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Terminology for Removal of Selected Constituents

Term	Definition
Carbonate hardness	Concentration of polyvalent ions that are associated with anions that comprise alkalinity (e.g. HCO_3^- , CO_3^{2-}).
Denitrification	Reduction or conversion of nitrate to nitrogen gas.
Enhanced softening	Process of removing hardness and TOC from water using the lime-softening process.
Greensand	Sand that contains a greenish colored mineral called glauconite (iron potassium phyllosilicate) and is typically coated with manganese oxide, known as manganese greensand, and is used to remove insoluble ferric iron and manganese.
Hardness	Sum of the soluble concentrations of polyvalent ions (e.g., Ca^{2+} , Mg^{2+}).
Natural radionuclides	Molecules (e.g., radium-226, radon-222, uranium-238) that dissolve in groundwater as a result of radioactive gases and rock formations, and have unstable nuclei and emit energy in the form of ionizing radiation.
Noncarbonate hardness	Concentration of polyvalent ions in water that are associated with nonalkalinity anions (e.g., SO_4^{2-} , Cl^-).
Recarbonation	Process of adding carbon dioxide to water lower the pH after softening.
Single-stage softening	Process of adding lime to water to remove only the calcium hardness from the water, leaving the magnesium hardness.
Softening	Process of removing hardness from water.
Split-flow lime treatment	Process of separating the water stream into two or more streams, softening the streams to various degrees and then blending them to obtain the desired water quality.
Two-stage excess lime-soda treatment	Process of adding an excess of lime to water to bring about the removal of both calcium and magnesium followed by stabilization of the water with soda ash treatment.

Water purveyors are continuously striving to provide their communities with potable water that is safe for human consumption and aesthetically acceptable. The primary focus of the previous chapters of this textbook has been the removal of the traditional constituents found in most natural waters. There are, however, a number of nontraditional constituents that must also be removed from some natural waters to provide potable water. The purpose of this chapter is to introduce and discuss the removal

of the most common of these nontraditional and emerging constituents, including arsenic, calcium, magnesium, nitrate, radionuclides, pharmaceutical and personal care products. However, before discussing the individual constituents, it will be helpful to review what constitutes traditional, nontraditional, and emerging constituents.

20-1 Traditional, Nontraditional, and Emerging Constituents

As discussed in Chap. 2, there are many constituents in water that impact potable water. The more common, also called traditional, constituents in most surface water supplies include turbidity, NOM, biological agents, taste and odor compounds, and low levels of synthetic organic compounds (SOCs). Low, but measurable, levels of SOCs are usually not specifically treated in present water treatment practices if their concentrations do not exceed their maximum contaminant level (MCL). In addition to the conventional constituents identified above, a variety of other constituents may be present in both surface waters and groundwaters. These other constituents are considered nontraditional in the sense that they are not encountered in most natural waters. For example, surface waters may contain inorganic constituents such as iron, manganese, hardness (Ca^{2+} , Mg^{2+}), and other trace dissolved metals (e.g., Ba, Se, Ra). Groundwater sources may also contain iron, manganese, hardness, and other dissolved metals such as those described above. These nontraditional constituents in one way or another also impact the provision of potable water.

In addition to the traditional and nontraditional constituents in water, water purveyors need to be aware of emerging constituents. For example, perchlorate, *N*-nitrosodimethylamine (NDMA), methyl tertiary butyl ether (MTBE), arsenic, radium, and disinfection by-products are now cause for health concern and some are being regulated. Many of these emerging constituents can be difficult and expensive to remove using conventional water treatment practices. New innovative water treatment practices are also being developed to meet regulatory demands for these emerging constituents. For example, new-iron-oxide-based adsorbents were developed to treat water sources containing arsenic, UV technology is being used to treat NDMA in some water supplies, and modifications to conventional water treatment practices are being employed to reduce disinfection by-products (see Chaps. 13 and 19).

Several constituents in water that impact potable water and treatment processes that may be used to remove them are reported in Table 20-1. The performance of these treatment processes for a given constituent is presented subjectively in terms of removal efficiencies reported in various studies. The information presented in Table 20-1 can be used as a general guideline when a particular constituent must be removed. However,

Table 20-1General effectiveness of water treatment processes for selected nontraditional constituents^a

Selected Contaminant	MCL, mg/L	Water Treatment Processes													References	
		Coagulation Sedimentation,			Ion Exchange, Ch. 16		Membrane Processes		Chemical Oxidation Disinfection		Adsorption, Ch. 15					
		Aeration, Stripping, Ch. 14	Granular Media Filtration, Ch. 9, 10, 11	Lime Softening Ch. 20	Anion	Cation	Reverse Osmosis Ch. 17	Membrane filtration Ch. 12	Ch. 8, 13, 18	GAC	PAC	Ferric Hydroxide	Activated Alumina			
Inorganic Constituents																
Arsenic (+3)	0.010	P	G-E	F-E	G-E	P	E	P	P	F-G	P-F	E	F-E	1-22, 33, 36		
Arsenic (+5)	0.010	P	G-E	F-E	G-E	P	E	F	P	F-G	P-F	E	F-E	1-22, 33, 36		
Barium	2.0	P	P-F	G-E	P	E	E	NA	P	P	P	NA	P	31, 33, 35, 36		
Chromium (+3)	0.10	P	G-E	G-E	P	E	E	NA	P	F-G	F	NA	P	31, 33, 35, 36		
Chromium (+6)	0.10	P	P	P	E	P	E	NA	F	F-G	F	NA	P	32, 33, 35, 36, 39		
Copper	1.3 ^b	P	G	G-E	P	F-G	E	NA	P-F	F-G	P	NA	NA	31, 33, 35, 36		
Fluoride	4.0	P	F-G	P-F	P-F	P	E	NA	P	G-E	P	NA	E	23, 24, 35, 36, 41		
Hardness	NA	P	P	E	P	E	E	NA	P	P	P	NA	P	35, 36		
Iron	0.30 ^c	F-G	F-E	E	P	G-E	G-E	NA	G-E	P	P	NA	F-G	25, 26, 38		
Lead	0.0 ^b	P	E	E	P	F-G	F-G	NA	P	F-G	P-F	NA	P	31, 32, 33, 35, 36		
Manganese	0.05 ^c	P-G	F-E	E	P	G-E	G-E	NA	G-E	F-E	P	NA	P	26, 33, 36		
Mercury (inorganic)	0.002	P	F-G	F-G	P	F-G	F-G	NA	P	F-G	F	NA	P	29, 36, 39		
Nitrate	10.0	P	P	P	G-E	P	G	NA	P	P	P	NA	P	35, 36		
Perchlorate	0.018 ^{b,d}	P	NA	NA	G-E	P	G-E	NA	NA	F-G	NA	NA	NA	35, 36		
Radium	5.0 ^e	P	P-F	G-E	P	E	E	NA	P	P-F	P	NA	P-F	30, 35, 36, 41, 43		
Uranium	0.030	P	G-E	G-E	E	G-E	E	NA	P	F	P-F	NA	G-E	42		

Organic Constituents

VOCs	NA	G-E	P	P-F	P	P	F-E	F-E	P-G	F-E	P-G	NA	P	36, 40
SOCs	NA	P-F	P-G	P-F	P	P	F-E	F-E	P-G	F-E	P-E	NA	P-F	36, 40, 50
Color	15 ^f	P	F-G	F-G	P-G	NA	NA	NA	F-E	E	G-E	NA	P	35, 36
TTHMs	0.080	G-E	P	P	P	P	F-G	F-G	P-G	F-E	P-F	NA	P	27, 28, 37
MTBE	0.020 ^g	G-E	P	P	P	P	F-E	F-E	P-G	F-E	P-E	NA	NA	44, 45
NDMA	0.02 ^h	P	NA	NA	NA	NA	NA	NA	E ⁱ	NA	NA	NA	NA	46-48

^aAbbreviations: P—poor (0–20% removal); F—fair (20–60% removal); G—good (60–90% removal); E—excellent (90–100% removal); NA, not applicable/insufficient data.

References: 1. Aus Planer-Friedrich, 2001; 2. Benjamin et al., 2000; 3. Brandhuber and Amy, 1998; 4. Chang et al., 1994; 5. Cheng et al., 1993; 6. Clifford, 1999; 7. Clifford and Lin, 1986; 8. Clifford and Ghurye, 1998a; 9. Driehaus et al., 1998; 10. Edwards, 1994; 11. Ferguson and Anderson, 1974; 12. Ferguson and Gavis, 1972; 13. Frey et al., 2000; 14. Gupta and Chen, 1978; 15. Hering and Elimelech, 1996; 16. Pontius et al., 1994; 17. Rubel and Williams, 1980; 18. Rubel and Hathaway, 1985; 19. Scott et al., 1995; 20. Simms and Azizian, 1977; 21. Smith et al., 1992; 22. Thompson and Chowdhury, 1993; 23. Sollo et al., 1984; 24. Rubel and Woosley, 1979; 25. Singer and Stumm, 1970; 26. Sly et al., 1990; 27. Blanck, 1979; 28. Weil, 1975; 29. Logsdon and Symons, 1979; 30. Brinck, 1976; 31. McRae and Parsi, 1974; 32. Mixon, 1973; 33. Logsdon et al., 1974; 34. Argo, 1984; 35. Sorg 1978a,b; 36. Sorg and Love, 1984; 37. Symons and Carswell, 1981; 38. Wood and DeMarco, 1980; 39. Zemansky, 1974; 40. Singley, 1979; 41. Sigworth and Smith, 1972; 42. Sorg, 1988; 43. Valentine et al., 1990; 44. Brown et al., 1997; 45. U.S. EPA, 1999; 46. Fleming et al., 1996; 47. Calgon, 1998; 48. Bolton et al., 1999; 49. Taylor and Jacobs, 1996; 50. Duranceau et al., 1992.

^bMaximum contaminant limit goal.

^cSecondary standard.

^dProposed standard.

^epCi/L.

^fCFU (colony-forming units).

^gOdor threshold.

^hCalifornia Department of Health Services.

ⁱUltraviolet light.

constituents that comprise background water matrices can vary widely with respect to their number and concentration and can impact treatment process performance. Treatment processes that can be used in combination are not considered in Table 20-1.

20-2 Arsenic

Arsenic is widespread throughout our environment. For example, the crust of the Earth contains about 1.8 mg/kg of arsenic. Arsenic is typically composed of the minerals arsenopyrite (FeAsS), orpiment (As_2S_3), and realgar (AsS). The lithosphere varies from less than 0.2 to about 15 mg As/kg of soil. In addition, the atmosphere contains about 0.02 to 2.8 ng/m³ while the aquatic environment contains less than 0.010 µg/L (Aus Planer-Friedrich, 2001). Most commercial arsenic is obtained by heating arsenopyrite. Because arsenic is tasteless and colorless, it was well known as a poison for humans in the Middle Ages and was used as far back as AD 55 in the poisoning by Nero of Britannicus. Arsenic has also been used for medicinal purposes. In the early 1800s, arsenic was used as a remedy for curing anorexia, rheumatism, asthma, tuberculosis, and diabetes and the treatment of malaria until the discovery of penicillin. Commercial uses of arsenic today include wood preservatives (accounts for 90 percent usage), paints, dyes, metals, drugs, soaps, rat poison, and semiconductors.

In the past few decades, the long-term exposure to arsenic has become a major health concern throughout the world. More than 100 million people worldwide are ingesting drinking water from wells that contain arsenic. Among other potential health risks, recent research shows a strong dose-dependent relationship between arsenic exposure and accelerated development of atherosclerosis in the arteries leading to the brain. Studies have suggested that arsenic may cause liver, kidney, and bladder cancer (Smith et al., 1992). Pontius et al. (1994) summarized the health implications of arsenic on humans. More recently, the water industry has focused some of its efforts on arsenic occurrence in water supplies and methodologies for its removal.

The concentrations of arsenic in water from various places throughout the world are summarized in Table 20-2. Perhaps the most well known area of the world noted for arsenic problems is in Bangladesh. It is estimated that 28 to 35 million people are exposed to arsenic in drinking water wells with arsenic concentrations exceeding 0.05 mg/L, and between 200,000 to 270,000 arsenic-related deaths from cancer are expected in this country alone (Smith et al., 1992). The U.S. EPA has estimated that some 13 million people in the United States, primarily in the western states, are exposed to arsenic in drinking water at levels greater than 0.01 mg/L.

The World Health Organization (WHO) proposed limit on arsenic in drinking water is 0.01 mg/L, which is largely based on analytical capability.

Table 20-2

Summary of waters with elevated arsenic concentrations throughout world

Water Body and Location	Arsenic Concentration, $\mu\text{g/L}$	
	Range	Typical
River water		
Baseline, various	0.13–2.1	0.83
Norway	<0.02–1.1	0.25
Southeast United States	0.15–0.45	0.30
Madison and Missouri Rivers, United States (geothermal influenced)	10–370 10–370	
United States		2.1
Dordogne, France		0.7
Po River, Italy		1.3
Polluted European rivers	4.5–45	
High-As groundwater influenced		
Northern Chile	190–21800	
Northern Chile	400–450	
Ron Phibun, Thailand (mining influenced)	4.8–583	218
Ashanti, Ghana	<2.0–7900	284
British Columbia, Canada	<0.2–556	17.5
Lake water		
Baseline	<0.2–0.42	0.28
British Columbia		
France	0.73–9.2	
Japan	0.38–1.9	
Sweden	0.06–1.2	
Western United States (geothermal influenced)	0.38–1000	
Estuarine water		
Oslofjord, Norway	0.7–2.0	
Saanich Inlet, British Columbia	1.2–2.5	
Rhone, France	1.1–3.8	2.2
Krka Estuary, Yugoslavia	0.13–1.8	
Seawater		
Deep Pacific and Atlantic Oceans	1.0–1.8	
Coastal Malaysia	0.7–1.8	1.0
Coastal Spain	0.5–3.7	1.5
Coastal Australia	1.1–1.6	1.3
Groundwater		
Baseline United Kingdom	<0.5–10	
As-rich provinces: Bengal Basin, Argentina, Mexico, northern China, Taiwan, Hungary	10–5000	

Source: Adapted from WHO (2001) Draft Report.

Developed countries such as the United States, European community, Japan, and Canada have adopted the 0.01-mg/L limit. The implications of these new regulations in terms of health and cost to society are discussed in several references (U.S. EPA, 2000, 2001; WHO, 2001; Health Canada, 2006). Presented below is a short summary of the forms of arsenic found in water followed by present treatment technologies for removing arsenic from water supplies.

Chemical Properties

A brief review of the chemical properties of arsenic in water is useful in understanding the treatment processes available for arsenic removal. Arsenic can occur in four oxidation states in water (+5, +3, 0, -3) but is usually found only in the trivalent [arsenite, As(III)] and pentavalent [arsenate, As(V)] states.

The predominance diagrams for arsenite and arsenate as a function of pH are shown on Fig. 20-1. In the pH range from 2 to 9, the undissociated form of arsenite (H_3AsO_3) is the predominate species. Most natural As(III)-containing surface and groundwaters in the pH range of 6.5 to 8.5 will have As in the H_3AsO_3 form. Arsenate ($HAsO_4^{2-}$) will be present in the pH range from 7 to 11.5, which will most likely occur in the normal pH range for most water supplies. For pH values less than 7.0, $H_2AsO_4^-$ will be the predominate species.

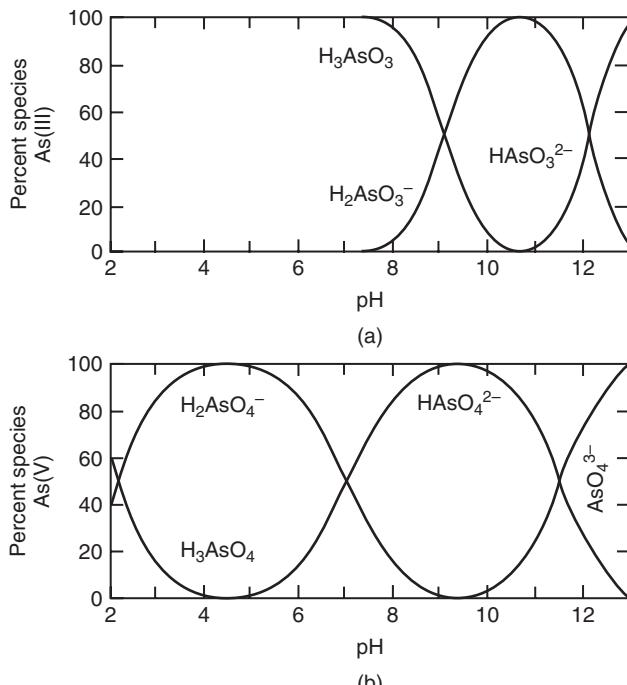
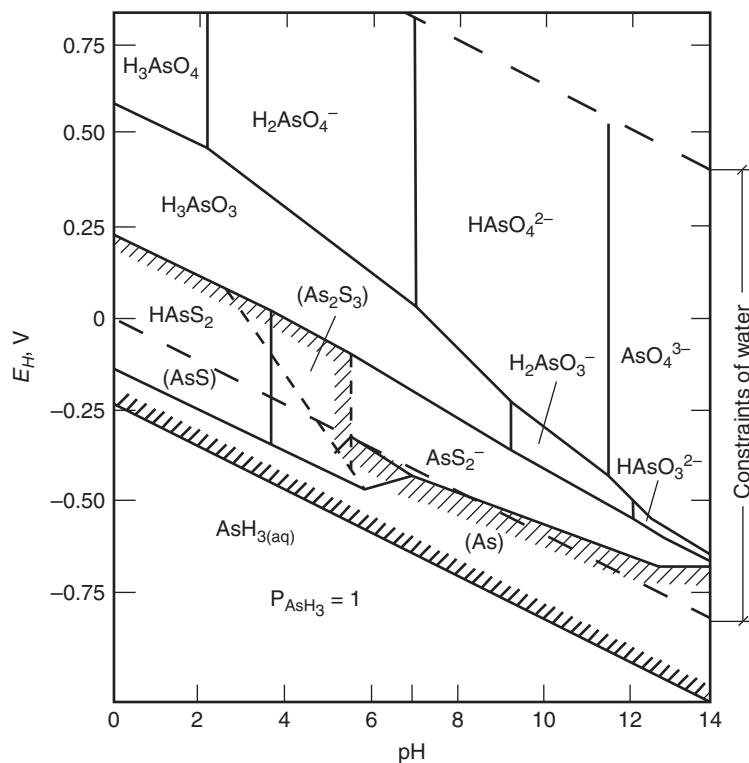


Figure 20-1

Predominance diagram for As(III) and As(V) as function of pH. (Adapted from Gupta and Chen, 1978.)

**Figure 20-2**

The E_H -pH diagram for arsenic at 25°C and 1 atm with total arsenic 10^{-5} mol/L and total sulfur 10^{-3} mol/L. Solid species are enclosed in parentheses in cross-hatched area, which indicates solubility less than $10^{-5.3}$ mol/L. (adapted From Ferguson and Gavis, 1972. Reprinted with permission.)

The E_H -pH diagram for arsenic in the presence of oxygen, sulfur, and water at 25°C and 1 atm is presented on Fig. 20-2. The E_H -pH diagram represents the equilibrium condition of arsenic under various redox potentials and pH conditions. For surface waters that are well aerated (oxidizing or high E_H conditions), $H_2AsO_4^-$ becomes the dominant species at pH values less than about 6.9 and $HAsO_4^{2-}$ becomes the dominant species at higher pH values. Usually little or no As(III) is present under oxidizing conditions. For well waters that contain little dissolved oxygen (mildly reducing or low E_H values), H_3AsO_3 should be the dominant species for pH values less than about 9.2.

In the presence of relatively high concentrations of reduced sulfur, dissolved arsenic-sulfide species can be present. Reducing, acidic conditions will favor the formation of reduced sulfur species such as orpiment (As_2S_3), realgar (AsS), or other sulfide-arsenic species. Waters high in arsenic are usually not expected where there is a high concentration of free sulfide. Thioarsenate species are more likely to be present at neutral and alkaline pH in the presence of very high sulfide concentrations. In addition, organic arsenic forms can be produced by biological activity in some surface waters but are not routinely measured.

Treatment Strategies

Treatment strategies for arsenic removal from water supplies include (1) conventional coagulation, (2) sorption with ferric and aluminum oxides, (3) ion exchange, and (4) membranes. More recently, the use of nonconventional adsorbents such as ferric and aluminum oxides have been evaluated as potential treatment alternatives for the removal of arsenic. A brief discussion of these treatment practices is presented and references are provided for further reading in this section.

COAGULATION PROCESSES

Traditionally, coagulation and filtration processes have been used to remove arsenic. Coagulants such as alum, ferric chloride, ferric sulfate, and lime have been used to remove arsenic to varying degrees. Coagulation processes usually require arsenic to be in the form of As(V); if arsenite, As(III), is present, it is usually oxidized first using chlorine, permanganate, or ozone. The mechanisms for As(V) removal by coagulation processes may be a combination of precipitation, coprecipitation, and adsorption. Edwards (1994) provides a discussion of the mechanisms associated with arsenic removal.

The performance results from several pilot- and full-scale studies using various coagulation processes are summarized in Table 20-3. Observed removals using ferric chloride have ranged from 81 to 100 percent using coagulant dosages from 5 to 304 mg/L. Typical doses for ferric salts are 5 to 30 mg/L and the pH is usually below 8.0. Alum coagulation has resulted in removals ranging from 23 to 100 percent with dosages from 6 to 50 mg/L. Typical dosages for alum are 10 to 50 mg/L and the pH is usually between 6 and 7.0. For Fe-Mn treatment processes, where the Fe^{2+} concentrations are greater than about 1.5 mg/L, around 80 to 90 percent of the As is removed. Plants that remove only Mn did not achieve significant removals of arsenic (McNeill and Edwards, 1997). Arsenic removals ranging from 60 to 90 percent have been observed in softening plants that use excess lime for Mg^{2+} treatment. For single-stage softening plants that only remove Ca^{2+} , arsenic removals of 0 to 40 percent have been observed. For source waters containing high levels of phosphate or silicate, coagulation can be less effective for arsenic removal. For waters containing sulfides, As(III) is precipitated as AsS and As_2S_3 . Jar test screening is recommended at the bench level to evaluate different options for arsenic removal when using coagulants.

SORPTION PROCESSES

Because adsorption onto alum, ferric, and lime precipitates is a major arsenic removal mechanism, adsorbents composed of similar surface adsorption properties have been tested and also found to be promising for the removal of arsenic. Two promising granular adsorbents are activated alumina and granular ferric hydroxide (GFH) based adsorbents. The properties of these two granular adsorbents are reported in Table 20-4. In the fixed-bed

Table 20-3

Summary of some pilot- and full-scale results for As removal using coagulation processes

Type of Study	Water Type	Coagulant Conditions	Initial As Concentration, $\mu\text{g/L}$	Final As Concentration, $\mu\text{g/L}$	Percent As Removal, %	Reference
Pilot plant	Groundwater Anoxic well water (natural As)	Ferric hydroxide (2.4 – 2.7 mg/L Fe), pH 8.8 Alum (7–46 mg/L), pH 7.4	40–43 640–830 ^a	<10 <10–470	75–82 38–100	Ghurye et al., (2004) Sorg and Logsdon (1978)
		Ferric chloride (18–77 mg/L) pH 7.0–8.5	560–920 ^a	<10–290	60–100	Sorg and Logsdon (1978)
		Ferric chloride (17–304 mg/L) pH 7.0–7.6, prechlorinated	580–940 ^b	<10–130	81–100	Sorg and Logsdon (1978)
	Surface water [spiked As(V)]	Alum (10–30 mg/L), pH 6.3–7.6, cationic polymer 2 mg/L	2.42–5.83 ^c	0.26–3.50	13–94	Cheng et al. (1993)
		Ferric chloride (10–30 mg/L), pH 6.3–7.3, cationic polymer 3 mg/L	3.17–5.33 ^c	0.02–0.43	91–98	Cheng et al. (1993)
	Surface water (natural As)	Ferric Hydroxide (2.7 mg/L Fe), pH 8.8	40–43	<10	>80	Ghurye et al. (2004)
Full-scale plant	Surface water (natural As)	Ferric chloride (3–10 mg/L), pH 7.18–7.8, chlorine 3–5 mg/L, cationic polymer 2–3 mg/L Alum (6–20 mg/L), pH 7.18–7.8, chlorine 3–5 mg/L, cationic polymer 2–3 mg/L	1.2–1.7 ^a 2.1–2.2 ^c 2.1–2.2 ^c	0.07–0.32 0.63–1.7 0.63–1.7	81–96 23–71 23–71	Scott et al. (1995) Scott et al. (1995) Scott et al. (1995)
	Groundwater (natural As)	Fe–Mn treatment (aeration, oxidation, filtration), pH 7.5 Fe–Mn treatment (aeration, oxidation, filtration), pH 7.5	20.5 ^d 5.2 ^d	2.7 0.88	86.7 83.1	McNeill and Edwards (1995) McNeill and Edwards (1995)

(continues)

Table 20-3 (Continued)

Type of Study	Water Type	Coagulant Conditions	Initial As Concentration, $\mu\text{g/L}$	Final As Concentration, $\mu\text{g/L}$	Percent As Removal, %	Reference
Blended surface and groundwater (natural As)	Blended surface and groundwater (natural As)	Single-stage calcium softening, pH 8.7	3.1 ^d	2.9	6.1	McNeill and Edwards (1995)
	Surface water (natural As)	Excess lime enhanced softening, lime dose 120 mg/L, ^e pH 8.2	3.9 ^d	1.26	67.7	McNeill and Edwards (1995)
	Groundwater (natural As)	Excess lime enhanced softening, pH 7.6	8.2 ^d	1.75	78.6	McNeill and Edwards (1995)
	Surface water (natural As)	Excess lime enhanced softening, lime dose 450 mg/L, ^e pH 7.1	32.4 ^d	13.9	57.1	McNeill and Edwards (1995)
		Alum coagulation, alum dose 55 mg/L, pH 7.8	12.0 ^d	3.4	71.3	McNeill and Edwards (1995)
		Alum coagulation, alum dose 10 mg/L, pH 7.8	4.3 ^d	2.48	42.3	McNeill and Edwards (1995)
		Alum coagulation, alum dose 10 mg/L, pH 7.8	4.4 ^d	3.06	30.4	McNeill and Edwards (1995)

^aAs(III) (assumed).^bAs(V) (assumed).^cAs(V) (known).^dAs (unknown).^eAs CaO.

