10

Chemical Water and Wastewater Treatment Processes

Robert M. Sykes
The Ohio State University

Harold W. Walker
The Ohio State University

Linda K. Weavers
The Ohio State University

10.1 Coagulation

Surface waters contain a variety of suspended, colloidal solids that have aesthetic, economic, or health impacts. Simple sedimentation and direct, unaided filtration are not practical in the case of clays and organic detritus, because the overflow and filtration rates required for their removal lead to facilities that are 100 to 200 times larger than those built today (Fanning, 1887; Fuller, 1898). Consequently, all surface water treatment plants incorporate processes that destabilize and agglomerate colloids into larger, fast-settling particles.

Colloids

Properties

Colloidal systems (dispersoids, colloidal dispersions, colloidal suspensions, colloidal solutions, and sols) consist of particles suspended in some sort of medium. The chemical composition of the particles is usually different from that of the medium, but examples where they are the same are known. Colloidal systems are distinguished from true solutions and mechanical suspensions by the following criteria (Voyutsky, 1978).

Opalescence

Colloidal systems scatter visible light. If a light beam is passed through a suspension of colloidal particles, some of the light beam will be scattered at right angles, and a cloudy streak will be seen running along its path. This is called a “Tyndall cone” after its discoverer.

A consequence of scattering is that colloidal systems do not transmit images of objects; when the transmitted light is viewed along its path, only a uniform glow is seen. This property is called "turbidity," and colloidal systems are said to be "turbid." By contrast, true solutions, even if they are colored, transmit clear images of objects.

Opalescence is the basis of colloid measurement. If light intensity measurements are made collinearly with the beam, the procedure is called "turbidimetry." If the measurements are made at right angles to the path of the beam, the procedure is called "nephelometry."

Turbidimetry requires subtraction of the light intensity leaving the sample from the light intensity entering the sample. For low turbidities, this difference is small, and its measurement is inherently inaccurate. Nephelometry is preferred at low turbidities, because only the intensity of the scattered light need be known, and very low light intensities can be measured accurately.

In Rayleigh's theory, the scattered light intensity is given by the following (Jirgensons and Straumanis, 1956):

$$H_s = 24\pi^3 \cdot \left(\frac{n_p^2 - n_m^2}{n_p^2 + 2n_m^2} \right) \cdot \frac{nV_p^2}{\lambda^4} \cdot I_o \qquad (10.1)$$

where H_s = the total scattered light intensity summed over all angles from nonconducting, spherical particles (W or ft·lbf/sec)
I_0 = the irradiance of the incident beam (W/m^2 or ft·lbf/ft^2·sec)
n = the concentration of particles (number/m^3 or number/ft^3)
n_m = the refractive index of the suspending medium (dimensionless)
n_p = the refractive index of the particle (dimensionless)
λ = the wavelength of the incident beam (m or ft)

The observed intensity of scattered light varies with (a) the angle at which the light is measured, (b) the size and properties of the particles, (c) the properties of the suspending medium, (d) the wavelengths in the incident light, and (e) whether or not the light is polarized. Consequently, the units of turbidity are somewhat arbitrary, and the weight concentrations of particles in different waters may be different, even if the turbidities are the same.

The turbidity units used in environmental engineering are based on several different but related standards. The earliest standard was based on the silica frustules of diatoms (Committee on Standard Methods of Water Analysis, 1901). The shells were cleaned of organic matter and ground and sieved through a 200 mesh screen, so the particles were smaller than 74 µm. This means the original standard suspension includes some particles that were larger than colloids. A suspension containing 1 mg/L of these prepared particles was defined to have a turbidity of 1.

Nowadays, the clay kaolin, the organic colloid formazin, and styrene divinylbenzene beads are used instead of diatomaceous earth, but the concentrations of these materials are adjusted so that one turbidity unit of any of them produces approximately the same degree of scattering as 1 mg/L of diatomaceous earth (Joint Editorial Board, 1992). All these modern standards also include particles that are larger than colloids. However, many of the suspended particles in surface waters are supracolloidal, so the use of standards containing supracolloidal particles is not an error.

If the turbidity is between 25 and 1000 units, it is often measured using a Jackson Tube. This is an example of turbidimetry. In this device, a standardized candle is viewed through a layer of sample contained in a glass tube with opaque sides and a clear bottom. Sample can be added to or withdrawn from the tube until the image of the candle disappears and a uniformly illuminated field remains. The depth of sample is correlated with the turbidity. For example, if the turbidity is 100 units, the image of the candle disappears at a sample depth of 21.5 cm; it disappears at 39.8 cm, if the turbidity is 50 units. Turbidity measurements performed this way are reported as "JTU," i.e., Jackson turbidity units.

For turbidities less than 25 units, the scattered light intensity at 90° from the incident path is measured. Various commercial instruments are used, and they are calibrated against standard suspensions.

Measurement at 90° is called nephelometry, and the instruments are called nephelometers. The measured turbidity is reported as "NTU," i.e., nephelometric turbidity units.

The treatment goal for potable waters is to produce a final turbidity less than 0.5 units.

Dialysis

Colloidal particles can be dialyzed. This means that they cannot pass through a semipermeable membrane. True solutes of low molecular weight will. Consequently, if a system containing water, true solutes, and colloidal particles is placed on one side of a semipermeable membrane, and pure water is placed on the other side of the membrane, the true solutes pass through the membrane, equilibrating their concentrations on either side, but the colloids do not. This is one way of purifying colloidal systems from dissolved salts. The process is dependent on the sizes of the membrane's pores, and so this is another size classification scheme: colloids are larger than true solutes. The traditional membranes were animal tissues like bull's bladders and parchment, but nowadays, various synthetic membranes are used, and the pore sizes can be specified (Voyutsky, 1978).

Osmotic Pressure

If a colloidal system is dialyzed, it will exhibit an osmotic pressure on the dialysis membrane, just like a true solution. Osmotic pressure is proportional to the number of particles suspended in the dispersing medium. It does not depend on the size of the particles, so it does not matter whether the particles are single atoms, large molecules, or sols.

The osmotic pressure of the colloidal system is calculated using Einstein's formula, which is the same as the osmotic pressure equation for true solutes (Einstein, 1956):

$$p = \frac{RTn}{VN_A} \tag{10.2}$$

where N_A = Avogadro's number ($6.022\,136\,7 \times 10^{23}$ particles/mole)
n = the concentration of particles (number/m^3)
p = the osmotic pressure of the colloidal system ($\mathrm{N/m}^2$)
R = the gas constant (8.314 510 J/mol·K)
T = the absolute temperature (K)

It is estimated that a 0.5% by wt. gold sol, which is about the highest concentration that can be achieved, consisting of particles about 1 nm in diameter, would develop an osmotic pressure of only 1 to 2 mm water head (Svedberg, 1924).

Brownian Movement

Colloidal particles exhibit the so-called "Brownian movement," which is visible in the case of the larger particles under a microscope. The Brownian movement is due to the momentum transmitted to the colloidal particles by the thermal motion of the suspending medium. The resulting paths of the colloidal particles consist of connected, broken straight lines oriented at random and with random lengths. The result is that the particles diffuse according to Fick's Law. Einsteins's formula for the diffusivity of colloidal particles is (Einstein, 1956):

$$D = \frac{RT}{6\pi N_A \mu r} \tag{10.3}$$

where D = the diffusivity of the suspended particles (m^2/s)
r = the radius of the suspended particle (m)
μ = the absolute viscosity of the suspending medium (N·s/m^2)

Colloidal particles have a small settling velocity, which may be estimated from Stoke's Law. Consequently, in a perfectly quiescent container, the particles will tend to settle out. This will establish a concentration gradient, with higher concentrations toward the bottom, and the resulting upward diffusion will, at some point, balance the sedimentation. At equilibrium, the particles are distributed vertically in the container according to the “hypsometric” law, which was first derived for the distribution of gases in a gravitational field (Svedberg, 1924):

$$\frac{n_2}{n_1} = \exp\left\{-\frac{gN_A V_p\left(\rho_p - \rho\right)\left(z_2 - z_1\right)}{RT}\right\} \tag{10.4}$$

where g = the acceleration due to gravity (9.80665 m/s^2);
n_1 = the number (or concentration) of particles at height z_1
n_2 = the number (or concentration) of particles at height z_2
V_p = the volume of a single particle (m^3)
z_1 = the elevation of particle concentration n_1 (m)
z_2 = the elevation of particle concentration n_2 (m)
ρ = the mass density of the suspending medium (kg/m^3)
ρ_p = the mass density of the particles (kg/m^3)

Electrophoresis

If an electric field is applied to a colloidal system, *all* the particles will migrate slowly to *one* electrode. This means that the particles are charged and that they all have the same kind of charge, positive or negative, although the absolute values of the charges may differ. This should be contrasted with solutions of electrolytes, which contain equal numbers of positive and negative charges: when true solutions are electrolyzed, particles are attracted to both electrodes.

Stability

Many colloidal systems are unstable, and the particles can be coagulated in a variety of ways. In fact, one of the main problems of colloid chemistry is how to make the particles stay in suspension.

Composition

The particles usually have a different composition from the suspending medium. Therefore, the systems consist of more than one chemical phase, usually two but sometimes more, and they are heterogeneous. True solutions consist of a single phase.

Particle Size

The traditional range of sizes of colloidal particles was set by Zsigmondy (1914) at 1 to 100 nm. The upper size limit was chosen because it is somewhat smaller than the smallest particle that can be seen under a light microscope. Also, particles smaller than 100 nm do not settle out of suspension, even under quiescent conditions, but particles around 1 µm, the size of bacteria, will. The lower limit is somewhat smaller than can be detected by an ultramicroscope. Consequently, these are operational limits determined by the available instrumentation; they are not fundamental properties of colloidal systems.

These sizes may be compared to those of other particles:

- Atoms — 0.1 to 0.6 nm
- Small molecules — 0.2 to 5 nm
- Small polymers — 0.5 to 10 nm
- Colloids — 1 to 100 nm
- Clay — <2000 nm (Smaller clays are colloidal.)
- Bacteria — 250 to 10,000 nm (These and larger particles are settleable.)
- Silt — 2000 to 50,000 nm
- Visible particles — >50,000 nm
- Very fine sand — 50,000 to 100,000 nm

Dispersions of particles with diameters between 100 and 1000 nm are sometimes called “fine” dispersions; if the diameters are larger than 1000 nm, the dispersion is called “coarse.” Fine and coarse dispersions are maintained by turbulence in the suspending medium, not by the random thermal motion of their molecules.

Kinds of Colloidal Dispersions

Colloids can also be classified according to chemistry. The simplest scheme, due to Ostwald (1915), is:

- Gas in gas (impossible)
- Liquid in gas (fogs, mists, clouds)
- Solid in gas [smokes, fumes (ammonium chloride)]
- Gas in liquid (foams)
- Liquid in liquid (emulsions, cream)
- Solid in liquid (colloidal gold)
- Gas in solid (meershaum, pumice)
- Liquid in solid [metallic mercury in ointments, opal (water in amorphous silica)]
- Solid in solid [ruby glass (gold in glass), cast iron (carbon in iron)]

The important colloids in water and sewage treatment are foams, emulsions, and solids-in-liquids. Smokes, fumes, fogs, and mists are important in air pollution.

Classification by Stability

Colloidal systems are traditionally divided into two broad groups:

- “Reversible,” “lyo(hydro)philic,” or “emulsoid”
- “Irreversible,” “lyo(hydro)phobic,” or“suspensoid”

The various terms used to describe each class are not exact synonyms, because they emphasize different aspects of colloidal stability. Furthermore, they are probably best thought of as endpoints on a continuous spectrum rather than separate groups. Lyophilic colloids are typically organic materials, especially naturally occurring ones, and lyophobic colloids are primarily inorganic materials.

The dichotomy reversible/irreversible, proposed by Zsigmondy (1914), is based on the idea of thermodynamic spontaneity. A colloidal system is called reversible if after drying it can be reformed simply by adding the dispersion medium. It is called irreversible if it does not reform spontaneously.

The distinctions lyophilic/lyophobic, introduced by Neumann (Ostwald, 1915), and hydrophilic/hydrophobic, which was introduced by Perrin (Ostwald, 1915), refer to the sensitivity of the system to the addition of electrolytes. A lyo(hydro)philic colloidal particle remains in suspension and uncoagulated over relatively wide ranges of electrolyte concentration, but lyo(hydro)phobic colloidal particles are stable only over narrow ranges of electrolyte concentration.

Suspensoid comprehends the ideas of irreversiblility and electrolyte sensitivity.

Emulsoid comprehends reversibility and insensitivity to electrolytes.

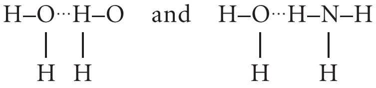
Because these definitions are not fully equivalent, they sometimes lead to contradictory classifications. For example, clays spontaneously form stable suspensions when mixed with natural waters, so they can be classified as reversible and, by extension, hydrophilic (Fridrikhsberg, 1986). On the other hand, the stability of clay suspensions is sensitive to the electrolyte concentration, so they can also be classified as hydrophobes (James M. Montgomery, Consulting Engineers, Inc., 1985). Aluminum hydroxide and ferric hydroxide, which are discussed below, also exhibit these contrary tendencies (Voyutsky, 1978). Furthermore, some colloid scientists maintain that organic substances like cellulose and protein are not properly classified as any kind of colloid; they are really high molecular weight molecules in true solution (Voyutsky, 1978). By implication, the only true colloids are suspensoids. Most workers, however, continue to include organic materials among the colloids.

Stability

Colloidal dispersions are said to be stable, if the particles remain separated from one another for long times. If the particles coalesce, the dispersion becomes unstable. There are two phenomena that affect stability: solvation and surface charge (Kruyt, 1930).

Hydrophilic colloids are naturally stabilized by solvation and surface charge. Hydrophobic colloids are not solvated and depend entirely on surface charge for stability. Clays and metallic hydroxides are partially solvated but are stabilized in part by surface charges.

A particle is solvated if its surface bonds to water. The particular kind of bonding involved is called "hydrogen bonding." This is a sort of weak electrostatic bonding. It occurs whenever the system contains surfaces that have strongly electronegative atoms like O, N, or F. Even when these atoms are covalently bonded into molecules, their attraction for electrons is so strong that the electron cloud is distorted and concentrated in their vicinity. This produces a region of excess negative charge. Hydrogen atoms tend to be attracted to these zones of excess negativity, and this attraction leads to a weak bonding between molecules. For example, water molecules hydrogen bond both to each other and to ammonia:



$$\begin{array}{ccccccc} \mathrm{H} & - & \mathrm{O} & \cdots & \mathrm{H} & - & \mathrm{O} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array} \quad \text{and} \quad \begin{array}{ccccccccc} \mathrm{H} & - & \mathrm{O} & \cdots & \mathrm{H} & - & \mathrm{N} & - & \mathrm{H} \\ & & | & & & & | & & \\ & & \mathrm{H} & & & & \mathrm{H} & & \end{array}$$

Here the solid lines indicate normal covalent bonds, and the three dots indicate hydrogen bonds. Typical hydrogen bond energies are about 5 kcal/mole, compared to about 50 to 100 kcal/mole for covalent bonds.

Hydrogen bonding leads to a competition between water molecules and other colloids for the particle surface, and in the case of hydrophilic colloids, the water wins. Consequently, the particles are prevented from coalescing, because they are coated with a film of water that cannot be displaced.

The surface charge on colloids is developed in three ways. Some colloids contain surface groups that readily ionize in water or take up protons, e.g., (Stumm and Morgan, 1970):

$$-\mathrm{OH} \rightarrow -\mathrm{OH}^-$$

$$-\mathrm{NH_2} \rightarrow -\mathrm{NH_3^+}$$

$$-\mathrm{COOH} \rightarrow -\mathrm{COO}^-$$

These ionizations and protonations are strongly pH dependent, and the resulting surface potential varies with the pH.

The second method is selective bonding of ions from the surrounding solution. This occurs because the plane of the crystal lattice that forms the particle surface has unsatisfied electrostatic and covalent bonds that ions in the suspending medium can complete. The bonding is very specific and depends on the detailed chemistry of the particle surface and the kinds of ions dissolved in the water.

