute (BSI) presents the British view on this subject. Both the ASME and BSI are held in high regard.

The ASME and BSI test codes enable users to obtain accurate information on the adaptability of equipment, best methods of operation, and equipment capacity and efficiency. They provide means for verifying manufacturers' guarantees. The codes also provide checklists before testing, required instrumentation and testing equipment, special precautions, and computation instructions for interpretation of test results.

Boiler Circulation

An adequate flow of water and water-steam mixture is necessary for steam generation and control of tube metal temperatures in all the circuits of the boiler. The force of gravity available to produce flow in natural circulation comes from the difference between the densities [lb/ft^3 (g/cm^3)] of the fluids in the downcomer (downflow) and riser (upflow) tubes (Fig. 9.24).

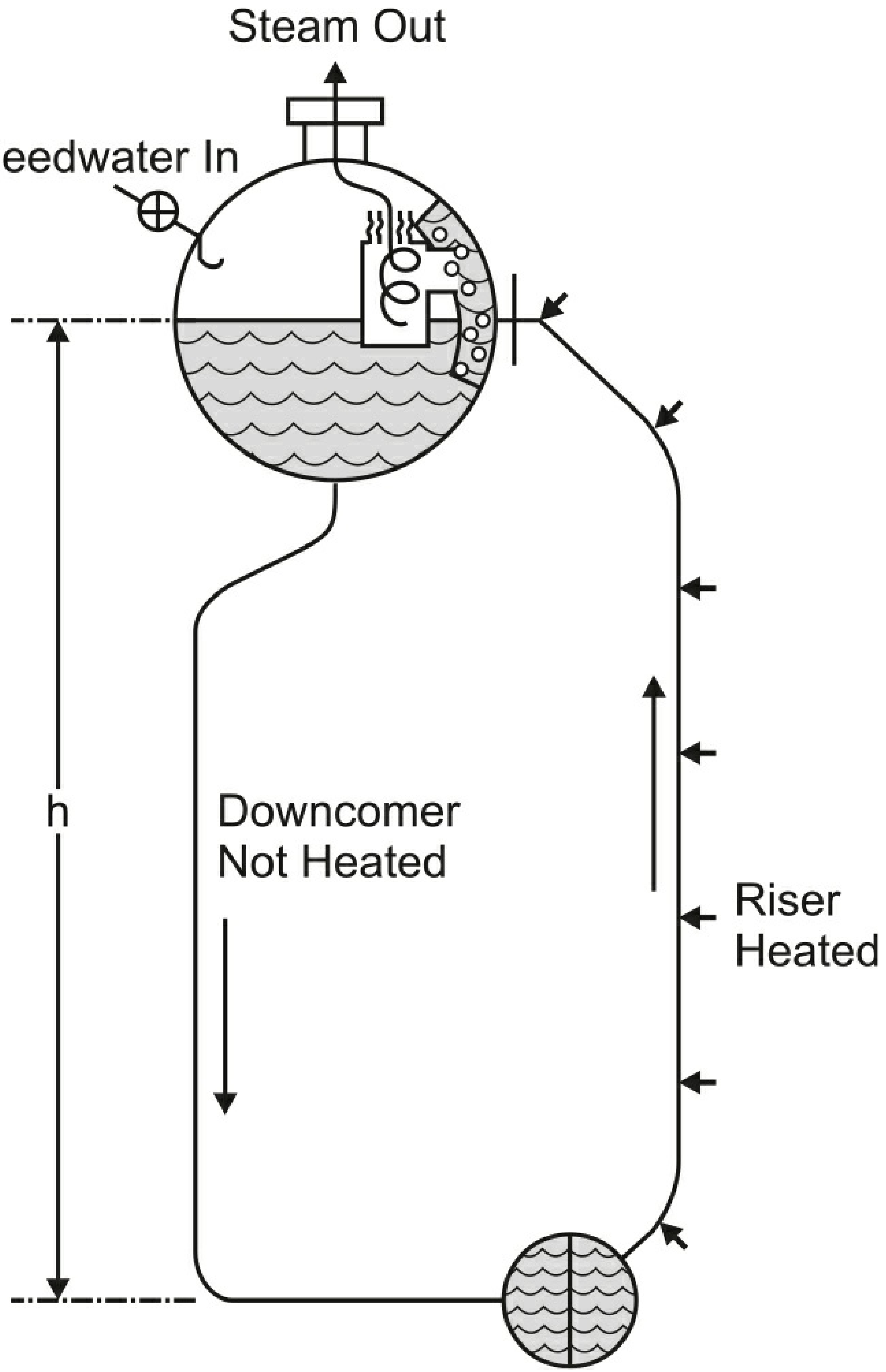

FIGURE 9.24 Simple natural circulation, including primary steam separator in drum.

This flow of water and steam within the boiler is called natural circulation. When heated, water decreases in density and tends to rise to the top of the vessel; conversely, cooler feedwater entering the boiler drum is heavier than the bulk water. Thus, it tends to drop to the bottom of the vessel.

When water is heated to its boiling point, small steam bubbles form on the heated surface. These bubbles cling to the metal due to surface tension until they are large enough to overcome the surface tension or until they are swept away by the circulating water in the tube. This phenomenon is known as nucleate boiling. The steam is much lighter than water and rises rapidly. This movement of the steam through the water creates turbulence and circulation. Figure 9.25 shows the effect of pressure and temperature on steam and water density.

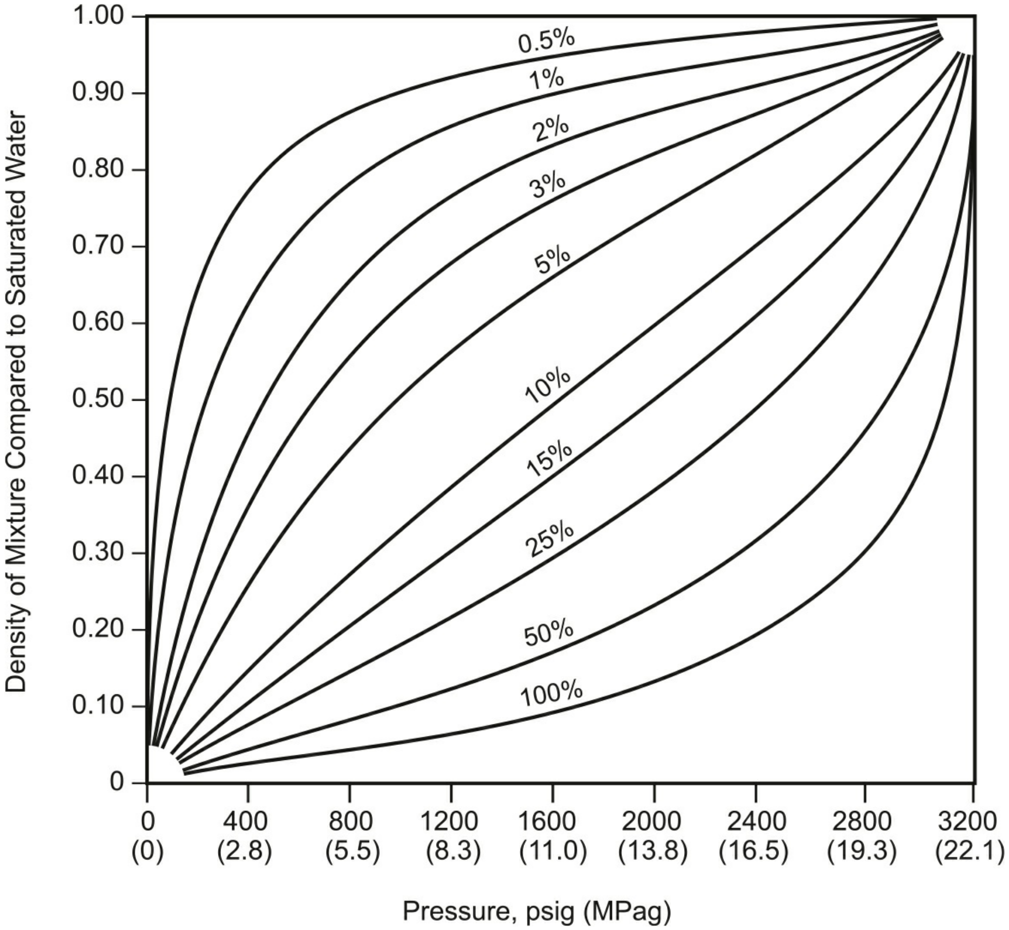

FIGURE 9.25 Density relationship of steam and water mixture.