Table 20-4
Properties of activated alumina and GFH adsorbents

Parameter	Unit	Activated Alumina,	
		Alcoa F-1	GFH
Media size	mm	0.29–0.50	0.32–2.0
Grain density	g/cm ³	3.97	1.59
Bulk density	g/cm ³	0.641–0.960	1.22–1.29
Porosity of grains	%	—	72–77
Specific surface area	m ² /g (dry weight)	300–350	250–300

mode of operation, these adsorbents were tested successfully at both the pilot and full scale in the United States and Europe on natural waters. The results of some studies that have been performed on these adsorbents are given in Table 20-5. The reported range of capacities for activated alumina is from 1000 to 13,000 bed volumes (BV) but typically around 10,000 BV. The GFH adsorbent capacities have ranged from 32,000 up to 85,000 BV depending upon the water quality. The GFH adsorbents are very attractive from a performance standpoint; however, at this time the cost is rather prohibitive for large systems. For both adsorbents, the capacities will depend upon water quality parameters such as temperature, pH, and competing constituents in the water matrix, which may include NOM and competing ions (e.g., phosphate, silicate, sulfate). For example, activated

Table 20-5
Comparison of results for adsorbents in fixed beds in removing arsenic from water supplies

Adsorbent	Influent Arsenic Concentration, µg/L	Treatment Objective, µg/L	Bed Volumes Treated	Reference
Activated alumina	70	10	1,000	Benjamin et al. (2000)
	50	10	10,000	Benjamin et al. (2000)
	21	10	13,000	Clifford (1999)
	23	10	110,500	Simms and Azizian (1997)
	98	50	16,000	Clifford (1999)
	22	10	15,600	Clifford (1999)
	100	10	9,000	Rubel and Hathaway (1985)
Granular ferric hydroxide (GFH) based adsorbent	15–20	10	85,000	Driehaus et al. (1998)
	100	10	25,000	Thomson et al. (2005)
	100–180	—	34,000	Driehaus et al. (1998)
	21	—	37,000	Driehaus et al. (1998)
	16	—	32,000	Driehaus et al. (1998)

alumina performs best at pH values around 5.5 to 6.0 and drops off sharply above 7.0. It should also be noted that preoxidation of the water to convert any As(III) to As(V) is usually performed before the adsorption process.

In some cases, activated alumina can be regenerated with a strong base followed by a strong acid. Reported recoveries of arsenic from the regeneration process are about 75 percent. For small systems, one-time use may be more economical than regeneration, which will be required for large systems. A good discussion of the design and regeneration of activated alumina for fluoride removal is presented by Clifford (1999). The design parameters for arsenic removal may be similar; however, rapid small-scale and pilot testing may be used to develop site-specific design information. In addition, the use of powdered activated alumina coupled with membranes (microfiltration and ultrafiltration) may also be a promising treatment process.

Presently, the GFH adsorbent is used once and disposed of in a landfill. Regeneration techniques for GFH may be necessary to make it an economically viable process for large systems. Other adsorbents such as manganese greensand, manganese dioxide, hydrous iron oxide particles, and iron-oxide-coated sand may be promising if verified through pilot testing and if it can be demonstrated that these processes are viable and economically feasible at full scale.

ION EXCHANGE

Ion exchange can be a viable process for the removal of arsenic from natural waters. Design considerations for arsenic removal by ion exchange include (1) oxidation state of arsenic, (2) resin type, (3) background ion concentrations and type of ion, (4) empty-bed contact time (EBCT), (5) regenerant strength and level, and (6) spent-brine reuse and treatment. Some of the design considerations for arsenic removal by ion exchange are discussed in this section, and an in-depth discussion is presented in Clifford (1999).

From the speciation diagram given on Fig. 20-1, As(V) is present as monovalent H_2AsO_4^- and divalent HAsO_4^{2-} in the pH range of natural waters, 6 to 9. If As(III) is present in the water, it usually exists as a neutral species, which cannot be removed by ion exchange and must be oxidized to As(V) prior to ion exchange treatment. For waters with total dissolved solids (TDS) concentrations less than about 500 mg/L and sulfate concentrations less than about 120 mg/L, anion ion exchange can be an economically attractive process for arsenic removal (Frey and Edwards, 1997). At low TDS and sulfate concentrations the competition for resin exchange sites with arsenic is low, and reasonable exchange capacity for arsenic can be achieved. However, for waters containing high sulfate and TDS levels, ion exchange may not be a viable process (Clifford and Ghurye, 1998b). For waters having high pH and alkalinity and low sulfate concentration, As(V) can be effectively treated with an anion exchange resin in the chloride form (Clifford and Lin, 1986).

Type of strong-base resin

With respect to the type of strong-base anion (SBA) exchange resin, no significant difference in performance has been observed among the various resins and both type 1 and type 2 polystyrene resins may provide slightly higher breakthrough capacities than other SBA resins. For waters containing arsenic and nitrate, HAsO_4^{2-} has a poor affinity for monovalent nitrate-selective resins and should be avoided. When using conventional SBA resins, another concern is nitrate peaking or chromatographic overshoot due to the ions having different affinities for the resin. Nitrate has a slightly lower affinity than arsenic for standard SBA resins (see Chap. 16, Table 16-4) and will increase in liquid-phase concentration as it is pushed through the column and eventually will be present in the effluent at a much higher concentration than the influent concentration. The nitrate effluent concentration can sometimes exceed the effluent guidelines for nitrate in the water. Care should be taken to shorten the arsenic loading cycle time such that the nitrate standard is not exceeded. Nitrate will typically appear in the effluent just before arsenic breakthrough. In addition, lowering the pH to produce monovalent arsenic is not effective because H_2AsO_4^- affinity is much less than HAsO_4^{2-} (Clifford, 1999).

Based on pilot studies for arsenic removal, it has been shown that arsenic leakage (see Chap. 16) can develop during exhaustion cycles, but the observed concentrations (0.2 to 0.8 $\mu\text{g/L}$) are well below the proposed MCL of 10 $\mu\text{g/L}$. Arsenic leakage increases when particulate iron concentrations in the water increase due to the adsorption of the arsenic onto the iron particles. Steps should be taken to provide particulate filtration prior to the ion exchange process.

General design considerations

Typical EBCTs for arsenic removal range from 1.5 to 3.0 min and other operational parameters are similar to those presented in Table 16-1 in Chap. 16. Arsenic-loaded SBA resins can be regenerated easily with NaCl. Because arsenic is a divalent ion, it undergoes selectivity reversal in the presence of high-ionic-strength solutions and consequently is easy to remove from the resin during regeneration. In addition, regeneration superficial velocities greater than 0.02 m/h were found to work best for arsenic because they resulted in higher arsenic recoveries.

Down-flow co-current regeneration has been shown to be more effective for regenerating arsenic-laden resins than the conventional countercurrent mode of regeneration (Clifford and Ghurye, 1998a). Co-current is more effective because at the end of the exhaustion cycle the arsenic that is exchanged onto the resin bed is located near the feed end of the bed. Consequently, when the regenerant is passed through the bed in the down-flow mode, the regenerant is contacted with the highest arsenic resin concentration. Down-flow co-current regeneration will reduce arsenic leakage.

Brine management

Brine reuse and treatment are important in the removal of arsenic by ion exchange (see also Chap. 21). Field studies have demonstrated that arsenic-laden resin could be regenerated successfully using spent brine for over 20 regeneration cycles before arsenic leakage exceeded 10 µg/L (Clifford, 1999). Sodium chloride was added to the spent-brine solution to maintain a 1.0 N NaCl solution concentration. The concept of brine reuse should be investigated because it can provide significant cost savings with respect to lowering the salt requirements and brine disposal volume. Waste brine containing arsenic needs to be treated prior to disposal. Arsenic can be precipitated using FeCl₃, alum, or lime. For a brine waste containing 90 mg/L of As(V) and 50,000 mg/L TDS, about 12 times the stoichiometric quantity of FeCl₃ is required to reduce the As(V) concentration to less than 5 mg/L. Arsenic removal is very pH dependent, and greater than 99 percent As(V) can be removed from the brine solution using an iron-to-arsenic ratio of 20 : 1 at a final pH of around 5.5. Consequently, pH adjustment should be included in brine disposal evaluations.

MEMBRANES

A number of studies have been conducted to evaluate the use of membranes for arsenic removal (Moore et al., 2008; Ghurye et al., 2004; Brandhuber and Amy, 1998; Chang et al., 1994; Hering and Elimelech, 1996; Thompson and Chowdhury, 1993). In one study, several ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes were evaluated for arsenic removal from two spiked groundwater sources from Southern California (Brandhuber and Amy, 1998). Based on these studies, guidelines for arsenic removal using membrane treatment are summarized in Table 20-6. The combined treatment using coagulation and membranes can be used to effectively remove arsenic, and if arsenic is in particulate form, large-pore-size membranes may be effective in As removal. The As(III) form can only be removed by RO; otherwise it must be preoxidized, forming As(V) before membrane treatment. Reverse osmosis and NF can effectively remove the dissolved form of As(V), and tight UF membranes may be effective as well. Waters high in dissolved organic carbon (DOC) may inadvertently cause poor arsenic removal due to membrane fouling.

20-3 Iron and Manganese Removal

The fundamental concepts involved with removal of soluble iron and manganese are similar and the two often occur together in water supplies. These soluble species are typically unstable when exposed to oxidants such as dissolved oxygen and when processed in a water treatment plant will usually form precipitate during treatment, in the distribution piping system, or at the point of use. However, depending upon which treatment processes are used, it may be important to control these precipitation reactions. The

Table 20-6

Guidelines for the use of membranes for arsenic removal in water treatment^a

Source Water Characteristic	Membrane Treatment Only				Oxidation Pretreatment
	RO	NF	UF	MF	
As speciation					
As(III)	R	PE	NR	NR	R
As(V)	R	R	NR	NR	NR
As size distribution					
Dissolved	R	PE	NR	NR	NR
Particulate	NR	NR	PE	PE	NR
Co-occurrence					
NOM	PE	NR	NR	NR	NR
Inorganic	R	NR	NR	NR	NR

^aRemoval of other forms possible with ferric coagulants.

^bR—Recommended, NR—not recommended, PE—possibly effective.

Source: Brandhuber and Amy (1998).

most common treatment approach is to precipitate all the soluble forms of iron and manganese so that these constituents can be removed in other processes such as sedimentation and filtration. In addition to controlling the soluble species, colloidal and/or particulate iron and manganese are also important and must be considered in the overall removal. Consequently, the following sections provide a brief discussion of the background of these species, as well as their chemistry as related to redox properties, followed by control methods.

Iron is the fourth most abundant element in the Earth's crust, making up about 5.6 percent of the mass (McMurtry and Fay, 2003). Common mineral sources (deposits) of iron include ferric oxides and hydroxides such as hematite (Fe_2O_3) and ferric hydroxide $[\text{Fe}(\text{OH})_3]$. Ferric hydroxide gives rocks and soils their red and yellowish color. Sedimentary forms of iron may include sulfides, such as pyrite and marcasite; two minerals with identical composition (FeS_2) but different crystalline structures; carbonates such as siderite (FeCO_3); and mixed oxides such as magnetite (Fe_3O_4). The ferrous oxides and sulfides are the usual sources of dissolved iron in groundwaters. Weathering of iron silicates can produce dissolved iron in surface water; however, this is a relatively slow process.

Iron

OCCURRENCE AND IMPORTANCE IN WATER SUPPLIES

The interactions between iron-bearing soils or rock formations and water surrounding it can dissolve iron into the water. Iron is relatively soluble in a reducing environment or in natural waters, such as some low-oxygen-containing groundwaters and low-oxygen surface water, such as hypolimnetic waters of eutrophic lakes, large rivers, and reservoirs. In these waters, iron may be found in the reduced or ferrous form (Fe^{2+}) such as

Table 20-7

Maximum iron and manganese concentrations for selected industrial and commercial applications

Application	Maximum Concentration or Threshold Range (mg/L)		
	Mn	Fe + Mn	Fe
Air conditioning	0.5	0.5	—
Baking	0.2	0.2	0.2
Brewing	0.1	0.1	0.1–1.0
Canning	0.2	0.2	—
Carbonated beverages	0.2	0.1–0.2	0.1–0.2
Cooling water	0.2–0.5	0.2–0.5	0.5
Confectionary	0.2	0.2	0.2
Dyeing	0.0	0.0	—
Electroplating	—	—	Trace
Food processing, general	0.0	0.2	0.2
Ice	0.2	0.2	—
Laundering	—	—	0.2–1.0
Milk industry	0.03–0.1	—	—
Oil well flooding	—	—	0.1
Photographic processing	0.0	0.0	0.1
Pulp and paper			
Ground wood	0.5	1.0	0.3
Kraft pulp	0.1	0.2	—
Soda pulp	0.05	0.1	0.1
Kraft pulp, unbleached	0.5	—	—
Kraft pulp, bleached	0.1	—	0.05
Fine paper pulp	0.05	0.1	0.10
High-grade paper pulp	0.05	0.1	—
Plastics (clear)	0.02	0.02	—
Rayon pulp	0.03	0.05	—
Rayon manufacturing	0.0–0.02	0.0	0.05
Sugar manufacturing	—	—	0.1
Tanning	0.2	0.2	0.1–2.0

ferrous sulfate (FeSO_4) and ferrous bicarbonate [$\text{Fe}(\text{HCO}_3)_2$], hydroxide forms, or complexed with NOM. Low-alkalinity (<50 mg/L as CaCO_3) groundwaters may contain up to 10 mg/L of total iron. Also, some water treatment plant operators have observed high concentrations of iron in the raw water obtained from the hypolimnetic zone of reservoirs during periods of stagnation and stratification as it is seasonally mobilized from reduced lake sediments (Stumm and Lee, 1961).

Correspondingly, iron is very insoluble in an oxidizing environment or in natural waters containing sufficient quantities of dissolved oxygen. Depending upon the water quality, iron can exist in three physical forms: as large oxidized particles, small oxidized colloidal particles, and the soluble

reduced form. The smaller particles can often pass through filters of 0.45 μm pore size or smaller and are therefore classified as soluble in many operational schemes. For example, oxygenated surface waters (pH 5 to 8) typically have total iron concentrations in the range of 0.05 to 0.2 mg/L. In these waters, iron species present may consist of solids of large oxidized particles or small colloidal particles of ferric hydroxide sorbed onto clay particles, organic colloids, and other suspended solids and precipitates.

The U.S. EPA (1991) Secondary Drinking Water Regulations limit iron to 0.3 mg/L for taste and aesthetic reasons. The only advantage of having iron in water is for nutritional value, but only 1 to 2 mg/d is needed and most humans intake about 7 to 35 mg/d. Thus, daily consumption of water is not a major source of iron. There are several disadvantages of having iron in water supplies. Iron ions impart a metallic taste, and the taste threshold is reported to be around 0.1 to 0.2 mg/L of ferrous sulfate or ferrous chloride as Fe^{2+} . Ferrous iron may precipitate as ferric hydroxide after oxidation and stain laundry and household fixtures such as bathtubs, porcelain basins, glassware, and dishes. Iron may discolor industrial products such as textiles and paper. Threshold values for industrial and commercial uses of iron are listed in Table 20-7. Iron precipitates can clog pipes and support the growth of iron bacteria (*Crenothrix* and *Gallionella*), which can cause taste and odor problems.

CHEMICAL PROPERTIES

While the chemistry of iron oxidation is complex and not clearly understood, there are some useful physical/chemical relationships that can be used to interpret observations made in water treatment facilities. Parameters that affect iron oxidation and its rate include water temperature and pH and constituents in the water such as dissolved oxygen (DO), bicarbonate, NOM, sulfate, dissolved silica, and particles. Many of these parameters are discussed below to help explain iron oxidation.

An E_H -pH diagram for iron is presented on Fig. 20-3. The equilibrium form of various iron species that would be expected under the conditions stated, at any specific E_H -pH combination, is shown with the boundary defined by the E_H -pH limit of water. The solid forms of iron are shown with an (s). Under reducing conditions ($E_H < 0$), over a wide range of pH, iron solubility is low and pyrite tends to precipitate. Under oxidizing conditions ($E_H > 0$) and pH values above 5.0, iron tends to precipitate to ferric hydroxide $[\text{Fe(OH)}_3]$. Between these two regions ferrous iron is quite soluble, and this region corresponds to typical E_H -pH conditions of groundwater (pH 5 to 9 and E_H 0.20 to -0.10 V).

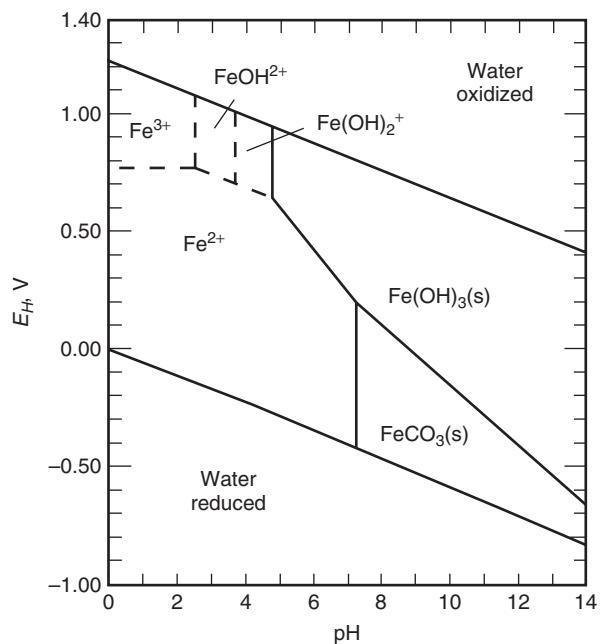
The stoichiometric expressions for the oxidation of ferrous iron using DO and some commonly used oxidants are shown in Table 20-8. In addition, the quantity of oxygen required, the alkalinity consumed, and an estimate of the sludge produced are also provided in Table 20-8.

Table 20-8

Oxidation reactions for iron

Oxidant	Reaction	Equation Number	Oxidant Needed, mg/mg Fe ²⁺	Alkalinity Used, mg/mg Fe ²⁺	Sludge Produced, ^a kg/kg Fe ²⁺
Oxygen	$4\text{Fe}(\text{HCO}_3)_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}(\text{OH})_3 + 8\text{CO}_2$	20-1	0.14	1.80	1.9
Chlorine	$2\text{Fe}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 + \text{Cl}_2 \rightarrow 2\text{Fe}(\text{OH})_3 + \text{CaCl}_2 + 6\text{CO}_2$	20-2	0.64	2.70	1.9
Chlorine dioxide	$\text{Fe}(\text{HCO}_3)_2 + \text{NaHCO}_3 + \text{ClO}_2 \rightarrow \text{Fe}(\text{OH})_3 + \text{NaClO}_2 + 3\text{CO}_2$	20-3	1.21	2.70	1.9
Potassium permanganate	$3\text{Fe}(\text{HCO}_3)_2 + \text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{OH})_3 + \text{MnO}_2 + \text{KHCO}_3 + 5\text{CO}_2$	20-4	0.94	1.50	2.43

^aSludge weight is based on $\text{Fe}(\text{OH})_3$ as the precipitate; however, it is likely that portions of the sludge will contain FeCO_3 .
Source: Adapted from ASCE/AWWA (1990).

**Figure 20-3**

Forms of iron in water as function of redox potential versus pH constructed with total iron activity 10^{-7} M or 5.6 $\mu\text{g/L}$, 96 mg/L SO_4^{2-} , CO_2 species at 1000 mg/L HCO_3^- , temperature at 25°C , and pressure of 1 atm (adapted from Langmuir, 1997).

KINETICS OF IRON OXIDATION

In the absence of iron complexed with NOM and pH values greater than 5.5, the rate of oxygenation of Fe^{2+} iron was found to be first order with respect to Fe^{2+} and O_2 and second order with respect to OH^- ion (Stumm and Lee, 1961). Based on these experimental observations, the following expression was proposed:

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k [\text{Fe}^{2+}] [\text{OH}^-]^2 P_{\text{O}_2} = k_r [\text{Fe}^{2+}] \quad (20-5)$$

where $[\text{Fe}^{2+}]$ = aqueous-phase ferrous iron concentration, mol/L

k = rate constant, typically $8.0(\pm 2.5) \times 10^{13} \text{ L}^2/\text{mol}^2 \cdot \text{min} \cdot \text{atm}$ at 20°C (Stumm and Morgan, 1996)

$[\text{OH}^-]$ = aqueous-phase hydroxide ion concentration, mol/L

P_{O_2} = partial pressure of oxygen, atm

k_r = pseudo-first-order constant, $\text{min}^{-1} = k [\text{OH}]^2 P_{\text{O}_2}$

The oxygenation rate of $[\text{Fe}^{2+}]$ is very dependent upon pH, as shown in Eq. 20-5. The dependence of the oxygenation rate of Fe^{2+} on pH is shown on Fig. 20-4. The y axis represents the log of the rate of oxygenation of Fe^{2+} with respect to time and is obtained by rearrangement of Eq. 20-5 as

$$k [\text{OH}^-]^2 P_{\text{O}_2} = -\frac{d[\text{Fe}^{2+}]}{[\text{Fe}^{2+}] dt} = -\frac{d \ln [\text{Fe}^{2+}]}{dt} \quad (20-6)$$

Example 20-1 Theoretical stoichiometric calculation

A 100,000-m³/d raw-water source containing 5 mg/L ferrous iron is oxidized to ferric hydroxide with oxygen. Calculate the quantity of oxygen required, alkalinity consumed as CaCO₃, and quantity of sludge produced as ferric hydroxide.

Solution

1. Determine the quantity of oxygen required using Eq. 20-1 in Table 20-8:

Dissolved oxygen required

$$\begin{aligned}
 &= (5 \text{ Fe}^{2+} \text{ mg/L}) (0.14 \text{ mg O}_2/\text{mg Fe}^{2+}) \\
 &\quad (100,000 \text{ m}^3/\text{d}) (1 \text{ kg}/10^6 \text{ mg}) (10^3 \text{ L/m}^3) \\
 &= 70 \text{ kg/d}
 \end{aligned}$$

2. Determine the quantity of alkalinity consumed as CaCO₃ using the values shown in Table 20-8:

Quantity alkalinity consumed

$$\begin{aligned}
 &= (5 \text{ mg Fe}^{2+}/\text{L}) (1.80 \text{ mg alkalinity/mg Fe}^{2+}) \\
 &\quad (100,000 \text{ m}^3/\text{d}) (1 \text{ kg}/10^6 \text{ mg}) (10^3 \text{ L/m}^3) \\
 &= 900 \text{ kg/d}
 \end{aligned}$$

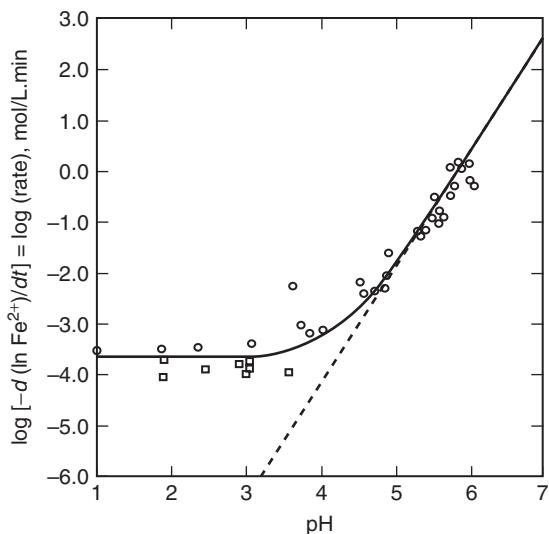
3. Estimate the quantity of sludge produced as ferric hydroxide using values from Table 20-8:

Sludge produced as Fe(OH)₃

$$\begin{aligned}
 &= (5 \text{ mg Fe}^{2+}/\text{L}) (1.90 \text{ mg sludge/mg Fe}^{2+}) \\
 &\quad (100,000 \text{ m}^3/\text{d}) (1 \text{ kg}/10^6 \text{ mg}) (10^3 \text{ L/m}^3) \\
 &= 950 \text{ kg/d}
 \end{aligned}$$

Comment

Oxygen addition is seldom used to precipitate iron because iron is typically complexed to NOM and the oxidation kinetics are too slow.

**Figure 20-4**

Oxidation rate of Fe^{2+} by oxygen for $P_{\text{O}_2} = 0.20 \text{ atm}$ and temperature = 25°C . (Adapted from Singer and Stumm, 1970.)

Assuming the oxygen partial pressure is constant, Eq. 20-6 can be written as

$$-\frac{d \ln [\text{Fe}^{2+}]}{dt} = k' [\text{OH}^-]^2 \quad (20-7)$$

where k' = rate constant, $\text{L/mol} \cdot \text{min}$, $= kP_{\text{O}_2}$

Taking the logarithms of both sides and substituting $K_w/[\text{H}^+]$ for $[\text{OH}^-]$, the following expression for the log of the rate of oxygenation of Fe^{2+} can be obtained (Snoeyink and Jenkins, 1980):

$$\log (\text{rate}) = \log (k'') + 2 \text{ pH} \quad (20-8)$$

where k'' = constant, $k' K_w^2$

Effect of pH

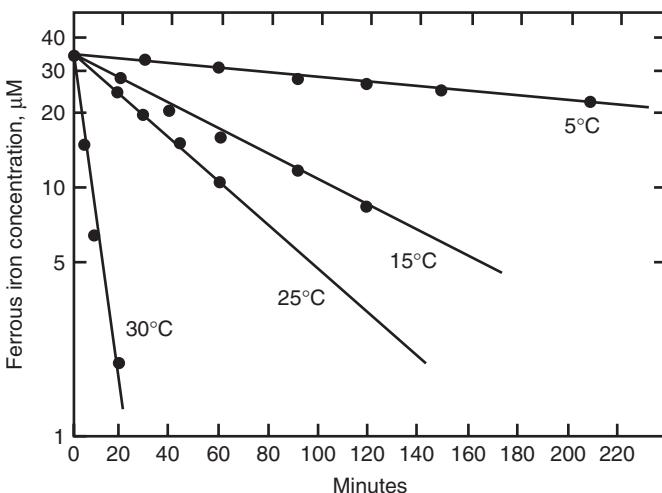
For pH values greater than 5.5, the experimental data and Eq. 20-5 are in agreement, and the rate of oxygenation of Fe^{2+} increases by 100-fold per pH unit. For pH values less than about 3.5, the oxygenation of Fe^{2+} is independent of pH.

Effect of temperature

The effect of temperature on the rate of oxygenation of Fe^{2+} appears to be large when data are plotted as shown on Fig. 20-5 (Sung and Morgan, 1980). However, when the data on Fig. 20-5 are normalized with respect to changes in K_w and O_2 solubility with temperature, the change in the value of the rate constants is small (Sung and Morgan, 1980).