The third method is ion exchange. Some ions, usually cations, diffuse out of the crystal lattice of the colloidal particle into the surrounding medium, and they are replaced by other ions that diffuse from the medium into the particle. If the two ions have different charges, the lattice will acquire or lose charge. Ion exchange is not very specific, except that small, highly charged ions tend to replace large, weakly charged ions.

All three mechanisms may occur on a single particle. The net result is the surface potential, ψ_0.

The surface potential influences the remaining ions in the suspending medium by electrostatic repulsion and attraction; the result is the so-called "electrical double layer" (Voyutsky, 1978). If the particle has a net negative charge (which is typical of clays), positive ions in the suspending medium adsorb electrostatically to the exterior of the particle surface in a layer one or more ions thick. This adsorbed layer is called the "Stern" layer, and it reduces the net potential on the particle from ψ_0 to ψ_δ. The reduced electrostatic field repels and attracts ions in the suspending medium depending on whether they are of like or unlike sign, respectively. Consequently, the solution is not electrically neutral near the particle surface, and any given thin layer of solution will contain an excess of charge opposite in sign to ψ_δ. The ions in the solution layer bearing the charges of opposite sign are called the counterions, and the layer itself is called the "diffuse" or "Gouy" layer. Away from the particle surface, the net observed charge is the sum of the charges due to the particle surface charge, the Stern layer and the intervening Gouy layer. It falls off with distance, until at large distances, the system appears to be electrically neutral.

The surface potential of colloids is usually determined by measuring their velocity in an electrical field. Because moving particles have an attached boundary layer of water, what is actually determined is the net of the voltage on the particle and the counterions in the boundary layer. The result is called the electrokinetic potential or the zeta potential, and it is calculated using the Helmholtz–Smoluchowski equation (Voyutsky, 1978):

$$\zeta = \frac{k\pi\mu v}{\varepsilon \cdot \boldsymbol{E}} \tag{10.5}$$

where E = the imposed potential gradient (V/m)
k = a constant in the Helmholtz–Smoluchowski equation that depends on the particle shape and imposed electric field, generally between 4 and 8 (dimensionless)
ν = the particle velocity (m/s)
ε = the dielectric constant of the suspending medium (dimensionless)
μ = the absolute viscosity of the suspending medium ($N{\cdot}s/m^2$)
ζ = the zeta potential (V)

The ratio ν/E is called the electrophoretic mobility.

The thickness of the boundary layer will depend upon the velocity of the particle. Consequently, the volume of water and the number of counterions associated with a moving colloid varies with the imposed electric field and other factors. This means that ζ also varies with these conditions, and it cannot be identified with ψ_δ. Nevertheless, as long as the experimental conditions are standardized, the zeta potential remains a useful index of the surface potential on the particles. Furthermore, many colloids coagulate spontaneously if the Stern layer potential, ψ_δ, is near zero, and the zeta potential is also zero in this case.

Coagulation Chemistry

Coagulation Mechanisms

Colloidal particles can be coagulated in four ways:

- Surface potential reduction
- Compression of the Gouy layer
- Interparticle bridging
- Enmeshment

Reduction of surface potential is effective only against hydrophobic colloids. If the surface potential arises because of ionization or protonation of surface groups, a change in pH via the addition of acid or base will eliminate it. Addition of counterions that adsorb to the surface of the particles also can reduce the surface potential.

Compression of the Gouy layer permits colloidal particles to approach each other closely before experiencing electrostatic repulsion, and their momentum may overcome the residual repulsion and cause collision and adhesion. The Gouy layer can be compressed by the addition of counterions that do not adsorb to the particles. The compression is greatest for highly charged ions, because the electrostatic attraction per ion increases with its charge. According to the Schulze–Hardy Rule (Voyutsky, 1978), the molar concentration of an ion required to coagulate a colloid is proportional to the reciprocal of its charge raised to the sixth power. Consequently, the relative molar concentrations of mono-, di-, tri-, and tetravalent ions required to coagulate a colloid are in the ratios $1{:}(1/2)^6{:}(1/3)^6{:}(1/4)^6$ or 1:0.016:0.0013:0.00024.

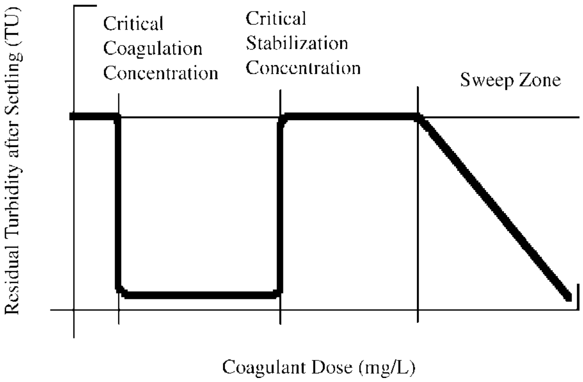


FIGURE 10.1 Residual turbidity after settling vs. coagulant dose.

Interparticle bridging is accomplished by adding microscopic filaments to the suspension. These filaments are long enough to bond to more than one particle surface, and they entangle the particles forming larger masses. The filaments may be either uncharged in water (nonionic), positively charged (cationic), or negatively charged (anionic).

Enmeshment occurs when a precipitate is formed in the water by the addition of suitable chemicals. If the precipitate is voluminous, it will surround and trap the colloids, and they will settle out with it.

Coagulant Dosage

A typical example of coagulation by aluminum and iron salts is shown in Fig. 10.1, in which residual turbidity after settling is plotted against coagulant dose. At low coagulant dosages, nothing happens. However, as the dosage is increased a point is reached at which rapid coagulation and settling occurs. This is called the "critical coagulation concentration" (CCC). Coagulation and settling also occur at somewhat higher concentrations of coagulant. Eventually, increasing the dosage fails to coagulate the suspension, and the concentration marking this failure is called the "critical restabilization concentration" (CSC). At still higher coagulant dosages, turbidity removal again occurs. This second turbidity removal zone is called the "sweep zone."

Figure 10.1 can be explained as follows. Between the CCC and the CSC, aluminum and iron salts coagulate silts and clays by surface charge reduction (Dentel and Gossett, 1988: Mackrle, 1962; Stumm and O'Melia, 1968). Aluminum and iron form precipitates of aluminum hydroxide [$Al(OH)_3$] and ferric hydroxide [$Fe(OH)_3$], respectively. These precipitates are highly insoluble and hydrophobic, and they adsorb to the silt and clay surfaces. The net charge on the aluminum hydroxide precipitate is positive at pHs less than about 8; the ferric hydroxide precipitate is positive at pHs less than about 6 (Stumm and Morgan, 1970). The result of the hydroxide adsorption is that the normally negative surface charge of the silts and clays is reduced, and so is the zeta potential. Coagulation and precipitation of the silts and clays occurs when enough aluminum or iron has been added to the suspension to reduce the zeta potential to near zero, and this is the condition between the CCC and the CSC.

At dosages below the CCC, the silts and clays retain enough negative charge to repel each other electrostatically.

As the aluminum or iron dosage approaches the CSC, aluminum and ferric hydroxide continue to adsorb to the silts and clays, the silts and clays become positive, and they are stabilized again by electrostatic repulsion, although the charge is positive.

If large amounts of aluminum or iron salts are used, the quantity of hydroxide precipitate formed will exceed the adsorption capacity of the silt and clay surfaces, and free hydroxide precipitate will accumulate in the suspension. This free precipitate will enmesh the silts and clays and remove them when it settles out. This is the sweep zone.

When the coagulant dosages employed lie between the CCC and the CSC, the coagulation mechanism is surface charge reduction via adsorption of aluminum or ferric hydroxides to the particle surfaces. Consequently, there should be a relationship between the raw water turbidity and the dosage required to destabilize it. Examples of empirical correlations are given in Stein (1915), Hopkins and Bean (1966), Langelier, Ludwig, and Ludwig, (1953), and Hudson (1965). For particles of uniform size, regardless of shape, the surface area is proportional to the two-thirds power of the concentration. This rule is also true for different suspensions having the same size distribution. Hazen's (1890) rule of thumb, Eq. (10.6), follows this rule very closely:

$$C_{Alum} = 0.349 + 0.0377 \cdot C_{TU}^{2/3}; \qquad R^2 = 0.998 \tag{10.6}$$

where C_{Alum} = the filter alum dosage in grains/gallon
C_{TU} = the raw water turbidity in JTU

However, when waters from several different sources are compared, it is found that the required coagulant dosages do not follow Hazen's rule of thumb. The divergences from the rule are probably due to differences in particle sizes in the different waters. For constant turbidity, the required coagulant dosage varies inversely with particle size; the required dosage nearly triples if the particle size is reduced by a factor of about ten (Langelier, Ludwig, and Ludwig, 1953).

The Jar Test

Although Eq. (10.6) is useful as a guideline, in practice, coagulant dosages must be determined experimentally. The determination must be repeated on a frequent basis, at least daily but often once or more per work shift, because the quantities and qualities of the suspended solids in surface waters vary. The usual method is the "jar test."

The jar test attempts to simulate the intensity and duration of the turbulence in key operations as they are actually performed in the treatment plant: i.e., chemical dosing (rapid mixing), colloid destabilization and agglomeration (coagulation/flocculation), and particle settling. Because each plant is different, the details of the jar test procedure will vary from facility to facility, but the general outline, developed by Camp and Conklin (1970), is as follows:

- Two-liter aliquots of a representative sample are placed into each of several standard 2L laboratory beakers or specially designed 2L square beakers (Cornwall and Bishop, 1983). Typically, six beakers are used, because the common laboratory mixing apparatus has space for six beakers. Beakers with stators are preferred because there is better control of the turbulence. The intensity of the turbulence is measured by the "root-mean-square velocity gradient," "G." (The r.m.s. characteristic strain rate, $\overline{\Gamma}$, is nowadays preferred.)
- The mixer is turned on, and the rotational speed is adjusted to produce the same r.m.s. velocity gradient as that produced by the plant's rapid-mixing tank.
- A known amount of the coagulant is added to each beaker, usually in the form of a concentrated solution, and the rapid mixing is allowed to continue for a time equal to the hydraulic detention time of the plant's rapid mixing tank.
- The mixing rate is slowed to produce a r.m.s. velocity gradient equal to that in the plant's flocculation tank, and the mixing is continued for a time equal to the flocculation tank's hydraulic detention time.
- The mixer is turned off, and the flocculated suspension is allowed to settle quiescently for a period equal to the hydraulic detention time of the plant's settling tanks.
- The supernatant liquid is sampled and analyzed for residual turbidity.

Hudson and Singley (1974) recommend sampling the contents of each beaker for residual suspended solids as soon the turbulence dies out, in order to develop a settling velocity distribution curve for the flocculated particles.

The supernatant liquid should be clear, and the floc particles should be compact and dense, i.e., “pinhead” floc, so-called because of its size. Large, feathery floc particles are undesirable, because they are fragile and tend to settle slowly, and they may indicate dosage in the sweep zone, which may be uneconomic.

If the suspension does not coagulate or if the result is “smokey” or “pinpoint” floc, either:

- More coagulant is needed.
- The raw water has insufficient alkalinity, and the addition of lime or soda ash is required. (This necessitates a more elaborate testing program to determine the proper ratios of coagulant and base.)
- The water is so cold that the reactions are delayed. (The test should be conducted at the temperature of the treatment plant.)

The jar test is also used to evaluate the performance of various coagulant aids, as well as the removal of color, disinfection by-product precursors, and taste and odor compounds.

Finally, it should be noted that the jar test simulates an ideal plug flow reactor. This means that it will not accurately simulate the performance of the flocculation and settling tanks unless they exhibit ideal plug flow, too. In practice, flocculation tanks must be built as mixed-cells-in-series, and settling tanks should incorporate tube modules.

Aluminum and Iron Chemistry

The chemistries of aluminum and ferric iron are very similar. Both cations react strongly with water molecules to form hydroxide precipitates and release protons:

$$\mathrm{Al^{3+} + 3\ H_2O \rightarrow Al(OH)_3(s) + 3\ H^+} \tag{10.7}$$

$$\mathrm{Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3(s) + 3\ H^+} \tag{10.8}$$

Furthermore, at high pHs both precipitates react with the hydroxide ion and redissolve, forming aluminate and ferrate ions:

$$\mathrm{Al(OH)_3(s) + OH^- \rightarrow Al(OH)_4^-} \tag{10.9}$$

$$\mathrm{Fe(OH)_3(s) + OH^- \rightarrow Fe(OH)_4^-} \tag{10.10}$$

Both cations also form a large number of other dissolved ionic species, some of which are polymers, and many of yet unknown structure.

The dissolution of aluminum and ferric hydroxide at high pH is not a significant problem in water treatment, because the high pHs required do not normally occur. However, the hydrolysis reactions of Eqs. (10.7) and (10.8) are. Both reactions liberate protons, and unless these protons are removed from solution, only trace amounts, if any, of the precipitates are formed. In fact, if aluminum salts are added to pure water, no visible precipitate is formed. There are also many natural waters in which precipitate formation is minimal. These generally occur in granitic or basaltic regions.

Filter Alum

The most commonly used coagulant is filter alum, also called aluminum sulfate. Filter alum is made by dissolving bauxite ore in sulfuric acid. The solution is treated to remove impurities, neutralized, and evaporated to produce slabs of aluminum sulfate. The product is gray to yellow-white in color, depending on the impurities present, and the crystals include variable amounts of water of hydration: $Al_2(SO_4)_3(H_2O)_n$, with n taking the values 0, 6, 10, 16, 18, and 27. It is usually specified that the water-soluble alumina [Al_2O_3]

content exceed 17% by weight. This implies an atomic composition of $Al_2(SO_4)_3(H_2O)_{14.3}$. The commercial product also should contain less than 0.5% by wt insoluble matter and less than 0.75% by wt iron, reported as ferric oxide [Fe_2O_3] (Hedgepeth, 1934; Sidgwick, 1950).

Filter alum can be purchased as lumps ranging in size from 3/4 to 3 in., as granules smaller than the NBS No. 4 sieve, as a powder, or as a solution. The solution is required to contain at least 8.5% by wt alumina. The granules and powder must be dissolved in water prior to application, and the lumps must be ground prior to dissolution. Consequently, the purchase of liquid aluminum sulfate, sometimes called "syrup alum," eliminates the need for grinders and dissolving apparatus, and these savings may offset the generally higher unit costs and increased storage volumes and costs.

The dissolution of filter alum and its reaction with alkalinity to form aluminum hydroxide may be described by,

$$\mathrm{Al_2(SO_4)_3(H_2O)_{14.3}(s) + 6\ HCO_3^- \rightarrow 2\ Al(OH)_3(s) + 6\ CO_2 + 3\ SO_4^{2-} + 14.3\ H_2O} \qquad (10.11)$$

The aluminum hydroxide precipitate is white, and the carbon dioxide gas produced will appear as small bubbles in the water and on the sides of the jar test beaker. The sulfate released passes through the treatment plant and into the distribution system. One mole of filter alum releases six moles of protons, so its equivalent weight is 1/6 of 600 g or 100 g. The alkalinity consumed is six equivalents or 300 g (as $CaCO_3$). This is the source of the traditional rule-of-thumb that *1 g of filter alum consumes 0.5 g of alkalinity.*

The acid-side and base-side equilibria for the dissolution of aluminum hydroxide are (Hayden and Rubin, 1974):

$$\mathrm{Al^{3+} + H_2O \leftrightarrow Al(OH)_3(s) + 3\ H^+} \qquad (10.12)$$

$$K_{s1} = \frac{[\mathrm{H^+}]^3}{[\mathrm{Al^{3+}}]} = 10^{-10.40} \quad (25°\mathrm{C}) \qquad (10.13)$$

$$\mathrm{Al(OH)_3(s) + OH^- \leftrightarrow Al(OH)_4^-} \qquad (10.14)$$

$$K_{s2} = \frac{[\mathrm{Al(OH)_4^-}]}{[\mathrm{OH^-}]} = 10^{1.64} \quad (25°\mathrm{C}) \qquad (10.15)$$

Substituting the ionization constant for water produces:

$$K_{s2} \cdot K_w = [\mathrm{Al(OH)_4^-}] \cdot [\mathrm{H^+}] = 10^{-12.35} (25°\mathrm{C}) \qquad (10.16)$$

Equations (10.13) and (10.16) plot as straight lines on log/log coordinates. Together they define a triangular region of hydroxide precipitation, which is shown in Fig. 10.2. Figure 10.2 shows the conditions for the precipitation of aluminum hydroxide. However, it is known that this triangular region also corresponds to the region in which silts and clays are coagulated (Dentel and Gossett, 1988; Hayden and Rubin, 1974). The rectangular region in the figure is the usual range of pH levels and alum dosages seen in water treatment. It corresponds to Hazen's recommendations.