All once-through units and most hot water boilers depend upon positive (forced) recirculation of the water and steam mixture. Nearly all other boilers, however, depend upon natural circulation to ensure that sufficient water is fed to each tube receiving heat to keep its surface thoroughly wetted and at the desired operating temperature. Lack of adequate flow will result in tube overheating and failure.

Design Considerations

The prime requisite in designing a natural circulating boiler is to maintain nucleate boiling under all anticipated operating conditions. Equally important is the proper distribution of water to all the tubes, especially in multiple-drum, water-wall boilers.

Water in a large container, for example, a firetube boiler, has a relatively sluggish movement until circulation is established. Staggering of tubes causes greater water turbulence when circulation is initiated. Circulation in watertube boilers, on the other hand, is established quite quickly, beginning as soon as the heat input is sufficient to produce steam bubbles. The steam bubbles create enough density difference within the confines of the tubes to cause water and steam to rise in the riser tubes.

In design, the riser circuits are normally fixed by the general arrangement of the boiler. They form the enclosure of the furnace and provide the surface area required for nucleate boiling, based upon the expected heat absorption (heat transfer rates).

The effect of uneven heating, improper firing, and the burning of different fuels on nucleate boiling must also be considered. The water flow rate velocities in properly designed boilers will ensure that enough water flows over the tubes to pick up the heat required to generate steam, maintain nucleate boiling conditions, and minimize tube overheating and failure. Flow rate velocities vary from 1 to 10 ft/s (0.3–3 m/s), depending upon the type of boiler.

For example, in boilers with inclined tubes, heat flux may be on only half the tube, and the geometry is prone to steam/water stratification (steam blanketing). Therefore, higher mass flows are required to prevent departure from nucleate boiling (DNB). DNB occurs when steam bubbles form faster than they are removed, resulting in an insulating steam blanket. When DNB occurs, the heat transfer through the tube is greatly reduced, overheating occurs, and tubes eventually fail. In boilers that have nearly vertical tubes and total heat flux spread over the entire tube circumference, lower mass flows are adequate.

From an efficiency standpoint, it would be highly desirable to evaporate all the water circulating through the generating tubes in one pass. If this were to happen though, the amount of solids (for a low-purity feedwater system) that would deposit on the high heat transfer surfaces would result in overheating and failure. Total evaporation also presents two other problems:

1. Maintaining a constant water level is almost impossible when load changes occur.
2. Severe foaming occurs due to uncontrolled bubble release.

To overcome these difficulties, boilers are designed to recirculate anywhere from 3 to 30 times more water than is necessary for steam formation. This excess water circulation prevents boiling to dryness and permits easier control of water levels.

The ratio of water fed to the steam generating tubes, and the steam actually generated (mass of water to mass of steam), is called the circulation ratio. Thus, for most recirculating boilers, circulation ratios are normally between 3:1 and 30:1.

As indicated previously, severe tube damage can occur if a boiler does not have proper circulation and flow velocities. The result will be evaporation to dryness, which leads to deposition, tube overheating, and eventual rupture. Evaporation to dryness or steam blanketing may also lead to concentration of chemicals, such as chelates or caustic, causing severe tube corrosion and failure.

Improper heat input and tube design may result in lack of proper circulation velocity. This can be the result of too much heat to the downcomers, causing them to act like riser tubes. Lack of heat to the risers results in insufficient steam generation, causing them to act like downcomers. In either case, the result is inverse circulation or stagnation in the tubes. With these conditions, flow rates are so low that impurities will not be swept along and tend to deposit and accumulate within the tubes, until they are eventually corroded or plugged.

Natural Circulation Systems

As discussed earlier, water circulates naturally because of its change in density with temperature. Thus, in natural circulating systems, boiler circulation increases with increased heat input, until a maximum flow rate is reached. Beyond this maximum point, any further increase in heat input results in a decrease in flow, because the pressure drop in the risers exceeds the head supplied by the downcomers. Properly designed units operate in the rising part of the curve shown in Fig. 9.26, to the left of the maximum peak. Operating in this area of the curve permits a natural circulating boiler to be self-compensating under varying load conditions (e.g., increased steam generation under increased load conditions), changes in heat absorption surface cleanliness, and varying fuel and burner conditions.

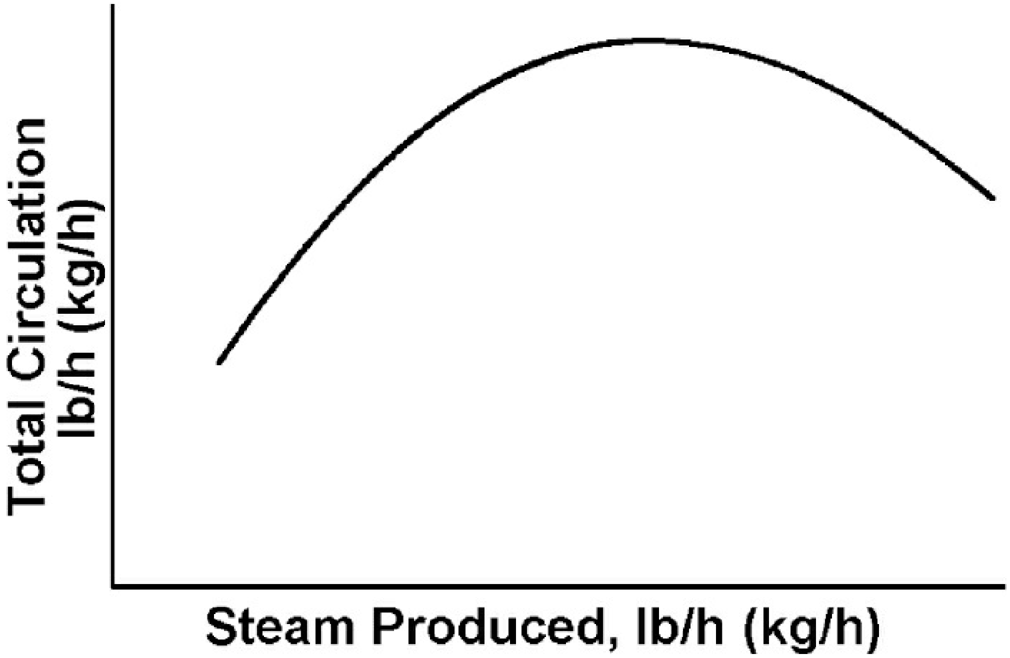

FIGURE 9.26 Relationship between boiler circulation at a given pressure and steaming rate (scale arbitrary).

A natural circulating boiler is the most prevalent type found in today's watertube boilers. Natural circulation is a result of the difference in densities between water and a water-steam mixture. At operating pressures greater than 2500 psig (17.2 MPag) and in some cases where the water-wall tubing is not vertical in orientation, some boiler manufacturers choose to use a forced circulation design rather than natural circulation.

As indicated earlier, too high a heat input can result in restricted circulation and tube starvation. Normally, the first several rows of tubes that are exposed to higher gas temperatures act as risers and the rest as downcomers. With increasing firing rates (higher heat input), the number of tubes acting as risers increases, and the number acting as downcomers decreases correspondingly. When this happens, two problems may occur:

1. There will not be enough downcomers to supply enough water to the risers, and tube starvation results.
2. Some tubes will act as both downcomers and risers, causing reduced flow or stagnation (dead spot).

Boilers with water-cooled furnace walls may experience problems if there is not proper circulation. These tubes absorb radiant heat at such a rapid rate that steam forms a large part of the tube contents near the top of the wall. Boiler manufacturers take extreme caution to ensure that water-wall downcomers are large enough to supply sufficient water to the wall riser tubes, and are properly insulated to protect against becoming risers as well. Lack of proper circulation in the water-wall tubes results in rapid and massive tube failures.

Positive (Forced) Circulating Systems

Essentially, positive circulation uses recirculating pumps to force the water to circulate through the boiler, for example, as cooling water must be circulated. Some manufacturers choose to use the forced circulation design for units operating at 2500 psig (17.2 MPag) or greater because of the low density ratio between steam and water. For example, at 500 psig (3.4 MPag), the density ratio between water and steam is 50:1; however, at 2500 psig (17.2 MPag), this ratio is only 5:1.

Because positive circulating boilers do not require natural circulation, they can be designed to make the most efficient use of available space. Tubes may be arranged horizontally and of any number of different sizes and passes, because water flow can be proportioned at the inlet when utilizing positive circulation to flow through all tubes at desired rates.