Figure 20-5

Impact of temperature on oxygen kinetics of Fe^{2+} . The experiments were conducted in 0.11 M ionic strength and adjusted with NaClO_4 . The alkalinity was equal to 9.0×10^{-3} M as HCO_3^- , pH was equal to 6.82, P_{O_2} was 0.2 atm, and the initial Fe^{2+} concentration was 0.0347 M. (Adapted from Sung and Morgan, 1980.)



Effect of ionic strength

The impact of ionic strength on the oxygenation rate of Fe^{2+} is shown in Table 20-9. Increasing the ionic strength by a factor of about 10 from 0.009 to 0.11 M decreases the rate by about a factor of 4 from 4.0×10^{13} to $1.2 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$. The time required for 50 percent reduction of the Fe^{2+} concentration in seawater is nearly 100 times larger than values observed for freshwater (Kester et al., 1975). The presence of Cl^- and SO_4^{2-} is believed to form complexes with the Fe^{2+} ion and inhibit oxygenation (Tamura et al., 1976).

Table 20-9

Impact of ionic strength on oxygenation rate constant for Fe^{2+}

Ionic Strength, mol/L	<i>k</i> , (mol/L) ⁻² · atm ⁻¹ · min ⁻¹
0.009	$4.0 \pm 0.6 \times 10^{13}$
0.012	$3.1 \pm 0.7 \times 10^{13}$
0.020	$2.9 \pm 0.6 \times 10^{13}$
0.040	$2.2 \pm 0.5 \times 10^{13}$
0.060	$1.8 \pm 0.3 \times 10^{13}$
0.110	$1.2 \pm 0.2 \times 10^{13}$

^aT = 25°C; alkalinity = 9×10^{-3} M HCO_3^- ; $[\text{Fe}^{2+}]_0 = 34.7 \mu\text{M}$; $P_{\text{O}_2} = 0.20$ atm; pH = 6.84.

Sources: Adapted from Faust and Aly (1998).

Effect of complexing agents

Organic complexing agents can also impact the oxygenation of Fe^{2+} . Humic and tannic acids or other NOM can bind or complex iron and slow down the kinetics of oxidation. Iron complexed with NOM, often referred to as filterable iron because it is soluble, is usually associated with water sources high in organic color. The chemistry of NOM and its interactions with metals are very complex and considerable research has been performed to elucidate the chemical nature of these yellow-colored organic iron complexes (Liao et al., 1982; Thurman, 1985). Soluble Fe^{2+} has been shown to not complex in the presence of humic acid at low pH values ($\text{pH} < 5$), but increasing the pH ($\text{pH} > 8.0$) can result in the formation of a soluble Fe^{2+} complex. This complexing ability was attributed to greater dissociation of carboxyl groups of the humic acid. It was proposed that humic acids could chemically reduce Fe^{3+} to Fe^{2+} followed by complexation of the Fe^{2+} with the humic acids. The presence of humic and tannic acids has also been shown to inhibit the oxygenation of Fe^{2+} (Theis and Singer, 1974). In addition, organically bound Fe^{2+} cannot be effectively oxidized by the use of aeration (Kawamura, 2000).

Even though manganese makes up a very small percentage of the Earth's crust (<0.1 percent), it is abundant in rocks and soils. Manganese is an essential nutrient for both humans and plants. Typical daily intake is about 10 mg, the majority of which comes from food sources. For plants, manganese moves as an enzyme activator and in animals it is important in growth and in nervous system functioning.

Manganese**OCCURRENCE AND IMPORTANCE IN WATER**

Manganese is similar to iron in that it is usually present in the +2 oxidation state (Mn^{2+}) in anoxic groundwaters and in the hypolimnion region of reservoirs and eutrophic lakes. When the groundwater is pumped to the surface and when the hypolimnetic waters are mixed, the Mn^{2+} is exposed to oxygen and begins to undergo a series of oxidation reactions to Mn^{4+} . This oxidation is accompanied by a decrease in pH and DO concentration and the formation of MnO_2 precipitate. Manganese may cause aesthetic problems such as laundry and fixture staining. Manganese concentrations around 0.2 to 0.4 mg/L may also impart an unpleasant taste to water and can promote the growth of microorganisms in reservoirs and distribution systems. Consumer complaints have been documented with manganese concentrations as low as 20 $\mu\text{g}/\text{L}$ (Sly et al., 1990). The U.S. EPA (1991) specifies a secondary MCL for manganese of 50 $\mu\text{g}/\text{L}$.

CHEMICAL PROPERTIES

Typically manganese occurs in the form of oxides and hydroxides. Manganese has eight oxidation states [Mn^0 , Mn^{2+} , $\text{Mn}_3\text{O}_4(\text{s})$, $\text{Mn}_2\text{O}_3(\text{s})$, MnO_2 , MnO_4^{3-} , MnO_4^{2-} , and MnO_4^-]. At pH values of most natural waters,

Example 20-2 Time required for Fe²⁺ oxidation from a groundwater

Groundwater with a soluble Fe²⁺ concentration of 5.0 mg/L is to be oxidized by aeration to a Fe²⁺ concentration of 0.3 mg/L. The raw-water pH is 7.0 with a temperature of 10°C, and it is assumed that P_{O_2} is in equilibrium with the atmosphere. A typical pseudo-first-order rate constant for the oxygenation of Fe²⁺ is 0.168 min⁻¹. For steady-state operation and a flow rate of 10,000 m³/d (2.64 mgd), calculate and compare the minimum hydraulic detention time and reactor volume for the oxidation of Fe²⁺ to Fe³⁺ for a completely mixed flow reactor (CMFR) and for a plug flow reactor (PFR).

Solution

1. Determine the steady-state residence time for the CMFR using Eq. 6-37:

$$\tau_{CMFR} = \frac{C_{A0} - C_A}{kC_A} = \frac{Fe_0^{2+} - Fe^{2+}}{k'Fe^{2+}} = \frac{(5.0 - 0.3) \text{ mg/L}}{(0.168 \text{ min}^{-1})(0.3 \text{ mg/L})} \\ = 93 \text{ min}$$

2. Determine the CMFR volume:

$$V_{CMFR} = Q\tau_{CMFR} = (93 \text{ min})(10,000 \text{ m}^3/\text{d})(1 \text{ d}/1440 \text{ min}) \\ = 645 \text{ m}^3$$

3. Determine the steady-state residence time for the PFR using Eq. 6-65:

$$\tau_{PFR} = \frac{1}{k} \ln \left(\frac{C_{A0}}{C_A} \right) = \frac{1}{0.168 \text{ min}^{-1}} \ln \left(\frac{5.0}{0.3} \right) = 16.7 \text{ min}$$

4. Determine the PFR volume:

$$V_{PFR} = (16.7 \text{ min})(10,000 \text{ m}^3/\text{d})(1 \text{ d}/1440 \text{ min}) = 116 \text{ m}^3$$

5. Compare the PFR and CMFR detention times and values. As discussed in Chap. 6, the PFR is much more efficient than a CMFR. In most cases bench and/or pilot tests will be used to determine the kinetics for the water source of interest because the impact of both colloidal and particulate iron will have to be evaluated. However, this calculation can be used to provide some preliminary insight into the minimum contact times required for Fe²⁺ removal.

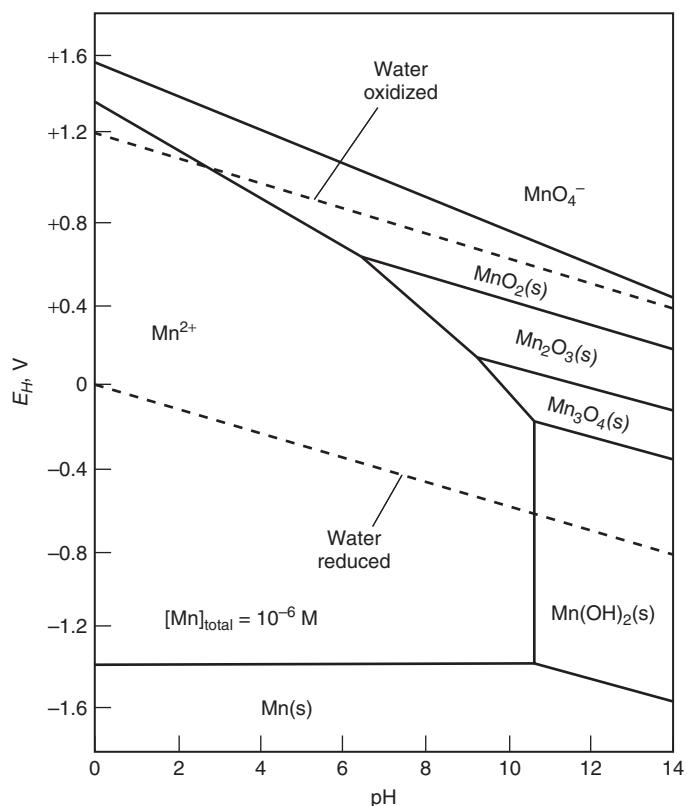


Figure 20-6
Forms of manganese in water as function of redox potential versus pH at a water temperature of 25°C. (Adapted from Pourbaix, 1966, 1974.)

aqueous Mn²⁺ is the predominant form of manganese, as shown on the E_H-pH diagram on Fig. 20-6. Concentrations of Mn²⁺ on the order of 0.1 to 1.0 mg/L are common, although in low-pH waters higher concentrations can occur. Oxidation of Mn²⁺ can thermodynamically lead to three different oxides of manganese depending upon the E_H and pH—MnO₂, Mn₂O₃, and Mn₃O₄, with the predominant form being MnO₂.

KINETICS OF OXIDATION

Three oxidation states of manganese important in drinking water are Mn²⁺ (soluble), Mn⁴⁺ (as MnO₂ precipitate), and Mn⁷⁺ (as MnO₄⁻ strong oxidant). The Mn²⁺ state can be removed from water via oxidation, but aeration is not a very effective treatment option unless the pH is greater than about 9.0. The reaction sequence for oxygenation of Mn²⁺ is suggested as (Faust and Aly, 1998)

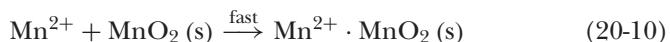
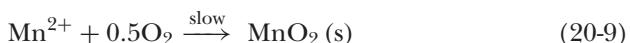


Table 20-10

Oxidation reactions for manganese

Oxidant	Reaction	Equation Number	Oxidant Needed, mg/mg Mn ²⁺	Alkalinity Used, mg/mg Mn ²⁺	Sludge Produced ^a , kg/kg Mn ²⁺
Oxygen	$2\text{MnSO}_4 + 2\text{Ca}(\text{HCO}_3)_2 + \text{O}_2 \rightarrow 2\text{MnO}_2 + 2\text{CaSO}_4 + 2\text{H}_2\text{O} + 4\text{CO}_2$	20-12	0.29	1.80	1.58
Chlorine	$\text{Mn}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 + \text{Cl}_2 \rightarrow \text{MnO}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O} + 4\text{CO}_2$	20-13	1.29	3.64	1.58
Chlorine dioxide	$\text{Mn}(\text{HCO}_3)_2 + 2\text{NaHCO}_3 + 2\text{ClO}_2 \rightarrow \text{MnO}_2 + 2\text{NaClO}_2 + 2\text{H}_2\text{O} + 4\text{CO}_2$	20-14	2.46	3.64	1.58
Potassium permanganate	$3\text{Mn}(\text{HCO}_3)_2 + 2\text{KMnO}_4 \rightarrow 5\text{MnO}_2 + 2\text{KHCO}_3 + 2\text{H}_2\text{O} + 4\text{CO}_2$	20-15	1.92	1.21	2.64

^aSludge weight is based on MnO₂ as the precipitate. It may be conservative in some cases.

Source: ASCE/AWWA (1990).

The rate of conversion of Mn²⁺ to MnO₂ also involves an autocatalytic process where the formation of MnO₂ solid provides for adsorption of Mn²⁺ and accelerates conversion of Mn²⁺ to MnO₂. Because of this catalytic effect, not all the Mn²⁺ that is removed from the process is converted to MnO₂ and may simply be adsorbed onto MnO₂. The products of manganese oxygenation appear to be nonstoichiometric and show various degrees of oxidation ranging from about MnO_{1.3} to MnO_{1.9} depending upon the pH (Stumm and Morgan, 1996). The general stoichiometric expressions for the oxidation of manganese using DO and some commonly used oxidants are displayed in Table 20-10 along with the quantity of oxygen required, the alkalinity consumed, and an estimate of the sludge produced. The values shown in Table 20-10 may be used to estimate the quantity of oxidant required, alkalinity consumed, and quantity of sludge produced for manganese oxidation. As discussed above, the extent of oxygenation of manganese is not accounted for by the stoichiometry of the oxidation alone and assuming that the sludge is MnO₂ will be conservative in terms of oxidant requirement.

Although the mechanism of this reaction is not understood completely, the following general expression may be used to describe the oxidation in a CMBR:

$$-\frac{d[\text{Mn}^{2+}]}{dt} = k_1[\text{Mn}^{2+}] + k_2[\text{Mn}^{2+}][\text{MnO}_2(\text{s})] \quad (20-16)$$

where k_1, k_2 = respective rate constants for oxidative and autocatalytic pathways

$[\text{Mn}^{2+}]$ = aqueous-phase manganese ion concentration, mol/L

$[\text{MnO}_2(\text{s})]$ = manganese oxide precipitate concentration, mol/L

An alternative rate expression has been presented for the oxidation of Mn²⁺ to MnO₂ using potassium permanganate (Knocke et al., 1991):

$$\begin{aligned} -\frac{d[\text{Mn}^{2+}]}{dt} = & k_1[\text{Mn}^{2+}][\text{KMnO}_4][\text{OH}^-]^{1.1} \\ & + k_2([\text{Mn}^{2+}] - [\text{Mn}^{2+}]_e)[\text{MnO}_2(\text{s})] \end{aligned} \quad (20-17)$$

where k_1 = rate constant for oxidative pathway, $9.55 \times 10^{12} \text{ s}^{-1}$
 $(\text{mol/L})^{-2.1}$

$[\text{Mn}^{2+}]$ = aqueous-phase Mn²⁺ ion concentration, mol/L

$[\text{KMnO}_4]$ = aqueous-phase KMnO₄ concentration, mol/L

$[\text{OH}^-]$ = aqueous-phase hydroxide ion concentration, mol/L
 k_2 = rate constant for autocatalytic pathway, $8.7 \times 10^3 \text{ s}^{-1}$
 $(\text{mol/L})^{-1}$

$[\text{Mn}^{2+}]_e$ = aqueous-phase Mn²⁺ ion concentration in finished water, mol/L

$[\text{MnO}_2(\text{s})]$ = manganese oxide precipitate concentration, mol/L

Similar to Fe^{2+} , the rate of Mn^{2+} oxidation is dependent on P_{O_2} and $[\text{OH}^-]$, as shown in the equation

$$\frac{d[\text{Mn}^{2+}]}{dt} = k_3 P_{\text{O}_2} [\text{OH}^-] [\text{Mn}^{2+}] = k [\text{Mn}^{2+}] \quad (20-18)$$

where k_3 = rate constant, $\text{L}^2/\text{mol}^2 \cdot \text{min} \cdot \text{atm}$

k = pseudo-first-order constant, $\text{min}^{-1} = k_3 P_{\text{O}_2} [\text{OH}^-]$

The oxygenation rate dependence of both Fe^{2+} and Mn^{2+} as a function of pH is shown on Fig. 20-7 (Stumm and Morgan, 1996). The Fe^{2+} and Mn^{2+} states have the same slope but occur at much different pH ranges. The oxidation rate of Mn^{2+} is very low for pH values less than about 9.0. In the pH range encountered in water treatment, the use of oxygenation for the removal of manganese is not practical and alternative oxidants are typically used.

The presence of DOC in the water is not considered in Examples 20-2 and 20-3. Typically, the DOC in natural water will react with Fe^{2+} or Mn^{2+} to form organic complexes. Knocke et al. (1991) found that Mn^{2+} does not appear to be readily complexed by humic and fulvic acids, but Fe^{2+} is readily complexed. Complexed Fe^{2+} is not well oxidized by either KMnO_4 or ClO_2 . However, preliminary studies indicated that alum coagulation may have an important role in the removal of complexed Fe^{2+} .

Treatment Strategies for Iron and Manganese

Several different treatment methods have been used to remove iron and manganese from drinking water supplies, including (1) oxidation using oxygen (aeration), chlorine, chlorine dioxide, potassium permanganate, or ozone followed by precipitate removal by sedimentation and filtration; (2) ion exchange; (3) lime softening; and (4) sequestering chemicals. Design considerations and performance information are provided for each process in the following discussion.

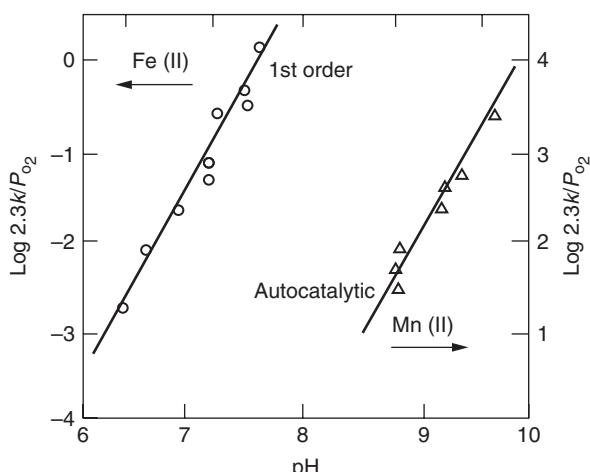


Figure 20-7

Comparison of impact of pH on oxidation rate of Fe^{2+} and Mn^{2+} by oxygen. (Adapted from Stumm and Morgan, 1996.)

Example 20-3 Time required for Mn²⁺ oxidation by potassium permanganate

The flow rate through a treatment process is 10,000 m³/d (2.64 mgd). After removing the soluble iron from groundwater by aeration, 2 mg/L of Mn(II) ion is present. Potassium permanganate (KMnO₄) is added at a dose of 4.0 mg/L (2.53×10^{-5} mol/L) to oxidize Mn(II) ion (Mn²⁺) to a concentration of 0.1 mg/L. The groundwater pH is 7.0 with a temperature of 10°C, and it is assumed that 5 mg/L (5.75×10^{-5} mol/L) of manganese dioxide (MnO₂) is in equilibrium with 0.1 mg/L of Mn²⁺. For steady-state operation, calculate and compare the minimum hydraulic detention time and volume for the oxidation of Mn²⁺ to MnO₂ for a completely mixed flow reactor (CMFR) and for a plug flow reactor (PFR). Assume the [Mn²⁺]_e concentration is zero.

Solution

- Calculate the pseudo-first-order rate constant.
 - Write the rate equation for the oxidation of Mn²⁺. The rate equation for the oxidation of Mn²⁺ to MnO₂ shown in Eq. 20-17 can be simplified to a pseudo-first-order reaction rate as follows:

$$-\frac{d[\text{Mn}^{2+}]}{dt} = k_1[\text{Mn}^{2+}][\text{KMnO}_4][\text{OH}^-]^{1.1}$$

$$+ k_2([\text{Mn}^{2+}] - [\text{Mn}^{2+}]_e)[\text{MnO}_2(\text{s})]$$

$$-\frac{d[\text{Mn}^{2+}]}{dt} = k'[\text{Mn}^{2+}]$$

where k' = pseudo-first-order rate constant

- Determine k' for the given reaction conditions:

$$k' = k_1[\text{KMnO}_4][\text{OH}^-]^{1.1} + k_2[\text{MnO}_2(\text{s})]$$

$$= [9.55 \times 10^{12} \text{ s}^{-1} \cdot (\text{mol/L})^{-2.1}]$$

$$\times (2.53 \times 10^{-5} \text{ mol/L})(10^{-7} \text{ mol/L})^{1.1}$$

$$+ [8.7 \times 10^3 \text{ s}^{-1}(\text{mol/L})^{-1}](5.75 \times 10^{-5} \text{ mol/L})$$

$$= 4.82 + 0.50 = 5.3 \text{ s}^{-1} = 319 \text{ min}^{-1}$$

2. Determine the steady-state residence time and volume for the CMFR using Eq. 6-24.

- a. Determine the steady-state residence time:

$$\tau_{\text{CMFR}} = \frac{[\text{Mn}^{2+}]_0 - [\text{Mn}^{2+}]}{k'[\text{Mn}^{2+}]} = \frac{(2 - 0.1)\text{mg/L}}{(319 \text{ min}^{-1})(0.1 \text{ mg/L})}$$

$$= 5.96 \times 10^{-2} \text{ min}$$

- b. Estimate the CMFR volume:

$$V_{\text{CMFR}} = \tau_{\text{CMFR}} Q$$

$$= (5.96 \times 10^{-2} \text{ min})(10,000 \text{ m}^3/\text{d})(1 \text{ d}/1440 \text{ min})$$

$$= 0.414 \text{ m}^3$$

3. Determine the steady-state residence time and volume for the PFR.

- a. Calculate the required residence time using Eq. 6-70:

$$\tau_{\text{PFR}} = \frac{1}{k'} \ln \left(\frac{[\text{Mn}^{2+}]_0}{[\text{Mn}^{2+}]} \right) = \frac{1}{319 \text{ min}} \ln \left(\frac{2}{0.1} \right) = 9.4 \times 10^{-3} \text{ min}$$

- b. Estimate the required volume:

$$V_{\text{PFR}} = \tau_{\text{PFR}} Q$$

$$= (9.73 \times 10^{-3} \text{ min})(10,000 \text{ m}^3/\text{d})(1 \text{ d}/1440 \text{ min})$$

$$= 0.065 \text{ m}^3$$

OXIDATION WITH AIR

Aeration can be used to provide DO to the water to convert Fe^{2+} and Mn^{2+} to Fe(OH)_3 and MnO_2 , respectively. From a stoichiometric standpoint, 1 mg of oxygen can oxidize 7 mg of soluble Fe^{2+} and 3.4 mg soluble Mn^{2+} (see Tables 20-8 and 20-10). However, the rate of oxidation is slow and not practical for Mn^{2+} at typical pH values for natural waters. Even at a pH of 9.5, it takes about 1 h detention time for Mn^{2+} to oxidize. In comparison, iron can be completely oxidized in about 15 min at pH values around 7.5 to 8.0 when not complexed with NOM.

A number of aeration devices used to supply oxygen to water have been discussed in Chap. 14. Diffused aeration is one process where air diffusers are located along or near the bottom of a tank that is 3 to 5 m (12 to 15 ft) deep. The volumetric air-to-water ratio is typically around 0.75 to 1.0

and the average oxygen transfer efficiency is only around 5 to 10 percent. Diffused aeration is not used very often because it is not very effective in terms of oxygen transfer.

A more commonly used and effective aeration device is the coke tray aerator. This process contains a series of three to five perforated stainless steel trays 0.3 to 0.45 m (1.0 to 1.5 ft) apart that contain 5- to 10-cm-diameter crushed coke or limestone or plastic random packing. The packing provides air–water contact area as the water flows down through the trays while air flows across the trays providing oxygen to the water for oxidation to take place. The water-loading rate is typically around 600 to 800 L/m² · min (15 to 20 gpm/ft²). After a short period of operation, the iron deposits will coat the surface of the coke and assist in the oxidation process. Eventually the oxidation products will build up on the coke and begin to clog the system and the coke must be cleaned or replaced (ASCE/AWWA, 1990). This process is effective for soluble iron removal but not for iron that is organically bound. A baffled basin, which will provide 15 to 30 min additional contact time for oxidation to take place, is used following the aeration device. The oxidized insoluble iron is then removed by filtration. When iron concentrations are greater than 5 mg/L, the addition of alum after aeration followed by flocculation and sedimentation may be required prior to filtration (Kawamura, 2000).

OXIDATION WITH CHLORINE

Traditionally, iron and manganese were controlled using chlorine alone or combined with potassium permanganate under alkaline pH conditions followed by alum coagulation, clarification, and filtration. Free-chlorine doses as high as 5 mg/L have been used effectively to oxidize soluble Fe²⁺ ions as well as organically bound iron. However, in the current regulatory climate using such high doses of chlorine may not be desirable from a disinfection by-product (DBP) formation control standpoint. The stoichiometric reactions for chlorination of Fe²⁺ and Mn²⁺ are shown in Tables 20-8 and 20-10, respectively. Oxidation of Fe²⁺ requires about 0.64 mg chlorine/mg Fe²⁺ while Mn²⁺ oxidation requires 1.29 mg chlorine/mg Mn²⁺. Because the rate of oxidation is pH dependent, a pH of 8.0 to 8.5 is needed to provide Fe²⁺ oxidation times of about 15 to 30 min. Oxidation of Mn²⁺ requires 2 to 3 h and is not effective under these conditions. If ammonia is present in the water, it will consume chlorine and form chloramines, which will significantly reduce the rate of oxidation for both Fe²⁺ and Mn²⁺.

A common process for iron and manganese removal incorporates prechlorination, alum coagulation, sedimentation, and filtration. In this process, the filter media is conditioned with permanganate to form a manganese oxide coating on the surface of the media. The Mn²⁺ and Fe²⁺ will readily adsorb onto the media but can desorb if not oxidized. Chlorine addition just prior to filtration can be used to oxidize the adsorbed Mn²⁺.

and Fe^{2+} and convert them to oxides providing further adsorption sites for oxidation to take place. Any DO in the water can also oxidize adsorbed Fe^{2+} . This process has proven to be effective for Mn^{2+} removal to levels less than 0.02 mg/L and requires minimum process control. The advantage of this process is that the chlorine addition can be easily controlled depending upon the concentration of Mn^{2+} in the water, thus minimizing the formation of DBPs. When Mn^{2+} concentrations in the raw water are low and chlorination is shut off, the oxides will gradually be stripped off but can be reestablished when the chlorine is again added.

OXIDATION WITH CHLORINE DIOXIDE

Chlorine dioxide (ClO_2) is a stronger oxidant than free chlorine and can effectively oxidize soluble Fe^{2+} and Mn^{2+} ions. The observed removal of soluble Mn^{2+} is slightly greater than predicted from the stoichiometry shown in Table 20-10, due to adsorption of Mn^{2+} on the MnO_x solids that are formed during oxidation (Knocke et al., 1991). When the ClO_2 dosages used are greater or equal to the theoretical stoichiometric quantity, the observed Mn^{2+} removal is very close to the theoretical prediction, which is attributed to the adsorbed Mn^{2+} on the MnO_x being oxidized. Overall, the observed oxidation reaction of Mn^{2+} by ClO_2 appears to be a one-electron transfer with chlorite being the oxidant by-product. Oxidation of Fe^{2+} by ClO_2 shows a five-electron transfer resulting in Cl^- being the oxidant by-product. Consequently, the dosage requirement for Fe^{2+} oxidation is about 10 times less than for Mn^{2+} . These results have been verified by tests using ClO_2 as the oxidant (Knocke et al., 1991).