Other aluminum species not indicated in Fig. 10.2 are $AlOH^{2+}$ and $Al_8(OH)_{20}^{4+}$. These species are significant under acid conditions. The general relationship among the aluminum species may be represented as (Rubin and Kovac, 1974):

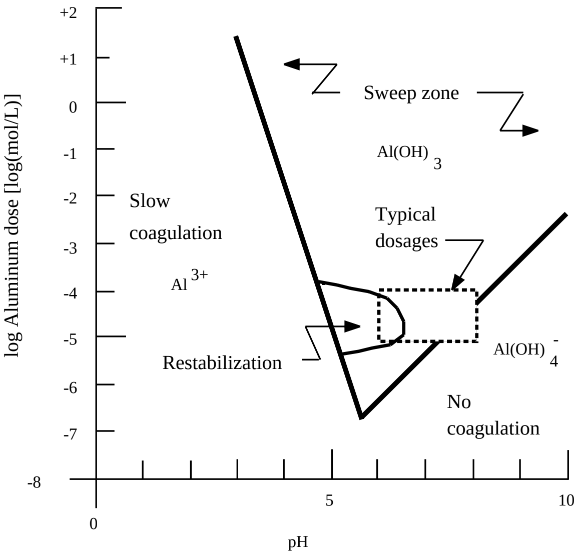


FIGURE 10.2 Alum hydroxide precipitation zone (Hayden and Rubin, 1974).

$$Al^{3+} \leftrightarrow \begin{Bmatrix} AlOH^{2+} \\ Al_8(OH)_{20}^{4+} \end{Bmatrix} \leftrightarrow Al(OH)_3(s) \leftrightarrow Al(OH)_4^-$$

$$\updownarrow$$

$$AlOOH(s)$$

$$\updownarrow$$

$$Al_2O_3(s)$$

The aluminum ion, Al^{3+}, is the dominant species below pH 4.5. Between pH 4.5 and 5, the cations $AlOH^{2+}$ and $Al_8(OH)_{20}^{4+}$ are the principal species. Aluminate, $Al(OH)_4^-$ is the major species above pH 9.5 to 10. Between pH 5 and 10, various solids are formed. The fresh precipitate is aluminum hydroxide, but as it ages, it gradually loses water, eventually becoming a mixture of bayerite and gibbsite. As the solid phase ages, the equilibrium constants given in Eqs. (10.13) and (10.15) change. The values given are for freshly precipitated hydroxide.

The usual aluminum coagulation operating range intersects the restabilization zone, so coagulation difficulties are sometimes experienced. These can be overcome by (Rubin and Kovac, 1974):

- Increasing the alum dosage to get out of the charge reversal zone (This is really a matter of increasing the sulfate concentration, which compresses the Gouy layer.)
- Decreasing the alum dosage to get below the CSC (The floc is generally less settleable, and the primary removal mechanism is filtration, which is satisfactory as long as the total suspended solids concentration is low.)
- Adding lime to raise the pH and move to the right of the restabilization zone
- Adding polyelectrolytes to flocculate the positively charged colloids or coagulant aids like bentonite or activated silica, which are negatively charged and reduce the net positive charge on the silt-clay-hydroxide particles by combining with them (Bentonite and activated silica also increase the density of the floc particles, which improves settling, and activated silica improves flow toughness.)

The same problems arise with iron coagulants, and the same solutions may be employed.

Ferrous and Ferric Iron

The three forms of iron salts usually encountered in water treatment are ferric chloride [$FeCl_3 \cdot 6H_2O$], ferric sulfate [$Fe_2(SO_4)_3(H_2O)_9$], and ferrous sulfate [$FeSO_4(H_2O)_7$]. Anhydrous forms of the ferric salts are available.

Ferrous sulfate is known in the trade as "copperas," "green vitriol," "sugar sulfate," and "sugar of iron." Ferrous sulfate occurs naturally as the ore copperas, but it is more commonly manufactured. Copperas can be made by oxidizing iron pyrites [FeS_2]. The oxidation yields a solution of copperas and sulfuric acid, and the acid is neutralized and converted to copperas by the addition of scrap iron or iron wire. However, the major source is waste pickle liquor. This is a solution of ferrous sulfate that is produced by soaking iron and steel in sulfuric acid to remove mill scale. Again, residual sulfuric acid in the waste liquor is neutralized by adding scrap iron or iron wire. The solutions are purified and evaporated, yielding pale green crystals. Although the heptahydrate [$FeSO_4(H_2O)_7$] is the usual product, salts with 0, 1, or 4 waters of hydration may also be obtained. Copperas is sold as lumps and granules. Because of its derivation from scrap steel, it should be checked for heavy metals.

Ferrous iron forms precipitates with both hydroxide and carbonate (Stumm and Morgan, 1970):

$$\mathrm{Fe(OH)_2(s)} \leftrightarrow \mathrm{Fe^{2+}} + 2\ \mathrm{OH^-} \tag{10.17}$$

$$K_{OH^-} = \left[\mathrm{Fe^{2+}}\right] \cdot \left[\mathrm{OH^-}\right] = 2 \times 10^{-15} \quad (25°\mathrm{C}) \tag{10.18}$$

$$\mathrm{FeCO_3(s)} \leftrightarrow \mathrm{Fe^{2+}} + \mathrm{CO_3^{2-}} \tag{10.19}$$

$$K_{CO_3^{2-}} = \left[\mathrm{Fe^{2+}}\right] \cdot \left[\mathrm{CO_3^{2-}}\right] = 2.1 \times 10^{-11} \quad (25°\mathrm{C}) \tag{10.20}$$

In most waters, the carbonate concentration is high enough to make ferrous carbonate the only solid species, if any forms.

The alkalinity of natural and used waters is usually comprised entirely of bicarbonate, and copperas will not form a precipitate in them. This difficulty may be overcome by using a mixture of lime and copperas, the so-called "lime-and-iron" process. The purpose of the lime is to convert bicarbonate to carbonate so a precipitate may be formed:

$$\mathrm{Fe^{2+}} + \mathrm{HCO_3^-} + \mathrm{OH^-} \rightarrow \mathrm{FeCO_3} + \mathrm{H_2O} \tag{10.21}$$

If the raw water has a significant carbonate concentration, less lime will be needed, because the original carbonate will react with some of the copperas. If the raw water has a significant carbonic acid concentration, additional lime will be required to neutralize it. In either case, enough lime should be used to form an excess of carbonate and, perhaps, hydroxide, which forces the reaction to completion. Hazen's (1890) rule-of-thumb for raw water with carbonate ($pH > 8.3$) is as follows:

$$\left\{\mathrm{CaO}\right\} = 1.16 \cdot \left\{\mathrm{FeSO_4(H_2O)_7}\right\} - \left\{\text{phenolphthalein alkalinity}\right\} + 0.6 \tag{10.22}$$

For raw water without carbonate ($pH < 8.3$),

$$\left\{\mathrm{CaO}\right\} = 1.16 \cdot \left\{\mathrm{FeSO_4(H_2O)_7}\right\} + 0.50 \cdot \left\{\mathrm{H_2CO_3^*}\right\} + 0.6 \tag{10.23}$$

The curly braces indicate that the concentration units are equivalents per liter. One mole of ferrous sulfate is two equivalents.

The lime-and-iron process produces waters with a pH of around 9.5, which may be excessive and may require neutralization prior to distribution or discharge. Consequently, copperas is normally applied in combination with chlorine. The intention is to oxidize the ferrous iron to ferric iron, and the mixture of copperas and chlorine is referred to as “chlorinated copperas:”

$$\mathrm{FeSO_4(H_2O)_7 + \tfrac{1}{2}\ Cl_2 \rightarrow Fe^{3+} + Cl^- + SO_4^{2-} + 7\ H_2O} \tag{10.24}$$

The indicated reaction ratio is about 7.84 g ferrous sulfate per g of chlorine, but dissolved oxygen in the raw water will also convert ferrous to ferric iron, and the practical reaction ratio is more like 7.3 g ferrous sulfate per g chlorine (Hardenbergh, 1940).

Ferric sulfate [$Fe_2(SO_4)_3 \cdot 9H_2O$] is prepared by oxidizing copperas with nitric acid or hydrogen peroxide. Evaporation produces a yellow crystal. Besides the usual nonahydrate, ferric sulfates containing 0, 3, 6, 7, 10, and 12 waters of hydration may be obtained (Sidgwick, 1950).

Ferric chloride is made by mixing hydrochloric acid with iron wire, ferric carbonate, or ferric oxide. The solid is red-yellow in color. The usual product is $FeCl_3 \cdot 6H_2O$, but the anhydrous salt and salts with 2, 2.5, and 3.5 waters of hydration are also known (Hedgepeth, 1934; Sidgwick, 1950).

Both ferric salts produce ferric cations upon dissolution:

$$\mathrm{Fe_2(SO_4)_3(H_2O)_9 \rightarrow 2\ Fe^{3+} + 3\ SO_4^{2-} + 9\ H_2O} \tag{10.25}$$

$$\mathrm{FeCl_3(H_2O)_6 \rightarrow Fe^{3+} + 3\ Cl^- + 6\ H_2O} \tag{10.26}$$

The chemistry of the ferric cation is similar to that of the aluminum cation, except for the species occurring under acidic conditions (Rubin and Kovac, 1974):

$$\begin{array}{c}
\mathrm{Fe^{3+}} \leftrightarrow \left\{\begin{array}{c} \mathrm{FeOH^{2+}} \\ \mathrm{Fe(OH)_2^+} \\ \mathrm{Fe_2(OH)_2^{4+}} \end{array}\right\} \leftrightarrow \mathrm{Fe(OH)_3(s)} \leftrightarrow \mathrm{Fe(OH)_4^-} \\
\updownarrow \\
\mathrm{FeOOH(s)} \\
\updownarrow \\
\mathrm{Fe_2O_3(s)}
\end{array}$$

In the case of iron, the equilibrium involving $Fe(OH)_2^+$ must be considered, as well as Eqs. (10.27) and (10.29) (Stumm and Morgan, 1970):

$$\mathrm{Fe^{3+} + 3\ H_2O \leftrightarrow Fe(OH)_3(s) + 3\ H^+} \tag{10.27}$$

$$K_{so} = \frac{\left[\mathrm{H^+}\right]^3}{\left[\mathrm{Fe^{3+}}\right]} = 10^{-3.28} \quad (25°\mathrm{C}) \tag{10.28}$$

$$\mathrm{Fe(OH)_3(s) + OH^- \leftrightarrow Fe(OH)_4^-} \tag{10.29}$$

$$K_{s1} = \frac{\left[\mathrm{Fe(OH)_4^-}\right]}{\left[\mathrm{OH^-}\right]} = 10^{-4.5} \quad (25°\mathrm{C}) \tag{10.30}$$

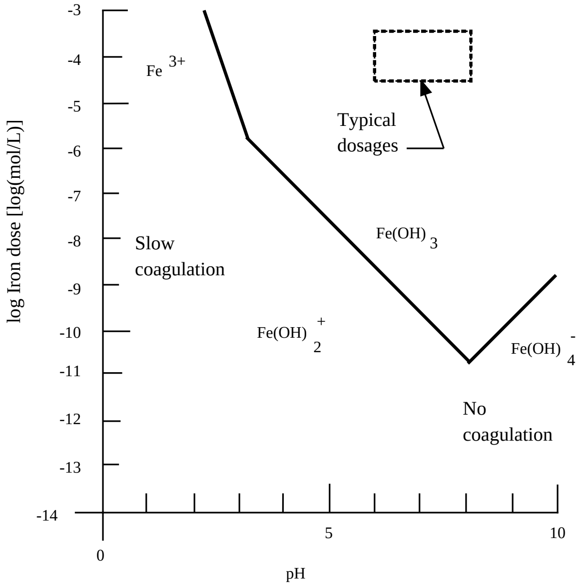


FIGURE 10.3 Ferric hydroxide precipitation zone (Stumm and Morgan, 1970).

$$\mathrm{Fe(OH)_3(s)} \leftrightarrow \mathrm{Fe(OH)_2^+} + \mathrm{OH^-} \tag{10.31}$$

$$K_{s2} = \left[\mathrm{Fe(OH_2^+)}\right]\cdot\left[\mathrm{OH^-}\right] = 10^{-16.6} \quad (25°\mathrm{C}) \tag{10.32}$$

The lines defined by Eqs. (10.28), (10.30), and (10.32) are plotted on log/log coordinates in Fig. 10.3. They define a polygon, which indicates the region where ferric hydroxide precipitate may be expected.

Lime

Lime is usually purchased as "quick lime" [CaO] or "slaked lime" [$Ca(OH)_2$]. The former is available as lumps or granules, the latter is a white powder. Synonyms for quick lime are "burnt lime," "chemical lime," "unslaked lime," and "calcium oxide." If it is made by calcining limestone or lime/soda softening sludges, quick lime may contain substantial amounts of clay. The commercial purity is 75 to 99% by wt CaO. The synonyms for slaked lime are "hydrated lime" and "calcium hydroxide." The commercial product generally contains 63 to 73% CaO.

Lime is used principally to raise the pH to change the surface charge on the colloids and precipitates or provide the alkalinity needed by aluminum and iron.

The lime dosage required for the formation of aluminum and ferric hydroxide, in equivalents per liter, is simply the aluminum or ferric iron dosage less the original total alkalinity:

$$\{\mathrm{CaO}\} + \{\mathrm{Ca(OH_2)}\} = \{\mathrm{Al^{3+}}\} + \{\mathrm{Fe^{3+}}\} - \{\text{total alkalinity}\} \tag{10.33}$$

All concentrations are in meq/L.

As a practical matter, the coagulant and the lime dosages are determined experimentally by the jar test; the calculation suggested by Eq. (10.33) cannot be used to determine lime dosages, although it may serve as a check on the reasonableness of the jar test results. Equation (10.33) also does not take into account finished water stability and issues associated with corrosion and scale.

The jar test is also used to determine the lime dosage needed to reduce the surface charge. The charge reduction is usually checked by an electrophoresis experiment to measure the zeta potential associated with the particles.

It is possible to coagulate many waters simply by adding lime. In a few instances, chiefly anoxic groundwaters, the coagulation occurs because the raw water contains substantial amounts of ferrous iron, and one is really employing the lime-and-iron process. Usually, the precipitate formed with lime is calcium carbonate, perhaps with some magnesium hydroxide. This is the lime/soda softening process.

Coagulant Aids

The principal coagulant aids are lime, bentonite, fuller's earth, activated silica, and various organic polymers. These aids are used to perform several functions, although any given aid will perform only one or a few of the functions:

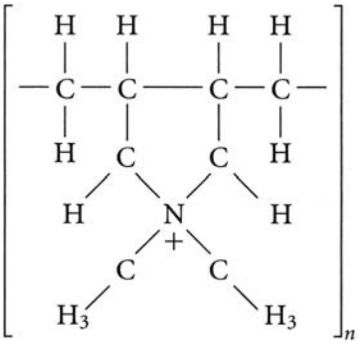
- They may change the pH of the water, which alters the surface charge on many colloids.
- They may provide the alkalinity needed for coagulation by aluminum and ferric iron.
- They may reduce the net surface charge on the colloids by adsorbing to the colloid surface; this is especially useful in escaping the restabilization zone.
- They may link colloidal particles together, forming larger masses; in some cases, the coagulant aid may totally replace the coagulant, but this is often expensive.
- They may increase the strength of the flocculated particles, which prevents floc fragmentation and breakthrough during filtration.
- They may increase the concentration of particles present, thereby increasing the rate of particle collision and the rate of flocculation.
- They may increase the density of the flocculated particles, which improves settling tank efficiencies.

Bentonite and fuller's earth are clays, and both are members of the montmorrillonite-smectite group. The clays are used during periods of low turbidity to increase the suspended solids concentration and the rate of particle collision and to increase the density of the floc particles. Because they carry negative charges when suspended in water, bentonite and fuller's earth may also be used to reduce surface charges in the restabilization zone. Clay dosages as high as 7 gr/gal (120 mg/L) have been used (Babbitt, Doland, and Cleasby, 1967). The required coagulant dosages are also increased by the added clay, and voluminous, fluffy flocs are produced, which, however, settle more rapidly than the floc formed from aluminum hydroxide alone.