Once-Through Circulation

In once-through units, feedwater is forced through the circuits with all of the water turning to steam. In other words, unlike recirculating systems that require circulation ratios of 3:1 to 30:1, a once-through unit has a circulation ratio of 1:1. Once-through units can be likened to a long pipe, where water is put into one end and comes out as steam at the other end. These units may operate either at subcritical or supercritical pressures [3200.2 psia (22.1 MPaa) is defined as the critical pressure of water]. They have limited application in industry, but are widely accepted in electric utilities.

For a further explanation of the design and operation of once-through units, refer to once-through boilers earlier in this chapter.

CHAPTER 10

Oxygen Removal

After pretreatment, corrosive gases such as carbon dioxide (CO_2) and oxygen (O_2) must still be removed from the feedwater system. Mechanical deaeration can remove these gases, especially oxygen, reducing them to a level that is either acceptable to the boiler system or suitable for further application of scavenging chemicals. Because oxygen is highly corrosive to metal, it must be reduced to the lowest possible concentration. Mechanical deaeration can reduce the concentration to less than 7 µg/L, depending on the equipment design and operation.

Oxygen is a highly active element. Even in small amounts, it can cause serious corrosion in feedwater lines, economizers, boiler internals, steam-operated equipment, and condensate return piping. Corrosion increases with increasing oxygen content. The corrosion rate of oxygen dissolved in water doubles for each 18°F (10°C) increase in temperature. In addition, portions of a system that are exposed to high flow rates or turbulent flow conditions are more susceptible to oxygen attack.

When oxygen and carbon dioxide are present together, the resulting corrosion rate may be 10 to 40% greater than the sum of the corrosion rates of the two gases acting separately. The combination of oxygen and ammonia is very corrosive to copper alloys.

Corrosion Mechanisms

Corrosion is an electrochemical process. Iron dissolves at the anodes, releasing electrons that are subsequently consumed by oxygen at the cathode (see Fig. 10.1). At a pH of approximately 7, the half-cell reactions are as follows:

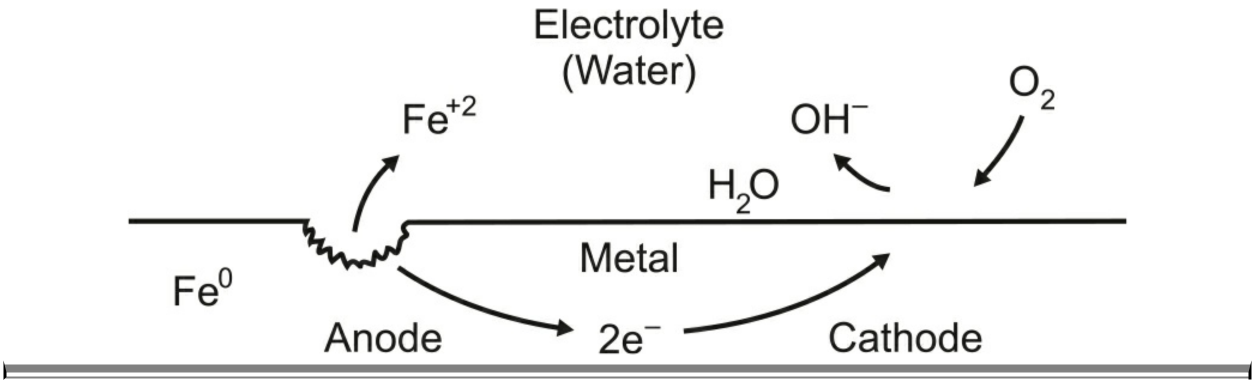

FIGURE 10.1 Corrosion cell mechanism.

$$\text{Anode:} \qquad Fe^0 \rightarrow Fe^{+2} + 2e^- \tag{10.1}$$

$$\text{Cathode:} \qquad 2e^- + H_2O + \tfrac{1}{2}O_2 \rightarrow 2OH^- \tag{10.2}$$

Penetration at the anodic area depends on the relative size of the cathodic and anodic areas. A small anodic area and a large cathodic area, for example, results in a concentrated dissolution of the iron at the anode to provide electrons for the larger cathode. As a result, a deep pit forms at the anode. Conditions that favor the formation of relatively small anodic areas are oxygen concentration differentials under areas of sludge accumulation, localized stress, and breaks in the passive magnetite layer on the steel surface.

Figure 10.2 illustrates oxygen corrosion located under a typical tubercle. Figure 10.3 illustrates the pitting of a similar metal surface after all sludge and iron oxide buildups have been removed.

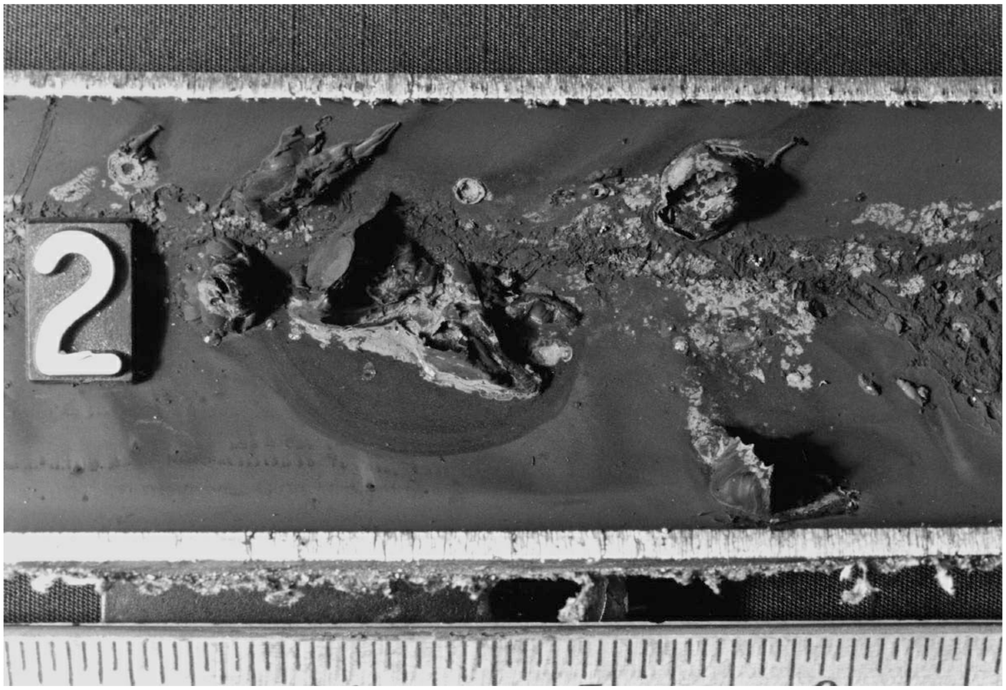

FIGURE 10.2 Oxygen corrosion tubercle.

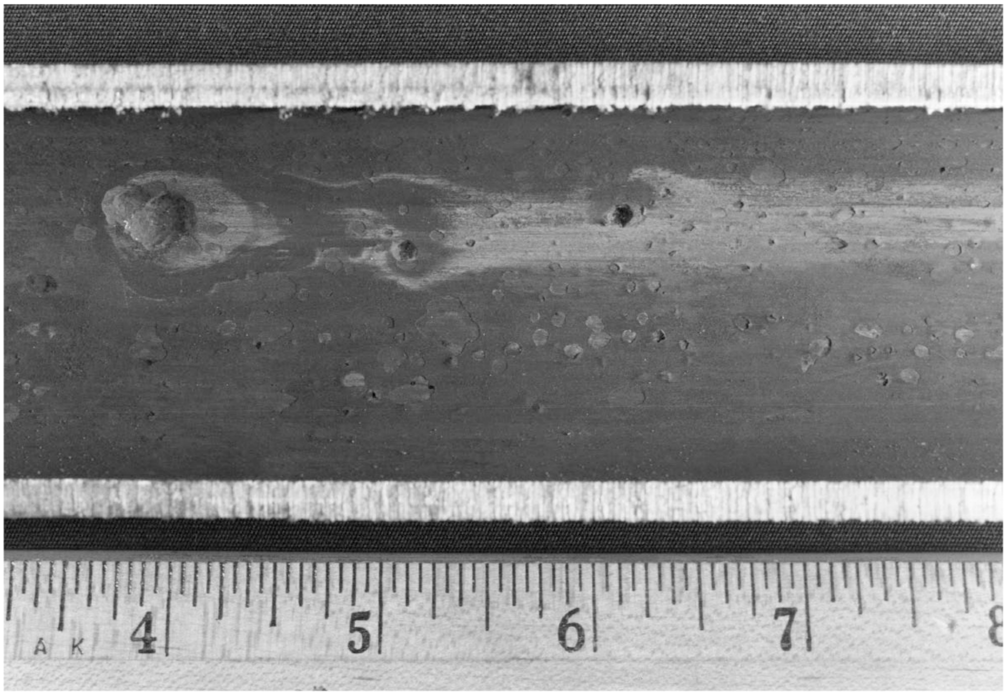

FIGURE 10.3 Pitting caused by oxygen corrosion.