The rate of reaction for Mn^{2+} and Fe^{2+} with ClO_2 is quite fast. In the absence of NOM and for pH values of 5.5 or greater, complete oxidation for Mn^{2+} can occur in about 20 s or less. In the presence of NOM and the same pH range, complete Mn^{2+} oxidation also requires about 20 s. The impact of NOM on Mn^{2+} oxidation is observed to be small, as it does not appear to complex with NOM (Knocke et al., 1991). Oxidation of soluble Fe^{2+} by ClO_2 requires about 5 s at a pH value of 5.5, and faster rates are possible at higher pH values. However, when Fe^{2+} is complexed with NOM, it becomes highly resistant to oxidation and must be removed by other processes that remove NOM, such as coagulation, or activated carbon treatment.

POTASSIUM PERMANGANATE AND GREENSAND FILTRATION

Soluble Fe^{2+} can also be oxidized using KMnO_4 at a similar rate, but the cost of KMnO_4 is higher than the cost of chlorine. Oxidation times for soluble and particulate Mn^{2+} in the presence of NOM are very fast (<20 s) at pH 5.5 and the rate increases as the pH increases. Soluble Fe^{2+} can also be oxidized using KMnO_4 at a similar rate, but because the cost of KMnO_4 is much higher than the cost of chlorine, the process is usually not practical. In applications where Fe^{2+} and Mn^{2+} are both present, Fe^{2+} is usually oxidized first using chlorine followed by the addition of KMnO_4 .

Example 20-4 Stoichiometric calculation for Fe²⁺ oxidation by chlorine

A process treating 100,000 m³/d groundwater containing 5 mg/L of ferrous iron (Fe²⁺) is being treated with chlorine. Calculate the quantity of chlorine required to oxidize ferrous to ferric hydroxide, alkalinity consumed as CaCO₃, and quantity of sludge produced given the oxidation reactions for iron using chlorine as shown in Table 20-8.

Solution

- Determine the quantity of chlorine required using the values for the chlorine reaction shown in Table 20-8:

$$\begin{aligned}\text{Chlorine required} &= (5 \text{ mg Fe}^{2+}/\text{L})(0.64 \text{ mg Cl}_2/\text{mg Fe}^{2+}) \\ &\quad (100,000 \text{ m}^3/\text{d})(10^3 \text{ L/m}^3)(1 \text{ kg}/10^6 \text{ mg}) \\ &= 320 \text{ kg/d}\end{aligned}$$

- Determine the quantity of alkalinity consumed for the chlorine reaction shown in Table 20-8:

$$\begin{aligned}\text{Alkalinity consumed} &= (5 \text{ mg Fe}^{2+}/\text{L})(2.70 \text{ mg alkalinity/mg Fe}^{2+}) \\ &\quad (100,000 \text{ m}^3/\text{d})(10^3 \text{ L/m}^3)(1 \text{ kg}/10^6 \text{ mg}) \\ &= 1350 \text{ kg/d}\end{aligned}$$

- Determine the quantity of sludge produced for the chlorine reaction shown in Table 20-8:

$$\begin{aligned}\text{Sludge produced as Fe(OH)}_3 &= (5 \text{ mg Fe}^{2+}/\text{L})(1.90 \text{ mg sludge/mg Fe}^{2+}) \\ &\quad (100,000 \text{ m}^3/\text{d})(10^3 \text{ L/m}^3)(1 \text{ kg}/10^6 \text{ mg}) \\ &= 950 \text{ kg/d}\end{aligned}$$

for Mn²⁺ oxidation. The oxidation of Fe²⁺ complexed with NOM requires contact times greater than 1 h and oxidant dosages above the theoretical stoichiometric amount. As a result, oxidation with KMnO₄ is not a practical process for removal of Fe²⁺ complexed with NOM.

A typical process for the removal of soluble Fe²⁺ and Mn²⁺ involves adding KMnO₄ as a solution ahead of a filter. After the addition of KMnO₄

and an alkali (if required), the oxidized water is delivered to a specially prepared filter. The contact time after the oxidant addition is typically 5 min at 20°C or 10 min at 1°C which is more than enough time for Fe²⁺ and Mn²⁺ oxidation as mentioned above. The filter media may be natural greensand, but silica sand and/or anthracite may also be used. Silica sand or anthracite are first treated with KMnO₄ to provide a manganese oxide coating on the media. Under normal conditions, the coating can be applied by controlled operation for several days with optimum KMnO₄ feed rates. Partial or marginal treatment may occur during the coating process. Once the coating is applied completely, satisfactory removals are usually maintained. The process is more efficient at pH values above 7.5.

The filtration process generally used for iron and manganese removal is pressure filtration. Filtration and backwash rates typically range from 240 to 480 m/d (4 to 8 gpm/ft²) and 480 to 1200 m/d (8 to 20 gpm/ft²), respectively, depending on the media size, temperature, and supplemental scour. Greensand media require periodic regeneration with a KMnO₄ solution. Greensand filter depths are similar to those used in conventional filtration applications; however, greensand media usually have an effective size less than 0.3 mm.

The applied dose of KMnO₄ should be controlled carefully because permanganate gives an easily detectable pink color in water at concentrations in the 0.05-mg/L range. Controlling the dose range is critical in avoiding consumer complaints. Some waters, such as reservoirs, experiencing periodic hypolimnologic episodes, may have seasonal variations in Mn²⁺. Consequently, bench-and pilot-scale studies are important in determining the required dosing rate associated with these variations.

OXIDATION WITH OZONE

Ozone can be used to oxidize Fe²⁺ and Mn²⁺ but is more costly than other oxidation methods and consequently is not practiced in the United States. However, ozonation has been used successfully in Europe for both Fe²⁺ and Mn²⁺ removal with conventional treatment processes combined with preozonation, and when preozonation is part of a process train for other treatment purposes, Fe²⁺ and Mn²⁺ oxidation occurs as incidental to the primary process purpose. The stoichiometric requirements for oxidation of Fe²⁺ and Mn²⁺ are 0.43 mg O₃/mg Fe²⁺ and 0.87 mg O₃/mg Mn²⁺. Ozonation will not impact the removal of Fe²⁺ complexed with NOM in subsequent conventional processes. Based on practical experience, overdosing with ozone will lead to the formation of various forms of permanganate and, if present, result in a pink color.

ION EXCHANGE PROCESS

Ion exchange processes may be used for removing low concentrations (<0.5 mg/L) of Fe²⁺ and Mn²⁺ from groundwaters. The majority of ion exchange applications for Fe²⁺ and Mn²⁺ are limited to treatment of

Example 20-5 Theoretical stoichiometric calculation for Fe²⁺ and Mn²⁺ removal using KMnO₄

A groundwater containing 5 g/m³ Fe²⁺ and 2 g/m³ Mn²⁺ is processed at a flow rate of 100,000 m³/d. Potassium permanganate (KMnO₄) is used to oxidize the Fe²⁺ and Mn²⁺. Calculate the quantity of potassium permanganate required, alkalinity consumed as CaCO₃, and quantity of sludge produced. Use the oxidation reactions for iron and manganese using KMnO₄ as shown in Tables 20-8 and 20-10, respectively.

Solution

- Determine the quantity of potassium permanganate required.
 - Compute the amount of KMnO₄ needed for Fe²⁺ oxidation for the reaction shown with potassium permanganate in Table 20-8:

$$\begin{aligned} \text{KMnO}_4 \text{ required due to Fe}^{2+} \\ = & (5 \text{ g Fe}^{2+}/\text{m}^3) (0.94 \text{ g KMnO}_4/\text{g Fe}^{2+}) \\ & (100,000 \text{ m}^3/\text{d}) (1 \text{ kg}/10^3 \text{ g}) \\ = & 470 \text{ kg/d} \end{aligned}$$

- Calculate the KMnO₄ required due to Mn²⁺ for the reaction shown with potassium permanganate in Table 20-10:

$$\begin{aligned} \text{KMnO}_4 \text{ required due to Mn}^{2+} \\ = & (2 \text{ g Mn}^{2+}/\text{m}^3) (1.92 \text{ g KMnO}_4/\text{g Fe}^{2+}) \\ & (100,000 \text{ m}^3/\text{d}) (1 \text{ kg}/10^3 \text{ g}) \\ = & 384 \text{ kg/d} \end{aligned}$$

- Calculate the total KMnO₄ required:

$$\text{Total KMnO}_4 \text{ required} = 470 + 384 = 854 \text{ kg/d}$$

- Determine the quantity of alkalinity consumed as CaCO₃.
 - Calculate the quantity of alkalinity consumed due to Fe²⁺ for the reaction shown with potassium permanganate in Table 20-8:

$$\begin{aligned} \text{Alkalinity consumed due to Fe}^{2+} \\ = & (5 \text{ g Fe}^{2+}/\text{m}^3) (1.50 \text{ g alkalinity/g Fe}^{2+}) \\ & (100,000 \text{ m}^3/\text{d}) (1 \text{ kg}/10^3 \text{ g}) \\ = & 750 \text{ kg/d} \end{aligned}$$

- b. Calculate the quantity of alkalinity consumed due to Mn^{2+} for the reaction shown with potassium permanganate in Table 20-10:

Alkalinity consumed due to Mn^{2+}

$$= \left(2 \text{ g } Mn^{2+}/m^3\right) \left(1.21 \text{ g alkalinity/g } Fe^{2+}\right) \\ \left(100,000 \text{ m}^3/d\right) \left(1 \text{ kg}/10^3 \text{ g}\right) \\ = 242 \text{ kg/d}$$

- c. Calculate the total quantity of alkalinity consumed:

$$\text{Total alkalinity consumed} = 750 + 242 \text{ kg/d} = 992 \text{ kg/d}$$

3. Determine the quantity of sludge produced.

- a. Calculate the sludge produced from Fe^{2+} oxidation for the reaction shown with potassium permanganate in Table 20-8:

Sludge produced due to Fe^{2+}

$$= \left(5 \text{ g } Fe^{2+}/m^3\right) \left(2.43 \text{ g sludge/g } Fe^{2+}\right) \\ \left(100,000 \text{ m}^3/d\right) \left(1 \text{ kg}/10^3 \text{ g}\right) \\ = 1215 \text{ kg/d}$$

- b. Calculate the sludge produced from Mn^{2+} oxidation for the reaction shown with potassium permanganate in Table 20-10:

Sludge produced due to Mn^{2+}

$$= \left(2 \text{ g } Mn^{2+}/m^3\right) \left(2.64 \text{ g sludge/g } Fe^{2+}\right) \\ \left(100,000 \text{ m}^3/d\right) \left(1 \text{ kg}/10^3 \text{ g}\right) \\ = 528 \text{ kg/d}$$

- c. Calculate the total sludge produced from Mn^{2+} and Fe^{2+} oxidation:

$$\text{Sludge produced due to } Mn^{2+} = 1215 + 528$$

$$= 1743 \text{ kg dry solids/d}$$

Comment

The values computed in this example were derived from a theoretical stoichiometric calculation point of view. In practical application, Fe^{2+} is usually oxidized first using chlorine followed by the addition of $KMnO_4$ for Mn^{2+} because the cost of $KMnO_4$ is much higher than the cost of chlorine.

industrial water and for point-of-use treatment systems for single-family dwellings using groundwater. Usually a strong-acid cation (SAC) exchange resin in the sodium form is used. The separation factors for several cations for a polystyrene resin sometimes found in groundwater are shown in Table 16-7. The separation factors for Fe^{2+} and Mn^{2+} are slightly lower than for Ca^{2+} , and the Mn^{2+} separation factor is slightly lower than Mg^{2+} . For waters containing moderate to high hardness, Fe^{2+} and Mn^{2+} may be removed, but the regeneration frequency will be higher than for waters that are low in hardness.

The use of SAC resins will not remove Fe^{2+} complexed with NOM; however, SBA resins have been reported to remove up to 95 percent of Fe^{2+} complexed with NOM (Clifford, 1999). The City of Santa Monica, California, removes about 1.0 mg/L of iron from a 30,000-m³/d (7.5-mgd) groundwater flow by a process of aeration and filtration through 0.762 m (30 in.) of ion exchange media. The water is softened in the filtering stage. The principal design parameters for this system include aeration with 10 min contact time and volumetric air-to-water ratio of 0.75; unbaffled contact basin with 60 min contact time; and 9.8 m/h (4 gpm/ft²) filtration rate through a polystyrene resin bed with an effective size of 0.4 mm. The resin requires periodic acid treatment due to fouling of the surface by oxidation. Effective resin life is about 12 years.

MEMBRANE PROCESS

Reverse osmosis membranes can be very effective for the removal of soluble Fe^{2+} and Mn^{2+} . However, as discussed in Chap. 17, even a small amount of oxidized iron and manganese can foul membranes and cause a decrease in their effectiveness. Pretreatment systems are typically used to remove oxidized iron and manganese prior to treatment with RO. In recent work in the Netherlands, it was found that Fe^{2+} and Mn^{2+} were removed effectively when the feed water was under anaerobic conditions (Kartinen and Martin, 2001). Two full-scale RO plants were involved in these studies, with Fe^{2+} concentrations ranging from 11 to 25 mg/L Fe^{2+} . In addition, fouling of the membranes was found to be considerably less under anaerobic operating conditions.

STABILIZATION PROCESS

Stabilization of soluble Fe^{2+} and Mn^{2+} is the opposite of oxidation. The chemical used for stabilization in water treatment is sodium hexametaphosphate ($\text{NaPO}_3)_6$ (SHMP), commonly known as polyphosphate, glassy phosphate, or polysilicate. This chemical is available in crystal, granular, or liquid form and is highly soluble. Chemical addition should occur before the water has a chance to come in contact with air or chlorine to ensure that the Fe^{2+} and Mn^{2+} are still in the soluble state. However, stabilization agents can be aggressive compounds with respect to metals, and

they may dissolve precipitated iron and manganese or promote dissolution of metallic pipe materials.

The high phosphate content (66 percent P₂O₅) of SHMP results in the formation of phosphate as a by-product of the reaction, which can promote biological growth. Where treated water is stored in open reservoirs, SHMP must be used with caution; otherwise, algal blooms and slimes may result. It should also be noted that stabilization does not remove Fe²⁺ and Mn²⁺ but merely holds it in an aesthetically acceptable condition that will degrade with time. Stabilized Fe²⁺ and Mn²⁺ will also appear on analytical tests. Feed rates for SHMP are typically less than 2 mg/L but should be determined by testing. Stabilization may be considered for waters if the Fe²⁺ is in the range of 0.3 to 1.0 mg/L and/or if the Mn²⁺ content is between 0.05 and 0.1 mg/L. The additive demand of polyvalent cations must be considered.

LIME TREATMENT

Lime treatment is effective in removing both Fe²⁺ and Mn²⁺. Excellent removals are obtained if the water is preaerated, the pH exceeds 9.8 during the process, and sufficient alkalinity (>20 mg/L as CaCO₃) is present. Softening is more costly than other processes for Fe²⁺ and Mn²⁺ removal because of the high capital costs. High iron and manganese removals preclude recalcination of lime sludge due to impurity of the sludge.

20-4 Softening

Theoretically, the hardness of water is defined as the sum of the soluble concentrations of polyvalent cations—all expressed as equivalent concentrations of calcium carbonate. *Carbonate hardness* is defined as the concentration of Ca²⁺ and Mg²⁺ and other polyvalent cations in water that are associated with the anions that comprise alkalinity (e.g., HCO₃⁻, CO₃²⁻). Similarly, *noncarbonate hardness* is defined as the concentration of Ca²⁺ and Mg²⁺ and other polyvalent cations in water that are associated with nonalkalinity anions (e.g., SO₄²⁻, Cl⁻). For example, carbonate hardness would be present in water after dissolution of CaCO₃ and MgCO₃, whereas noncarbonate hardness would appear if CaSO₄, CaCl₂, MgSO₄, and MgCl₂ were dissolved in the water. In water treatment, total hardness is usually expressed as the sum of the carbonate hardness and noncarbonate hardness.

Water treatment issues related to hardness removal have traditionally been related to aesthetics, although there is some nutritional benefit. The presence of hardness causes scale in pipes and hot-water heaters, high soap consumption, and the deterioration of fabrics. Removing hardness, termed *softening*, may be accomplished either by chemical precipitation as insoluble compounds, ion exchange, or membrane processes. Hardness has been removed successfully using ion exchange or low-pressure softening membranes. These processes are discussed in Chaps. 16 and 17, respectively.

The purpose of this section is to present the removal of hardness by means of chemical precipitation. Topics to be considered include (1) sources of hardness, (2) occurrence of hardness, (3) chemical precipitation methods, and (4) types of process configurations.

Hardness in natural waters usually comes from the dissolution of minerals from geologic formations that contain calcium and magnesium. Two of the most common forms are calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$]. Calcite, or *chalix*, the Greek word for “lime,” is one of the most common minerals and makes up about 4 percent by weight of the Earth’s crust. Calcite can dissolve in weak acidic environments such as in some groundwaters. Dolomite makes up approximately 2 percent by weight of the Earth’s crust. The mineral was named after French geologist Deodat de Dolomieu (1750–1801). Dolomite does not easily dissolve in acidic environments as calcite and is more often found in tropical marine environments. Groundwaters rich in dissolved magnesium usually contain a significant quantity of salt, which is thought to be essential in the formation of dolomite.

Sources of Hardness

The distribution of hard waters in the United States is shown on Fig. 20-8. Although waters above 150 mg/L hardness (as CaCO_3) are considered very

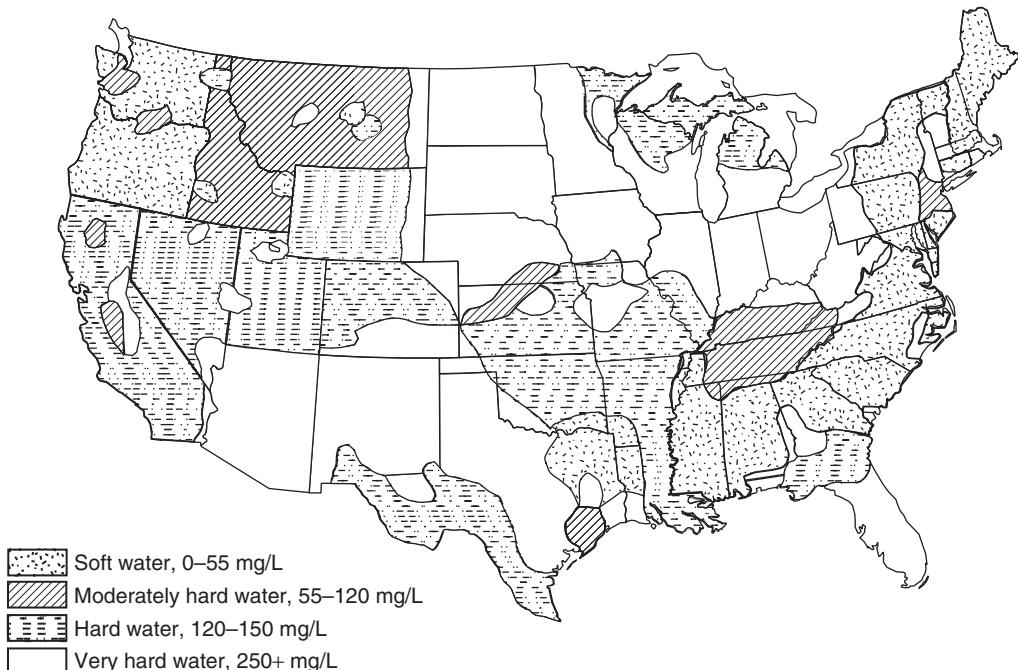


Figure 20-8

Distribution of hard water in United States. The areas shown define approximate hardness values for municipal water supplies. (Reprinted with permission from Ciaccio, 1971.)

hard, many utilities do not soften the water. Some utilities soften water when the total hardness exceeds 150 mg/L. The finished water hardness produced by a utility softening plant may vary from a low of 50 mg/L to a high of 150 mg/L depending upon the process configuration, economics, and public acceptance. A historical goal has been between 80 and 100 mg/L for both aesthetics and corrosion control (AWWA, 1969).

Softening by Chemical Precipitation

Precipitation softening relies on the relative insolubilities of calcium carbonate and magnesium hydroxide. The choice of precipitating chemicals depends upon the raw-water quality, which complicates the selection of the optimum treatment process, although the chemistry is straightforward. The equilibrium solubilities of calcium carbonate and magnesium hydroxide for typical water chemistry are shown on Figs. 20-9 and 20-10. As shown,

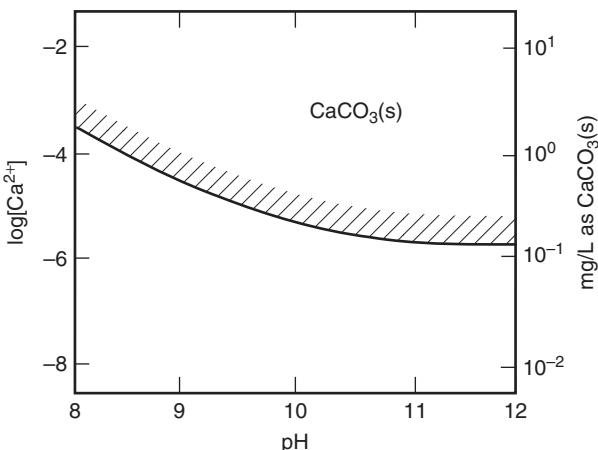


Figure 20-9
Solubility of CaCO_3 as function of pH ($K_{\text{sp}} = 4 \times 10^{-9}$); $C_T = 2 \times 10^{-3} \text{ mol/L}$.

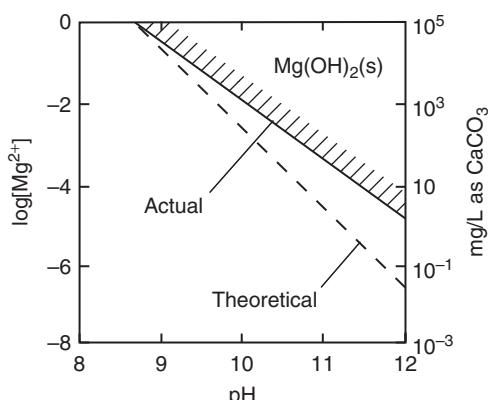


Figure 20-10
Solubility of $\text{Mg}(\text{OH})_2$ as function of pH ($K_{\text{sp}} = 2.5 \times 10^{-11}$).
Solid line is for solubility in 23 waters determined by Thompson et al. (1972).

within the normal concentration range of each cation and pH found in water treatment, it is necessary to increase the pH for both calcium and magnesium precipitation. The chemicals most commonly used to precipitate calcium and magnesium are lime and caustic soda. The choice of the two depends upon the water quality and economics. When the carbonate hardness is adequate, the softening required can be accomplished by pH adjustment alone, and both calcium carbonate and magnesium hydroxide can be precipitated.

When carbonate hardness is too low, the carbonate content must be supplemented by soda ash (sodium carbonate). The minimum hardness that can be achieved depends on the solubilities of the calcium carbonate and magnesium hydroxide at the pH of softening as well as the subsequent processes. Lime–soda ash softening has been a traditional process for the removal of hardness, consisting of both carbonate and noncarbonate hardness, from water supplies.

Lime is sold commercially in the forms of quicklime and hydrated lime. Quicklime is granular and usually greater than 90 percent CaO with magnesium oxide the primary impurity. Although quicklime is less expensive than hydrated lime, it must be hydrated or slaked to $\text{Ca}(\text{OH})_2$ before it is used for softening. Quicklime is usually crushed in a slaker and fed to form a slurry containing about 5 percent calcium hydroxide. Powdered, hydrated lime contains about 70 percent $\text{Ca}(\text{OH})_2$ and is prepared for use in the softening process by fluidizing in a tank containing a turbine mixer. Soda ash is a grayish-white powder and is nearly 98 percent sodium carbonate. Soda ash may be added simultaneously with lime to the treatment train or it may be added sequentially, following the addition of lime.

Aside from eliminating the aesthetic problems associated with hardness, lime softening has many potential health benefits as well. The use of lime softening can effectively remove heavy metals (e.g., lead, chromium, mercury, arsenic), iron and manganese, turbidity, and some organic compounds including a substantial amount of NOM and kill algae, bacteria, and viruses. More recently, the U.S. EPA has termed a variation of the lime-softening process as *enhanced softening* because the TOC removals can be as high as 40 to 80 percent depending upon the pH. When TOC removals are high, significant control of THMs and HAAs can be achieved when using chlorine for disinfection.

The principal reactions involved in the precipitation of hardness depend on whether the hardness is carbonate or noncarbonate. Chemical reactions for the removal of carbonate and noncarbonate hardness are presented and discussed below, along with treatment process options.

Chemistry of Water Softening by Precipitation

LIME SOFTENING: CARBONATE HARDNESS

The chemical reactions for lime softening are



When lime is added to water, it will first react with any free CO_2 , forming a calcium carbonate precipitate as shown in Eq. 20-19, and does not reduce any hardness. This reaction will take place first as CO_2 is a stronger acid than HCO_3^- . The conversion of bicarbonate to carbonate as a function of pH is shown on Fig. 20-11. Complete conversion would require a pH value greater than 12 to attain complete utilization of the bicarbonate alkalinity for calcium precipitation, as shown on Fig. 20-11. In practice, when alkalinity is present as bicarbonate, the optimum pH for maximum calcium carbonate precipitation may be as low as 9.3 because a significant amount of carbonate is in equilibrium with bicarbonate and more carbonate is formed as precipitation occurs.

The overall reaction for the removal of magnesium when alkalinity is present as bicarbonate (i.e., magnesium carbonate hardness) is given by Eq. 20-21. Based on practical experience, it has been found that a pH value of at least 10.5 or greater is required for effective Mg(OH)_2 precipitation. The range of lime dosages in excess of the stoichiometric amount required to raise the pH for precipitation of MgCO_3 as Mg(OH)_2 has been reported to be from 30 to 70 mg/L as CaCO_3 (Degrémont, 2007; Faust and Aly, 1998; Hammer and Hammer, 2001). Jar testing is recommended to obtain

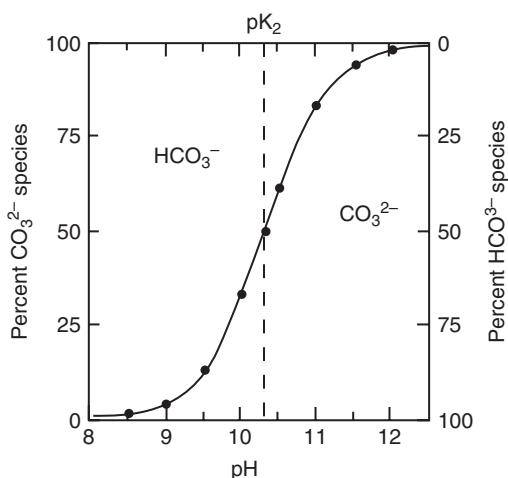


Figure 20-11

Distribution of carbonate and bicarbonate species as function of pH (25°C).

a more precise amount of excess lime required for effective $Mg(OH)_2$ precipitation for a given water source.