Activated silica is an amorphous precipitate of sodium silicate [Na_2SiO_3]. Sodium silicate is sold as a solution containing about 30% by wt SiO_2. This solution is very alkaline, having a pH of about 12. The precipitate is formed by diluting the commercial solution to about 1.5% by wt. SiO_2 and reducing the alkalinity of the solution to about 1100 to 1200 mg/L (as $CaCO_3$) with sulfuric acid. Chlorine and sodium bicarbonate have also been used as acids. The precipitate is aged for 15 min to 2 hr and diluted again to about 0.6% by wt. SiO_2. This second dilution stops the polymerization reactions within the precipitate. The usual application rate is 1:12 to 1:8 parts of silica to parts of aluminum hydroxide. The activated silica precipitate bonds strongly to the coagulated silts/clays/hydroxides and strengthens the flocs. This reduces floc fragmentation due to hydraulic shear in sand filters and limits floc "breakthrough" (Vaughn, Turre, and Grimes, 1971; Kemmer, 1988).

The organic polymers used as coagulant aids may be classified as nonionic, anionic, or cationic (James M. Montgomery, Consulting Engineers, Inc., 1985; O'Melia, 1972; Kemmer, 1988):

- Nonionic — polyacrylamide, $[–CH_2–CH(CONH_2)–]_n$, mol wt over 10^6; and polyethylene oxide, $[–CH_2–CH_2–]_n$, mol wt over 10^6
- anionic — hydrolyzed polyacrylamide, $[–CH_2–CH(CONH_2)CH_2CH(CONa)–]$, mol wt over 10^6; polyacrylic acid, $[–CH_2–CH(COO^-)–]_n$, mol wt over 10^6; polystyrene sulfonate, $[–CH_2–CH(øSO_{3^-})–]_n$, mol wt over 10^6
- cationic — polydiallyldimethylammonium, mol wt below 10^5; polyamines, $[–CH_2–CH_2–NH_{2^-}]_n$, mol wt below 10^5; and quarternized polyamines, $[–CH_2–CH(OH)–CH_2–N(CH_3)_2\text{-}]_n$, mol wt below 10^5



These materials are available from several manufacturers under a variety of trade names. The products are subject to regulation by the U.S. EPA. They are sold as powders, emulsions, and solutions.

All polymers function by adsorbing to the surface of colloids and metal hydroxides. The bonding may be purely electrostatic, but hydrogen bonding and van der Waals bonding occur too, and may overcome electrostatic repulsion.

Anionic polymers will bind to silts and clays, despite the electrostatic repulsion, if their molecular weight is high enough. The bonding is often specific, and some polymers will not bind to some colloids.

The charges on cationic and anionic polymers are due to the ionization and protonation of amino [$–NH_2$], carboxyl [–COOH] and amide [$–CONH_2$] groups and are pH dependent. Consequently, cationic polymers are somewhat more effective at low pHs, and anionic polymers are somewhat more effective at high pHs.

Cationic polymers reduce the surface charge on silts and clays and form interparticle bridges, which literally tie the particles together. Cationic polymers are sometimes used as the sole coagulant. Anionic and nonionic polymers generally function by forming interparticle bridges. Anionic and nonionic polymers are almost always used in combination with a primary coagulant. Dosages are generally on the order of one to several mg/L and are determined by jar testing.

Coagulant Choice

The choice of the coagulants to be employed and their dosages is determined by their relative costs and the jar test results. The rule is to choose the least cost combination that produces satisfactory coagulation, flocculation, settling, and filtration. This rule should be understood to include the minimization of treatment chemical leakage through the plant and into the distribution system. The important point here is that the choice is an empirical matter, and as such, it is subject to change as the raw water composition changes and as relative costs change.

Nevertheless, there are some differences between filter alum and iron salts that appear to have general applicability:

- Iron salts react more quickly to produce hydroxide precipitate than does alum, and the precipitate is tougher and settles more quickly (Babbitt, Doland, and Cleasby, 1967).
- Ferric iron precipitates over a wider range of pHs than does alum, 5 to 11 vs. 5.5 to 8. Ferrous iron precipitates between pH 8.5 and 11 (Committee on Water Works Practice, 1940).
- Alum sludges dewater with difficulty, especially on vacuum filters; the floc is weak and breaks down so that solids are not captured; the sludge is slimy, requiring frequent shutdowns for fabric cleaning; and the volume of sludge requiring processing is larger than with iron salts (Rudolfs, 1940; Joint Committee, 1959).
- Iron salts precipitate more completely, and the iron carryover into the distribution system is less than the aluminum carryover. The median iron concentration in surface waters coagulated with iron salts is about 80 μg/L, and the highest reported iron concentration is 0.41 mg/L (Miller et al., 1984). The median aluminum concentration in finished waters treated with alum is about 90 to 110 μg/L, and nearly 10% of all treatment plants report aluminum concentrations in their product

in excess of 1 mg/L (Letterman and Driscoll, 1988; Miller et al., 1984). Aluminum carryover is a problem because of indications that aluminum may be involved in some brain and bone disorders in humans, including Alzheimers disease (Alfrey, LeGendre, and Kaehny, 1976; Crapper, Krishnan, and Dalton, 1973; Davison et al., 1982; Kopeloff, Barrera, and Kopeloff, 1942; Klatzo, Wismiewski, and Streicher, 1965; Platts, Goode, and Hislop, 1977). The aluminum may be present as Al^{3+}, and its concentration in finished waters appears to increase with increases in flouride (caused by fluoridation) and dissolved organic matter, both of which form soluble complexes with Al^{3+} (Driscoll and Letterman, 1988).

- Alum is easy to handle and store, but iron salts are difficult to handle. Iron salts are corrosive, and they absorb atmospheric moisture, resulting in caking. This precludes feeding the dry compound (Rudolfs, 1940; Babbitt, Doland and Cleasby, 1967).
- There is no marked cost advantage accruing to either alum or iron salts.

Iron salts are often recommended for the coagulation of cold, low turbidity waters. However, a recent study suggests there is no substantial advantage for iron coagulation under these conditions (Haarhoff and Cleasby, 1988). There is an optimum aluminum dosage of about 0.06 mmol/L (1.6 mg Al^{3+}/L), and dosages above this degrade settling and removal. Iron does not exhibit such an optimum.

Sludge handling practices are also important. Water treatment sludges do not usually require processing prior to disposal. This situation arises because water treatment sludges consist of relatively inert inorganic materials, and in the past (but no longer), plants were often permitted to dispose of their sludges by discharge to the nearest stream. Nowadays, the sludges are simply lagooned or placed in landfills. In contrast, sewage treatment sludges are putrescible and require processing prior to disposal. This usually involves a dewatering step. The comparative ease and economy of dewatering iron sludges results in iron salts being the coagulant of choice in sewage treatment. Ferric iron also precipitates the sulfides found in sewage sludges, reducing their nuisance potential.

There are important disadvantages to ferric iron. First, ferric iron solutions are acidic and corrosive and require special materials of construction and operational practices. Second, any carryover of ferric hydroxide into a water distribution system is immediately obvious and undesirable. Alum hydroxide carryover would not be noticed.

References

Adamson, A.W. 1982. *Physical Chemistry of Surfaces*, 4th ed. John Wiley & Sons, Inc., Wiley-Interscience, New York.

Alfrey, A.C., LeGendre, G.R., and Kaehny, W.D. 1976. "The Dialysis Encephalopathy Syndrome. A Possible Aluminum Intoxification," *New England Journal of Medicine*, 294(1): 184.

Babbitt, H.E., Doland, J. J., and Cleasby, J.L. 1967. *Water Supply Engineering,* 6th ed. McGraw-Hill Book Co., Inc., New York.

Camp, T.R. and Conklin, G.F. 1970. "Towards a Rational Jar Test for Coagulation," *Journal of the New England Water Works Association*, 84(3): 325.

Committee on Standard Methods of Water Analysis. 1901. "Second Report of Progress," *Public Health Papers and Reports,* 27: 377.

Committee on Water Works Practice. 1940. *Manual of Water Quality and Treatment*, 1st ed., American Water Works Association, New York.

Cornwall, D.A. and Bishop, M.M. 1983. "Determining Velocity Gradients in Laboratory and Full-Scale Systems," *Journal of the American Water Works Association*, 75(9): 470.

Crapper, D.R., Krishnan, S.S., and Dalton, A.J. 1973. "Brain Aluminum in Alzheimers Disease and Experimental Neurofibrillary Degeneration," *Science*, 180(4085): 511.

Davison, A.M., Walker, G.S., Oli, H., and Lewins, A.M. 1982. "Water Supply Aluminium Concentration, Dialysis Dementia, and Effect of Reverse Osmosis Water Treatment," *The Lancet*, vol. II for 1982 (8302): 785.

Dentel, S.K. and Gossett, J.M. 1988. "Mechanisms of Coagulation with Aluminum Salts," *Journal of the American Water Works Association*, 80(4): 187.

Driscoll, C.T. and Letterman, R.D. 1988. "Chemistry and Fate of Al(III) in Treated Drinking Water," *Journal of Environmental Engineering,* 114(1): 21.

Einstein, A. 1956. *Investigations on the Theory of the Brownian Movement*, trans. A.D. Cowper, R. Fürth, ed. Dover Publications, Inc., New York.

Fanning, J.T. 1887. *A Practical Treatise on Hydraulic and Water-Supply Engineering*. D. Van Nostrand, Publisher, New York.

Fuller, G.W. 1898. *Report on the Investigations into the Purification of the Ohio River Water at Louisville, Kentucky, made to the President and Directors of the Louisville Water Company.* D. van Nostrand, Publisher, New York.

Haarhoff, J. and Cleasby, J.L. 1988. "Comparing Aluminum and Iron Coagulants for In-line Filtration of Cold Water," *Journal of the American Water Works Association* 80(4): 168.

Hardenbergh, W.A. 1940. *Operation of Water-Treatment Plants*. International Textbook Co., Scranton, PA.

Hayden, P.L. and Rubin, A.J. 1974. "Systematic Investigation of the Hydrolysis and Precipitation of Aluminum(III)," p. 317 in *Aqueous-Environmental Chemistry of Metals*, A.J. Rubin, ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Hazen, A. 1890. "Report of Experiments upon the Chemical Precipitation of Sewage made at the Lawrence Experiment Station During 1889," p. 735 *in Experimental Investigations by the State Board of Health of Massachusetts, upon the Purification of Sewage by Filtration and by Chemical Precipitation, and upon the Intermittent Filtration of Water made at Lawrence, Mass., 1888–1890: Part II of Report on Water Supply and Sewerage.* Wright & Potter Printing Co., State Printers, Boston, MA.

Hedgepeth, L.L. 1934. "Coagulants Used in Water Purification and Why," *Journal of the American Water Works Association,* 26(9): 1222.

Hopkins, E.S. and Bean, E.L. 1966. *Water Purification Control*, 4th ed. The Williams & Wilkins Co., Inc**.** **,** Baltimore, MD.

Hudson, H.E., Jr. 1965. "Physical Aspects of Flocculation," *Journal of the American Water Works Association*, 57(7): 885.

Hudson, H.E., Jr. and Singley, J.E. 1974. "Jar Testing and Utilization of Jar-Test Data," p. VI-79 in *Proceedings AWWA Seminar on Upgrading Existing Water-Treatment Plants*. American Water Works Association, Denver, CO.

James M. Montgomery, Consulting Engineers, Inc. 1985. *Water Treatment Principles and Design*. John Wiley & Sons, Wiley-Interscience Publication, New York.

Jirgensons, B. and Straumanis, M.E. 1956. *A Short Textbook of Colloid Chemistry.* John Wiley & Sons, Inc., New York.

Joint Committee of the American Society of Civil Engineers and the Water Pollution Control Federation. 1959. *Sewage Treatment Plant Design*, ASCE Manual of Engineering Practice No. 36, WPCF Manual of Practice No. 8, American Society of Civil Engineers and Water Pollution Control Federation, New York.

Joint Editorial Board. 1992. *Standard Methods for the Examination of Water and Wastewater*, 18th ed. American Public Health Association, Washington, DC.

Kemmer, F.N., ed. 1988. *The NALCO Water Handbook*, 2nd ed. McGraw-Hill, Inc., New York.

Klatzo, I., Wismiewski, H., and Streicher, E. 1965. "Experimental Production of Neurofibrillary Degeneration," *Journal of Neuropathology and Experimental Neurology*, 24(1): 187.

Kopeloff, L.M., Barrera, S.E., and Kopeloff, N. 1942. "Recurrent Conclusive Seizures in Animals Produced by Immunologic and Chemical Means," *American Journal of Psychiatry*, 98(4): 881.

Kruyt, H.R. 1930. *Colloids: A Textbook*, 2nd ed., trans. H.S. van Klooster. John Wiley & Sons, Inc., New York.

Langelier, W.F., Ludwig, H.F., and Ludwig, R.G. 1953. "Flocculation Phenomena in Turbid Water Clarification," *Transactions of the American Society of Civil Engineers*, 118: 147.

Letterman, R.D. and Driscoll, C.T. 1988. "Survey of Residual Aluminum in Filtered Water," *Journal of the American Water Works Association*, 80(4): 154.

Mackrle, S. 1962. "Mechanism of Coagulation in Water Treatment," *Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers,* 88(SA3): 1.

Miller, R.G., Kopfler, F.C., Kelty, K.C., Stober, J.A., and Ulmer, N.S. 1984. "The Occurrence of Aluminum in Drinking Water," *Journal of the American Water Works Association*, 76(1): 84.

O'Melia, C.R. 1972. "Coagulation and Flocculation," p. 61 in *Physicochemical Processes: for Water Quality Control*, W.J. Weber, Jr., ed. John Wiley & Sons, Inc., Wiley-Interscience, New York.

Ostwald, W. 1915. *A Handbook of Colloid-Chemistry*, trans. M.H. Fischer. P. Blaikston's Son & Co., Philadephia, PA.

Platts, M.M., Goode, G.C., and Hislop, J.S. 1977. "Composition of Domestic Water Supply and the Incidence of Fractures and Encephalopathy in Patients on Home Dialysis," *British Medical Journal*, vol. 2 for 1977 (6088): 657.

Rubin, A.J. and Kovac, T.W. 1974. "Effect of Aluminum(III) Hydrolysis on Alum Coagulation," p. 159 in *Chemistry of Water Supply, Treatment, and Distribution*, A.J. Rubin, ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Rudolfs, W. 1940. "Chemical Treatment of Sewage," *Sewage Works Journal*, 12(6): 1051.

Sidgwick, N.V. 1950. *The Chemical Elements and Their Compounds, Vols. I and II.* Oxford University Press, London.

Stein, M.F. 1915.*Water Purification Plants and Their Operation*. John Wiley & Sons, Inc., New York.

Stumm, W. and Morgan, J.J. 1970. *Aquatice Chemistry: An Introduction Emphasizing Equilibria in Natural Waters*. John Wiley & Sons, Inc., Wiley-Interscience, New York.

Stumm, W. and O'Melia, C.R. 1968. "Stoichiometry of Coagulation," *Journal of the American Water Works Association*, 60(5): 514.

Svedberg, T. 1924. *Colloid Chemistry: Wisconsin Lectures.* The Chemical Catalog Co., Inc., New York.

Vaughn, J.C., Turre, G.J., and Grimes, B.L. 1971. "Chemicals and Chemical Handling," p. 526 in *Water Quality and Treatment: A Handbook of Public Water Supplies*, 3rd ed., P.D. Haney et al., eds. McGraw-Hill, Inc., New York.

Voyutsky, S. 1978. *Colloid Chemistry*, trans. N. Bobrov. Mir Publishers, Moscow.

Zsigmondy, R. 1914. *Colloids and the Ultramicroscope: A Manual of Chemistry and Ultramicroscopy*, trans. J. Alexander. John Wiley & Sons, Inc., New York.