Because of oxygen's corrosive tendencies, feedwater is usually deaerated to remove as much of the gas as possible. Commonly, this is accomplished mechanically in a pressure deaerator. However, other devices and methods of removal are available and are discussed in the sections that follow. These include:

- Vacuum deaerators
- Feedwater heaters
- Deaerating condensers
- Gas transfer membrane systems
- Carbon beds with scavenger activation (catalysis)
- Ion exchange resin catalysis

Because such units or systems (including pressure deaerators) rely on equilibrium conditions, they cannot completely remove all oxygen present; so supplemental chemicals are needed to reduce the remaining residual oxygen further.

Mechanical Deaeration

Mechanical deaeration is the physical removal of dissolved gases from water. The primary goal is to remove oxygen from the boiler feedwater, but carbon dioxide and ammonia (NH_3) can also be reduced by deaeration. Effective removal of ammonia by mechanical deaeration requires a special design, as removal in standard deaerators is inefficient.

Mechanical deaeration is influenced by the following physical-chemical considerations.

Ionization

The degree to which gases can be deaerated depends on the ionization state of the gases involved. Oxygen does not ionize; therefore, it is easily removed. Carbon dioxide and ammonia do ionize, as shown in the following equations:

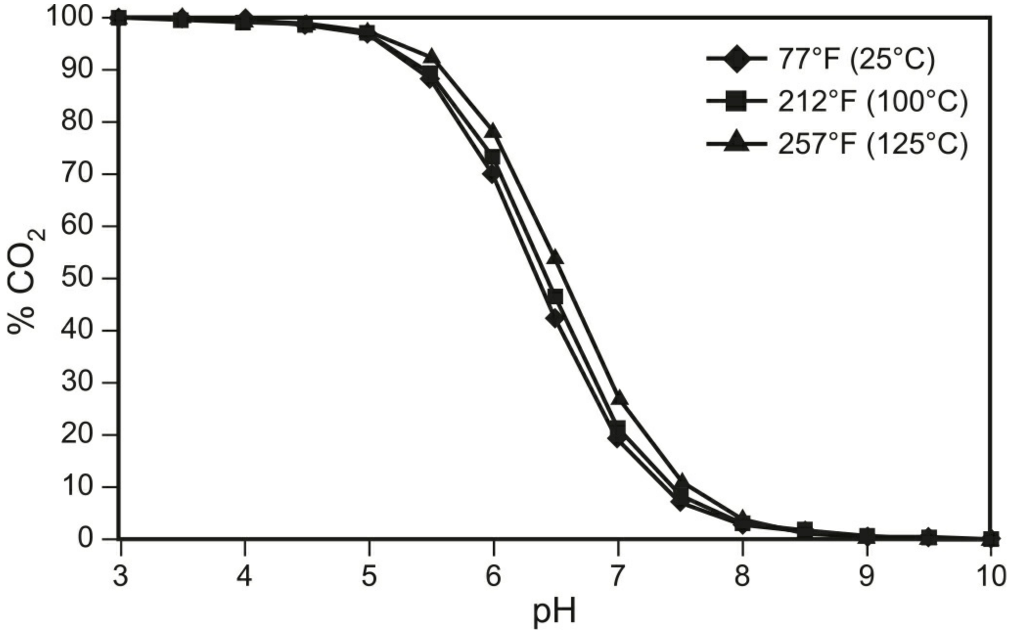

FIGURE 10.4 Carbon dioxide concentration versus pH.

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{10.3}$$

$$NH_3 + H_2O \rightarrow NH_4OH \rightarrow NH_4^+ + OH^- \tag{10.4}$$

Only that portion of these gases that remains in nonionized molecular form (CO_2 and NH_3) can be removed by mechanical deaeration. However, since ionization is an equilibrium state, adding mineral acids to the carbonic acid and alkali to the ammonium will shift these equilibria back toward the formation of CO_2 and NH_3. Figures 10.4 and 10.5 show the effect of pH on the portions of these two gases that are available for mechanical removal.

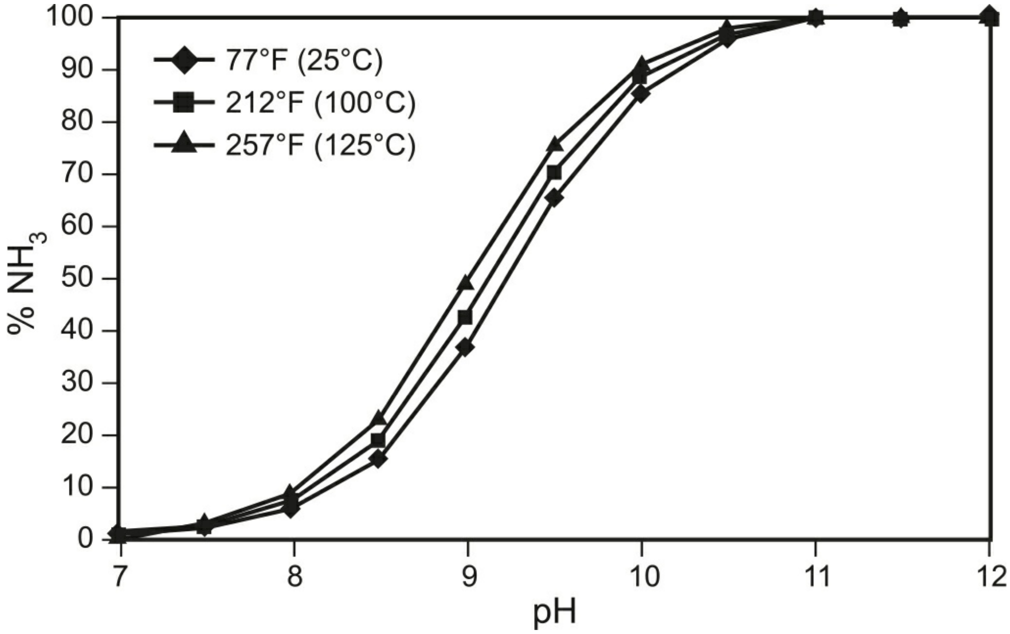

FIGURE 10.5 Ammonia concentration versus pH.

Thus, a mechanical decarbonator inserted after a hydrogen cycle cation exchanger, can remove carbonate alkalinity by stripping CO_2 from the water. This operation is quite efficient and removes CO_2 down to 5 to 10 mg/L in an atmospheric, blower-type unit, and down to virtually zero in a vacuum unit. If the decarbonator were placed into the flow before the hydrogen cycle cation exchanger acidified the water, CO_2 removal would be very poor.

Relative Partial Pressure

Water will dissolve a free (nonionized) gas only to the point at which equilibrium is reached between the partial pressure of the gas in the water and the partial pressure of the gas in the atmosphere with which it is in contact. This is Henry's law.

Air contains approximately 20% oxygen (O_2) and 79% nitrogen (N_2). The partial pressure exerted by oxygen in air is 1/5 atmosphere (20/100). Water surrounded by air, therefore, can dissolve oxygen up to the point at which oxygen in the water exerts a partial pressure of 1/5 atmosphere (see Fig. 10.6).

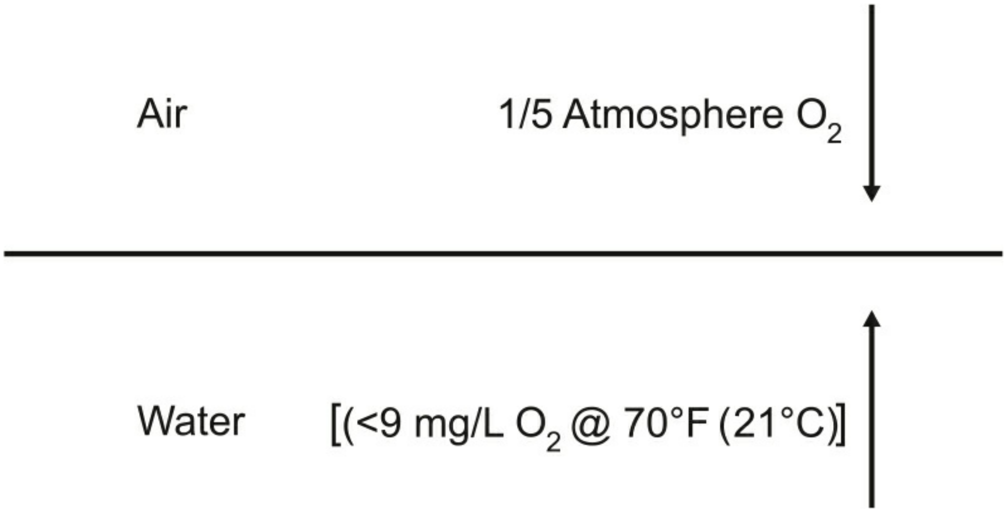

FIGURE 10.6 Equilibrium between O_2 in air and O_2 in water.