LIME-SODA SOFTENING: CARBONATE AND NONCARBONATE HARDNESS

Sometimes there may be a lack of carbonate alkalinity present to react with the lime and it becomes necessary to add an external source. Typically, soda ash, Na_2CO_3 , is used, as shown in the reaction

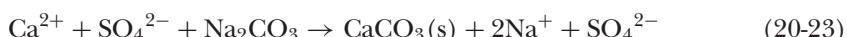
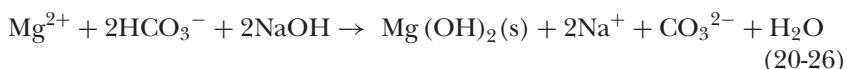
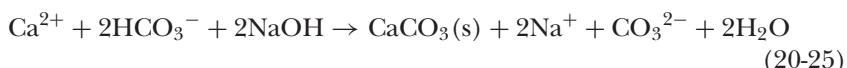


The calcium noncarbonate hardness in Eq. 20-23 may be present in the untreated water or may result from the precipitation of magnesium non-carbonate hardness, as shown in Eq. 20-22. For both reactions, the amount of soda ash required depends upon the amount of noncarbonate hardness to be removed.

CAUSTIC SODA SOFTENING: CARBONATE AND NONCARBONATE HARDNESS

Caustic soda ($NaOH$) is an alternative to the use of lime softening when there is insufficient carbonate hardness present in the raw water to react with lime. The choice between using soda ash and caustic soda will depend upon the economics and other factors such as the ease of handling ($NaOH$ is purchased as a 50 percent solution) and magnesium content. Some concern has been expressed about the use of sodium-containing compounds because, when noncarbonate hardness is removed, both use of soda ash and caustic soda result in the replacement of the divalent hardness ions with sodium.

The reactions for caustic soda are

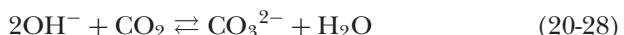


In Eqs. 20-24, 20-25, and 20-26 the sodium carbonate that is formed is available for calcium carbonate precipitation. In situations where more sodium carbonate is formed than there is calcium noncarbonate hardness to remove, the excess must remain in solution. This presents a problem of very high carbonate alkalinity, which can be reduced by acidification, but none of the excess sodium will precipitate. In contrast, when lime is used, the excess calcium is precipitated as the carbonate. Calcium carbonate precipitation is particularly important in those cases where high pH (and

the concomitant high caustic alkalinity) must be attained to precipitate magnesium as $\text{Mg}(\text{OH})_2$.

RECARBONATION: PH ADJUSTMENT

When the pH of the water after softening is greater than the saturation pH (pH_s), it is necessary to reduce the pH. The addition of CO_2 is the most common and economical method for precipitation of excess calcium and pH reduction. When excess caustic (noncarbonate) alkalinity is present, the following reaction occurs:

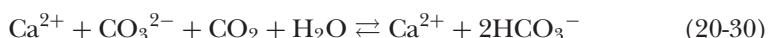


When CO_3^{2-} is formed, it will react to precipitate any calcium that is present above the saturation of calcium carbonate. Adding additional CO_2 will then lower the pH to a point of saturation equilibrium, as shown in the reaction

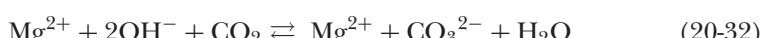
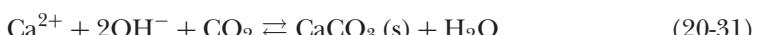


Historically, CO_2 was produced by the combustion of diesel fuel or natural gas either under water or in external burners, but the combustion process only yields about 12 percent CO_2 . Bulk pressurized/liquefied CO_2 is now commonly available and widely used because it is more convenient and the operation and maintenance problems associated with CO_2 generation are eliminated.

In the case of waters that only require selective calcium removal, the lime-treated water will be supersaturated with calcium carbonate and the pH will be between 10.0 and 10.6. The addition of carbon dioxide to the water will convert the carbonate ions, to bicarbonate ions, as shown by the reaction

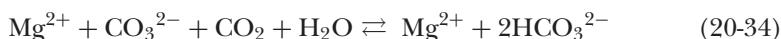


For waters that require calcium and magnesium removal, excess lime is added to precipitate the magnesium carbonate as magnesium hydroxide at a pH above 11.0. Enough carbon dioxide is needed to convert the excess hydroxide ions to carbonate ions and then all the carbonate ions to bicarbonate ions. Conversion of the excess hydroxide ions to carbonate ions will drop the pH to about 10.0 to 10.5, and the calcium hydroxide is converted to calcium carbonate precipitate and the magnesium hydroxide is converted to soluble magnesium carbonate (if it has not been removed), as shown in the reactions (Benefield and Morgan, 1999)



As stated above, additional carbon dioxide is required to lower the pH to about 8.4 to 8.6 (Benefield and Morgan, 1999). In this case, the calcium carbonate that was precipitated will dissolve in the bicarbonate form and

the magnesium carbonate will also convert to the bicarbonate form, as shown by the reactions



In a water treatment plant, the recarbonation process may take place in single or double stages. The double-stage process, sometimes called the “split recarbonation” process, according to Eqs. 20-29 and 20-30, is only practiced in a few plants as it is much more mechanically and land intensive than a single-stage process. However, the water quality produced by the two-stage process is softer and lower in alkalinity than single-stage softening when magnesium reduction is desired.

When the softened water contains little or no excess caustic alkalinity, only single-stage recarbonation is possible. It is used to reduce the pH to the saturation pH. Usually the final pH is around 8.5 to 9.0.

As discussed in Chap. 10, reactor/clarifiers and sludge blanket clarifiers are typically used for lime-softening plants. For these systems, flocculation and sedimentation times are around 20 min and 1 to 2 h, respectively. Based on kinetic studies, it has been found that about 20 to 30 min of contact time is required for Ca^{2+} to precipitate as $\text{CaCO}_3(\text{s})$ and approach equilibrium conditions (Alexander and McClanahan, 1975). The pH is also a factor in the kinetics of Ca^{2+} precipitation, as the kinetics of CaCO_3 formation increase with an increase in pH in the range of 9.0 to 12 (Faust and Aly, 1998). Recycling CaCO_3 sludge to provide a seeding effect for Ca^{2+} precipitation will increase the kinetics of CaCO_3 formation in a significant way.

The kinetics of recarbonation are more efficient than CaCO_3 precipitation and contact times in the CO_2 diffusion and recarbonation tanks are typically a minimum of 3 and 20 min, respectively. A typical basin has baffled channels and walls and is about 3.7 m (12 ft) deep.

For the softening processes describe above, there are several process trains that are used in practice. Specific process train selection depends upon the raw-water quality and the treated-water quality objectives. Single-stage, two-stage, and split-stream treatment softening are discussed below.

SINGLE-STAGE SOFTENING

Single-stage softening, sometimes called *undersoftening*, is used for waters that do not require the removal of magnesium hardness. A typical process schematic of the single-stage process is shown on Fig. 20-12a. Lime is added to the raw water either upstream of the reactor/clarifier in a separate flash mix process or into the reactor/clarifier. Flash mixers are used because mixing with a conventional mechanical mixer will cause precipitation

Kinetics of Lime Softening and Recarbonation

Types of Softening Process Configurations

formation on the blades, resulting in the dislodging and release of CaCO_3 . The pH of the water leaving the flash mixer is about 10.2 to 10.5. Soda ash can be added in the flash mix if noncarbonate hardness is present either with the lime or sequentially after the lime has been added.

As discussed in Chap. 10 (see Table 10-8), reactor/clarifiers and sludge blanket clarifiers are typically used for water-softening processes. Where reactor/clarifiers are used, lime sludge is frequently recycled to the head of the process train to improve the efficiency of the softening process. This recycle provides a seeding effect for the CaCO_3 particles to flocculate.

Following sedimentation, the lime-treated water will pass through a recarbonation reactor where the addition of CO_2 is used to reduce the pH from 10.2 to 10.5 to around 8.7 to 9.0. After recarbonation, particles that may form are removed by filtration. The water is usually softened to a final hardness of about 70 to 100 mg/L as CaCO_3 and it is very close to the pH_s value. Sometimes postchlorination is sufficient to reduce the pH to the pH_s , eliminating the need for the recarbonation step.

TWO-STAGE SOFTENING

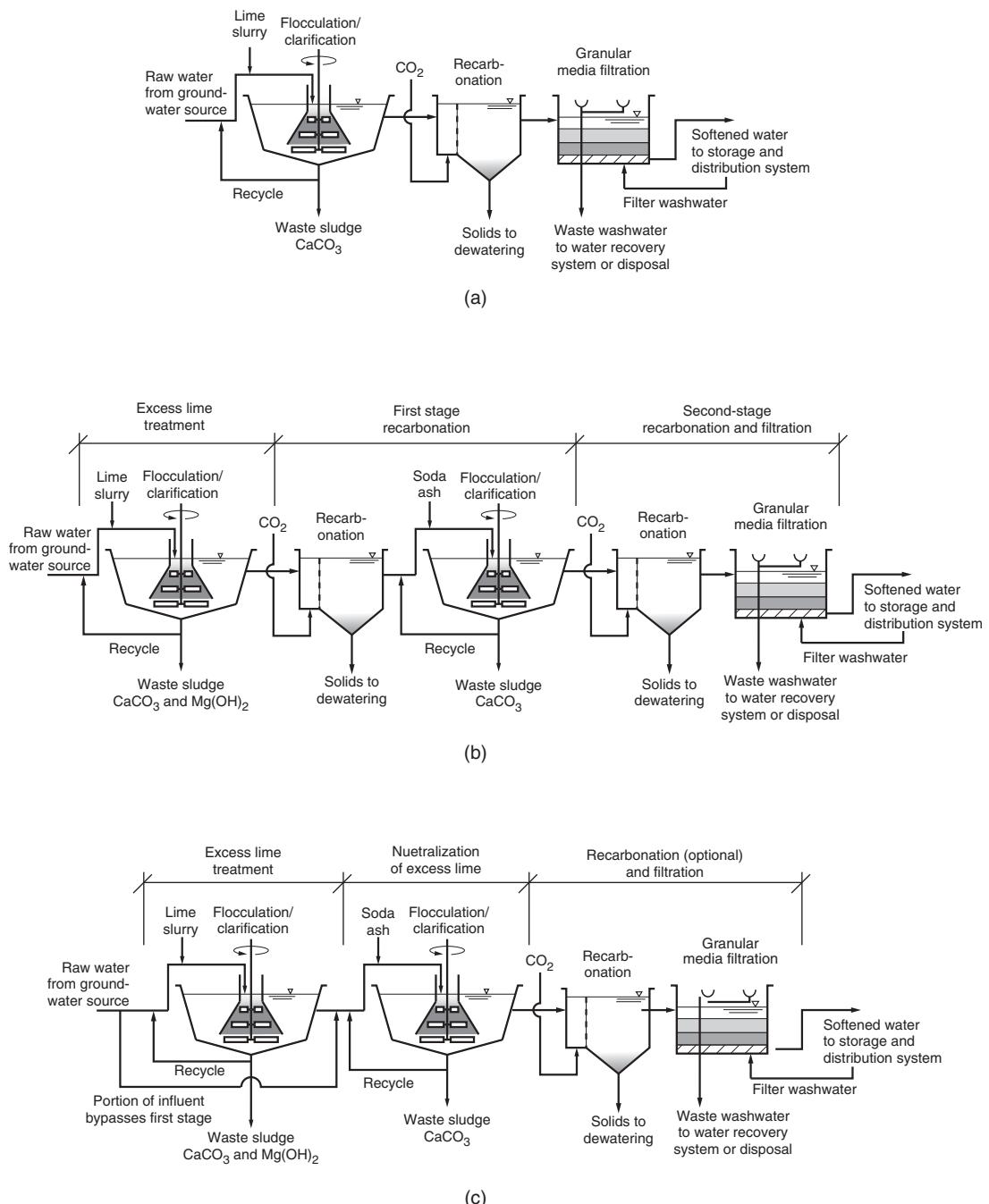
Sometimes postchlorination is sufficient to reduce the pH to the saturation pH (pH_s), eliminating the need for the recarbonation step. A schematic of the split recarbonation process is shown on Fig. 20-12b. Excess lime is added with a flash mixer to raise the pH to 11.0 or higher to precipitate magnesium. After sedimentation, CO_2 recarbonation is used to reduce the pH to about 10.0 to 10.6 and soda ash is added to precipitate the excess lime added for magnesium removal. The second-stage precipitation step is followed by sedimentation and then the second stage of CO_2 recarbonation is used to lower the pH value around 8.3 to 8.5. Filtration is used to remove any particles formed from the second recarbonation step.

SPLIT-TREATMENT SOFTENING

Split-treatment configurations consist of separating the process water into two or more streams, treating the streams to various degrees with different process treatment techniques, and then blending them to obtain the desired effluent water quality. Three split-stream configurations that have been practiced are (1) parallel softening and coagulation, (2) parallel lime softening and ion exchange or reverse osmosis, and (3) split treatment with excess lime. The first two processes are discussed briefly first, as they are used less frequently, followed by a more detailed discussion of the split treatment with excess lime process.

PARALLEL SOFTENING AND COAGULATION

For waters high in magnesium, turbidity, and/or color, parallel softening and coagulation can sometimes be economical and cost effective. In this process, part of the water to be treated is softened with excess lime to remove calcium and magnesium hardness. The remaining part of the water to be treated is coagulated to remove turbidity and color and as a result will

**Figure 20-12**

Process flow diagrams of common softening treatment techniques: (a) single-stage lime treatment; (b) two-stage excess lime–soda treatment, and (c) split-flow lime treatment.

be low in alkalinity. The waters are then blended to a balance of good color, turbidity, and hardness. A third stream has also been used in some cases to provide additional hardness for neutralization of excess caustic alkalinity in the softened water stream.

PARALLEL LIME SOFTENING AND ION EXCHANGE OR REVERSE OSMOSIS

This process modification can be used to soften raw waters with high noncarbonate and dissolved solids concentrations. Part of the water stream is treated with lime softening and the other part is softened with ion exchange or reverse osmosis. The use of ion exchange can be attractive when there is high noncarbonate hardness in the raw water, when the use of soda ash or caustic soda would not be economical, or in the case of an existing ion exchange plant. Reverse osmosis can be used instead of ion exchange for demineralization if the raw water requires additional reduction in dissolved solids.

SPLIT TREATMENT WITH EXCESS LIME

This process is used when magnesium must be reduced and the raw water contains very little noncarbonate hardness. A schematic of the excess lime split-stream process is shown on Fig. 20-12c. Part of the water is treated with excess lime softening for both calcium and magnesium hardness removal. In this part, the magnesium hardness can be removed down to its practical solubility limit of 10 mg/L. The other part of the water is bypassed and blended with the softened water prior to sedimentation. The alkalinity of the bypassed raw water is used to neutralize the excess caustic alkalinity required to reduce the magnesium in the treated water. Because the free carbon dioxide in the bypassed water is used to neutralize the excess lime of the processed stream, a recarbonation step is usually not needed. When the treatment objective of magnesium is chosen, a mass balance on the magnesium is used to determine the ratio of the bypass to treated flow, as given by the equation

$$X = \frac{[\text{Mg}^{2+}]_e - [\text{Mg}^{2+}]_t}{[\text{Mg}^{2+}]_0 - [\text{Mg}^{2+}]_t} \quad (20-35)$$

where

X = ratio of bypassed flow

$[\text{Mg}^{2+}]_e$ = magnesium hardness concentration, mg/L as CaCO_3 in finished water (Typically magnesium hardness is less than 50 mg/L as CaCO_3 such that the level of total hardness in the finished water is less than 80 to 100 mg/L as CaCO_3)

$[\text{Mg}^{2+}]_0$ = magnesium hardness concentration (mg/L as CaCO_3) in raw water

$[\text{Mg}^{2+}]_t$ = magnesium hardness concentration (mg/L as CaCO_3) in excess lime treated water before blending

Split treatment works best for groundwaters. For surface waters, where color, taste, and odor may cause problems, the two-stage process is usually

preferred. As discussed above, total hardness levels up to 120 mg/L as CaCO₃ are acceptable by some consumers so the calcium hardness in the finished water can be as high as 80 mg/L as CaCO₃.

An estimate of the chemical dosages for lime softening can be made using a number of different methods: (1) chemical stoichiometry, (2) the solution of simultaneous equilibria equations, (3) the use of softening diagrams, and (4) laboratory studies. All have applications in estimating chemical dosages with experimental methods providing results that most closely approximate plant performance. The chemical stoichiometry is typically used to obtain predesign information for planning and preliminary cost estimation. The solution of simultaneous equilibria equations is usually more rigorous as it involves numerical solution of a series of simultaneous equilibrium expressions. A number of programs such as RIDEQL, the MINEQL series, and the WATEQ series developed by the U.S. Geological Survey (Ball et al., 1979) can be used. These programs are typically used for research in the area of equilibrium and kinetics. The use of softening diagrams involves the use of Caldwell–Lawrence (CL) diagrams for estimating chemical dosages for the lime-softening process (Caldwell and Lawrence, 1953; Lowenthal and Marias, 1976; Merrill and Sanks, 1977). These diagrams were developed to enable equilibrium calculations to be made with less special training. A good discussion and application of this approach have been presented elsewhere (Benefield and Morgan, 1999; Sanks, 1978). The fourth approach, laboratory studies, is discussed in Chap. 9. Estimating chemical dosages for softening based on stoichiometry is illustrated below.

Chemical Dose Calculations for Lime–Soda Ash Softening

CHEMICAL DOSAGES BASED ON STOICHIOMETRY

The stoichiometric method is based on the assumption that all of the relevant reactions go to completion. Corrections can be made for the solubility of calcium carbonate and for the excess hydroxide alkalinity required for magnesium hydroxide precipitation. The chemical requirements can be estimated using the guidelines presented in Table 20-11. The guidelines were developed based on the stoichiometric expressions discussed previously (Eqs. 20-19 through 20-35) and the discussion of various lime-softening processes. The lime required as 100 percent CaO is calculated by noting that it serves the function of CO₂ removal, bicarbonate conversion to carbonate, and magnesium reduction. Use of the information in Table 20-11 for estimating the chemical dosages required for the various lime-softening processes is illustrated in Examples 20-6 and 20-7.

The soda ash requirement can be estimated from Eq. 20-23 by noting that soda ash is used only for noncarbonate hardness reduction because it requires about 1.9 times as much 100 percent Na₂CO₃ as 100 percent CaO to remove the same amount of hardness. Further, because soda ash is more expensive on a mass basis than CaO, it is desirable to minimize the amount of soda ash used (i.e., the amount of noncarbonate hardness

Table 20-11Summary of chemical dosage calculations required for lime and lime-soda ash softening^a

Process	Required Chemical Dosage Calculations
Single-stage lime: For waters with high calcium, low magnesium, and carbonate hardness	<p>Lime addition for softening: $\text{CaO} = \{\text{carbonic acid concentration}\} + \{\text{calcium carbonate hardness}\}$</p> <p>Soda ash addition for softening: $\text{Na}_2\text{CO}_3 = \text{none}$</p> <p>Carbon dioxide for pH adjustment after softening: $\text{CO}_2 = \left\{ \begin{array}{l} \text{estimated} \\ \text{carbonate alkalinity} \\ \text{of softened water} \end{array} \right\} = \left\{ \begin{array}{l} \text{source} \\ \text{water} \\ \text{alkalinity} \end{array} \right\} - \left\{ \begin{array}{l} \text{source} \\ \text{water calcium} \\ \text{hardness} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual} \\ \text{calcium hardness} \\ \text{of softened water} \end{array} \right\}$</p>
Excess lime: for waters with high calcium, high magnesium, and process may be one or two stages	<p>Lime addition for softening: $\text{CaO} = \left\{ \begin{array}{l} \text{carbonic acid} \\ \text{concentration} \end{array} \right\} + \left\{ \begin{array}{l} \text{total} \\ \text{alkalinity} \end{array} \right\} + \left\{ \begin{array}{l} \text{magnesium} \\ \text{hardness} \end{array} \right\} + \left\{ \begin{array}{l} \text{excess} \\ \text{lime dose} \end{array} \right\}$</p> <p>Soda ash addition for softening: $\text{Na}_2\text{CO}_3 = \text{none}$</p> <p>Carbon dioxide for pH adjustment after softening: $\text{CO}_2 = \left\{ \begin{array}{l} \text{source} \\ \text{water} \\ \text{alkalinity} \end{array} \right\} - \left\{ \begin{array}{l} \text{source} \\ \text{water total} \\ \text{hardness} \end{array} \right\} - \left\{ \begin{array}{l} \text{excess} \\ \text{lime} \\ \text{dose} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual} \\ \text{calcium hardness} \\ \text{of softened water} \end{array} \right\} + 2 \left\{ \begin{array}{l} \text{excess} \\ \text{lime} \\ \text{dose} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual} \\ \text{magnesium hardness} \\ \text{of softened water} \end{array} \right\}$</p>
Single-stage lime-soda ash: for water with high calcium, low magnesium, and carbonate and noncarbonate hardness	<p>Lime addition for softening: $\text{CaO} = \{\text{carbonic acid concentration}\} + \{\text{calcium carbonate hardness}\}$</p> <p>Soda ash addition for softening: $\text{Na}_2\text{CO}_3 = \{\text{calcium noncarbonate hardness}\} \text{ and/or } \{\text{magnesium noncarbonate hardness}\}$</p> <p>Carbon dioxide for pH adjustment after softening: $\text{CO}_2 = \left\{ \begin{array}{l} \text{source} \\ \text{water} \\ \text{alkalinity} \end{array} \right\} + \left\{ \begin{array}{l} \text{soda} \\ \text{ash} \\ \text{dose} \end{array} \right\} - \left\{ \begin{array}{l} \text{source} \\ \text{water} \\ \text{calcium} \\ \text{hardness} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual} \\ \text{calcium hardness} \\ \text{of softened water} \end{array} \right\}$</p>

Excess lime-soda ash: for waters with high calcium, high magnesium, and carbonate and noncarbonate hardness; process may be one or two stages

Lime addition for softening:

$$\text{CaO} = \left\{ \begin{array}{l} \text{carbonic acid concentration} \\ \text{calcium carbonate concentration} \end{array} \right\} + 2 \left\{ \begin{array}{l} \text{magnesium carbonate hardness} \\ \text{magnesium noncarbonate hardness} \end{array} \right\} + \left\{ \begin{array}{l} \text{excess lime requirement} \end{array} \right\}$$

Soda ash addition for softening:

$$\text{Na}_2\text{CO}_3 = \left\{ \begin{array}{l} \text{calcium noncarbonate hardness} \\ \text{magnesium noncarbonate hardness} \end{array} \right\}$$

Carbon dioxide for pH adjustment after softening:

$$\text{CO}_2, \text{ first stage} = \left\{ \begin{array}{l} \text{estimated hydroxide alkalinity of softened water} \end{array} \right\} = \left\{ \begin{array}{l} \text{excess lime dose} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual magnesium hardness of softened water} \end{array} \right\}$$

$$\text{CO}_2, \text{ second stage} = \left\{ \begin{array}{l} \text{estimated hydroxide alkalinity of softened water} \end{array} \right\} = \left\{ \begin{array}{l} \text{source water alkalinity} \end{array} \right\} + \left\{ \begin{array}{l} \text{soda ash dose} \end{array} \right\} - \left\{ \begin{array}{l} \text{source water total hardness} \end{array} \right\}$$

$$+ \left\{ \begin{array}{l} \text{estimated residual hardness of softened water} \end{array} \right\}$$

^aAll quantities are expressed as mg/L as CaCO₃.

removed). Minimizing the use of soda ash can be done by reducing the residual carbonate hardness to a minimum or allowing the hardness of the finished water to be higher or both.

Example 20-6 Single-stage selective calcium removal

A 50-ML/d raw-water source is to be softened to reduce the hardness. The mineral analysis of the raw water is given below. The average raw-water temperature and pH were found to be 10°C and pH 7.0, respectively. Using the given information, determine the total, carbonate, and noncarbonate hardness present in the raw and finished waters; the kilograms per day of lime, soda ash, and CO₂ needed for selective calcium softening; and the kilograms per day of CaCO₃ solids produced. Draw the initial and final bar diagrams of the raw and softened water. Assume the residual calcium hardness in the softened water is 30 mg/L as CaCO₃.

Constituent	Unit	Value
H ₂ CO ₃ *	mg/L	72
Ca ²⁺	mg/L	75
Mg ²⁺	mg/L	6.1
Na ⁺	mg/L	36.8
Alkalinity	mg/L as CaCO ₃	195
SO ₄ ²⁻	mg/L	60
Cl ⁻	mg/L	25

Solution

- Develop a summary table for the chemical constituents and the conversion of all the concentrations to meq/L and mg/L as CaCO₃:

Chemical Constituent	Concentration, mg/L	Equivalent	Molecular Weight	Equivalent Weight	Concentration, meq/L	mg/L as CaCO ₃
H ₂ CO ₃ *	72.0	2	62.0	31.0	2.32	116.0
Ca ²⁺	75.0	2	40.0	20.0	3.75	187.5
Mg ²⁺	6.1	2	24.4	12.2	0.50	25.0
Na ⁺	36.8	1	23.0	23.0	1.60	80.0
Total cation					5.85	292.5
Alk (HCO ₃)	195.0	2	100.0	50.0	3.90	195
SO ₄ ²⁻	60.0	2	96.0	48.0	1.25	62.5
Cl ⁻	25.0	1	35.5	35.5	0.70	35
Total anion					5.85	292.5

As a check, the constituent anions and cations should balance as shown.

2. Construct a bar diagram of the raw water that includes the chemical constituents that are important for softening. In the development of the bar diagrams, the cation constituents are placed on the top of the diagram and the anions are placed on the bottom. In relationship to the order of cations to anions on the bar diagram, they are placed according to their reactivity to lime. For example, as stated above, lime will first react with H_2CO_3^* ($[\text{CO}_2]_{\text{aq}}$) followed by HCO_3^- and then the rest of the nonreacting anions. The order for the cations is Ca^{2+} followed by Mg^{2+} and then the rest of the cations as shown below.