10.2 Softening, Stabilization, and Demineralization

Hardness

The natural weathering of limestone, dolomite, and gypsum produces waters that contain elevated levels of calcium and magnesium (and bicarbonate):

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2\ HCO_3^- \tag{10.34}$$

$$2\ CO_2 + 2\ H_2O + CaMg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 4\ HCO_3^- \tag{10.35}$$

$$CaSO_4(H_2O)_2 \rightarrow Ca^{2+} + SO_4^{2-} + 2\ H_2O \tag{10.36}$$

In the case of limestone and dolomite, weathering is an acid/base reaction with the carbon dioxide dissolved in the percolating waters. In the case of gypsum, it is a simple dissolution that occurs whenever the percolating water is unsaturated with respect to calcium sulfate.

Waters that contain substantial amounts of calcium and magnesium are called "hard." Waters that contain substantial amounts of bicarbonate are called "alkaline." Hard waters are usually also alkaline. For reasons connected to Clark's lime/soda softening process, the "carbonate hardness" is defined to be that portion of the calcium and magnesium that is equal to (or less than) the sum of the concentrations of bicarbonate and carbonate, expressed as meq/L. The "noncarbonate hardness" is defined to be the excess of calcium and magnesium over the sum of the concentrations of bicarbonate and carbonate, expressed as meq/L. Except for desert evaporite ponds, the concentrations of carbonate and hydroxide are negligible in natural waters.

Hardness is undesirable for two reasons:

- Hard waters lay down calcium and magnesium carbonate on hot surfaces, which reduces the heat transfer capacity of boilers and heaters and the hydraulic capacity of water and steam lines.
- Hard waters precipitate natural soaps; the precipitation consumes soaps uselessly, which increases cleaning costs, and the precipitate accumulates on surfaces and in fabrics, which requires additional cleaning and which reduces the useful life of fabrics.

It is generally believed that these costs become high enough to warrant municipal water softening when the water hardness exceeds about 100 mg/L (as $CaCO_3$).

Modern steam boilers require feedwaters that have mineral contents much lower than what can be achieved via lime/soda softening. Feedwater demineralization is usually accomplished via ion exchange or reverse osmosis.

Some scale deposition is desirable in water distribution systems in order to minimize lead and copper solubility.

Lime/Soda Chemistry

The excess lime process for the removal of carbonate hardness and the practice of reporting hardness in units of calcium carbonate were introduced by Thomas Clark in 1841 and 1856, respectively (Baker, 1981). The removal of noncarbonate hardness via the addition of soda ash or potash was introduced by A. Ashby in 1876.

The underlying principle is that calcium carbonate and magnesium hydroxide are relatively insoluble. Magnesium hydroxide is more insoluble than magnesium carbonate. The solubility products for dilute solutions of calcium carbonate are as follows (Shock, 1984):

$$K_{sp} = \left[\mathrm{Ca}^{2+}\right] \cdot \left[\mathrm{CO}_3^{2-}\right] \tag{10.37}$$

Calcite:

$$\log K_{sp} = -171.9065 - 0.077993T + \frac{2839.319}{T} + 71.595 \log T \tag{10.38}$$

Aragonite:

$$\log K_{sp} = -171.9773 - 0.077993T + \frac{2903.293}{T} + 71.595 \log T \tag{10.39}$$

Vaterite:

$$\log K_{sp} = -172.1295 - 0.077993T + \frac{3074.688}{T} + 71.595 \log T \tag{10.40}$$

where T = the absolute temperature in K.

For the magnesium solutions, one has the following (Stumm and Morgan, 1970),

$$\begin{aligned} K_{sp} &= \left[\mathrm{Mg}^{2+}\right]\cdot\left[\mathrm{OH}^{-}\right]^{2} \\ &= 10^{-9.2}\ (\text{active, 25°C}) \\ &= 10^{-11.6}\ (\text{brucite, 25°C}) \end{aligned} \tag{10.41}$$

$$\begin{aligned} K_{sp} &= \left[\mathrm{Mg}^{2+}\right]\cdot\left[\mathrm{CO}_3^{2-}\right] \\ &= 10^{-4.9}\ (\text{magnesite, 25°C}) \\ &= 10^{-5.4}\ (\text{nesquehonite, 25°C}) \end{aligned} \tag{10.42}$$

The solubility product for calcite varies nearly linearly with temperature from $10^{-8.09}$ at 5°C to $10^{-8.51}$ at 40°C. This is the basis of the "hot lime" process (Powell, 1954).

The reactions involved can be summarized as follows. First, a slurry of calcium hydroxide is prepared, either by slaking quick lime or by adding slaked lime to water. When this slurry is mixed with hard water, the following reactions occur in sequence:

1. Reaction with carbon dioxide and carbonic acid:

$$\mathrm{Ca(OH)_2} + \mathrm{H_2\ CO_3} \rightarrow \underline{\mathrm{CaCO_3}}{}_{-} + \mathrm{H_2O} \tag{10.43}$$

2. Reaction with bicarbonate:

$$\mathrm{Ca(OH)_2} + 2\ \mathrm{HCO_3^-} \rightarrow \underline{\mathrm{CaCO_3}}{}_{-} + \mathrm{CO_3^{2-}} + \mathrm{H_2O} \tag{10.44}$$

3. Reaction with raw water calcium:

$$\mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \rightarrow \underline{\mathrm{CaCO_3}} \tag{10.45}$$

4. Reaction with magnesium:

$$\mathrm{Ca(OH)_2} + \mathrm{Mg^{2+}} \rightarrow \underline{\mathrm{Mg(OH)_2}} + \mathrm{Ca^{2+}} \tag{10.46}$$

5. Reaction with soda ash:

$$\mathrm{Na_2\ CO_3} + \mathrm{Ca^{2+}} \rightarrow \underline{\mathrm{CaCO_3}} + 2\ \mathrm{Na^+} \tag{10.47}$$

The reaction with carbon dioxide is a nuisance, because it consumes lime and produces sludge but does not result in any hardness removal. Carbon dioxide concentrations are generally negligible in surface waters but may be substantial in groundwaters. In that case, it may be economical to remove the carbon dioxide by aeration prior to softening.

Equations (10.44) and (10.45) are the heart of the Clark process. First, hydrated lime reacts with bicarbonate to form an equivalent amount of free carbonate. The calcium in the lime precipitates out as calcium carbonate, and the free carbonate formed reacts with an equivalent amount of the raw water's original calcium, removing it as calcium carbonate, too. The net result is a reduction in the calcium concentration.

Equation (10.46) is called the "excess lime" reaction, because a substantial concentration of free, unreacted hydroxide is required to drive the precipitation of magnesium hydroxide. The net result is the replacement of magnesium ions by calcium ions. If there is any free carbonate left over from Eq. (10.45), it will react with an equivalent amount of the calcium removing it.

Equation (10.47) is Ashby's process for the removal of noncarbonate hardness. Any calcium left over from Eq. (10.45) is precipitated with soda ash or potash.

Calcium Removal Only

Unless the magnesium concentration is a substantial portion of the total hardness, say more than one-third, or if the total hardness is high, say more than 300 mg/L (as $CaCO_3$), only calcium is removed. The traditional rule of thumb is that cold water softening can reduce the calcium concentration to about 0.8 meq/L (40 mg/L as $CaCO_3$) (Tebbutt, 1992). The magnesium concentration is unchanged.

The reactions are most easily summarized as a bar chart. First, all the ionic concentrations and the concentration of carbon dioxide/carbonic acid are converted to meq/L. Carbon dioxide/carbonic acid acts like a diprotic acid, so its equivalent weight is one-half its molecular weight. The bar chart is drawn as two rows with the cations on top and the anions on the bottom. Carbon dioxide/carbonic acid is placed in a separate box to the left. The sequence of cations from left to right is calcium, magnesium, and all others. The sequence of anions from left to right is carbonate, bicarbonate, and all others:

<table>
<tr><td rowspan="2">CO_2</td><td colspan="3">Ca^{2+}</td><td>Mg^{2+}</td><td>Other cations</td></tr>
<tr><td>CO_3^{2-}</td><td>HCO_3^-</td><td colspan="3">Other anions</td></tr>
</table>

The lime requirement for calcium removal is the sum of the carbon dioxide/carbonic acid demand and the lime required to convert bicarbonate to carbonate. If the calcium concentration exceeds the carbonate and bicarbonate concentrations combined (as shown), then all the bicarbonate is converted. However, if the sum of carbonate and bicarbonate is greater than the calcium concentration, only enough bicarbonate is converted to remove the calcium. The calculation is,

$$\{CaO\} = \{CO_2 + H_2CO_3\} + \min\left[\{\text{original Ca}^{2+} - CO_3^{2-}\} \text{ or } \{HCO_3^-\}\right] \qquad (10.48)$$

where $\{x\}$ = the concentration of species x in meq/L.

The soda ash requirement is calculated as the calcium that cannot be removed by the original carbonate plus the bicarbonate converted to carbonate:

$$\{Na_2CO_3\} = \{\text{original Ca}^{2+}\} - \{CO_3^{2-}\} - \{HCO_3^-\} \qquad (10.49)$$

For the bar diagram shown, the calcium concentration is larger than the sum of the carbonate and bicarbonate, and therefore, the soda ash requirement is not zero.

The sludge solids produced consist of calcium carbonate. The concentration in suspension just prior to settling is,

$$X_{ss} = 50.04\left[\{CaO\} + \{\text{original Ca}^{2+}\}\right] \qquad (10.50)$$

where X_{ss} = the concentration of suspended solids in mg/L.

If the raw water contains any suspended solids, these will be trapped in the precipitate, and they must be included.

Calcium and Magnesium Removal

If magnesium must be removed, excess lime treatment is required. The traditional rule of thumb is that cold water excess lime softening will reduce the calcium concentration to about 0.8 meq/L and the magnesium concentration to about 0.2 meq/L.

The bar chart relevant to excess lime treatment would look as follows:

<table>
<tr><td rowspan="2">CO_2</td><td colspan="3">Ca^{2+}</td><td>Mg^{2+}</td><td>Excess lime Ca^{2+}</td><td>Other cations</td></tr>
<tr><td>CO_3^{2-}</td><td>HCO_3^-</td><td colspan="4">Other anions</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">← Noncarbonate Hardness →</td><td></td><td></td></tr>
</table>

The required lime dosage is,

$$\{CaO\} = \{CO_2 + H_2CO_3\} + \{HCO_3^-\} + \{Mg^{2+}\} + \{\text{excess lime}\} \tag{10.51}$$

where $\{x\}$ = the concentration of species x in meq/L.

Note that all the carbon dioxide/carbonic acid, all the bicarbonate, and all the magnesium must be reacted. The quantity of excess lime influences the concentration of magnesium that can be achieved and the rate of reaction. In cold water, a free hydroxide concentration of about 1 meq/L is required to reduce the magnesium concentration to 50 mg/L (as $CaCO_3$), and about 1.4 meq/L is required to produce a magnesium concentration of 8 mg/L (as $CaCO_3$) (Powell, 1954). The equivalent pHs are 11 and 11.2, respectively.

The soda ash requirement is,

$$\begin{aligned} \{Na_2CO_3\} &= \{Ca^{2+}\} + \{Mg^{2+}\} + \{\text{excess lime Ca}\} - \{CO_3^{2-}\} - \{HCO_3^-\} \\ &= \{\text{noncarbonate hardness}\} + \{\text{excess lime Ca}\} \end{aligned} \tag{10.52}$$

The solids formed consist of calcium carbonate and magnesium hydroxide and any silts and clays in the raw water. The total suspended solids concentration in mg/L prior to settling is,

$$X_{ss} = 50.04\left[\{CaO\} + \{\text{original } Ca^{2+}\}\right] + 29.16\{\text{original } Mg^{2+}\} \tag{10.53}$$

Any silts and clays in the raw water will be trapped in the precipitates and should be added to get the total suspended solids.

Recarbonation

When only calcium is removed, the settled water has a pH between 10 and 10.6, is supersaturated with respect to calcium carbonate, and contains suspended calcium carbonate crystals that did not settle out. The traditional rule of thumb is that the residual calcium hardness is about 0.8 meq/L, and the magnesium hardness is unchanged. In the case of excess lime treatment, the settled water is supersaturated with respect to calcium carbonate and magnesium hydroxide and contains suspended particles of both crystals. The final pH is between 11 and 11.5. Such waters will deposit hard scales in sand filters and distribution systems and corrode lead and copper. The usual practice is to convert carbonate and hydroxide to bicarbonate by reacting with carbon dioxide gas.

Consider the following bar chart that represents excess lime-softened water after sedimentation:

<table>
<tr><td>Ca^{2+}</td><td>Mg^{2+}</td><td colspan="2">Other cations</td></tr>
<tr><td>CO_3^{2-}</td><td>OH^-</td><td>Excess lime OH^-</td><td>Other anions</td></tr>
</table>

It is convenient to use concentration units of mmol/L, because the carbonate and carbon dioxide are both converted to bicarbonate and so behave as a monoprotic base and acid. The carbon dioxide requirement is in mmol/L,

$$\left[CO_2\right]=\left[CO_3^{2-}\right]+\left[OH^-\right]+\left[\text{excess lime } OH^-\right] \tag{10.54}$$

In the case of excess lime softening, the carbonate and hydroxide concentrations associated with calcium and magnesium would be about 0.4 and 0.2 mmol/L, respectively, and the excess lime hydroxide (which is associated with other cations) would be about 1 to 1.5 mmol/L. Therefore, the expected carbon dioxide dosage is about 1.6 to 2.1 mmol/L. In the case of calcium removal only, there is no hydroxide residual, so the expected carbon dioxide dosage would be about 0.4 mmol/L.

In either case, the final water pH will be 8.3 or a little higher. Whether or not such waters will deposit scale can be estimated by using the Larson–Buswell (1942) correction to Langelier's (Langelier, 1936, 1946; Hoover, 1938) equilibrium pH_{eq},

$$\text{pH}_{\text{eq}}=-\log\left\{\frac{K_2\left(\text{Ca}^{2+}\right)\left(\text{Alkalinity}\right)}{K_{sp}}\right\}+9.30+\frac{2.5\sqrt{\mu}}{1+5.3\sqrt{\mu}+5.5\mu} \tag{10.55}$$

or the formula derived by Singley et al. (1985):

$$\text{pH}_{\text{eq}}=-\log\left\{\frac{K_2\left[\text{Ca}^{2+}\right]\cdot\left[\text{Alkalinity}\right]}{K_{sp}}\right\}+\frac{2.5\sqrt{\mu}+3.63\mu}{1+3.30\sqrt{\mu}+2.61\mu} \tag{10.56}$$

Langelier's saturation index, I_{sat}, is calculated as,

$$I_{sat}=\text{pH}_{\text{act}}-\text{pH}_{\text{eq}} \tag{10.57}$$

where I_{sat} = Langeliers's saturation index
pH_{act} = the measured pH of the water
pH_{eq} = the equilibrium pH at which a water neither deposits nor dissolves calcium carbonate
K_2 = the second acid dissociation constant for carbonic acid
K_{sp} = the solubility product of calcium carbonate
(Ca^{2+}) = the calcium ion concentration in mg/L as $CaCO_3$
$[\text{Ca}^{2+}]$ = the calcium ion concentration in mol/L
(Alkalinity) = the total alkalinity in mg/L as $CaCO_3$
[Alkalinity] = the total alkalinity in eq/L
μ = the ionic strength in mol/L
≈ Total Dissolved Solids (mg/L)/40,000

The values of the calcium carbonate solubility product were given above. The second acid ionization constant of carbonic acid can be estimated by (Shock, 1984),

$$\log K_2=-107.8871-0.03252849T+\frac{5151.79}{T}+38.92561\log T-\frac{563713.9}{T^2} \tag{10.58}$$

where T = the absolute temperature in K.

A water is stable if its measured pH is equal to pH_{eq}. It will deposit calcium carbonate scale if its measured pH is greater than pH_{eq}, and it will dissolve calcium carbonate scale if its measured pH is less than pH_{eq}.

More information is provided by Ryznar's (1944) stability index, I_{stab}:

$$I_{stab}=2p\text{H}_{\text{eq}}-p\text{H}_{\text{act}} \tag{10.59}$$

A stability index between about 6.3 and 6.8 will result in virtually no calcium carbonate scale or iron corrosion. Indices below 6 result in scale deposition from hot water, and the deposition is heavy below an index of 5. Indices above 7 produce iron corrosion, and indices above 8 indicate very corrosive water.