At 77°F (25°C) and atmospheric pressure, this correlates to an approximate content of 8.4 mg/L oxygen in water. In traditional mechanical deaeration, the equilibrium between oxygen in the water and the atmosphere contacting it is deliberately upset. This is accomplished by blanketing the water with an atmosphere of steam that contains little oxygen (see Fig. 10.7).

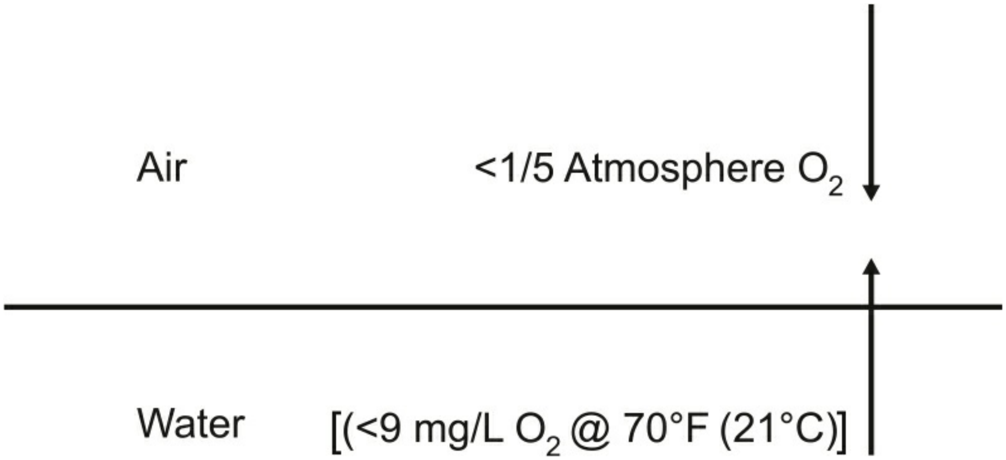

FIGURE 10.7 Equilibrium shift with steam.

Temperature

As the temperature of water is raised to its boiling point (saturation temperature for a specific pressure), all free (nonionized) gases theoretically become insoluble. Figure 10.8 graphically illustrates the solubility of oxygen as a function of temperature. In practice, total removal of gases does not occur.

Henry's law relates the steam oxygen content to the liquid water oxygen content. As a result, neither of these contents can reach zero, and a small amount of gas remains dissolved in the water phase.

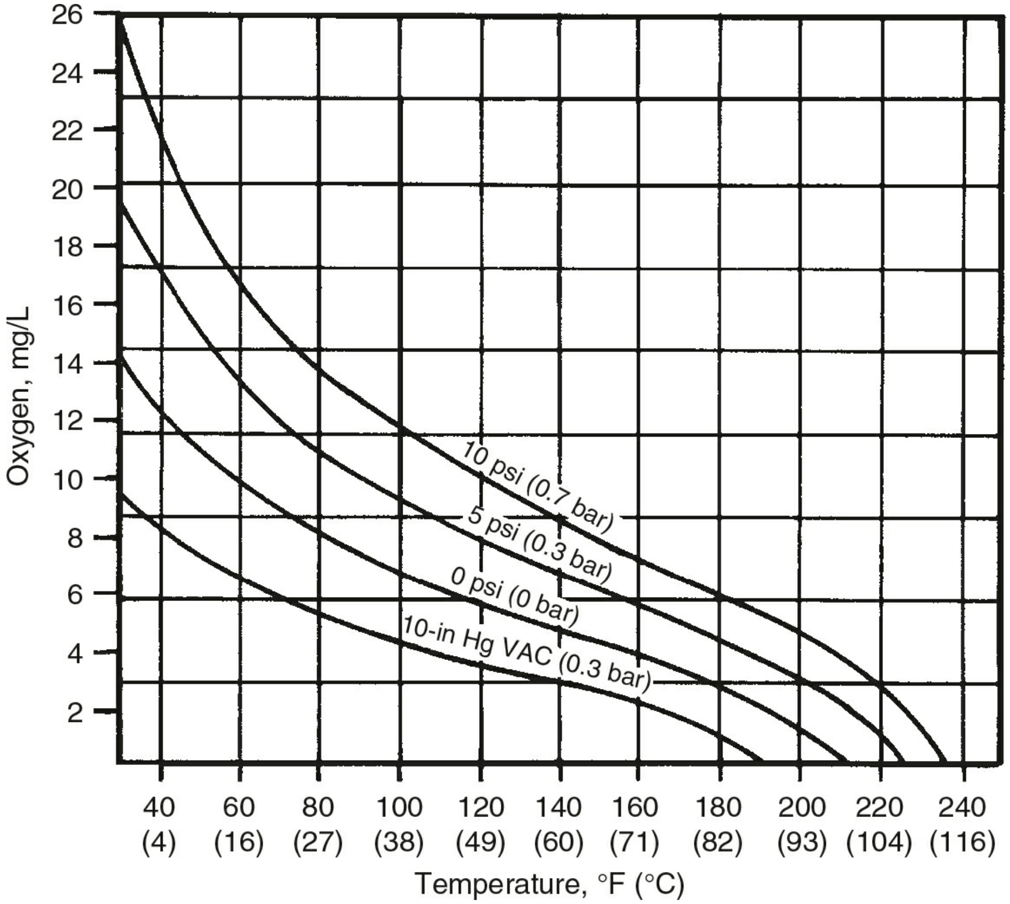

FIGURE 10.8 Solubility of oxygen in pure water versus temperature.

Agitation

A more complete removal of entrapped gases can be obtained by breaking the water stream into small droplets or thin films and then preventing these droplets from agglomerating. Smaller droplets can be heated more efficiently, and the vapor/liquid interface will be repeatedly broken, reducing the tendency of the gases to remain dissolved in the cooler liquid phase. With a smaller droplet, the entrapped gases have a shorter distance through which to diffuse before release from the water. Steam can more effectively scrub the smaller droplets. Finally, by continuously breaking and reforming the droplets of water, entrapped gases have a greater tendency to escape from the water (see Fig. 10.9).

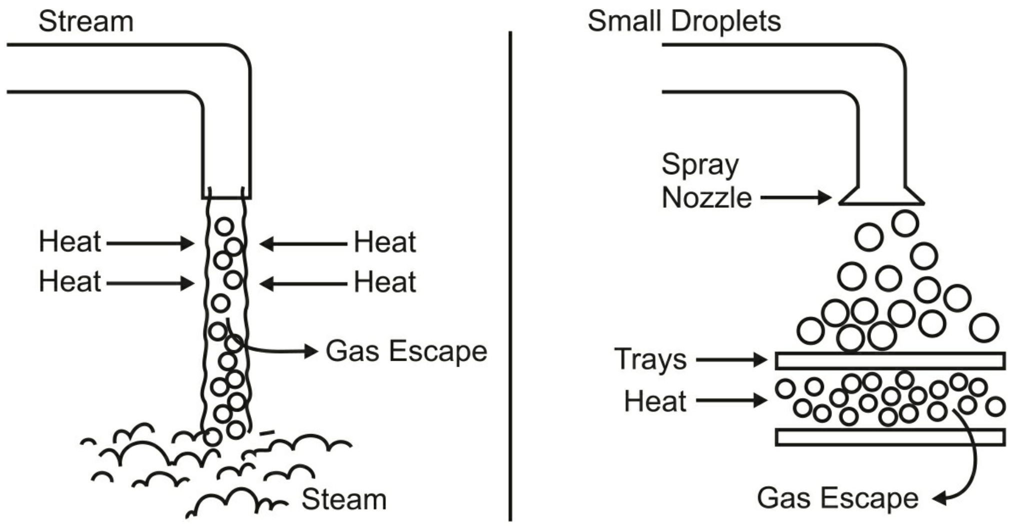

FIGURE 10.9 Gas removal from water droplets.