		116	0.0		187.5	212.5		292.5
H_2CO_3^*			Ca^{2+}		Mg^{2+}		Na^+	
			HCO_3^-			SO_4^{2-}		Cl^-
		116	0.0		195	257.5		292.5

3. Determine the total hardness, carbonate hardness, and noncarbonate hardness.

- a. The total hardness can be calculated from the table as the sum of the calcium and magnesium ions as CaCO_3 or taken directly from the bar chart:

$$\text{Total hardness} = (187.5 + 25) = 212.5 \text{ mg/L as CaCO}_3$$

- b. The carbonate hardness is simply the sum of the calcium and magnesium ions associated with bicarbonate ions. From the bar diagram of the raw water, all the calcium is associated with bicarbonate and only a small amount of the magnesium is associated with the rest of the bicarbonate. Because all the bicarbonate is associated with calcium and magnesium, the carbonate hardness is simply equal to bicarbonate alkalinity as CaCO_3 as shown by the following:

$$\begin{aligned}\text{Carbonate hardness} &= 187.5 + (195 - 187.5) \\ &= 195 \text{ mg/L as CaCO}_3\end{aligned}$$

- c. From the bar chart, the noncarbonate hardness is simply the magnesium ions not associated with carbonate hardness:

$$\begin{aligned}\text{Noncarbonate hardness} &= 212.5 - 195.0 \\ &= 17.5 \text{ mg/L as CaCO}_3\end{aligned}$$

4. Calculate the lime, soda ash, and carbon dioxide dosages required for selective calcium softening.
- From Table 20-11, the lime requirement for single-stage treatment is given as

$$\text{CaO required} = \text{carbonic acid concentration} \\ + \text{calcium carbonate hardness concentration}$$

or from the bar diagram:

$$\begin{aligned}\text{CaO required} &= [(116 \text{ mg CaCO}_3/\text{L}) + (187.5 \text{ mg CaCO}_3/\text{L})] \\ &\quad \times (28 \text{ mg CaO}/50 \text{ mg CaCO}_3) \\ &= 170 \text{ mg/L} \\ &= (170 \text{ mg CaO/L}) (1 \text{ kg}/10^6 \text{ mg}) (50 \times 10^6 \text{ L/d}) \\ &= 8500 \text{ kg/d}\end{aligned}$$

- Because there is sufficient alkalinity to precipitate calcium, no soda ash is required.
- From Table 20-11, the carbon dioxide requirement for selective calcium removal is equal to the estimated carbonate alkalinity of the softened water:

Estimated carbonate alkalinity of softened water

$$\begin{aligned}&= \text{source water alkalinity} \\ &- \text{source water calcium hardness} \\ &+ \text{estimated residual calcium hardness of softened water}\end{aligned}$$

Assuming the residual calcium hardness in the softened water is 30 mg/L as CaCO₃, the CO₂ can be calculated as

Estimated carbonate alkalinity of softened water

$$\begin{aligned}&= (195 - 187.5 + 30.0) \text{ mg CaCO}_3/\text{L} \\ &= 37.5 \text{ mg CaCO}_3/\text{L}\end{aligned}$$

CO₂ required

$$\begin{aligned}&= (37.5 \text{ mg CaCO}_3/\text{L}) \\ &\quad \times (22.0 \text{ mg CO}_2/50 \text{ mg CaCO}_3) = 16.5 \text{ mg/L} \\ &= (16.5 \text{ mg CO}_2/\text{L}) (1 \text{ kg}/10^6 \text{ mg}) (50 \times 10^6 \text{ L/d}) \\ &= 825 \text{ kg/d}\end{aligned}$$

5. Determine the quantity of precipitated solids. The quantity of precipitated solids will be equal to the sum of the H_2CO_3^* precipitated as CaCO_3 (see Eq. 20-19) and two times the calcium carbonate hardness precipitated as CaCO_3 (see Eq. 20-20) because an equivalent amount of lime was added to remove the calcium as bicarbonate, minus the solubility of CaCO_3 :

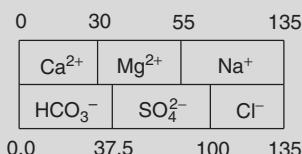
$$\begin{aligned}\text{CaCO}_3 \text{ solids produced} &= [(116.0 + 2 \times 187.5 - 30.0) \text{ mg CaCO}_3/\text{L}] \\ &\quad \times 1 \left(1 \text{ kg}/10^6 \text{ mg} \right) \left(50 \times 10^6 \text{ L/d} \right) \\ &= 23,050 \text{ kg/d}\end{aligned}$$

6. Calculate the total, carbonate, and noncarbonate hardness present in finished water. In this water, the final hardness will be the sum of the soluble calcium and the magnesium carbonate hardness plus the magnesium noncarbonate hardness:

$$\begin{aligned}&\text{Total final hardness of softened water} \\ &= [(30 + 7.5) + (17.5)] \text{ mg/L} \\ &= 55 \text{ mg/L as CaCO}_3\end{aligned}$$

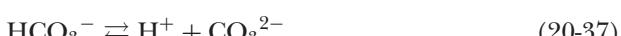
$$\begin{aligned}&\text{Final noncarbonate hardness of softened water} \\ &= 17.5 \text{ mg/L as CaCO}_3\end{aligned}$$

7. Draw a bar diagram of the finished water.



DETERMINATION OF CARBONIC ACID CONCENTRATION FOR SOFTENING CALCULATIONS

Some laboratories may provide the carbonic acid concentration, H_2CO_3^* . If the concentration of H_2CO_3^* is not given, then it can be calculated from carbonic acid equilibria. The applicable equilibrium equations for the carbonic acid system are



Because the dissolved fraction of the total CO_2 in water is small and hydrolyzes to H_2CO_3 , the H_2CO_3^* concentration is taken as the sum

of CO_2 and H_2CO_3 concentrations. The equilibrium constants for the stoichiometric equations (Eqs. 20-36 and 20-37) are

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \quad (20-38)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (20-39)$$

where K_1 = first dissociation constant for carbonic acid

K_2 = second dissociation constant for carbonic acid

Both K_1 and K_2 have been correlated to temperature and can be calculated from the expressions (Rossum and Merrill, 1983)

$$K_1 = 10^{14.8435 - 3404.71/T - 0.032786T} \quad (20-40)$$

$$K_2 = 10^{6.498 - 2909.39/T - 0.02379T} \quad (20-41)$$

where T = water temperature, K

The total carbonic species concentration, C_T , in water is represented by the expression

$$C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (20-42)$$

where C_T = total carbonic species concentration, mol/L

The ionization fractions of these species defined for each species are

$$\alpha_0 = \frac{[\text{H}_2\text{CO}_3^*]}{C_T} \quad (20-43)$$

$$\alpha_1 = \frac{[\text{HCO}_3^-]}{C_T} \quad (20-44)$$

$$\alpha_2 = \frac{[\text{CO}_3^{2-}]}{C_T} \quad (20-45)$$

Based on Eqs. 20-42 through 20-45, the following expressions can be used to calculate the ionization fractions based on acid reactions in natural waters (i.e., alkalinity is in the form of bicarbonate alkalinity):

$$\alpha_0 = \frac{1}{1 + K_1/[\text{H}^+] + K_1 K_2 / [\text{H}^+]^2} \quad (20-46)$$

$$\alpha_1 = \frac{1}{[\text{H}^+]/K_1 + 1 + K_2/[\text{H}^+]} \quad (20-47)$$

$$\alpha_2 = \frac{1}{[\text{H}^+]^2 / (K_1 K_2) + [\text{H}^+]/K_2 + 1} \quad (20-48)$$

Given the alkalinity, pH, and temperature of the water, Eqs. 20-42 through 20-48 can be used to calculate the H_2CO_3^* concentration (procedure adapted from Benefield and Morgan, 1999).

Example 20-7 Single-stage excess lime softening

A 50-ML/d raw-water source is to be softened to reduce the hardness. The mineral analysis of the raw water is given below. The average raw-water temperature and pH were found to be 15°C and 7.2, respectively. Using the given information, determine the carbonic acid concentration in the raw water; the total carbonate and noncarbonate hardness present in the raw and finished water; the kilograms per day of lime, soda ash, and CO₂ needed for selective calcium softening; and the kilograms per day of CaCO₃ solids produced. Draw the initial and final bar diagrams of the raw and softened water. The residual calcium and magnesium hardnesses in the softened water are 30 and 20 mg/L as CaCO₃, respectively. Use an excess lime dose of 30 mg/L as CaCO₃.

Constituent	Unit	Value
Ca ²⁺	mg/L	60
Mg ²⁺	mg/L	20
Na ⁺	mg/L	15.9
Alk(HCO ₃ ⁻)	mg/L as CaCO ₃	240
SO ₄ ²⁻	mg/L	12
Cl ⁻	mg/L	10

Solution

1. Develop a summary table for the chemical constituents and the conversion of all the concentrations to meq/L and mg/L as CaCO₃. Because the H₂CO₃* was not given, it must first be determined from the alkalinity, pH, and temperature.

- a. The carbonic acid concentration can be determined from Eq. 20-42 if it is assumed that at pH = 7.2 the alkalinity is primarily made up of bicarbonate alkalinity:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = [H_2CO_3^*] + [HCO_3^-] + 0$$

- b. The C_T value can be determined from the pH, temperature, and bicarbonate alkalinity using Eqs. 20-44, 20-47, 20-40, and 20-41 as shown:

$$\alpha_1 = \frac{1}{[H^+]/K_1 + 1 + K_2/[H^+]}$$

$$C_T = \frac{[HCO_3^-]}{\alpha_1}$$

$$\begin{aligned}
 K_1 &= 10^{14.8435 - 3404.71/T(K) - 0.032786T(K)} \\
 &= 10^{14.8435 - 3404.71/288\text{ K} - 0.032786 \times 288\text{ K}} = 3.79 \times 10^{-7} \\
 K_2 &= 10^{6.498 - 2909.39/T(K) - 0.02379T(K)} \\
 &= 10^{6.498 - 2909.39/288\text{ K} - 0.02379 \times 288\text{ K}} = 3.50 \times 10^{-11} \\
 \alpha_1 &= \frac{1}{(1.0 \times 10^{-7.2}) / 3.79 \times 10^{-7} + 1 + 3.5 \times 10^{-11} / (1.0 \times 10^{-7.2})} \\
 &= 0.86 \\
 C_T &= \frac{[\text{HCO}_3^-]}{\alpha_1} = \frac{(240\text{ mg/L}) [1/(100\text{ g/mol})] (1\text{ g}/10^3\text{ mg})}{0.86} \\
 &= 2.79 \times 10^{-3}\text{ mol/L}
 \end{aligned}$$

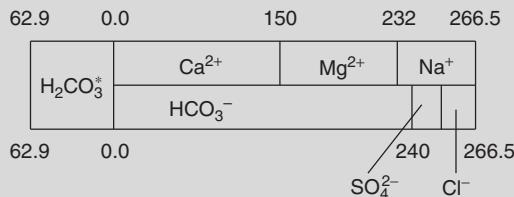
c. The carbonic acid concentration can be determined as

$$\begin{aligned}
 [\text{H}_2\text{CO}_3^*] &= C_T - [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \\
 &= 2.79 \times 10^{-3} - 2.4 \times 10^{-3} - 0 \\
 &= (3.9 \times 10^{-4}\text{ mol/L})(100\text{ g/mol})(10^3\text{ mg/g}) \\
 &= 39.0\text{ mg/L as CaCO}_3
 \end{aligned}$$

d. A summary of the chemical constituents in terms of CaCO_3 is shown in the following table:

Chemical Constituent	Concentration mg/L	Equivalents	Molecular Weight	Equivalent Weight	meq/L	mg/L as CaCO_3
H_2CO_3^*	39	2	62.0	31.0	1.26	62.9
Cations						
Ca^{2+}	60	2	40.0	20.0	3.00	150
Mg^{2+}	20	2	24.4	12.2	1.64	82
Na^+	15.9	1	23.0	23.0	0.69	34.5
Total					5.33	266.5
Anions						
Alk as CaCO_3	240	2	100	50.0	4.8	240
SO_4^{2-}	12	2	96.0	48	0.25	12.5
Cl^-	10	1	35.5	35.5	0.28	14
Total					5.33	266.5

2. Construct a bar diagram of the raw water that includes the chemical constituents (as CaCO_3) that are important for softening (see step 2 in Example 20-6 for a discussion of the development of the bar diagram).



3. Determine the total hardness, carbonate hardness, and noncarbonate hardness.

- a. The total hardness can be calculated from the summary table as the sum of the calcium and magnesium ions as CaCO_3 or taken directly from the bar chart:

$$\begin{aligned}\text{Total hardness} &= (150 + 82) \text{ mg/L as } \text{CaCO}_3 \\ &= 232 \text{ mg/L as } \text{CaCO}_3\end{aligned}$$

- b. The carbonate hardness is the same as the total hardness because there is no noncarbonate hardness present:

$$\text{Carbonate hardness} = 232 \text{ mg/L as } \text{CaCO}_3$$

- c. In this case the noncarbonate hardness is zero.

4. Calculate the lime, soda ash, and carbon dioxide dosages required for excess lime softening.

- a. From Table 20-11 for excess lime treatment, the following expression can be used to calculate the lime dose:

$$\begin{aligned}\text{CaO required} &= \text{carbonic acid concentration} + \text{calcium hardness} \\ &\quad + \text{magnesium hardness} + \text{excess lime dose} \\ &= [(62.9 + 240 + 82 + 30) \text{ mg } \text{CaCO}_3/\text{L}] \\ &\quad \times (28 \text{ mg CaO}/50 \text{ mg } \text{CaCO}_3) \\ &= 232 \text{ mg/L} \\ &= (232 \text{ mg CaO/L})(1 \text{ kg}/10^6 \text{ mg})(50 \times 10^6 \text{ L/d}) \\ &= 11,600 \text{ kg/d}\end{aligned}$$

- b. Because all the hardness is in the carbonate form, no soda ash dose is required.

- c. The carbon dioxide requirement for selective calcium removal is equal to the estimated carbonate alkalinity of the softened water plus two times the excess lime dose and the estimated residual magnesium hardness of the softened water or as given by the expression

CO_2 required

$$\begin{aligned} &= \text{estimated carbonate alkalinity of softened water} \\ &+ 2 \times \text{excess lime dose} \\ &+ \text{estimated residual magnesium hardness of softened water} \end{aligned}$$

- d. Carbonate alkalinity of the softened water is calculated as

Estimated carbonate alkalinity of softened water

$$\begin{aligned} &= \text{source water alkalinity} - \text{source water total hardness} \\ &- \text{excess lime dose} \\ &+ \text{estimated residual calcium hardness of softened water} \\ &= (240 - 232 - 30 + 30) \text{ mg CaCO}_3/\text{L} = 8 \text{ mg CaCO}_3/\text{L} \end{aligned}$$

- e. Consequently, the CO_2 dosage requirement is calculated as

CO_2 required

$$\begin{aligned} &= [(8 + 2 \times 30 + 20) \text{ mg CaCO}_3/\text{L}] (22 \text{ mg CO}_2/50 \text{ mg CaCO}_3) \\ &= 39 \text{ mg CO}_2/\text{L} \\ &= (39 \text{ mg CO}_2/\text{L}) (1 \text{ kg}/10^6 \text{ mg}) (50 \times 10^6 \text{ L/d}) = 1,950 \text{ kg/d} \end{aligned}$$

- f. The CaCO_3 solids precipitated can be calculated from the table where it will be equal to the sum of the H_2CO_3^* precipitated as CaCO_3 , 2 times the calcium carbonate hardness precipitated as CaCO_3 (see Eq. 20-20), 2 times the magnesium hardness precipitated, precipitation of the excess lime added, and minus the solubility of CaCO_3 :

CaCO_3 solids produced

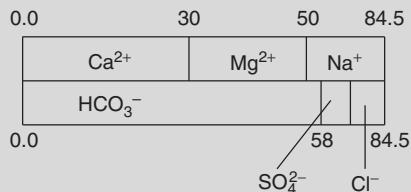
$$\begin{aligned} &= [(62.9 + 2 \times 150 + 2 \times 82 - 30) \text{ mg CaCO}_3/\text{L}] \\ &(1 \text{ kg}/10^6 \text{ mg}) (50 \times 10^6 \text{ L/d}) \\ &= 24,845 \text{ kg/d} \end{aligned}$$

5. Calculate the total, carbonate, and noncarbonate hardness present in finished waters. The carbonate hardness will be the sum of the

soluble calcium and the magnesium carbonate hardness and the noncarbonate hardness is equal to zero. Therefore, the total hardness is equal to the total carbonate hardness:

$$\text{Total carbonate hardness} = (30 + 20) = 50 \text{ mg/L as CaCO}_3$$

6. The final bar diagram of the finished water in terms of CaCO_3 is given below.



20-5 Nitrate

The principal sources of nitrogen are from (1) nitrogeneous compounds produced by plant and animals, (2) the mining of sodium nitrate for use in fertilizers, and (3) the atmosphere. The most oxidized form of nitrogen is nitrate (NO_3^-). In the United States, the average dietary intake of nitrate is about 75 to 100 mg/d, of which approximately 80 to 90 percent comes from vegetables. Vegetables with high nitrate levels are lettuce, beets, celery, and spinach. It is interesting that people on a vegetarian diet may consume as much as 250 mg/d of nitrate. Accordingly, drinking water accounts for only 5 to 10 percent of nitrates consumed. However, if the nitrate levels in the water are five times the MCL (10 mg/L), water may supply a person about half the daily diet requirements.

Although nitrate occurs naturally in drinking water sources, elevated levels usually come from human activity such as municipal and industrial wastes, unmanaged solid waste landfills, onsite wastewater systems, runoff or groundwater from manured and fertilized agricultural lands, stormwater drainage, and animal feed lots. Because nitrates are extremely soluble in water, they can easily seep through the soil and into drinking water supplies. Surface waters such as lakes, reservoirs, and rivers are also susceptible to nitrate contamination from these sources. Nitrate concentrations in surface and groundwaters may be increasing worldwide (Nixon, 1992; Spalding and Exner, 1993).

Nitrate is of primary concern for infants younger than 6 months of age. Infants are very susceptible to methemoglobinemia, a condition known as “blue baby syndrome.” High nitrate levels that are reduced in the stomach and/or the saliva of an infant to nitrite cause blue baby syndrome. Nitrite

Occurrence and Importance in Water Supplies

in the blood combines with hemoglobin to form methemoglobin, which reduces the capability of the blood to transport oxygen throughout the body. This results in the skin of a baby turning blue and can be fatal. The present MCL in the United States is 10 mg/L as nitrate and Canada has established a maximum acceptable concentration (MAC) of 10 mg NO_3^- /L. The European Union recommends a level of 11.3 mg NO_3^- /L.

Treatment Strategies

Because nitrate is a stable, highly soluble ion, it is difficult to remove by conventional coagulation and adsorption processes. Present technologies for nitrate removal from water supplies include chemical and biological denitrification, reverse osmosis, electrodialysis, and ion exchange.

CHEMICAL DENITRIFICATION

Chemical denitrification involves the reduction of nitrate to nitrogen gas using metals such as iron and aluminum. This process was evaluated and found to be very expensive due to the high metal dosages and other costs associated with the process (Murphy, 1991; Sorg, 1978a,b).

BIOLOGICAL DENITRIFICATION

Biological denitrification takes place in an anoxic environment where nitrate is converted to nitrogen gas through the following series of steps:



To provide an anoxic environment, the DO concentration in the water must be less than about 0.1 mg/L. Both heterotrophic and autotrophic bacteria can be used to denitrify water. Heterotrophic bacteria require an organic carbon source to be used as an electron acceptor for the denitrification reaction. For drinking water, the microorganisms can utilize NOM if the concentration is high enough and the form of NOM is amenable to biodegradation. In most cases, it is necessary to add in an organic source such as methanol, ethanol, or acetic acid. The carbon-to-nitrogen ratios required for methanol, ethanol, and acetic acid are reported to be 0.93, 1.05, and 1.32, respectively (Mateju et al., 1992).

Autotrophic bacteria are also capable of denitrification. Bacteria such as *Thiobacillus denitrificans* can use hydrogen or reduced sulfur species as substrate and carbon dioxide or bicarbonate as carbon sources for cell synthesis. Autotrophic bacteria require a minimum sulfur-to-nitrogen ratio of 4.3 when using thiosulfate and a minimum hydrogen-to-nitrogen ratio of 0.38 when using hydrogen as the substrate. Autotrophic bacteria have also been used in *in situ* denitrification in groundwater (Gayle et al., 1989).

Attached and suspended growth

Pilot studies have been performed to evaluate the feasibility and performance of several biological denitrification processes. The results from a number of biological denitrification pilot- and some full-scale studies that were designed to evaluate the biological denitrification process are reported

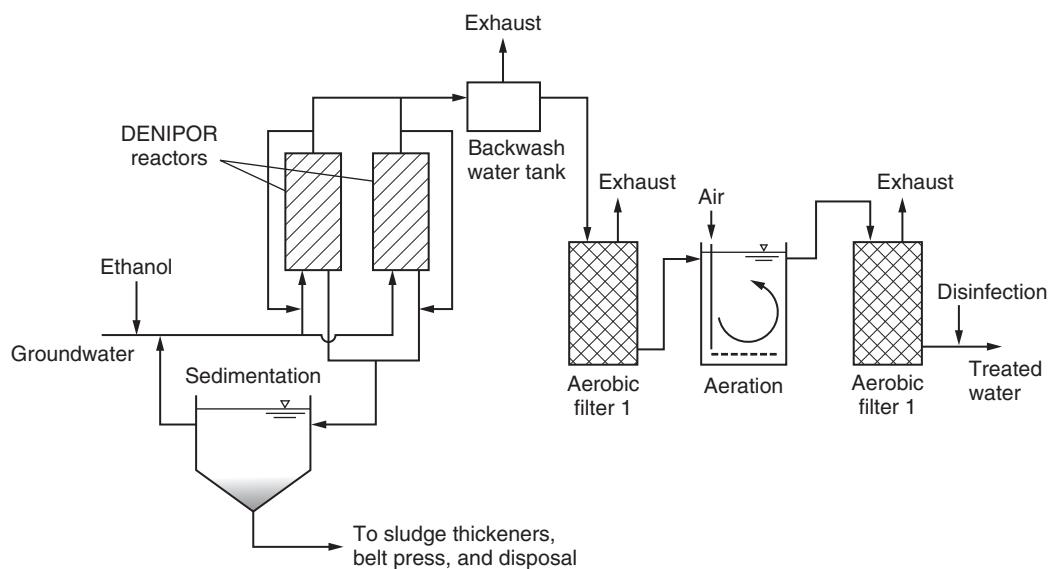
Table 20-12

Summary of several reported biological denitrification studies

Study	Reactor Type(s)	Water Source	Performance	Comments
1	1. Packed bed 2. Suspended growth 3. Fluidized sand bed (heterotrophic)	Thames water with methanol added	Reported denitrification rate 1. $12 \text{ g N/m}^3 \cdot \text{h}$ 2. $12\text{--}160 \text{ g N/m}^3 \cdot \text{h}$ 3. $160 \text{ g N/m}^3 \cdot \text{h}$	Fluidized-bed reactor reduced nitrate by 45 mg/L at 2°C using upflow velocity of 12 m/h
2	Packed sand bed (heterotrophic)	Groundwater with sucrose added	With initial nitrate concentration of 22.6 mg/L, 100% removal was obtained with carbon-to-nitrogen ratio of 2.0	Vacuum used to remove trapped nitrogen gas in packed column
3	Static bed upflow reactor with spherical support medium (heterotrophic)	Groundwater with acetic acid added	With initial nitrate concentration of 100 mg/L, 100% removal was obtained with carbon-to-nitrogen ratio of 1.5	Retention time 9 h, effluent high in suspended solids and turbidity
4	Fluidized sand bed (heterotrophic)	Groundwater with methanol added	With initial nitrate concentration of 75 mg/L, 100% removal was observed for EBCT of 15 min	Flow rate 0.95 ML/d (0.25 mgd), reactor loading was $9.0 \text{ kg NO}_3^-/\text{m}^3 \cdot \text{d}$, methanol added 20–25% higher than stoichiometric requirement
5	DENITROPUR process, fixed-bed reactor (heterotrophic)	Groundwater with hydrogen added	With initial nitrate concentration of 75 mg/L, 99% removal observed	Flow rate 2.4 ML/d (0.63 mgd) with loading rate of $0.12 \text{ kg N/m}^3 \cdot \text{d}$
6	DENIPOR process, fixed-bed reactor with polystyrene medium (autotrophic)	Groundwater with ethanol and phosphate added	Removal rate of 95% reported	Process loading rate $0.7\text{--}1.0 \text{ kg N/m}^3 \cdot \text{d}$

Source: Adapted from Kapoor and Viraraghavan (1997).

in Table 20-12. Two processes developed in Germany are the DENIPOR and DENITROPUR processes. A schematic of the DENIPOR process used for full-scale microbiological denitrification in Mönchengladbach, Germany, is shown on Fig. 20-13. As shown, buoyant polystyrene spherical beads are used to support the biomass in the fixed-bed reactors. A periodic downward flushing is used to remove excess biofilm that can cause plugging.

**Figure 20-13**

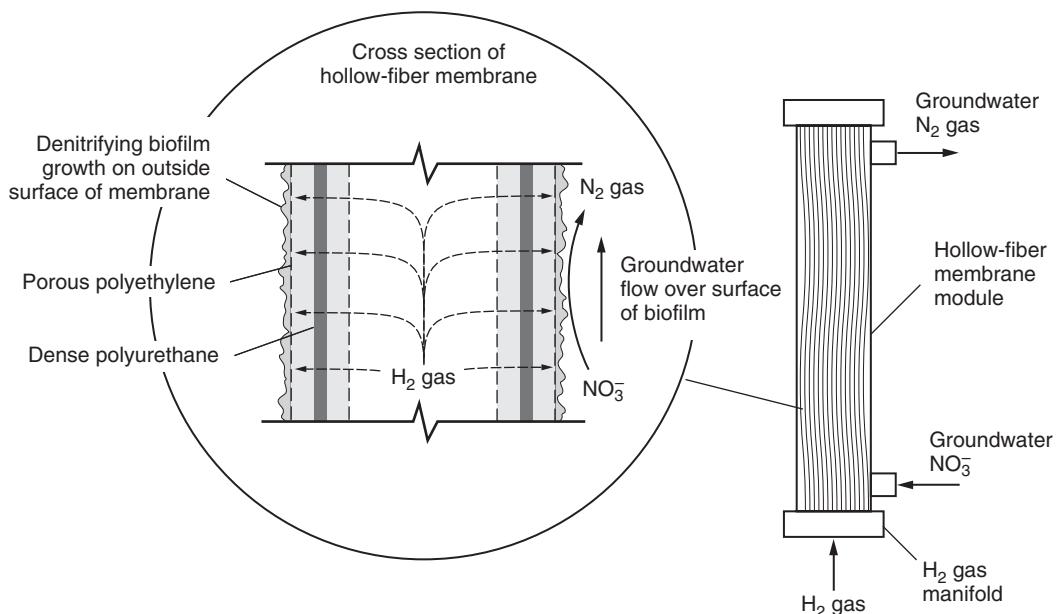
Schematic of DINIPOR process for biological denitrification.