Lead and Copper Control

The action level for lead is 0.015 mg/L, and the maximum contaminant level goal (MCLG) for lead is zero. The action level for copper is 1.3 mg/L, and the MCLG for copper is also 1.3 mg/L. If 10% of the taps sampled exceed either of the action levels, one or more of the following must be done to the water system (EPA, 1991):

- Install corrosion control for the distribution system
- Treat the raw water to remove lead and copper
- Replace lead service lines
- Conduct public education to help the public reduce their exposure to lead

The general corrosion reaction is an oxidation in which the metallic element becomes an ion that may react with other solution ions:

$$\mathrm{Me} \rightarrow \mathrm{Me}^{n+} + ne^- \tag{10.60}$$

Corrosion can be discussed under three heads (Schock, 1990):

- Immunity — Immunity to corrosion means that the water chemistry is such that the metal is thermodynamically stable and will not corrode and go into solution. However, lead metal in contact with water is unstable and will corrode. Immunity generally requires some kind of cathodic protection, and the protected metal survives only as long as the sacrificial metal exists. In potable waters, zinc, aluminum, steel, and iron provide cathodic protection to lead, lead-tin solders, and copper.
- Passivation — Metal surfaces may be passivated by the deposition of a stable, nonporous film that protects the thermodynamically unstable metal from corrosion. In waters containing carbonate ion, the lead surface may be coated with a layer of plumbous carbonate (cerrusite, $PbCO_3$), hydroxyplumbous carbonate [hydrocerrusite, $Pb(CO_3)_2(OH)_2$], or plumboacrite [$Pb_{10}(CO_3)_6(OH)_6O$] (Schock, 1990). The minimum equilibrium lead concentration is 0.069 mg/L, and it occurs at pH 9.8 and a dissolved carbonate concentration of 4.8 mg/L as C (Schock, 1990). The equilibrium lead concentrations for pHs between 8 and 9 and carbonate concentrations of less than 10 mg/L are less than 0.2 mg Pb/L. At pH 9.8, lead concentrations increase as carbonate concentrations increase or decrease. At a carbonate concentration of 4.8 mg C/L, lead concentrations increase as the pH increases or decreases.
- All of these lead concentrations are above the action level of 0.015 mg/L, but water in distribution systems is seldom in equilibrium with the piping and appurtenances, and measured lead concentrations may be less than the equilibrium values.
- Lead surfaces can also be passivated by zinc orthophosphate. Typical dosages are 0.4 to 0.6 mg/L as PO_4^{3-}. Theoretically, an equilibrium lead concentration of 0.01 mg/L can be achieved if the pH is adjusted to 7.6, the phosphate dosage is 4.5 mg/L as PO_4^{3-}, and the bicarbonate concentration is 5 to 10 mg/L as C (Schock, 1989). Zinc concentrations should not exceed 5 mg/L (for aesthetics), and this may limit the usefulness of zinc orthophosphate.
- Polyphosphate solubilizes lead, but it is slowly hydrolyzed to orthophosphate.
- In low alkalinity waters, sodium silicate at concentrations above 20 mg/L as SiO_2 and pHs around 8.2 slowly forms protective coatings on lead surfaces.
- Protection — Protection occurs when a layer of material is deposited that reduces the diffusion of material to and from the metal surface. The most common protective layer is calcium carbonate scale. This would require recarbonation to stop at a positive Langelier saturation index or a Ryznar stability index less than 6.

It should be noted that corrosion is not inhibited at Langelier indices as high as 2. The corrosion rate is more strongly influenced by dissolved oxygen and total dissolved solids than by water stability. For mild steel, the empirical formula for the rate of penetration is (Singley et al., 1985),

$$R_{pen} = \frac{C_{TDS}^{0.253} \cdot C_{DO}^{0.820}}{10^{0.0876 I_{sat}} \cdot t^{0.373}} \tag{10.61}$$

where C_{DO} = the dissolved oxygen concentration in mg/L
C_{TDS} = the total dissolved solids concentration in mg/L
I_{sat} = Langelier's saturation index (dimensionless)
R_{pen} = the mild steel corrosion penetration rate in mils per year
t = the exposure time in days

Ion Exchange

Materials

An ion exchanger is a solid that adsorbs certain dissolved ions from solution and replaces them with other ions. Some materials exchange cations, and others exchange anions. The exchange maintains the electroneutrality of the exchanger and the solution, so the number of equivalents of cations or anions released is equal to the number of equivalents of cations or anions adsorbed.

The property of ion exchange is widely known among many kinds of naturally occurring and synthetic solid materials. However, the most useful ion exchange materials are synthetic organic polymers consisting of polystyrene chains cross-linked with divinylbenzene and various attached functional groups. The functional groups may be divided into four classes. Letting *R* represent the resin lattice, the groups are (Abrams and Beneza, 1967):

- Strong acid cation (SAC) exchangers that contain the sulfonate ($R\text{-}SO_3^-$) group — These exchangers operate over a wide pH range and can remove all cations from solution, replacing them with protons, or all doubly and triply charged cations, replacing them with sodium.
- Weak acid cation (WAC) exchangers that contain the carboxylate ($R\text{-}COO^-$) group — These exchangers operate in neutral to alkaline pHs, where the carboxylate group is ionized and can remove doubly charged and triply charged ions, if carbonate or bicarbonate is present in sufficient quantities to neutralize the protons released.
- Strong base anion (SBA) exchangers that contain the quarternary amine $[R\text{–}N(CH_3)_3^+]$ group — These exchangers can operate over a wide range of pHs and can remove all anions, replacing them with hydroxide or chloride ions.
- Weak base anion (WBA) exchangers that contain a primary, secondary, or tertiary amine ($R\text{-}NH_3^+$, $R = NH_3^+$, $R{+}NH^+$) group — These exchangers operate in the acidic range where the amino group is protonated.

Most commercial resins are homogeneous gels (Abrams and Beneza, 1967). The solid consists of an open crystalline matrix that adsorbs water and permits the free diffusion of ions. The charge of the functional groups is balanced by the diffusing ions. The degree of cross-linking influences the ionic diffusion rate, and large ions may be excluded from the gel.

Macroporous, highly cross-linked resins are available (Abrams and Beneza, 1967). In these materials, ion exchange is limited to the interior surfaces of the macropores. However, ionic diffusion in the macropores is rapid. Macroporous resins are largely limited to nonaqueous processes.

Equilibria

The exchange process can be described as a two-phase equilibrium involving ion *X* with charge *n* and ion *Y* with charge *m*:

$$\mathrm{R - X_m^n + nY^m \leftrightarrow R - Y_n^m + mX^n} \tag{10.62}$$

$$K = \frac{\left[\mathrm{R}-\mathrm{Y}_n^m\right]^n \left[\mathrm{X}^n\right]^n}{\left[\mathrm{R}-\mathrm{X}_m^n\right]^m \left[\mathrm{Y}^m\right]^n} \tag{10.63}$$

Note that the terms $[\mathrm{R}-\mathrm{X}_m^n]$ and $[\mathrm{R}-\mathrm{Y}_n^m]$ refer to the activities of ions in the solid phase, while the terms $[X^n]$ and $[Y^m]$ refer to the ionic activities in water. In practice, concentrations rather than activities are used, and the equilibrium constant is called a selectivity coefficient. The selectivity coefficient varies with the ionic strength of the solution. Concentrations of ions in the exchanger are generally reported as a mass-to-mass ratio, whereas concentrations in water are reported as a mass-to-volume ratio.

Sometimes another constant called the separation factor is used:

$$\alpha = \frac{\left[\mathrm{R}-\mathrm{Y}_\mathrm{n}^\mathrm{m}\right]\left[\mathrm{X}^\mathrm{n}\right]}{\left[\mathrm{R}-\mathrm{X}_\mathrm{m}^\mathrm{n}\right]\left[\mathrm{Y}^\mathrm{m}\right]} = K \cdot \frac{\left[\mathrm{R}-\mathrm{X}_\mathrm{m}^\mathrm{n}\right]^{m-1}\left[\mathrm{Y}^\mathrm{m}\right]^{n-1}}{\left[\mathrm{R}-\mathrm{Y}_\mathrm{n}^\mathrm{m}\right]^{n-1}\left[\mathrm{X}^\mathrm{n}\right]^{m-1}} \tag{10.64}$$

Note that the separation factor is not an equilibrium constant and will vary significantly with water composition. Some separation factors relative to sodium are given in Table 10.1.

In general, ion exchangers preferentially adsorb more highly charged ions over less highly charged ions, and smaller ions over larger ions. The general preference sequence for cation exchangers is (Kemmer, 1988),

$$\mathrm{Fe}^{3+} > \mathrm{Al}^{3+} > \mathrm{Pb}^{2+} > \mathrm{Ba}^{2+} > \mathrm{Sr}^{2+} > \mathrm{Cd}^{2+} > \mathrm{Zn}^{2+} > \mathrm{Cu}^{2+} > \mathrm{Fe}^{2+} >$$

$$\mathrm{Mn}^{2+} > \mathrm{Ca}^{2+} > \mathrm{Mg}^{2+} > \mathrm{K}^{+} > \mathrm{NH}_4^{+} > \mathrm{Na}^{+} > \mathrm{H}^{+} > \mathrm{Li}^{+}$$

In most natural waters, ferric iron and aluminum form precipitates, which should be removed prior to the ion exchange bed to prevent clogging. Ferrous iron may be oxidized by dissolved oxygen after exchange and precipitate in or on the resin beads. This can be prevented by applying a reductant like sodium sulfite to the raw water or mixing it with the regenerant.

TABLE 10.1 Separation Factors Relative to Sodium and Chloride for Various Ions (N = 0.01; TDS = 500 mg/L as $\mathrm{CaCO_3}$)

Strong Acid Cation Exchangers		Strong Base Anion Exchangers	
Cation	α	Anion	α
Ammonium, $\mathrm{NH_4^+}$	1.3	Acetate, $\mathrm{CHCOO^-}$	0.14
Barium, $\mathrm{Ba^{2+}}$	5.8	Arsenate, $\mathrm{HAsO_4^{2-}}$	1.5
Calcium, $\mathrm{Ca^{2+}}$	1.9	Bicarbonate, $\mathrm{HCO_3^-}$	0.27
Copper, $\mathrm{Cu^{2+}}$	2.6	Bisulfate, $\mathrm{HSO_4^-}$	4.1
Hydronium, $\mathrm{H^+}$	0.67	Bisulfite, $\mathrm{HSO_3^-}$	1.2
Iron, $\mathrm{Fe^{2+}}$	1.7	Bromide, $\mathrm{Br^-}$	2.3
Lead, $\mathrm{Pb^{2+}}$	5	Chloride, $\mathrm{Cl^-}$	1
Magnesium, $\mathrm{Mg^{2+}}$	1.67	Chromate, $\mathrm{CrO_4^{2-}}$	100
Manganese, $\mathrm{Mn^{2+}}$	1.6	Fluoride, $\mathrm{F^-}$	0.07
Potassium, $\mathrm{K^+}$	1.67	Nitrate, $\mathrm{NO_3^-}$	3.2
Radium, $\mathrm{Ra^{2+}}$	13	Nitrite, $\mathrm{NO_2^-}$	1.1
Sodium, $\mathrm{Na^+}$	1	Selenate, $\mathrm{SeO_4^{2-}}$	17
Strontium, $\mathrm{Sr^{2+}}$	4.8	Selenite, $\mathrm{SeO_3^{2-}}$	1.3
Zinc, $\mathrm{Zn^{2+}}$	1.8	Sulfate, SO	9.1

Source: Clifford, D.A. 1990. "Ion Exchange and Inorganic Adsorption," p. 561 in *Water Quality and Treatment: A Handbook of Community Water Supplies*, 4th ed. F.W. Pontius, ed., McGraw-Hill, Inc., New York.

TABLE 10.2 Ion Exchange Resin Properties

Parameter	Strong Acid Cation Exchanger	Strong Base Anion Exchanger
Effective size (mm)	0.45–0.55	0.45–0.55
Uniformity coefficient	1.7	1.7
Specific gravity of wet grains (dimensionless)	≤1.3	≥1.07
Moisture content of wet grains (%)	43–45	43–49
Iron tolerance (mg/L)	5	0.1
Chlorine tolerance (mg/L)	1	0.1
Silica tolerance (mg/L)	—	10 (<30% total anions)
Service flow rate (gpm/ft^3)	≤5	2–3
Minimum depth (in.)	30	30
Backwash flow rate (gpm/ft^2)	5–8	2–3
Backwash expansion (%)	50	50–75
Backwash duration (min)	5–15	5–20
Flushing flow rate (gpm/ft^3)	1.0–1.5	0.5
Flushing volume (empty bed volumes)	2–5	2–10
Flushing duration (min)	30–70	30–150
Operating ion exchange capacity (kgr $CaCO_3$/ft^3)	9–25	9–17
Regenerant concentration (% by wt)		
NaCl	3–12	1.5–12
H_2SO_4	2–4	—
NaOH	—	2–4
Regenerant dose (lb/ft^3)		
NaCl	5–20	5–20
H_2SO_4	2.5–10	—
NaOH	—	3.5–8
Regenerant efficiency (%)		
NaCl	30–50	—
H_2SO_4	20–40	—
NaOH	—	—
Regenerant application rate (gpm/ft^2)	0.5	0.5
Regenerant contact time (min)	50–80	60–90

Sources: Clifford, D.A. 1990. "Ion Exchange and Inorganic Adsorption," p. 561 in *Water Quality and Treatment: A Handbook of Community Water Supplies*, 4th ed. F.W. Pontius, ed., McGraw-Hill, Inc., New York.

Culp/Wesner/Culp, Inc. 1986. *Handbook of Public Water Systems*, R.B. Williams and G.L. Culp, eds. Van Nostrand Reinhold Co., Inc., New York.

Kemmer, F N., ed. 1988. *The Nalco Water Handbook*, 2nd ed. McGraw-Hill, Inc., New York.

Powell, S.T. 1954. *Water Conditioning for Industry*. McGraw-Hill, Inc., New York.

For anion exchangers, the preference sequence is,

$$CrO_4^{2-} > SO_4^{2-} > SO_3^{2-} > HPO_4^{2-} > CNS^- > CNO^- > NO_3^- >$$

$$NO_2^- > Br^- > Cl^- > CN^- \; HCO_3^- > HSiO_3^- > OH^- > F^-$$

These sequences are affected by the ionic strength of the solution and the chemical composition of the ion exchanger.

Operating parameters and important resin properties are summarized in Table 10.2. Note that the operating exchange capacity varies with the concentration of the regenerant solution. This is a consequence of the equilibrium nature of the process.

Sodium Cycle Softening

Health and Ecology Notes

The sodium concentration in the finished water is equal to the original hardwater sodium concentration plus the sodium required to replace the calcium and magnesium hardness removed:

$$C_{Naf} = C_{Nao} + \tfrac{23}{50} C_{HCao} + \tfrac{23}{50} C_{HMgo} \tag{10.65}$$

where C_{HCao} = the original calcium hardness [eq/m^3 or gr (as $CaCO_3$)/ft^3]
C_{HMgo} = the original magnesium hardness [eq/m^3 or gr (as $CaCO_3$)/ft^3]
C_{Naf} = the final sodium concentration [eq/m^3 or gr (as $CaCO_3$)/ft^3]
C_{Nao} = the original sodium concentration [eq/m^3 or gr (as $CaCO_3$)/ft^3]

If a hard water is softened, the resulting sodium concentration will be high, and drinking water may comprise a significant fraction of the dietary sodium intake. This may be of concern for people on restricted sodium diets.

A zero-hardness water is corrosive, because of the lack of scale-forming calcium ions. Such waters are not suitable for household use without further treatment, because lead and copper will be dissolved from plumbing fixtures. Zinc orthophosphate additions and pH adjustment may be required. Partially softened waters may be acceptable if the final pH and carbonate concentration are carefully adjusted.

Sodium cycle softening produces a waste brine that may adversely affect fresh water biota. Many states have restrictions on the increase in total dissolved solids concentration that they will permit in receiving waters. Common restrictions are an increase in TDS of 100 mg/L and an absolute upper limit of 750 mg/L.

Waste brines do not adversely affect the biological wastewater treatment processes (including septic tanks) at chloride concentrations up to several thousand mg/L (Ludzack and Noran, 1965).