Gas Removal

The gases released from the water must be physically removed, or they will redissolve. Removal is accomplished by maintaining a flow of fresh steam over the droplets, directing the oxygen contaminated steam away from the deaerated water, and finally by removing the liberated gases from the system. In mechanical deaeration, removal is accomplished by continuously venting the gases to atmosphere.

The following sections describe how these principles are incorporated in the designs of the various types of mechanical deaerators.

Pressure Deaerators

Deaerating equipment is designed to heat water to the temperature of saturated steam at the pressure maintained within the deaerator and to reduce oxygen in the feedwater to about 0.007 to 0.04 mg/L (7–40 μg/L). If the unit is guaranteed to reduce the oxygen to 7 μg/L or less, it is commonly designated as a deaerator. If the equipment is guaranteed to reduce oxygen to only 40 μg/L, it is commonly referred to as a deaerating heater.

Designs vary from manufacturer to manufacturer, so units encountered in plants may deviate from the examples illustrated or described here. It is wise to compare the actual internal and external configurations and operating conditions with the original drawings and specifications. Poorly planned retrofits, construction modifications, or changes in system conditions such as for energy recovery are often the cause of poor deaerator performance.

Deaerating units may be spray, tray, or atomization type, but all three types have two distinct sections. These are the primary preheating section and the secondary deaeration section. The preheating section in all types of modern pressure deaerators is of similar design, construction, and function regardless of the type of secondary deaeration element.

Primary Preheating Section

The function of the primary preheating section is to raise the temperature of the water entering the deaerator to within 1 to 2°F (0.6–1.1°C) of the saturation temperature of the steam being used. In addition, this section functions as the vent condenser to condense the steam, liberate the noncondensable gases, and release the gases to atmosphere. Continuous condensation of the steam at this point causes fresh steam to flow continuously through the secondary deaeration element in order to maintain the operating pressure. This action ensures the required atmosphere of oxygen-free steam is maintained to sustain good deaeration.

In older units, the vent condenser consisted of a tubular heat exchanger usually mounted in a cast iron housing located externally on the top of the unit. The liquid entering the deaerator flowed through the tubes inside the steam atmosphere of the cast iron shell. After being heated in the tubes, the liquid was usually sprayed into the steam atmosphere in the deaerator through one or more perforated spray pipes.

In newer deaerators, the heat exchanger and spray pipes have been replaced by a preheater section with a number of stainless steel, spring-loaded spray nozzles. The nozzles create very thin curtains of water that reach saturation temperature very rapidly and release over 90 to 95% of the dissolved oxygen and other noncondensable gases.

The preheater section also serves as an internal, direct-contact vent condenser, where noncondensable gases are separated and concentrated before being discharged to atmosphere. The mixture of steam and noncondensable gases (including oxygen) present in the preheater section, is in intimate contact with the incoming cold water, so that most of the steam is condensed in the heating of the water. Only a small amount of steam along with the oxygen and other noncondensable gases is discharged through the vent pipe to atmosphere. Condensation of the steam in the preheater is the only mechanism that maintains the required steam flow through the secondary section, since the amount of steam passing through the vent valve is very small.

In very large, horizontal deaerators installed in high-pressure utility stations, the preheater may still consist of perforated spray pipes. In such cases, the operating load tends to be almost constant, and makeup is a small percentage of the feedwater. Accordingly, the fixed orifices in the spray pipes usually can maintain the desired pressure drop, thin water curtains, and degree of preheating required to maintain guaranteed performance.

Regardless of the preheater or deaerator type, the operation of the preheater is crucial to successful deaeration. Unless the preheater reduces the oxygen level to a few hundred µg/L (<5–10% of the original concentration), the secondary deaeration section will be unable to reduce the final effluent oxygen residual to the guaranteed level. As long as the springs are intact and maintain the desired pressure drop, the preheater will function as required over much of the unit operating capacity range.

Basic Principles of Mechanical Deaeration Using Pressure Deaerators

Effective mechanical deaerators must accomplish the following:

- Heat the water to the saturation temperature corresponding to the steam pressure within the deaerator.
- Break the water stream into small droplets or thin films that allow rapid diffusion of gases to a water surface, where they can be liberated into the vapor phase.
- Vigorously boil and scrub the heated water with fresh, oxygenfree steam that removes any remaining traces of oxygen and other noncondensable gases.
- Maintain the partial pressures of oxygen and carbon dioxide as low as possible at the liquid and vapor interface, especially where deaerated water separates from steam.
- Continuously discharge the noncondensable gases from the space

within the deaerator dome through proper venting.

Spray Deaerator

Figure 10.10 illustrates a typical spray-type deaerator. It may be more accurately described as a fixed orifice scrubber or reboiler. As previously discussed, feedwater enters the primary preheater section through spring-loaded spray valves. Steam supplied to the primary preheater section comes from the secondary stage deaerator.

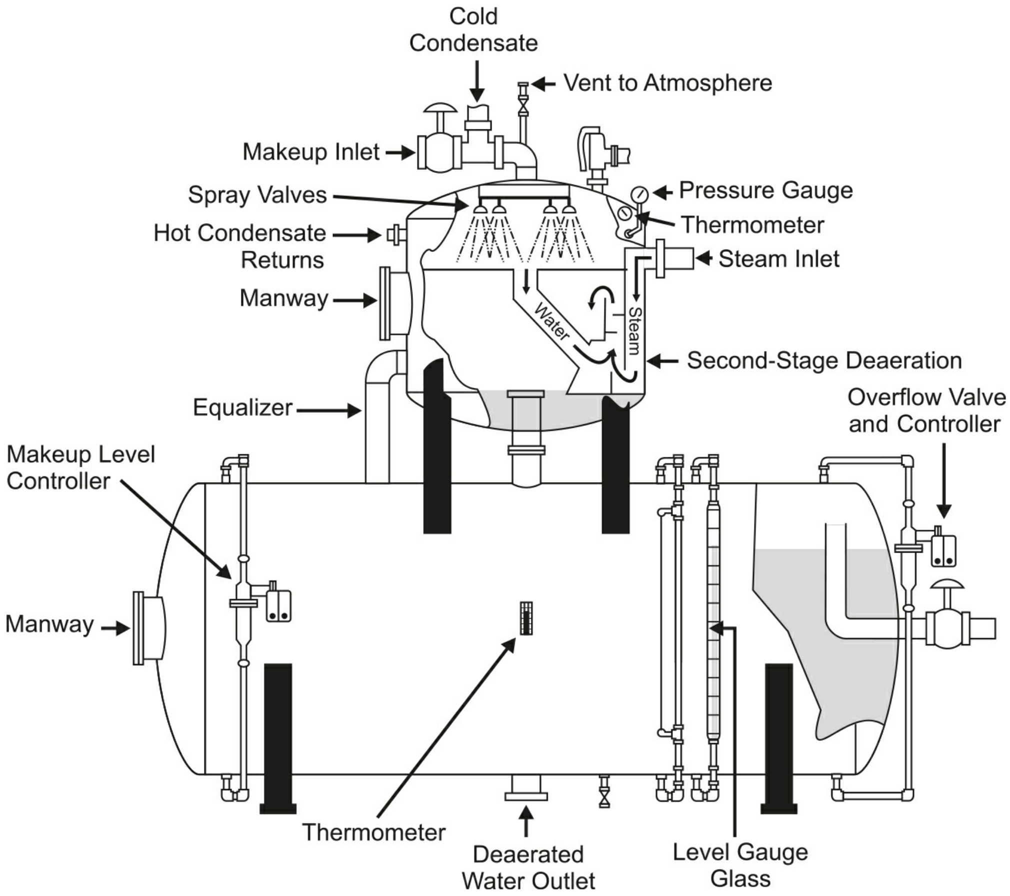

FIGURE 10.10 Spray deaerator.

Feedwater leaving the primary preheater section contains only traces of oxygen and other noncondensable gases. The water enters the second-stage scrubber section, flowing through internal piping or channels. The hot water mixes with live, fresh steam, which has entered the scrubber section through the steam inlet. It is important to realize that the volumetric ratio of the resulting mixture will be approximately 99.6% steam/0.4% water as opposed to a ratio of approximately 1% steam/99% water based on mass. For example, saturated steam at 20 psia (138 kPaa) has a specific volume of 20.079 ft^3/lb (1.253 m^3/kg), while the saturated liquid has a volume 0.017 ft^3/lb (0.001 m^3/kg). This vast difference in volume has an extremely vital impact on the performance of a spray deaerator.