The water from the denitrification reactors is treated further through two aerobic filters. The advantages of this process are (1) an organic substrate is not needed and (2) as the biomass production is low the sludge production is also low (a sludge production rate of only 0.2 kg organic matter/kg N was observed). The disadvantage of this process is that the kinetics of autotrophic bacteria is much slower than heterotrophic bacteria.

Hollow-fiber membrane bioreactor

An emerging autotrophic biological process for denitrification is called the hollow-fiber membrane bioreactor (HFMB) process, as shown on Fig. 20-14 (Lee and Rittmann, 1999). The HFMB process consists of membrane modules supporting several confined hollow-fiber membranes that contain a thin film of autotrophic bacteria on the outer portion of the hollow-fiber membranes. The inside of the confined hollow-fiber membranes contains hydrogen gas that diffuses outward in the radial direction through the membrane, providing dissolved hydrogen gas to the biofilm and creating a hydrogen atmosphere surrounding the biofilm. Biological denitrification is carried out by the autotrophic biofilm as NO_3^- is used as a terminal electron acceptor for respiration while hydrogen is used as the electron donor under anoxic conditions.

Results of pilot plant studies show the HFMB process is effective for the removal of nitrate from groundwater and is summarized in Table 20-13 (Falk and Ergas, 2002). Removal efficiencies of greater than 90 percent can be achieved with the HFMB process.

**Figure 20-14**

Schematic of bench-scale hollow-fiber membrane bioreactor process. (Adapted from Lee and Rittmann, 1999.)

Table 20-13

Performance data from studies evaluating HFMB process

Parameter	Unit	Study ^a		Lee and Rittmann, 2002	
		Influent	Effluent	Influent	Effluent
Nitrate	mg NO ₃ ⁻ -N/L	76	28	12.5	<1
Turbidity	NTU	2.4	2.9	nd	nd
Nitrite	mg NO ₂ ⁻ -N/L	0.08	0.75	0.9	0.74
TOC	mg/L	0.7	3.4	nd	nd
DOC	mg/L	0.7	2.7	1.4	2.3
pH	Unitless	7.5	7.8	7	7.2
Heterotrophic plate count	CFU/100 mL	0	2.3 × 10 ⁵	0	1.4 × 10 ³
Nitrate utilization rate	g NO ₃ ⁻ -N/m ²	Maximum = 1.4 Average = 0.8		Maximum = 1.4 Average = 0.8	
NO ₃ ⁻ -N removal rate	%	63		92	
Hydrogen utilization efficiency	%	>94		>96	

^and = nondetect.

Source: Adapted from Falk and Ergas (2002).

REVERSE OSMOSIS

Reverse osmosis and electrodialysis can be used to reduce nitrate levels in drinking water but is primarily used to treat high total dissolved solids and salt water. The cost of RO for treatment of nitrate only is much more expensive than the ion exchange process. Reverse osmosis is usually cost effective for nitrate removal if there are other water quality issues such as high TDS concentrations. Electrodialysis is a process that involves passing electric current through a series of semipermeable membranes to remove nitrate and other ions. The electrodialysis process provides about the same removal as reverse osmosis but is limited to treating soft waters, is expensive, and requires full-time monitoring.

ION EXCHANGE

Ion exchange is an effective treatment process for removal of nitrate. As discussed in Chap. 16, SBA exchange resins are used to remove anions. Typically major anions present in water supplies are sulfate, bicarbonate, and chloride. When nitrate is present in the water, these ions along with nitrate will be removed on SBA resins. The preference for anion exchange onto standard type 1 and type 2 SBA resins is sulfate > nitrate > bicarbonate > chloride. Because sulfate is preferred over nitrate, the impact of sulfate on nitrate exchange is very important and needs to be considered (see Chap. 16). For both type 1 and type 2 polystyrene resins and polyacrylic SBA resins, the quantity of nitrate removed in a given exchange cycle will depend upon the sulfate concentration, TDS, and nitrate concentration.

Resin types

There are also nitrate-specific resins that are specifically designed for nitrate removal. Nitrate-selective resins are usually used when chromatographic peaking in standard resins may impact the process performance (Clifford, 1999). Chromatographic peaking occurs when the more preferred sulfate ion migrates through the resin bed displacing the nitrate and concentrating it toward the end of the bed. When sulfate migrates to the end of the bed, it displaces the concentrated nitrate off the resin, resulting in a higher concentration of nitrate in the effluent than in the influent.

When treating a typical groundwater, the ion exchange effluent nitrate concentration can reach as high as 130 percent of the influent concentration. Consequently, resins used to treat nitrate are designed such that nitrate is preferred over sulfate. Some commercially available nitrate-selective resins are described in Table 20-14. Nitrate-selective resins are similar to standard type 1 resins but have ethyl, propyl, or butyl groups substituted for the methyl group on the trimethyl amine functionality [$\text{RN}(\text{CH}_3)_3$]. These substitutions separate the charged exchange sites along the backbone of the resins far enough apart so that the sulfate ion, which requires two charged sites close to each other, will not readily exchange. The nitrate-selective resins also have a higher hydrophobicity than the standard SBA

Table 20-14

Summary of commercially available SBA nitrate-selective resins

Resin	Functional Groups	Ionic Form	Total Volume Capacity Minimum, meq/mL	Shipping Weight (approx.), kg/m ³	Water Retention, %
Purolite A520E	Quaternary ammonium	Cl ⁻	1.0	684	52–56
SR-6 Symbron	Trimethyl amine	Cl ⁻	0.85	668	42–45
Amberlite-996, Rohm & Haas	Trimethyl amine	Cl ⁻	1.0	—	50–56

resins. Nitrate-selective resins are also required when brine reuse by denitrification is implemented when the sulfate concentration in the feed water is greater than 200 mg/L (Liu and Clifford, 1996). Nitrate-selective resins and their technical information can be obtained from several manufacturers (e.g., Purolite, London, England; Rohm and Haas, Philadelphia, PA; and Sybron/Bayer Corporation, Pittsburgh, PA).

Ion exchange process

A typical ion exchange process for nitrate removal is shown on Fig. 20-15. Strong-base anion resins are usually in the chloride form so that NaCl can

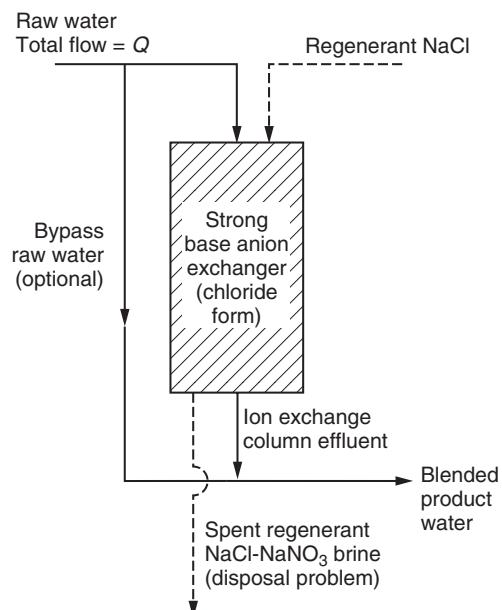


Figure 20-15
Schematic of typical ion exchange process using NaCl regeneration.

be used for regeneration of the resin. The fixed beds operate in the down-flow mode and co-current regeneration is usually used to reduce leakage of nitrate. An optional bypass of the water is sometimes used so that, when blended with the ion exchange process water, the nitrate concentration in the water is around 7 to 8 mg/L and is below the MCL. Depending on the water quality, nitrate breakthrough typically occurs around 100 to 500 BV. For example, field experiments showed that for an influent nitrate concentration of 21.5 mg/L and sulfate concentrations of 43 and 310 mg/L the nitrate breakthrough decreased from 400 to 180 BV (Clifford, 1999). Consequently, pilot studies are usually carried out to evaluate the breakthrough performance for a particular raw-water source.

Regeneration

Two types of regeneration techniques, partial and complete, can be used. However, for economic reasons, partial regeneration is used because significant leakage can be tolerated up to 10 mg/L of nitrate. For partial regeneration, it is important to completely mix the resin after each regeneration cycle to ensure leakage is not excessive. Performance for two full-scale plants using partial regeneration with NaCl is presented in Table 20-15. Both plants are used to treat 3.8 ML/d (1 mgd) using NaCl for resin regeneration. The water treated in the McFarland, California, plant contains 15 mg/L NO_3^- , 100 mg/L SO_4^{2-} , 90 mg/L Cl^- , and 100 mg/L HCO_3^- . In the plant in Binic, France, the surface water is pretreated with coagulation, sedimentation, and filtration ahead of the ion exchange process. The raw water treated in the Binic, France, plant contains 10 to 23 mg/L NO_3^- , 50 mg/L SO_4^{2-} , 50 mg/L Cl^- , and 85 mg/L HCO_3^- . This water is also

Table 20-15

Full-scale nitrate ion exchange plant performance

Description	Unit	McFarland, CA	Binic, France
Source water	—	Well water	Surface water
Polystyrene–DVB SBA	—	Duolite A101D	Dowex SBRP
Type I resin			
Regenerant concentration	N (%)	1.0 (6%)	—
Resin capacity, meq/L	meq/L	1.3	1.2
Brine utilization factor	eq Cl^- /eq	10	7.6
Run length to breakthrough	BV	260	400
Wastewater volume	% of blended product water	3.4	1.4
Bypass flow	% of blended product water	24	0
NaCl consumption for 3.8 ML/d blended product water	kg/d	1130	1150

Source: Clifford and Liu (1995).

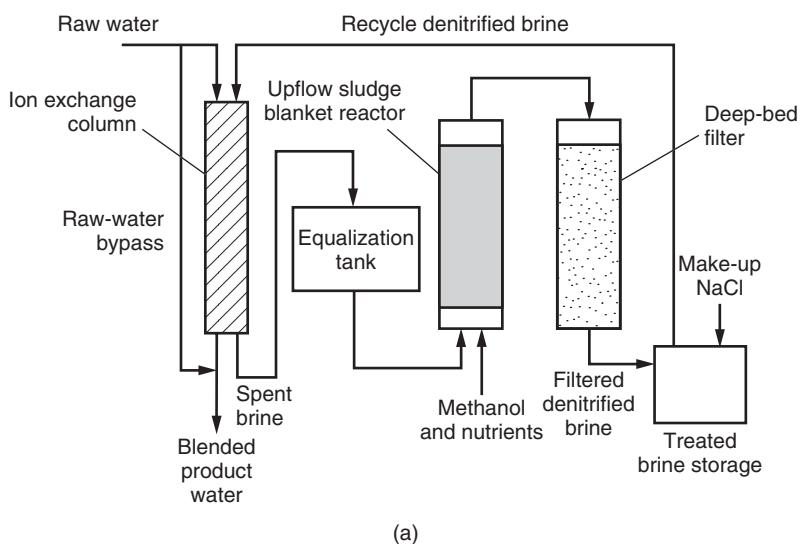
high in TOC and the resin is replaced every 3 years due to organic fouling. Because the Binic plant had lower TDS and sulfate concentrations than the McFarland plant, it could treat up to 135 more BVs. It should also be noted that the Binic plant was unable to utilize a bypass stream and, thus, required higher salt usage than the McFarland plant. If the Binic plant were allowed to have a leakage of 7.9 mg/L nitrate, then the salt consumption in that plant would have only been 530 kg/d (Clifford and Liu, 1995).

Brine disposal

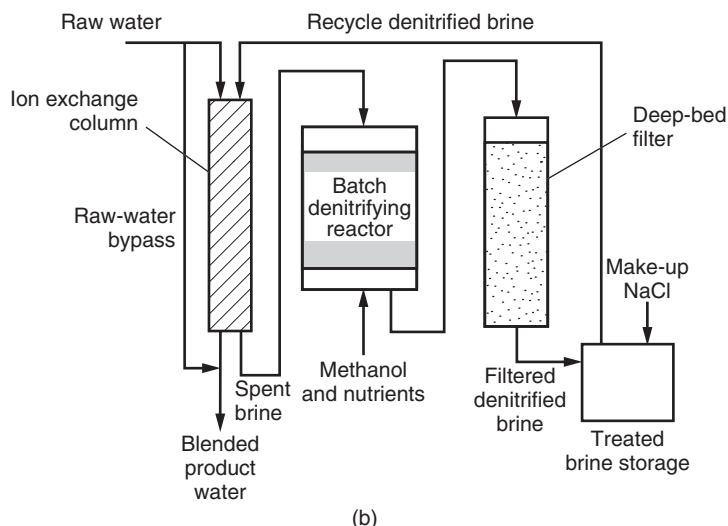
Nitrate-containing brine cannot be directly discharged into lakes and rivers due to its high salinity and nitrate, which causes eutrophication. For ion exchange plants near the coastal regions, ocean disposal may be an alternative if the conveyance system is available. For both the cities of McFarland, California, and Binic, France, the brine is disposed of in the sanitary sewer system as the brine waste is only a small portion of the total wastewater sent to the treatment plant and the biological treatment is not impacted. However, the McFarland plant, which uses aerated lagoons, discharges the water for irrigation of cotton crops. Unfortunately, salt concentrations are beginning to accumulate in the soil. While the exchange process is a cost-effective treatment process for nitrate removal from water, the issues of brine disposal must be carefully considered.

Recent studies have focused on brine treatment by denitrification and brine reuse to reduce the cost and problems associated with salt usage and brine disposal. The two processes shown on Fig. 20-16 are the biological denitrification of brine wastes using an upflow sludge blanket (USB) reactor (Hoek and Klapwijk, 1987, 1988) and a sequencing batch reactor (SBR) process (Liu and Clifford, 1996). The USB reactor is used to denitrify the spent nitrate-containing brine. An equalization tank is used to provide a constant nitrate influent in the USB and filtration is required for the denitrified brine before reuse. An advantage of the SBR process is that regeneration of an ion exchange column is also a batch process so the SBR process can also act as an equalization tank. Based on the results of bench and pilot studies for a methanol-to-nitrate ratio of 2.2, the nitrate removal efficiency is above 95 percent per batch. With the use of nitrate-selective resins, the brine has been reused over 38 times without significant sulfate buildup problems in the brine. With the SBR process there were no significant problems associated with resin performance. Compared to the conventional partial-regeneration process, with reuse of the denitrified brine it was possible to treat 70 percent more water per run, use 23 percent less salt, and produce 60 percent less wastewater (Clifford and Liu, 1995). While this process shows much promise, it has yet to be tested as a full-scale application.

A comparison of the various nitrate removal processes is presented in Table 20-16, including (1) conventional ion exchange, (2) direct biological



(a)



(b)

Figure 20-16

Dutch and American nitrate removal processes that incorporate biological denitrification into ion exchange process for spent-brine treatment: (a) Dutch ion exchange process with biological denitrification using upflow sludge blanket reactor (adapted from van der Hoek and Klapwijk, 1987) and (b) American ion exchange process with biological denitrification using sequencing batch reactor (adapted from Clifford and Liu, 1995).

denitrification, and (3) ion exchange with biological denitrification and reuse of the brine (Clifford and Liu, 1995). Both ion exchange and biological denitrification have been operated on a full-scale level, and the combined ion exchange and spent-brine denitrification process has only been tested on the pilot scale. If the nitrate-laden brine can be disposed of in a safe and cost-effective way, then the chloride ion exchange process may be the simplest and most cost-effective process. However, if there are problems with brine disposal, then direct biological denitrification or ion exchange with biological denitrification and brine reuse may be required.

Table 20-16
Comparison of nitrate removal techniques

Parameter	Ion Exchange	Direct Biological Heterotrophic Denitrification	Ion Exchange with Biological Denitrification and Brine Reuse
Raw-water quality (typically groundwater)	High TDS and sulfate reduce resin capacity for NO_3^-	Not influenced by water quality	Same as ion exchange
Treated-water quality	Increased chloride and corrosivity, variable anion concentrations	Posttreatment required to increase DO and eliminate TOC, NO_2^- , and turbidity	Same as ion exchange
Posttreatment required	Usually none	Biological oxidation, filtration, disinfection	Filtration of brine and possible disinfection required
Process complexity	Simple	Complex	Complex
Process control	Run length based on cumulative flow	Must control rate of ethanol and nutrient addition	Same as ion exchange plus addition of ethanol and nutrients ^a
Monitoring of treated water	NO_3^-	NO_3^- , NO_2^- , TOC, and bacteria	NO_3^- brine conductivity
Startup and shutdown	Operates on demand	Weeks to months required for startup; maintain viable denitrifying organisms	Maintain viable denitrifying organisms
Waste disposal	Large volume of brine containing NO_3^- and excess NaCl	Small volume of biomass sludge ^b	Small amount of nitrate-free brine and biomass sludge ^b

^aFor batch denitrification of brine, only batch addition of substrate and nutrients is required.

^bNitrate is converted to nitrogen gas by bacteria that grow slowly and produce a small amount of biomass for disposal.

20-6 Radionuclides

Natural radionuclides are the most common source of radioactivity in the environment. Natural radionuclides are formed from the dissolution of rock formations containing uranium ore and gases released from deep in the Earth's crust. The principal source of natural radionuclides is uranium ore (U_3O_8), and its abundance in the Earth's crust is only about 1 part per 10^{12} parts. The anthropogenic radionuclides come from sources such

as nuclear power plants used to supply electrical energy, medical facilities that provide nuclear medicines and x-ray services, academic and research facilities using nuclear materials for research, commercial products such as televisions and smoke detectors, and nuclear weapons for national defense.

Occurrence and Importance in Water Supplies

Most drinking water sources contain very low levels of radioactive nuclei, or radionuclides, which is not usually a public health concern. However, there are some groundwater sources, primarily areas of the Midwest and western United States, with radionuclide concentrations that exceed present drinking water standards. Presently, radionuclide contamination of drinking water has not been a concern for large water utilities, but for small water utilities using groundwater in some areas of the country treatment is required. Use of radionuclide materials by industry may become greater due to increases in energy demand and possible medical applications, and the increase in demand may impact some water utilities. In addition, the present threat of terrorist activities related to the use of nuclear material in the United States and abroad may also be a future source of contamination in water supplies.

Chemistry and Removal

The most common radionuclide of concern in water treatment are radium-226, radon-222, radium-228, uranium-234, which are ionic decay products of uranium-238 and thorium-232. With respect to aqueous systems, radium-226 and radium-228 exist in natural groundwaters primarily as divalent cations. Radon-222 is a gaseous radioactive element that can exist as 25 different isotopes. Radon-222 is highly volatile and has a Henry's law constant of 1.69 ($L_{\text{Water}}/L_{\text{Air}}$) at 20°C. Uranium has four oxidation states, U(III), U(IV), U(V), and U(VI). The oxidation states U(III) and U(V) are unstable in both air and water, U(IV) is stable in air, and U(VI) is stable in water. In aqueous solution, uranium exists as uranyl ion and readily complexes primarily with carbonate and hydroxide, as shown on Fig. 20-17. In the pH range of most natural waters, the uranyl ion complexes primarily with the carbonate and bicarbonate anions to form uranyl carbonate complexes. At pH values between 5.0 and 6.5, the primary species is UO_2CO_3^0 , and between pH values of 6.5 and about 7.5 the primary species is $\text{UO}_2(\text{CO}_3)_2^{2-}$. Small uranyl hydroxide complexes [UO_2OH^+ and $(\text{UO}_2)_3(\text{OH})_5^{+}$] are also formed as shown on Fig. 20-17.

Treatment Methods

Several conventional water treatment technologies are capable of removing radionuclides. The U.S. EPA's best available technology (BAT) for radon-222 removal is aeration; for combined radium-226 and radium-228 it is coagulation–filtration; for radium-226 and radium-228 separately it is ion exchange, reverse osmosis, or lime softening; and for uranium it is ion exchange. Performance data for various processes used to remove radionuclides are reported in Table 20-17. The highest removal efficiencies

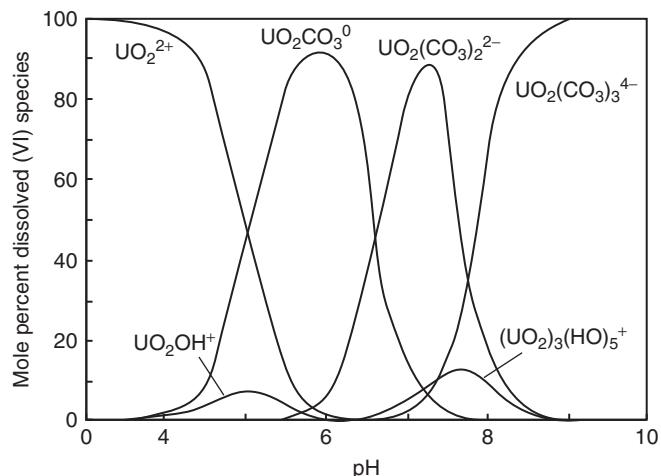


Figure 20-17
Distribution of uranium species in water.

Table 20-17

Summary of technology and performance of processes for removing radionuclides from drinking water

Method	Removal Efficiency, %		
	Radon	Radium	Uranium
Activated alumina			90
Aeration, packed tower	To 99+		
Aeration, diffused bubble	To 99+		
Aeration, spray	70–95+		
Coagulation–filtration			80–98
GAC adsorption–decay	62–99+		
Electrodialysis		90	
Greensand		25–50	
Hydrous manganese oxide filter		90	
Ion exchange		81–99	90–100
Lime softening		80–92	85–99
Reverse osmosis		90–95+	90–99

^aThe highest removal efficiencies for some technologies are associated with point-of-entry and point-of-use devices.

Source: Adapted from Lowery and Lowery (1988).

observed are for point-of-entry (POE) and point-of-use (POU) treatment systems. Water treatment processes for radionuclides are further discussed in the following sections.

AERATION

Radon-222 gas has a very high Henry's law constant and is very amenable to aeration. As discussed in Chap. 14, aeration methods such as spray, bubble,

and packed-tower systems are very effective methods for removing radon-222 from water. In packed towers, reported radon-222 removal efficiencies have been as high as 98 percent using an air-to-water ratio of only 8 : 1 (Dixon et al., 1991). Using higher air-to-water ratios can achieve removals greater than 99 percent. Design procedures discussed in Chap. 14 can be used to design aeration devices to remove radon-222.

ION EXCHANGE

Strong-acid cation resins in the sodium form and weak acid cation (WAC) resins in the hydrogen form can be used to remove radium-226 and radium-228 from aqueous systems. For normal sodium ion exchange softening, both radium isotopes can be removed completely. The advantage of using WAC resins is that they are easier to regenerate and require less regenerant per unit volume treated than SAC resins. However, the disadvantages of using WACs are that they swell during exhaustion, acid-resistant materials are required to prevent corrosion when using HCl as a regenerant solution, noncarbonate hardness is not removed, it will be necessary to strip the CO₂ from the treated water, and pH adjustment is needed (Faust and Aly, 1998).

For combined radium and uranium removal, a mixed bed containing SBA and SAC resins can be used. A mixture of 10 percent SBA and 90 percent SAC resins in a small fixed bed was able to treat water containing 25 pCi/L radium and 120 µg/L uranium to less than 1 pCi/L radium and 20 µg/L uranium (Clifford and Zhang, 1994). Potassium chloride was found to be a better regenerant than sodium chloride for radium removal. Design concepts and procedures discussed in Chap. 16 can be used to provide design guidance for ion exchange systems. With respect to disposal of contaminated brines, present practice is disposal to municipal sanitary sewers.

COAGULATION–FILTRATION

Conventional coagulation–filtration plants can be effective in removing uranium from drinking water supplies. Based on laboratory studies using jar tests, it has been found that uranium can be removed effectively using iron and aluminum coagulants (Lee and Bondietti, 1983; Lee et al., 1982).

The full-scale Moffat CO water treatment plant has an influent uranium concentration of 15 µg/L, and 75 percent removal was achieved at a raw-water pH of 7.5 using alum, lime, and polymer (Hanson, 1987; Lee et al., 1982). However, there was wide variation in the percent removals. For the same water treated at the Moffat plant, Hanson (1987) also reported that the alum plant in Arvada, Colorado, which uses the microfloc system, was able to achieve removals of 18 to 90 percent, and an average efficiency of 67±15 percent. High removals have also been observed using chemical clarification and dissolved air flotation.

LIME SOFTENING

In the same jar test study described above, Lee et al. (1982) showed the addition of lime (50 to 250 mg/L) raised the pH to 10.6 to 11.5 and obtained uranium removals of 85 to 90 percent. The impact of pH between 10.6 and 11.5 did not impact the removals. Jar tests were also performed with various doses of lime and magnesium carbonate ($MgCO_3$). At pH values between 9.8 and 10.6 $MgCO_3$ dosages reduced the effectiveness of lime softening on uranium removal. However, at pH values greater than 10.6, uranium removal increased with increasing $MgCO_3$ dosages. The critical pH value was determined to be 10.6. Above this value the addition of $MgCO_3$ with lime increased uranium removals to 93 to 99 percent. Further experiments showed that magnesium hydroxide precipitate plays an important role in the removal of uranium.

REVERSE OSMOSIS

Reverse osmosis provides excellent removal of radium and uranium isotopes. Operating results for several membranes used to remove natural uranium from a groundwater in Florida with an influent concentration of 300 $\mu\text{g}/\text{L}$ are displayed in Table 20-18. Removal efficiencies of 98 percent and greater were observed for each membrane. High removal efficiencies were also reported for radium-226. These results have been confirmed on similar waters containing uranium and radium (Sorg, 1988).