Operating Cycle

The sodium cycle ion exchange softening process consists of the following cycle:

- Hard water is passed through a bed of fresh ion exchange resin that is preloaded with sodium ions; calcium and magnesium ions are adsorbed from solution and replaced by a charge-equivalent amount of sodium ions.
- At the end of the ion exchange service run (which is indicated by a preset timer or by effluent monitoring), the ion exchange bed is backwashed to remove sediment, and the washwater is run to waste.
- The ion exchange material is then regenerated by slowly pumping through it a sodium chloride brine; the required brine volume normally exceeds the pore spaces in the bed; the spent regenerant brine is run to waste; and the concentration of the brine determines the exchange capacity of the resin.
- The bed is then flushed with several empty bed volumes of hard water to remove the spent regenerant brine, and the flushing water is run to waste; the bed is put back in service.

The design problem is to determine the following:

- Required bed volume and dimensions
- Duration of a cycle
- Mass of salt required for regeneration in each cycle
- Volume of regenerant brine required each cycle
- Volume of waste brine produced each cycle
- Composition of the waste brine

Bed Volume and Salt Requirement

For all intents and purposes, the removal of calcium and magnesium is nearly complete. Thus, the required ion exchange bed volume, V, can be calculated as follows:

$$V = \frac{Q t_s C_{Ho}}{q_{iec}} \tag{10.66}$$

where C_{Ho} = the hardness of the raw water [eq/m^3 or gr (as $CaCO_3$)/ft^3]
Q = the raw water flow rate (m^3/s or ft^3/sec)
q_{iec} = the capacity of the ion exchange resin [eq/m^3 or gr (as $CaCO_3$)/ft^3]
t_s = the time-in-service of the bed (sec)
V = the volume of the bed (m^3 or ft^3)

The time-in-service, t_s, is a design choice. The hard water flow rate, Q, the raw water hardness, C_{Ho}, and the bed exchange capacity, q_{iec}, are determined by the design problem.

The service flow rate in Table 10.2 yields a minimum bed volume, service time, and hydraulic detention time. The minimum depth requirement yields a maximum cross-sectional area, which is intended to control short-circuiting. Sometimes the service flow rate is given as an areal rate (approach velocity). In that case, the service flow rate and minimum depth combine to yield a minimum bed volume, service time, and hydraulic detention time.

Regeneration Scheduling

The cycle time is the sum of the required service time, backwash time, regeneration time, flushing time, and down time for valve opening and closing and pump startup and shutdown:

$$t_c = t_s + t_b + t_r + t_f + t_d \tag{10.67}$$

where t_b = the backwashing time (sec)
t_c = the cycle time (sec)
t_d = the down time for valve and pump adjustments (sec)
t_f = the flushing time (sec)
t_r = the regeneration time (sec)
t_s = the time-in-service of the bed (sec)

The last four components of the cycle time are more or less fixed, and the service time is freely adjustable (by adjusting the bed volume) and can be chosen so that the cycle time fits comfortably into a convenient work schedule.

Partial Softening

It is usually desirable to produce a finished hardness C_{Hf} greater than zero, in order to facilitate corrosion control. This is accomplished by bypassing some of the raw water around the exchanger and mixing it with softened water, as shown in Fig. 10.4. The finished water hardness is,

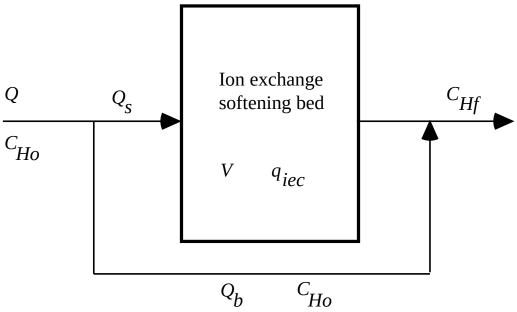


FIGURE 10.4 Flow scheme for partial ion exchange softening.

$$C_{Hf} = \frac{Q_b C_{Ho}}{Q_s + Q_b} = \frac{Q_b C_{Ho}}{Q} \tag{10.68}$$

where C_{Ho} = the hardness of the raw water [eq/m^3 or gr (as $CaCO_3$)/ft^3]
C_{Hf} = the hardness of the finished water [eq/m^3 or gr (as $CaCO_3$)/ft^3]
Q = the raw water flow rate (m^3/s or ft^3/sec)
Q_b = the raw water flow bypassed around the softener (m^3/s or ft^3/sec)
Q_s = the raw water flow processed through the softener (m^3/s or ft^3/sec)

The fractions of the raw water flow that are softened and bypassed are as follows:

$$f_s = \frac{Q_s}{Q} = 1 - \frac{C_{Hf}}{C_{Ho}} \tag{10.69}$$

$$f_b = \frac{Q_b}{Q} = \frac{C_{Hf}}{C_{Ho}} \tag{10.70}$$

where f_b = the fraction of the raw water that is bypassed (dimensionless)
f_s = the fraction of the raw water that is softened (dimensionless).

The bed volume is sized based on the volume of water softened, Q_s.

The salt requirement per cycle, M_{NaCl}, is the manufacturer's recommended dosage rate per unit bed volume, m_{NaCl}, times the bed volume:

$$M_{NaCl} = m_{NaCl}V \tag{10.71}$$

where M_{NaCl} = the mass of salt required to regenerate an ion exchange bed per cycle (kg or lb)
m_{NaCl} = the salt dosage per unit bed volume (kg/m^3 or lb/ft^3).

This will vary with the desired bed ion exchange capacity. The salt efficiency is defined to be the sodium exchanged divided by the sodium supplied. If equivalents are used to express masses, the efficiency is,

$$E_{Na} = \frac{Vq_{iec}}{M_{NaCl}/58.5} \tag{10.72}$$

where E_{Na} = the salt efficiency (dimensionless).

Large ion exchange capacities require disproportionate salt dosages, which significantly reduce the salt efficiency.

Waste Brine

The waste brine is composed of the wash water, the spent regenerant brine, and the flushing water.

The wash water volume is merely the backwash rate, U_b, times the backwash duration and bed cross-sectional area, A:

$$V_{ww} = U_b A t_b \tag{10.73}$$

where A = the cross-sectional area of the bed (m^2 or ft^2)
t_b = the backwash duration (sec)
U_b = the backwash rate (m/s or ft/sec)
V_{ww} = the wash water volume (m^3 or ft^3)

The regenerant brine volume is equal to the mass of salt that is required for regeneration, divided by the weight fraction of salt in the brine, and the density of the brine:

$$V_{rb} = \frac{M_{NaCl}}{\rho_{rb} f_{NaCl}} \tag{10.74}$$

where f_{NaCl} = the mass fraction of salt in regenerant brine (dimensionless)
M_{NaCl} = the mass of salt required to regenerate an ion exchange bed per cycle (kg or lb)
ρ_{rb} = the density of regenerant brine (kg/m^3 or lbm/ft^3)

Densities for various brine concentrations and compositions are given in standard handbooks like the *CRC Handbook of Chemistry and Physics*.

The amount of flushing water is equal to the empty bed volume times the number of bed volumes used for flushing:

$$V_f = nV \tag{10.75}$$

where n = the number of empty bed volumes of flushing water needed to remove spent brine from an ion exchange bed (dimensionless)
V = the empty bed volume (m^3 or ft^3)
V_f = the flushing water volume (m^3or ft^3)

The total waste brine volume per cycle is,

$$V_{wb} = V_{ww} + V_{rb} + V_f \tag{10.76}$$

The waste brine contains the following:

- All the calcium and magnesium removed
- All the chloride in the regenerant brine
- All the sodium not exchanged during regeneration

The composition is most easily calculated if the units are equivalents. If the equivalent fraction of calcium in the hard water is f_{Ca}, the masses of the various ions in the waste brine are as follows:

$$M_{Ca} = f_{Ca} V q_{iec} \left(\frac{20 \text{ g Ca}}{\text{eq}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{g}} \right) \quad (\text{as Ca}) \tag{10.77}$$

$$M_{Mg} = \left(1 - f_{Ca}\right) V q_{iec} \left(\frac{12.16 \text{ g Mg}}{\text{eq}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{g}} \right) \quad (\text{as Mg}) \tag{10.78}$$

$$M_{Na} = M_{NaCl} \left(\frac{23 \text{ g Na}}{58.5 \text{ g NaCl}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{g}} \right) - V q_{iec} \left(\frac{23 \text{ g Na}}{\text{eq}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{g}} \right) \quad (\text{as Na}) \tag{10.79}$$

$$M_{Cl} = M_{NaCl} \left(\frac{35.5 \text{ g Cl}}{58.5 \text{ g NaCl}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{g}} \right) \quad (\text{as Cl}) \tag{10.80}$$

where f_{Ca} = the equivalents fraction of calcium in the hard water (dimensionless)
M_{Ca} = the mass of calcium in waste brine from ion exchange in kg
M_{Cl} = the mass of chloride in waste brine from ion exchange in kg
M_{Mg} = the mass of magnesium in waste brine from ion exchange in kg
M_{Na} = the mass of sodium in waste brine from ion exchange in kg

Chloride Cycle Dealkalization and Desulfurization

Strong base anion exchange resins will release chloride ions and adsorb bicarbonate, carbonate, and sulfate. The regenerant is a sodium chloride brine, but the chloride is the exchangeable ion, and the sodium ion is passive. The calculations parallel those for sodium cycle softening.

Demineralization

Waters may be nearly completely demineralized by a combination of strong acid hydrogen cycle and strong base hydroxide cycle resins.

Raw waters are first processed through the hydrogen cycle resin, which removes all cations and replaces them with protons. The result is a dilution solution of mineral acids and carbonic acid. The pH will depend on the total amount of cations removed: each equivalent of cations is replaced by one equivalent of protons.

The carbonic acid is derived from the carbonate and bicarbonate originally present in the raw water. Carbonic acid decomposes to form carbon dioxide gas until it is in equilibrium with the gas-phase partial pressure of CO. If the initial alkalinity is high enough, a vacuum degassifier will be required after the hydrogen cycle exchanger to remove the carbon dioxide gas.

The initial bicarbonate and carbonate ions are removed by conversion to carbon dioxide gas and degassification. The remaining anions (Cl^-, SO_4^{2-}, NO_3^-, etc.) can be removed by hydroxide cycle ion exchange. Note that the hydrogen cycle exchanger must precede the hydroxide cycle exchanger in order to avoid the formation of calcium carbonate and magnesium hydroxide deposits.

The design calculations for hydrogen cycle and hydroxide cycle exchangers parallel those for sodium cycle softening, the differences being that H^+ and OH^- are being released to the water rather than Na^+, and that the regenerants are strong acids (H_2SO_4 or HCl) and strong bases (NaOH or KOH). The waste products are fairly strong acid and base solutions. The wastes do not exactly neutralize each other, because the acid and base efficiencies are usually different.

Strong acid hydrogen cycle exchangers are usually regenerated with sulfuric acid. However, the acidity required to drive the regeneration is generally on the order of 2 to 8% acid by wt, and in this range, sulfuric acid is only partially ionized. The result is a low acid efficiency, generally on the order of 30%. Furthermore, in hard waters, the calcium sulfate solubility limit in the waste acid may be exceeded, and a gypsum sludge may be produced. Both problems can be avoided by using hydrochloric acid, but it is expensive, and HCl vapors pose a venting problem.

If the removal of weak acid anions like HCO_3^-, $HSiO_3^-$ or CH_3 COO^- is not required or if such anions are absent, weak base anion exchanger resins can be used instead of strong base anion resins. WBA resins can be regenerated with a wide variety of bases.

Mixed-bed exchangers contain SAC and SBA resins. Cation exchange and anion exchange occur at every level of the bed. The proportions of the two resin types depend on their relative ion exchange capacities. SBA resins have much lower densities than SAC resins, so they can be separated by backwashing. Regeneration is accomplished by down-flowing base through the upper SBA resin and up-flowing acid through the lower SAC resin. The wastes are drawn off at the interface between the separated resins. A mechanism for remixing the beads after regeneration must be included in the bed design.

References

Abrams, I.M. and Beneza, L. 1967. “Ion Exchange Polymers,” p. 692 in *Encyclopedia of Polymer Science and Technology*, Vol. 7. John Wiley & Sons, Inc., New York.

Baker, M.N. 1981. *The Quest for Pure Water: The History of Water Purification from the Earliest Records to the Twentieth Century*, Volume I, 2nd ed. American Water Works Association, Denver, CO.

Clifford, D.A. 1990. “Ion Exchange and Inorganic Adsorption,” p. 561 in *Water Quality and Treatment: A Handbook of Community Water Supplies*, 4th ed. F.W. Pontius, ed., McGraw-Hill, Inc., New York.

Culp/Wesner/Culp, Inc. 1986. *Handbook of Public Water Systems,* R.B.Williams and G.L. Culp, eds. Van Nostrand Reinhold Co., Inc., New York.

Environmental Protection Agency. 1991. “Drinking Water Regulations: Maximum Contaminant Level Goals and National Primary Drinking Water Regulations for Lead and Copper,” *Federal Register*, 56(110): 26460.

Hoover, C.P. 1938. "Practical Application of the Langelier Method," *Journal of the American Water Works Association*, 30(11): 1802.

Kemmer, F.N., ed. 1988. *The Nalco Water Handbook*, 2nd ed., McGraw-Hill, Inc., New York.

Langelier, W.F. 1936. "The Analytical Control of Anti-corrosion Water Treatment," *Journal of the American Water Works Association,* 28(10): 1500.

Langelier, W.F. 1946. "Chemical Equilibria in Water Treatment," *Journal of the American Water Works Association*, 38(2): 169.

Larson, T.E. and Buswell, A.M. 1942. "Calcium Carbonate Saturation Index and Alkalinity Interpretations," *Journal of the American Water Works Association*, 34(11): 1667.

Lee, R.G., Becker, W.C., and Collins, D.W. 1989. "Lead at the Tap: Sources and Control," *Journal of the American Water Works Association,* 81(7): 52.

Ludzack, F.J. and Noran, D.K. 1965. "Tolerance of High Salinities by Conventional Wastewater Treatment Processes," *Journal of the Water Pollution Control Federation*, 37(10): 1404.

Powell, S.T. 1954. *Water Conditioning for Industry.* McGraw-Hill, Inc., New York.

Ryznar, J.W. 1944. "A New Index for Determining Amount of Calcium Carbonate Scale Formed by a Water," *Journal of the American Water Works Association,* 36(4): 472.

Shock, M.R. 1984. "Temperature and Ionic Strength Corrections to the Langelier Index — Revisisted," *Journal of the American Water Works Association,* 76(8): 72.

Schock, M.R. 1989. "Understanding Corrosion Control Strategies for Lead," *Journal of the American Water Works Association,* 81(7): 88.

Schock, M.R. 1990. "Internal Corrosion and Deposition Control," p. 997 in *Water Quality and Treatment: A Handbook of Community Water Supplies*, 4th ed., F.W. Pontius, ed. McGraw-Hill, Inc., New York.

Singley, J.E., Pisigan, R.A., Jr., Ahmadi, A., Pisigan, P.O., and Lee, T.-Y. 1985. *Corrosion and Carbonate Saturation Index in Water Distribution Systems*, EPA/600/S2–85/079. U.S. Environmental Protection Agency, Water Engineering Research Laboratory, Center for Environmental Research Information, Cincinnati, OH.

Stumm, W. and Morgan, J.J. 1970. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters.* John Wiley & Sons, Inc., Wiley-Interscience, New York.

Tebbutt, T.H.Y. 1992. *Principles of Water Quality Control*, 4th ed. Pergamon Press, Oxford, UK.

10.3 Chemical Oxidation

Chemical Oxidants

Chemical oxidants are used in water and wastewater treatment for a variety of purposes, including disinfection; oxidation of iron and manganese; oxidation of recalcitrant, refractory, or toxic organic compounds; taste, odor, and color removal; prevention of algal growth within the treatment plant; control of nuisance species; and improvement of coagulation and flocculation efficiency (EPA, 1999). The most common oxidants for water treatment are chlorine, chlorine dioxide, ozone, permanganate, and advanced oxidation processes (AOPs). The oxidation-reduction half-reactions and standard reduction potentials, E^0, of common water treatment oxidants are shown in Table 10.3. A larger E^0 indicates a thermodynamically stronger oxidant; however, the kinetics of the reaction may control whether a reaction occurs. For example, although chlorine dioxide may react with a reductant producing Cl^-, it often only gains $1e^-$ rather than $5e^-$ forming ClO_2^-.