Both steam and water enter the bottom of the scrubber pot or chamber, where the two form an intimate mixture that is heated to full saturation temperature. As the mixture flows upwards, it may first pass through a distribution orifice or port that imposes a negligible pressure drop. At the outlet or throat of the scrubber, the mixture must pass through a final fixed area orifice, which imparts a significant pressure drop on the mixture. The drop in pressure creates a superheated mixture that immediately boils as it leaves the scrubber. This action scrubs the final remnants of oxygen from the mixture. The deaerated water falls to the storage area, while the steam and noncondensables are drawn into the preheater section.

The scrubber is a fixed orifice device that is designed and sized relative to a certain steam volume and velocity. Any change in operating conditions that creates a substantial change in steam volume or velocity will have a negative impact on deaerator performance. For example, a sharp increase in influent temperature would reduce steam demand, decrease scrubber steam velocity, and reduce stripping action. The addition of heat recovery equipment upstream of the deaerator could be the cause of such a condition. On the other hand, a sharp decrease in influent temperature could increase steam demand so dramatically as to cause a sudden and inordinately large increase in steam velocity. This could prevent good stripping action, promote entrainment of water in the vent vapor, and even damage the deaerator internals. Cold system start-ups at heavy flow rates or sudden surges of cold makeup water are typical causes of this condition.

Spray deaerators work well in base-load applications, where variations in influent flows are minor and predictable. They work quite well when operated at or near average design flow conditions. However, with wide load swings and operating conditions that vary considerably, they fail to produce the low effluent oxygen desired.

Tray Deaerator

Figure 10.11 illustrates a tray-type deaerator. As previously discussed, feedwater enters the primary preheater section through spring-loaded spray valves. Steam supplied to the primary preheater section comes from the secondary stage deaerator.

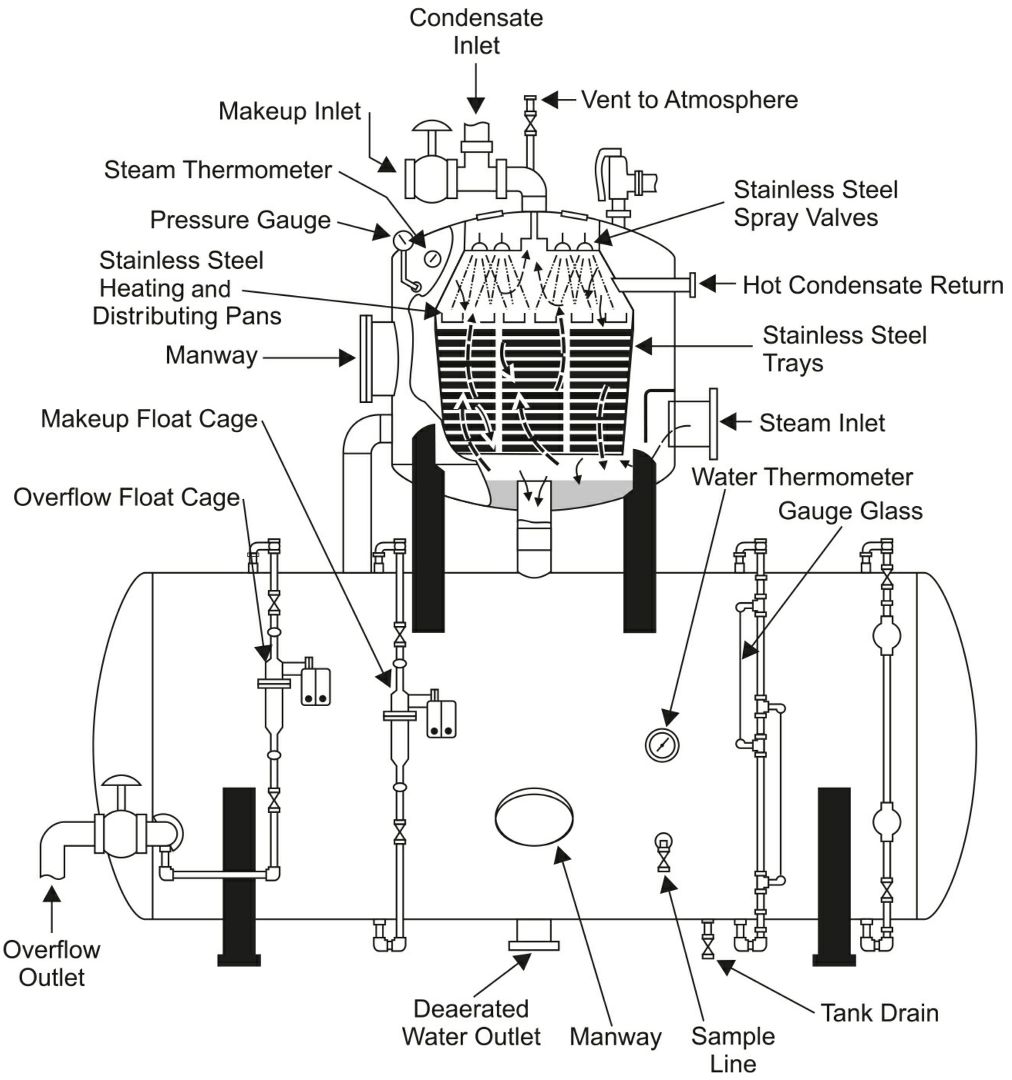

FIGURE 10.11 Tray deaerator.

The preheated water, which has little oxygen or noncondensables remaining (<5–10% of the original concentrations), is then directed into the secondary deaerating section. This is typically an enclosed stack of distributing pans or trays of stainless steel construction. In some designs, the lower trays may be replaced by stainless steel random ring packing.

The preheated water spills uniformly over the tray stacks or packing and cascades downward forming thin, uniform films. These thin films or curtains of water allow the oxygen to diffuse rapidly to the surface, where the equilibrium allows it to escape into the vapor phase or steam.

Steam flow in the tray section may take one of three configurations: co-flow, cross-flow, or counter-flow. In a co-flow unit, the steam is introduced at the top of the tray bank and flows down through the trays with the water. In a cross-flow unit, the steam passes from left to right as the water descends through it. In a counter-flow unit, the steam is introduced at the bottom of the tray stack and passes up through the descending water. This is probably the best of the three designs, since the cleanest steam mixes with the cleanest water at the bottom of the tray stack. Because of the condensing effect in the internal vent condenser/preheater section, and regardless of configuration or design, steam must flow from the steam inlet through the secondary tray section to the primary preheater section.

In the design using random packing, the steam is admitted at the bottom flowing upward through the packing in one pass and counter-current to the water flow. Again, steam flow is assured by the condensing effect in the preheater section. When the steam condenses, it falls back into the distributing pans with the incoming water that has been preheated. The noncondensable gases are released to atmosphere through the vent.

The tray deaerator is ideally suited for wide load swings or operation at partial loads, because of the capability of the tray stack to distribute and detain the falling water resulting in longer, more intimate steam-water contact. Thus, the tray deaerator is more tolerant of variations in steam flow and velocity. Steam flow through the tray section, however, must be sufficient to maintain water contact with oxygen-free steam and to maintain the desired equilibrium conditions necessary for full deaeration. Steam flow can only be maintained by condensation of steam in the preheater section as the feedwater is heated to saturation temperature.

Atomizing Deaerator

Figure 10.12 illustrates a typical design for a variable orifice atomizing deaerator. Note that this figure shows an external vent condenser.