ADSORPTION

A promising adsorbent for the removal of radium is hydrous manganese oxides (HMOs), which has been successfully used in bench and pilot studies. The HMOs are preformed by the addition of potassium permanganate ($KMnO_4$), which brings about the oxidation of manganese sulfate ($MnSO_4$). Radium will adsorb onto the preformed HMOs and be removed by filtration. For conventional water treatment plants, this process can be incorporated

Table 20-18

Radionuclide removal using membranes^a

Radionuclide	Feed Concentration Range	Contaminant Removal, %				
		Dow CTA, HF	DuPont ARAMIDHF	Filmtec TFC, SW	Hydranautics MCA, SW	
Radium, pCi/L	2.2–9.8	97	96	—	97	
Uranium(IV), $\mu\text{g}/\text{L}$	103–1650	99	98	99	99	

^aCA = cellulose acetate; CTA = cellulose triacetate; MCA = modified cellulose acetate; HF = hollow fiber; SW = spiral wound; TFC = thin-film composite.

Source: Adapted from Faust and Aly (1998).

easily into the process flow stream without significant plant modifications if radium removal is required. Periodic acid wash of the sand filters may be required to remove excess MnO₂. Preformed HMO was successfully used to remove radium from drinking water (Valentine et al., 1990).

20-7 Pharmaceuticals and Personal Care Products

Increasing interconnectedness between receiving waters for treated wastewater and source waters for potable water systems has created concern about whether trace contaminants can pass through wastewater treatment systems and enter the water supply. Many recent investigations have found evidence of low concentrations of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) in the source water for many communities throughout the United States and other developed nations. PPCPs are not currently regulated drinking water contaminants in the United States, but there is broad concern about their presence in drinking water supplies.

Pharmaceuticals include antibiotics, analgesics [painkillers such as aspirin, ibuprofen (e.g., Advil), acetaminophen (e.g., Tylenol)], lipid regulators (e.g., atorvastatin, the active ingredient in Lipitor), mood regulators (e.g., fluoxetine, the active ingredient in Prozac), antiepileptics (e.g., carbamazepine, the active ingredient in many epilepsy and bipolar disorder medications), and many other medications. Personal care products can include cosmetics and fragrances, acne medication, insect repellants, lotions, detergents, and other products. Ingested pharmaceuticals can be excreted with human waste and enter the wastewater system. Additional pharmaceuticals can enter the wastewater system because of the common practice of flushing unused medication down the toilet. Personal care products can be washed from the skin and hair during washing or showering. Discharge from wastewater treatment plants (WWTPs) have been shown to be a major source of many PPCPs (Wintgrens et al., 2004; Snyder et al., 2003) in the environment. Untreated animal waste, manufacturing residues, pesticides, and agricultural runoff are other sources of PPCPs (Kolpin et al., 2002).

Endocrine disrupting chemicals are chemicals that have the capability to interfere with the function of the human endocrine system (either stimulating or repressing hormonal function). EDCs can interfere with female sex hormones (estrogenic EDCs), male sex hormones (androgenic EDCs), or hormones that control metabolism and many other systems in the body (thyroidal EDCs). EDCs include natural hormones excreted from humans, ingested hormones such as estrogens subsequently excreted from females after use of birth-control pills, or synthetic compounds that mimic the function of hormones, such as bisphenol A.

PPCPs have been detected in wastewater in the United States since the 1960s and 1970s, and recent studies have detected them in a significant number of surface waters and even in treated drinking water supplies (Halling-Sorenson et al., 1998; Kolpin et al., 2002; Barnes et al., 2008; Focazio et al., 2008; Benotti et al., 2009). Analytical technologies have improved to the extent that the detection limit for many PPCPs is in the range of 5 to 10 ng/L, and these analytical capabilities have led to increased incidence of detection. In most cases, the concentrations of PPCPs and EDCs detected in source waters are below 1 µg/L. These concentrations are orders of magnitude below the therapeutic doses of many medications, which are typically tens to hundreds of milligrams per day. Example 20-8 demonstrates a comparison between level of exposure between concentrations found in water supplies and in therapeutic doses.

Occurrence and Significance in Water Supplies

Example 20-8 Comparison of therapeutic and environmental exposures to pharmaceuticals

A single adult tablet of a pain medication contains 200 mg of ibuprofen. Compare the amount of ibuprofen consumed in one tablet to the amount consumed in drinking water in (1) one day and (2) over a lifetime, if the drinking water contains 1 µg/L of ibuprofen.

Solution

1. Daily exposure. A typical human consumes about 2 L of water per day. Comparing one day of drinking water consumption to one tablet is

$$\frac{200 \text{ mg} (10^3 \mu\text{g/mg})}{(1 \mu\text{g/L}) (2 \text{ L})} = 100,000 = 10^5$$

One tablet of pain medication contains 100,000 times more ibuprofen than the amount consumed by drinking water for 1 day.

2. Lifetime exposure. The average life expectancy in several countries is just over 80 years. Consumption of water containing 1 µg/L of ibuprofen for 80 years would expose a person to:

$$(1 \mu\text{g/L}) (2 \text{ L/d}) (365 \text{ d/yr}) (80 \text{ yr}) (10^{-3} \text{ mg}/\mu\text{g}) = 58.4 \text{ mg}$$
$$\frac{58.4 \text{ mg}}{200 \text{ mg}} \times 100 = 29\%$$

The amount of ibuprofen consumed in drinking water over a lifetime is less than 30 percent of the amount in one tablet.

Example 20-8 demonstrates that environmental exposure to PPCPs can be low compared to exposure for medical purposes. Nevertheless, exposure to PPCPs and EDCs through drinking water remains an area of potential concern. Concern because of the increased incidence of detection that has been caused by improvements in analytical technologies has already been noted. Other possible reasons for recent concern about PPCPs and EDCs in water supplies include (1) increased interest in indirect potable reuse and increased awareness of the interconnections between wastewater discharge and water supplies, (2) the possibility of synergistic effects from exposure to trace concentrations of multiple PPCPs, and (3) the possibility that trace amounts of antibiotics in the environment may lead to the formation of resistant strains of bacteria.

Regardless of the public's concern regarding PPCPs and EDCs, it is important for the water treatment and regulatory communities to assess the concentration at which PPCPs and EDCs may pose health threats to consumers. An AWWARF study (Bruce et al., 2010) evaluated the toxicological relevance of PPCPs and indicated, for the compounds evaluated, the concentrations found in drinking water supplies were significantly below the concentrations considered to be significant from a toxicological perspective. Additional studies are ongoing to assess the human health significance of PPCPs and EDCs in drinking water.

Chemical Properties

Separation of constituents from water or wastewater is accomplished by exploiting differences in physical, chemical, and biological properties between the contaminants and water. These properties include molecular weight, solubility, charge, polarity, volatility, chemical reactivity, biodegradability, and others. Often, groups of compounds with similar properties can be removed by a single treatment process that exploits a specific property. However, there are thousands of different drugs and chemical compounds in use today that can, and do, end up in water with a correspondingly large variation in their physical, chemical, and biological properties (Dalton, 2004). The variability in properties means that these compounds will respond differently to different treatment techniques, so no treatment process will be effective for all PPCPs and EDCs.

Many PPCPs are organic compounds with relatively low molecular weight (< 1000 Da). However, they have differences in charge, polarity, volatility, and other properties that will make generalized treatment strategies more difficult. In addition, many pharmaceuticals are designed with specific properties to enhance their function as pharmacological agents that may interfere with treatment objectives. For instance, PPCPs may be designed with high chemical stability, high water solubility, low biodegradability, and low adsorbancy to nonpolar adsorbents, which may make treatment more difficult.

Treatment Strategies

Despite the wide range of chemical properties that may be expressed by PPCPs and EDCs, there are several treatment strategies that work well for many compounds. The most practical for the widest range of compounds are advanced oxidation, reverse osmosis, and adsorption onto activated carbon. The application of these treatment processes to PPCPs is described in the following sections.

ADVANCED OXIDATION

Oxidation and advanced oxidation processes (AOPs) achieve removal by chemical destruction. Advanced oxidation processes use combinations of chemical oxidants or combine a chemical oxidant with UV radiation to increase the rate of oxidation through generation of highly reactive free radicals such as the hydroxyl radical (OH^\cdot). Common AOPs include ozone/hydrogen peroxide, UV/ozone (UV/ O_3), and UV/hydrogen peroxide (UV/ H_2O_2). Advanced oxidation is discussed in more detail in Chap. 18.

Most conventional chemical oxidation processes are not very effective at removing many PPCPs at the doses used for disinfection (Snyder et al., 2008; Okuda et al., 2008). The same is generally true for UV light oxidation. UV irradiation alone achieves limited degradation of many PPCPs, particularly at doses used for disinfection (Kim et al., 2007, 2008; Canonica et al., 2008; Kruithof et al., 2007). However, doses at least 5 to 10 times higher than the typical doses for disinfection can achieve better removal of some PPCPs (Snyder et al., 2003; Kruithof et al., 2007).

Ozone, ozone-based, and UV-based AOPs can effectively degrade most PPCPs. Ozonation by itself can reduce both the concentration and number of compounds detected after treatment (Snyder et al., 2006; Andreozzi et al., 2004; Vieno et al., 2007). Okuda et al. (2008) found that ozone coupled with a biological activated carbon process reduced all residual pharmaceuticals to below quantification limits. As with other uses of ozonation, the formation of bromate is a consideration when using ozone for PPCP removal. In addition, ozonation of PPCPs may require longer contact times and/or higher doses than that used for disinfection (Andreozzi et al., 2004; Ternes et al., 2003). The combination of hydrogen peroxide and UV light has also been shown to be highly effective at degrading many PPCPs (Pereira et al., 2007a, 2007b; Chen et al., 2007).

Because of the differences in chemical properties, some compounds are slowly oxidized or poorly degraded by advanced oxidation processes. Cyclophosphamide, 2-quinoxaline carboxylic acid (2-QCA) and N,N-diethyl-m-toluatin (DEET) were poorly removed in one study (Kim et al., 2008). Other studies have found that clofibric acid (Westerhoff et al., 2005; Ternes et al., 2003) and ciprofloxacin (Vieno et al., 2007) are difficult to remove by advanced oxidation processes.

An important consideration in the use of advanced oxidation for PPCP removal is that the reaction products are almost certainly not fully mineralized to H₂O and CO₂. While an oxidation process may destroy the parent compound, it may produce degradation products with unknown biological activity. A subsequent process, such as biofiltration following ozone, may be appropriate to remove the oxidation products. Biofiltration is discussed in Sec. 11-8 of Chap. 11.

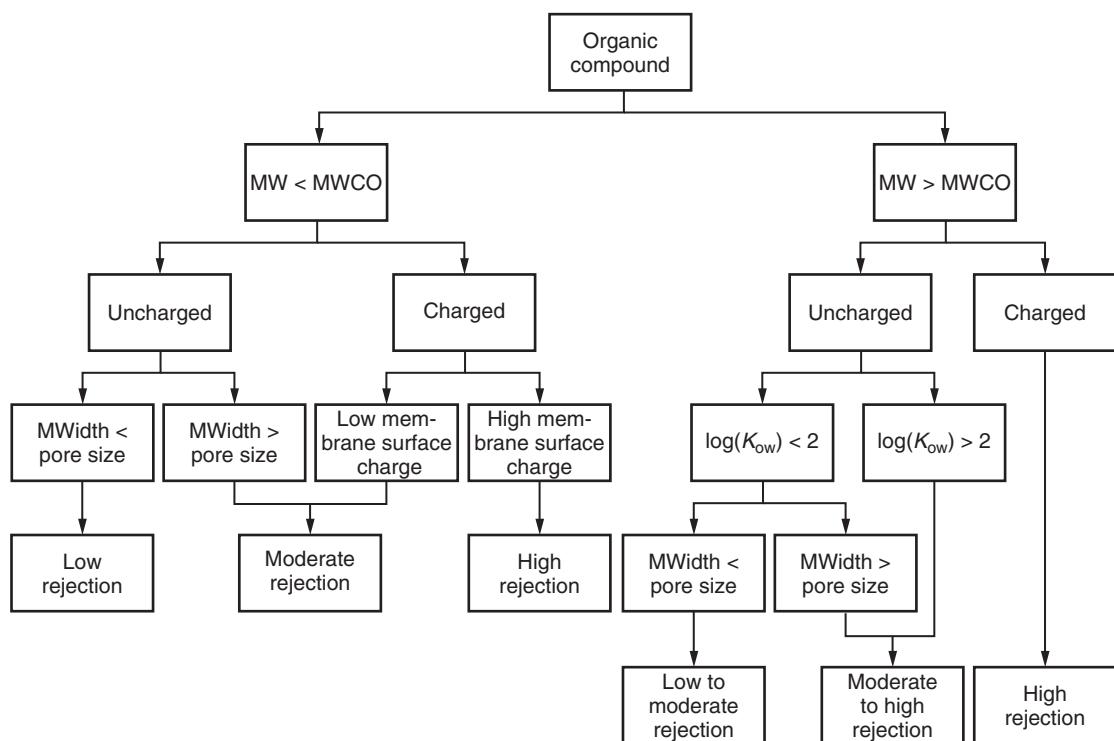
REVERSE OSMOSIS

Reverse osmosis is a membrane-based treatment process that separates contaminants from water by forcing water through the membrane under pressure. Dissolved contaminants are separated from the water as the water passes through the membrane. RO can effectively remove most PPCPs; removal efficiencies depend on properties of the feed water, membranes, and compounds to be removed. Reverse osmosis is discussed in Chap 17.

Many studies that have evaluated reverse osmosis for PPCP removal have found that RO can achieve excellent removal for most compounds (Snyder et al., 2003, 2007; Drewes et al., 2006). However, a number of factors can affect the level of removal. The most important parameters include the molecular weight or size, polarity, hydrophobicity, and charge of the compound, the membrane's surface charge and molecular weight cut-off (MWCO), and the fractional water recovery (Bellona et al., 2004; Kimura et al., 2003; Verliefde et al., 2007). The relationship between compound physicochemical properties and removal efficiency are qualitatively summarized in Fig. 20-18 (Drewes et al., 2006). Important compound properties reflected in this diagram are MWCO, charge, and hydrophobicity. As shown on the right side of Fig. 20-18, when the MWCO of the membrane is smaller than the MW of the compound, high rejection can be achieved for charged and hydrophobic [$\log(K_{ow}) > 2$] compounds, and lower rejection might be observed for small, neutral, hydrophilic compounds depending on the shape of the molecule. A number of researchers have shown that NF membranes do not achieve as good a rejection of PPCPs as tighter RO membranes (Xu et al., 2005; Yoon et al., 2002).

An operating parameter that can have a significant effect on PPCP removal is the feed water recovery. As noted in Chap. 17, osmotic pressure, concentration polarization, and the solubility of sparingly soluble salts can limit the recovery of water from an RO system. Higher recovery increases permeate volume but decreases its quality. Verliefde et al. (2007) showed that at a recovery of 10 percent, an NF membrane was able to remove >75 percent of all target compounds with most achieving >90 percent removal and a few compounds being removed at >99 percent. At 80 percent recovery, the same compounds were removed less effectively with one compound dropping to ~10 percent removal.

PPCP removal can be maximized by selecting membranes with a lower MWCO (i.e., seawater RO in lieu of brackish water RO membranes).

**Figure 20-18**

Rejection diagram for microconstituents using membrane processes as functions of both solute and membrane properties.
(Adapted from Drewes et al., 2006.)

Membranes with a lower MWCO, however, typically operate at lower water flux rates. As a result, it would be necessary to increase the size of the system or increase the feed pressure, which increases capital and operating costs.

As a treatment process, reverse osmosis has several negative aspects. These include (1) high loss of product water because of low recovery, (2) high energy consumption, (3) large volume waste stream, which increases disposal costs. These negative aspects should be considered when comparing reverse osmosis to other treatment processes for PPCP treatment.

ADSORPTION ONTO ACTIVATED CARBON

Activated carbon is an effective adsorbent that is used for removing many dissolved compounds from water. Granular activated carbon (GAC) and powdered activated carbon (PAC) have both been evaluated for their effectiveness in removing PPCPs and found to be effective for many PPCPs.

The compounds most effectively removed by activated carbon include the more nonpolar, more hydrophobic, lower MW, uncharged, and lower solubility compounds. Lower MW compounds are more efficiently removed because of increased accessibility to inner pores of the carbon. The pH is

also important for PPCPs that are weak acids because the pH affects the charge of the species.

Adsorption capacity affects the use of PAC and GAC differently. For PAC, a dose of carbon is added to the water and adsorption occurs until the capacity is reached, with the remaining pollutant staying in the water. Westerhoff et al. (2005) showed that protonated bases are well removed by PAC. Compounds with low K_{ow} values and deprotonated acid functional groups were the most difficult to remove. Increased removal efficiency for many compounds can be achieved by increasing the PAC dose and/or the contact time (Snyder et al., 2007; Baumgarten et al., 2007; Westerhoff et al., 2005).

For GAC, pollutants adsorb to the carbon bed and the pollutant concentration in the effluent can be unmeasurable until the capacity (measured as bed volumes) is reached, at which time the pollutant passes through the bed and the influent concentration of the pollutant is measured in the effluent. Studies have concluded that hydrophilic compounds break through the column sooner than the hydrophobic compounds (Snyder et al., 2007; Vieno et al., 2007). Vieno et al. (2007) found that the hydrophobic compound carbamazepine could be effectively removed by GAC even after treatment of >70,000 bed volumes of water, but that the more hydrophilic compounds could pass GAC treatment after only 2000 to 3000 bed volumes of water.

Once the adsorption capacity is reached, the media must be replaced or regenerated to restore removal effectiveness. Snyder et al. (2007) identified a facility with onsite and regular regeneration as having minimal breakthrough of organic contaminants and improved removal efficiency of selected PPCPs. In contrast, the study found little removal of trace organics in a facility with high levels of TOC that did not provide regular replacement/regeneration.

One parameter that affects both GAC and PAC is the NOM concentration (measured as DOC) in the feed water (Snyder et al., 2007). The presence of NOM can reduce the removal efficiency of PPCPs due to competition for adsorption sites. The NOM can block the pores within the activated carbon structure, leaving less opportunity for the PPCPs to be adsorbed. The quantity and characteristics of DOC in the feed water is an important parameter that can influence removal efficiencies for activated carbon (Westerhoff et al., 2005).

Studies have found that combined use of GAC or PAC with membrane processes is highly effective at removing PPCPs. One of the reported advantages is that this combination of processes effectively removes both DOC and DBPs. Verliefde et al. (2007) reported the combination of NF and GAC can provide a robust dual barrier for the removal of organic PPCPs. This is attributed to the NF membrane's ability to effectively remove high-molecular weight polar solutes, while activated carbon is more effective at removing nonpolar solutes. Similarly, use of RO to remove NOM would reduce the competition between NOM and PPCPs in a subsequent activated carbon process.

Problems and Discussion Topics

- 20-1 A 100 ML/d raw-water source containing 10-mg/L ferrous iron is oxidized to ferric hydroxide. Calculate the quantity of oxygen required, alkalinity consumed as CaCO_3 and quantity of sludge produced as ferric hydroxide.
- 20-2 A water supply containing a soluble Fe^{2+} concentration of 8.0 mg/L is to be oxidized by aeration to a concentration of 0.5 mg/L. The raw-water pH is 6.0, the temperature is 12°C, and it is assumed that P_{O_2} is in equilibrium with the atmosphere. Based on the results of laboratory studies, the pseudo-first-order rate constant for the oxygenation of Fe^{2+} is 0.17 min^{-1} . For steady-state operation and a flow rate of 40 ML/d (10.5 mgd), calculate and compare the minimum hydraulic detention time and reactor volume for the oxidation of Fe^{2+} to Fe^{3+} for plug flow and complete mixed flow reactors.
- 20-3 A 500-ML/d (132-mgd) flow of groundwater contains 2 mg/L of Mn(II) ion after aeration. A 5.0-mg/L (3.16×10^{-5} mol/L) dose of potassium permanganate (KMnO_4) is added to oxidize Mn(II) ion (Mn^{2+}) to a concentration of 0.1 mg/L. The groundwater pH is 6.5, the temperature is 15°C, and it is assumed that 5 mg/L (5.75×10^{-5} mol/L) of manganese dioxide (MnO_2) is in equilibrium with 0.1 mg/L of Mn^{2+} . For steady-state operation in a CMFR and plug flow reactor, calculate and compare the minimum hydraulic detention times for the oxidation of Mn^{2+} to MnO_2 .
- 20-4 A 20-ML/d flow of groundwater contains 5 mg/L of ferrous iron (Fe^{2+}). Calculate the quantity of chlorine required to oxidize ferrous to ferric hydroxide, alkalinity consumed, and the quantity of sludge produced.
- 20-5 A groundwater contains 8 mg/L of ferrous iron (Fe^{2+}) and 2 mg/L of Mn(II) ion (Mn^{2+}). Potassium permanganate (KMnO_4) is used to oxidize ferrous iron and Mn(II). If the well pumping rate is 9.81 ML/d (1500 gpm), calculate the quantity of potassium permanganate required, alkalinity consumed, and quantity of sludge produced.
- 20-6 The results of a mineral analysis of a raw water are as follows: H_2CO_3^* = 72 mg/L, Ca^{2+} = 100 mg/L, Mg^{2+} = 15 mg/L, Na^+ = 20 mg/L, $\text{Alk}(\text{HCO}_3^-)$ = 220 mg/L as CaCO_3 , SO_4^{2-} = 60 mg/L, Cl^- = 5.15 mg/L. If 50 ML/d of water from this source is to be softened to reduce the hardness, calculate the total, carbonate, and noncarbonate hardness present in the raw and finished waters; the kg/d of lime, soda ash, and CO_2 needed for selective calcium softening; and the kg/d of CaCO_3 solids produced. Draw bar diagrams

of the raw and softened water. Assume the residual hardness in the softened water is 30 mg/L as CaCO_3 .

- 20-7 If the water in Problem 20-6 had an alkalinity of 100 mg/L as CaCO_3 and an SO_4^{2-} concentration of 151 mg/L, calculate the total, carbonate, and noncarbonate hardness present in the raw and finished waters; the kg/d of lime, soda ash, and CO_2 needed for selective calcium softening; and the kg/d of CaCO_3 solids produced. Draw bar diagrams of the raw and softened water.
- 20-8 A two-stage excess lime-softening plant is designed to treat 57 ML/d (15 mgd) of a groundwater that contains the following constituents: $\text{Ca}^{2+} = 80 \text{ mg/L}$, $\text{Mg}^{2+} = 48.8 \text{ mg/L}$, $\text{Na}^+ = 23 \text{ mg/L}$, $\text{Alk}(\text{HCO}_3^-) = 270 \text{ mg/L}$ as CaCO_3 , $\text{SO}_4^{2-} = 125 \text{ mg/L}$, and $\text{Cl}^- = 35 \text{ mg/L}$. The water is to be softened by excess lime treatment. The average raw-water temperature and pH were found to be 10°C and 7.0, respectively. Draw a meq/L bar diagram, and determine the lime and soda ash dosages necessary in kg/d needed for softening. Assume that the soda ash is pure sodium carbonate and the lime is 85 percent CaO by weight. Also, calculate the kg/d of precipitated solids produced. Draw a meq/L bar graph of the water after the first stage of softening that includes the excess lime. Assume the practical limit of hardness removal for CaCO_3 is 30 mg/L, and that of $\text{Mg}(\text{OH})_2$ is 10 mg/L as CaCO_3 . Determine the kg/d of CO_2 required. Draw a meq/L bar diagram for the softened water after the second stage.
- 20-9 A 10-ML/d raw-water source is to be softened by two-stage lime softening to reduce the hardness. The results of a mineral analysis of the raw water are as follows: $\text{Ca}^{2+} = 112 \text{ mg/L}$, $\text{Mg}^{2+} = 20 \text{ mg/L}$, $\text{Na}^+ = 11 \text{ mg/L}$, $\text{Alk}(\text{HCO}_3^-) = 260 \text{ mg/L}$ as CaCO_3 , $\text{SO}_4^{2-} = 80.6 \text{ mg/L}$, $\text{Cl}^- = 38.0 \text{ mg/L}$. Calculate the total, carbonate, noncarbonate hardness present in the raw finished waters; the kg/d of lime, soda ash, and CO_2 needed for selective calcium softening; and the kg/d of CaCO_3 solids produced. Assume the residual calcium hardness in the softened water is 30 mg/L as CaCO_3 . Draw the initial and final bar diagrams of the raw and softened water. The average raw-water temperature and pH were found to be 15°C and 7.2, respectively.
- 20-10 A 50-ML/d raw-water source is to be softened using excess lime treatment to reduce the hardness. The results of a mineral analysis of the raw water are as follows: $\text{Ca}^{2+} = 70 \text{ mg/L}$, $\text{Mg}^{2+} = 15.9 \text{ mg/L}$, $\text{Na}^+ = 23 \text{ mg/L}$, $\text{Alk}(\text{HCO}_3^-) = 250 \text{ mg/L}$ as CaCO_3 and $\text{SO}_4^{2-} = 38.4 \text{ mg/L}$. Calculate the total, carbonate, and noncarbonate hardness present in the raw finished waters; the kg/d of lime, soda ash, and CO_2 needed for selective calcium softening;

- and the kg/d of CaCO_3 solids produced. Assume the residual calcium hardness in the softened water is 30 mg/L as CaCO_3 . Draw bar diagrams of the raw and softened water.
- 20-11 For the groundwater given in Problem 20-10, determine the lime dose required for softening by split treatment assuming the magnesium concentration in the finished water does not exceed 40 mg/L as CaCO_3 and the total hardness does not exceed 155 mg/L as CaCO_3 . Determine the final hardness of the finished water.
- 20-12 A 200-ML/d (53 mgd) raw-water source is to be softened using excess lime treatment to reduce the hardness. The results of a mineral analysis of the raw water are as follows: $\text{H}_2\text{CO}_3^* = 65.1$, $\text{Ca}^{2+} = 80$ mg/L, $\text{Mg}^{2+} = 19.5$ mg/L, $\text{Na}^+ = 23$ mg/L, $\text{Alk}(\text{HCO}_3^-) = 280$ mg/L as CaCO_3 , $\text{SO}_4^{2-} = 28.8$ mg/L, and $\text{Cl}^- = 14.2$ mg/L. Calculate the total, carbonate, and noncarbonate hardness present in the raw and finished waters; the kg/d of lime, soda ash, and CO_2 needed for selective calcium softening; and the kg/d of CaCO_3 solids produced. Assume the residual calcium hardness in the softened water is 30 mg/L as CaCO_3 . Draw bar diagrams of the raw and softened water.
- 20-13 Consider the precipitation softening by split-stream treatment of the raw water in Problem 20-12. Assume that only 75 percent of the water is treated by excess lime treatment and the other 25 percent bypasses the first stage and is mixed in the second stage. Compute the kg/d of chemicals required and the hardness of the water.

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