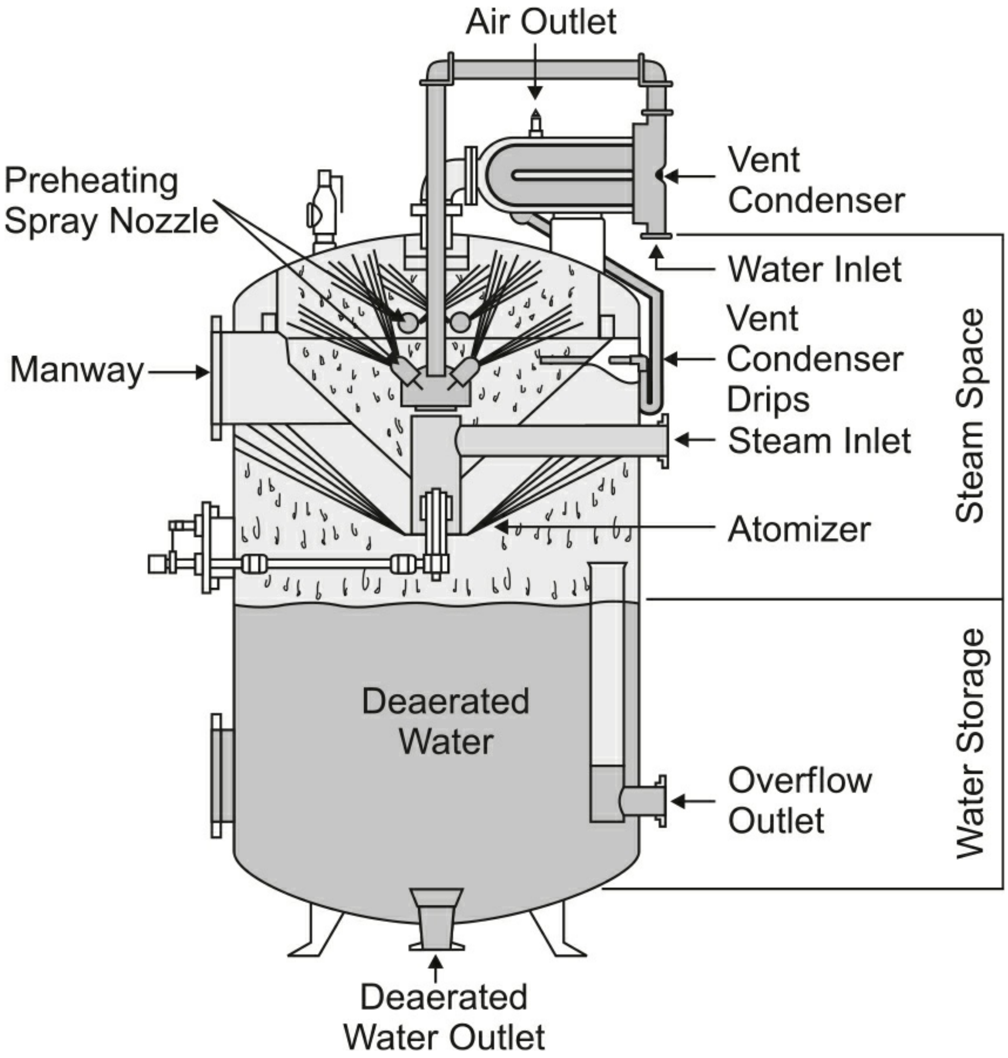

FIGURE 10.12 Atomizing deaerator.

As with the other types of deaerators, this type of unit is equipped with a primary preheater. The preheated, partially deaerated water then falls on the collecting cone, which directs the water to the atomizer.

Steam enters through the side of the deaerator and is conducted to the atomizing valve, where it is discharged as a constant high-velocity steam jet. The energy of the steam jet breaks up the water, producing a mist or fog of finely divided particles to assure maximum surface exposure to the scrubbing steam. Any remaining gas is removed and carried to the first stage by the steam, while the deaerated water falls to the storage section.

The atomizing valve is a variable orifice that is controlled either by integral, internal springs or weights or by an external weight-loaded arm. It is self-compensating and maintains a constant pressure differential on the steam supply, regardless of the load at which the deaerator is operated or the temperature at which the water is received. The steam jet is created by imposing a pressure drop through the orifice. As long as the internal valve is operable, the pressure drop is relatively constant. However, if the internal valve or lever linkage seizes or becomes inoperable, the unit becomes a fixed orifice device, and the resulting steam jet velocity is unpredictably variable.

Operating Considerations for Pressure Deaerators

All liquids having a temperature lower than the saturation temperature of the operating steam, should enter the deaerator through the spray nozzles or spray pipe. All liquids having a temperature higher than the saturation temperature of the operating steam, should enter the unit as follows:

- For spray-type deaerators, high-temperature liquids should enter directly into the scrubber pot upstream of the scrubber orifice.
- For tray-type deaerators, high-temperature liquids should enter such that the resulting flash steam travels through the trays using the same path as fresh steam.
- For atomizing-type deaerators, high-temperature liquids should enter directly into the preheater section above the atomizing valve, where the flash steam will be used in preheating.
- Introducing high-temperature liquids in other locations will adversely affect deaerator performance.

Changes in operating steam pressure will affect deaeration efficiency. Therefore, the sensing connection of the operating steam pressure control valve should be connected directly to the steam dome within the steam space of the preheater and should not be connected to the steam supply header outside the deaerator.

The differential between the mean temperature of the total liquid mixture entering the deaerator and the saturation temperature for the operating steam pressure should be more than 30°F (17°C), to assure adequate flow of scrubbing steam in the secondary deaeration section. A tray-type deaerator might perform satisfactorily down to a 10 to 20°F (6–11°C) temperature differential. Increased plant heat recovery initiatives may have a great impact on deaeration efficiency and chemical scavenger dosage by increasing the mean inlet liquid temperature.

If a tray or atomizing deaerator is operating below 25% of its design capacity, oxygen removal efficiency will be lower and scavenger chemical dosage will be higher than expected. A measurement greater than 15 µg/L O_2 is indicative of a poorly operating deaerator.

The temperature of the stored deaerated water should be within 1 to 4°F (0.6–2.2°C) of the saturation temperature for the operating steam pressure. Failure to achieve this temperature differential results in high effluent oxygen concentration and indicates mechanical issues within the unit.

Deaerating Heater

A deaerating heater is similar in most respects to tray, spray, and atomizing deaerators and typically cannot be discerned by external inspection. The major difference is the secondary deaeration section does not provide the same amount of steam/water contact or agitation as a full deaerator. In addition, the trays will probably be made of cast iron construction. Deaerating heaters will usually be guaranteed for an effluent oxygen of 40 µg/L, which is significantly higher than the effluent oxygen concentration from a full deaerator. Few new units are being built today, although deaerating heaters can still be found operating in older, low-pressure steam plants.

Proper Venting of Pressure Deaerators

One of the most common causes of poor deaerator performance is insufficient venting due to valve closure or restriction of vented steam, most typically for energy conservation purposes. The deaerator vent is one of the few points in the system where dissolved gases may be removed. Deaerator venting is analogous to the continuous blowdown of dissolved solids from a boiler. Dissolved solids cannot be discharged from a boiler drum without loss of some carrier water. Similarly, dissolved gases cannot be discharged from the deaerator without loss of some carrier steam. Noncondensable gases not vented from the deaerator will concentrate in the vapor phase, increasing their partial pressure. This in turn, increases their concentration in the liquid phase or deaerator effluent. Insufficient discharge of dissolved gases may cause major damage to power train components that can result in plant shutdown or equipment replacement.

Energy conservation measures frequently result in the installation of heat exchangers, cooling jackets, or other devices, to reclaim the heat content of the vent steam containing the noncondensables. Many of these devices cause a backpressure on the vent line and thus restrict flow. The result is higher noncondensable gases in the deaerator effluent.

In some cases, vent steam flow is reduced because of a choked or plugged orifice. Steam may condense in vertical or non-vertical vent pipes. This condensate flows back down the pipe walls, choking the vent orifice when steam flow is not sufficient. To minimize this type of problem, vent piping should be installed with no sharp bends or traps that could pool condensation and obstruct the flow of gases. Cooling water leaks in an external vent condenser, can cause excess water accumulation in the shell. If the drainpipe cannot discharge the excess liquid or is plugged, gas flow to the vent will be restricted.

Proper venting of a deaerator should result in a strong visible plume. There should be an invisible or clear area of approximately 6 to 18 inches (150–460 mm) between the end of the vent pipe and the visible portion of the plume. Irregular spitting of water with the vent discharge can indicate condensation, internal leaks, or water entrainment from broken or damaged spray nozzles. This condition, whatever the cause, can choke the vent gas flow.

Typically, the maximum quantity of steam required for venting a properly operating deaerator is less than 0.2% of the feedwater flow. This value varies relative to the percentage of fresh makeup used, but is less than 0.2% for tray or spray deaerators operating with 100% makeup. Some deaerator manufacturers might conservatively recommend 0.5% to assure sufficient venting.

Mixing Condensate and Makeup

One role of the deaerator is as a receiver for a variety of water, steam, and hot condensate streams that need to be recovered. It is important that these be introduced into the deaerator in such a manner as to avoid extreme temperature interfaces and to permit smooth operation.

A common practice is the separate introduction of the return condensate and cold makeup streams into the deaerator water box or preheater sprays. A large temperature differential between the two streams [more than 80°F (44°C)] can result in thermal stresses and water hammer that can damage deaerator