Chlorine

Chlorine can be purchased as pressurized liquid chlorine or as solid hypochlorite salts of calcium or sodium. Liquid chlorine is preferred for reasons of economy, but solid hypochlorite salts are preferred for reasons of safety.

TABLE 10.3 Standard Reduction Potentials of Common Oxidants

Reduction Half-Reaction	Standard Reduction Potential, E^0, V
$Cl_{2\,(aq)} + 2e^- = 2Cl^-$	+1.40
$HOCl + H^+ + 2e^- = H_2O + Cl^-$	+1.48
$OCl^- + 2H^+ + 2e^- = H_2O + Cl^-$	+1.71
$NH_2Cl + 2H^+ + 2e^- = Cl^- + NH_4^+$	+1.40
$ClO_2 + 5e^- + 2H_2O = Cl^- + 4OH^-$	+1.91
$ClO_2 + e^- = ClO_2^-$	+0.95
$ClO^- + 2H_2O + 4e^- = Cl^- + 4OH^-$	+0.76
$MnO_4^- + 4H^+ + 3e^- = MnO_2\ (s) + 2H_2O$	+1.68
$O_3 + 2e^- + 2H^+ = O_2 + H_2O$	+2.07
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	+1.77
$^\bullet OH + e^- = OH^-$	+2.80

Source: American Water Works Association. 1999. *Water Quality and Treatment: A Handbook of Community Water Supplies*, 5th edition, McGraw-Hill, New York.

Snoeyink, V.L. and Jenkins, D. 1980. *Water Chemistry,* John Wiley and Sons, New York.

Water Chemistry of Chlorine

Aqueous, often termed free chlorine, refers to elemental chlorine, Cl_2, as well as hypochlorous acid, HOCl, and hypochlorite, OCl^-. Combined chlorine is composed of monochloramine, NH_2Cl, and dichloramine, $NHCl_2$ (called chloramines). Combined chlorine is a relatively poor oxidant; thus, it is used primarily as a disinfectant. Cl_2 hydrolyzes in water, resulting in disproportionation (i.e., one Cl atom is oxidized, the other is reduced):

$$Cl_{2(aq)} + H_2O \leftrightarrow HOCl + H^+ + Cl^-; \qquad K_h = 4 \times 10^{-4} \tag{10.81}$$

Hypochlorous acid is a weak acid that dissociates to hypochlorite under moderate pH values:

$$HOCl \leftrightarrow H^+ + OCl^-; \qquad pK_a = 7.5 \tag{10.82}$$

Chlorine readily reacts with synthetic and naturally occurring organic compounds in water. Commonly, chlorine reacts with organic compounds by substitution for a hydrogen atom or addition, producing chlorinated organic products. However, chlorine may also oxidize a compound without chlorinating it (Snoeyink and Jenkins, 1980).

Chlorine Dioxide

Chlorine dioxide is an unstable greenish-yellow gas. Because of its instability, it cannot be stored or transported and is prepared on-site immediately prior to use. The usual methods are the reaction between hydrochloric acid and sodium chlorite and the reaction of sodium chlorite with chlorine, both in aqueous solution (Katz, 1980; Haas, 1990):

$$4\ HCl + 5\ NaClO_2 \rightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O \tag{10.83}$$

$$Cl_2 + 2\ NaClO_2 \rightarrow 2\ ClO_2 + 2\ NaCl \tag{10.84}$$

Excess chlorine is used to drive the chlorine/chlorite reaction to completion. The normal recommendation is 1 kg pure chlorine per kg pure sodium chlorite (1.3 mol/mol), but even this excess produces conversion of only about 60%. Some facilities use more chlorine, and others acidify the reaction. Chlorine dioxide can also be formed from sodium hypochlorite and sodium chlorite in aqueous solution:

$$NaOCl + 2\ NaClO_2 + H_2O \rightarrow 2\ ClO_2 + 3\ Na^+ + Cl^- + 2\ OH^- \tag{10.85}$$

In all these reactions, chloride, chlorite, and chlorate are formed in side reactions.

Chlorine dioxide is an oxidant; it acts as a one-electron acceptor forming chlorite:

$$ClO_2 + e^- \leftrightarrow ClO_2^- \tag{10.86}$$

Chlorite may gain four electrons, forming Cl^-:

$$ClO_2^- + 4e^- + 2H_2O \leftrightarrow Cl^- + 4OH^- \tag{10.87}$$

However, chlorite is less reactive; thus, the second reaction does not proceed readily. Large doses of chlorite cause anemia, therefore, EPA has established an MCL for chlorite of 1 mg/L (EPA, 2001a).

Ozone

Ozone is very unstable, thus it is prepared on-site by passing a dry, oil-free, particulate-free oxygen-containing gas between two high-voltage electrodes (generally 7500 to 20,000 volts) (Katz, 1980).

$$3\ O_2 \leftrightarrow 2\ O_3 \tag{10.88}$$

The yields are generally 1 to 3% ozone by volume in air and 2 to 6% in oxygen. The reaction liberates heat, and decomposition of ozone to oxygen is favored at high temperatures, so the ozone generators must be cooled (Weavers and Wickramanayake, 2000).

Ozone decomposes in water to yield free radicals including hydroxyl radical ($OH^\bullet$) and hydroperoxyl radical ($HO_2^\bullet$).

$$O_3 + OH^- \rightarrow HO_2^\bullet + O_2^{\bullet-} \tag{10.89}$$

$$HO_2 \leftrightarrow O_2^{\bullet-} + H^+ \tag{10.90}$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \tag{10.91}$$

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet \tag{10.92}$$

$$HO_3^\bullet \rightarrow OH^\bullet + O_2 \tag{10.93}$$

These, particularly $OH^\bullet$, are strong and reactive oxidants, typically resulting in diffusion-limited reactions with organic species. However, due to this reactivity, concentrations of $OH^\bullet$ in water reach concentrations up to 10^{-12} M, whereas concentrations of ozone reach concentrations of 10^{-3} M (EPA, 1999).

The rate of decomposition of ozone varies from hours to seconds, depending on water conditions such as temperature, pH, UV light, O_3 concentration, and concentration of radical scavengers (i.e., alkalinity and organic matter). Gurol and Singer (1982) developed the following empirical equation to incorporate some of these parameters:

$$-\frac{d[O_3]}{dt} = k[O_3][OH^-]^{-0.55} \tag{10.94}$$

where $[O_3]$ and $[OH^-]$ are O_3 and hydroxide ion concentrations, respectively, and k is the temperature-dependent rate constant.

Permanganate

Potassium permanganate is commercially available in a deep purple solid crystalline form that dissolves in water to form a pink or purple solution. Typically, 1 to 4% solutions of permanganate are generated on-site prior to application to a treatment stream.

As shown in Table 10.3, permanganate (MnO_4^-) contains oxidized manganese (+VII) that is reduced to manganese (+IV) in the form of manganese dioxide solid (MnO_2). Permanganate oxidizes a wide variety of organic and inorganic compounds in the pH 4 to 9 range. Typically, oxidation is more rapid under alkaline than acid conditions (Hazen and Sawyer, 1992). Unlike the other oxidants described above, permanganate is not an effective disinfectant at concentrations typically employed, and therefore, it is used strictly as an oxidizing agent (EPA, 1999). Permanganate is added prior to sedimentation in treatment to allow for removal of manganese dioxide solids.

Advanced Oxidation Processes

Advanced oxidation processes (AOPs) have been shown to be effective for the elimination of organic and inorganic pollutants from water (Glaze, 1987; Masten and Davies, 1994; Legrini et al., 1993; Hoffmann et al., 1995). AOPs are generally grouped together, because they all result in the *in situ* formation of radicals or, more specifically, hydroxyl radicals ($OH^{\bullet}$), in sufficient quantity to affect water treatment (Glaze, 1987). These processes are often needed when conventional approaches to water and wastewater treatment are ineffective. Examples of AOPs include ozone at high pH (O_3/OH^-), ozone combined with hydrogen peroxide (O_3/H_2O_2), photolysis of ozone (O_3/UV), photolysis of ozone and hydrogen peroxide (O_3/H_2O_2/UV), photo-Fenton reaction (Fe(II)/H_2O_2/UV), and semiconductor photocatalysis (TiO_2/UV). Hoffmann et al., 1995; Langlais et al., 1991; Legrini et al., 1993; and Masten and Davies, 1994 form an abbreviated list of review papers and books on various AOPs.

The effectiveness of AOPs is dependent on chemical components in water other than target compounds. Alkalinity, pH, NOM, and particulates may cause significant deviations in treatment time required. For example, alkalinity and NOM react with $OH^{\bullet}$ radicals formed, reducing the concentration available to react with target species. In addition, particulates and light-absorbing species in water limit light penetration in ultraviolet irradiation AOPs.

Nondisinfection Uses Of Oxidants

Chemical oxidants other than chlorine are playing an increasing role in minimizing disinfection by-products (DBPs). These oxidants may be used as primary disinfectants at the beginning or middle of the treatment process. Employing disinfectants other than chlorine early in the treatment process results in less trihalomethane (THM) formation due to oxidation of THM precursors and minimization of the interaction of chlorine with THM precursors.

Potassium permanganate is commonly used to control treatment plant fouling by nuisance aquatic species such as zebra mussels and Asiatic clams (EPA, 1999). Monochloramine is also effective at killing Asiatic clams without producing THMs.

Reduced iron (II) and manganese (II) are problematic in many groundwater sources but are uncommon in surface waters. Many oxidants may be used to remove iron and manganese from water sources. Oxidants act to oxidize iron (II) to iron (III) and manganese (II) to manganese dioxide [manganese (IV)]. The oxidized species are relatively insoluble and thus are removed in sedimentation treatment steps. Table 10.4 shows concentrations of various oxidants necessary to oxidize iron and manganese.

Taste and odor problems are more common in surface water than groundwater sources. This is due to the presence of algae and other microorganisms along with adequate nutrients from sources such as agricultural runoff. In addition, decaying vegetation is attributed to taste and color problems (James M. Montgomery, 1985). Moreover, disinfection can result in taste and odor. Taste and odor are extremely source specific, thus different oxidants may be effective, depending on factors such as location and season. Taste and odor associated with microorganisms and decaying vegetation are often resistant to traditional oxidation, thus ozone-containing AOPs such as ozone/hydrogen peroxide, ozone at high pH, or ozone/UV may be employed, although other oxidants may be effective as well.

TABLE 10.4 Oxidant Concentrations Required to Oxidize Reduced Iron and Manganese

Oxidant	Iron (II) mg/mg Fe	Manganese (II), mg/mg Mn
Chlorine, Cl_2	0.62	0.77
Chlorine dioxide, ClO_2	1.21	2.45
Ozone, O_3	0.43	0.88
Oxygen, O_2	0.14	0.29
Potassium permanganate, $KMnO_4$	0.94	1.92

Source: Environmental Protection Agency. 1999. "Alternative Disinfectants and Oxidants Guidance Manual," *EPA 815-R-99–014*.

Chemical oxidants are used in the removal of recalcitrant and toxic organic compounds when destruction rather than displacement into another phase (i.e., GAC or air stripping) is desired. Reactions are highly dependent on the target organic compound, the oxidant used, pH, temperature, and other constituents in the water (AWWA, 1999). In addition, the extent of oxidation is important to monitor. The oxidation of a target organic compound such as phenol will result in daughter products such as catechol, hydroquinone, and benzoquinone. These daughter products will vary depending on the oxidant, extent of oxidation, ratio of oxidant to target compound, and other constituents in water. Toxicity issues that may be present with parent compounds need to be considered for potential products formed.

References

American Water Works Association. 1999. *Water Quality and Treatment: A Handbook of Community Water Supplies*, 5th edition, McGraw-Hill, New York.

Environmental Protection Agency. 1999. "Alternative Disinfectants and Oxidants Guidance Manual," *EPA 815-R-99–014. (http://www.epa.gov/safewater/mdbp/mdbptg.html#disinfect).*

Environmental Protection Agency. 2001a. "Drinking Water Priority Rulemaking: Microbial and Disinfection Byproduct Rules," *EPA 816-F-01–012. (http://www.epa.gov/safewater/mdbp/mdbpfactsheet.pdf).*

Glaze, W.H. 1987. "Drinking-Water Treatment with Ozone." *Environmental Science and Technology*, 21: 224–230.

Gurol, M.D. and Singer, P.C. 1982. "Kinetics of Ozone Decomposition: A Dynamic Approach." *Environmental Science and Technology,* 16: 377–383.

Haas, C.N. 1990. "Disinfection," p. 877 in *Water Quality and Treatment: A Handbook of Community Water Supplies*, 4th ed., F.W. Pontius, ed. McGraw-Hill, Inc., New York.

Hoffmann, M.R., Martin, S.T., Choi, W., and Bahneman, D.W. 1995. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* 95: 69–96.

James M. Montgomery, Consulting Engineers, Inc. 1985. *Water Treatment Principles and Design*. John Wiley & Sons, New York.

Katz, J., ed. 1980. *Ozone and Chlorine Dioxide Technology for Disinfection of Drinking Water.* Noyes Data Corporation, Inc., Park Ridge, NJ.

Langlais, B., Reckhow, D.A., and Brink, D.R. 1991. *Ozone in Water Treatment Application and Engineering.* Chelsea, AWWA Research Foundation and Lewis Publishers.

Legrini, O., Oliveros, E., and Braun, A.M. 1993. Photochemical Processes for Water Treatment. *Chemical Reviews,* 93: 671–698.

Masten, S.J. and Davies, S.H.R. 1994. "Use of Ozone and Other Strong Oxidants for Hazardous Waste Management," In *Environmental Oxidants*. John Wiley & Sons, New York.

Snoeyink, V.L. and Jenkins, D. 1980. *Water Chemistry,* John Wiley and Sons, New York.

Weavers, L.K. and Wickramanayake, G.B. 2000. "Disinfection and Sterilization Using Ozone," pp. 205–214 in *Disinfection, Sterilization, and Preservation,* S.S. Block, ed., Lippincott Williams & Wilkins, New York.

10.4 Disinfection

Waterborne Diseases

The principal waterborne diseases in the U.S. are listed in Table 10.5. Almost all of these diseases are transmitted via fecal contamination of water and food, but a few are more commonly transmitted by direct person-to-person contact or by inhalation of microbially contaminated air. Most of these diseases are actually quite rare, there being only one or a few cases a year, and some like cholera have not been observed for decades. However, all of these diseases have permanent reservoirs among humans or wild animals both in the U.S. and abroad, and all of them have the potential to cause outbreaks unless careful sanitation is maintained.

For the last 30 years, the U.S. has averaged about 33 outbreaks of waterborne disease per year, and each outbreak has involved about 220 cases (Craun, 1988). The majority of the outbreaks occur in noncommunity and individual systems, but the majority of the cases occur in community systems. About one-fifth of the outbreaks occur in surface water systems that either do not treat the raw water or that provide only disinfection (Craun, 1988). About two-fifths of the outbreaks occur in groundwater systems that do not provide any treatment (Craun and McCabe, 1973). Only half of the outbreaks can be attributed to a specific organism, and in recent years, *Giardia lamblia* is the one most often identified, displacing *Salmonella*. However, *Cryptosporidium parvum*-induced diarrhea may be as common as giardiasis (Rose, 1988). In recent years, the U.S. has experienced nearly one proven *Cryptosporidium* outbreak per year (Pontius, 1993). In 1989–1990, there were 26 outbreaks of waterborne disease reported in the U.S. Of these, the causative organism was not identified in 14 outbreaks. *Giardia* was responsible in seven outbreaks, hepatitis A in two, and Norwalk-like viruses, *E. coli* O157:H7, and cyanobacteria were responsible for one each (Herwaldt et al., 1992). In 1993, over 400,000 people became ill as a result of contamination of drinking water by *Cryptosporidium* in Milwaukee, WI (Rowan and Behm, 1993).

The Total Coliform Rule

In the past, the sanitary quality of drinking water was judged by a most probable number (MPN) or membrane filter count (MFC) of coliform bacteria, and the maximum contaminant level was set at 1 total coliform per 100 mL. The U.S. Environmental Protection Agency (1989) has abandoned this method and now uses the following rule (Pontius, 1990):

- Total coliform must be measured in 100 mL samples using the multiple tube fermentation technique, the membrane filter technique, or the presence-absence coliform test [all of which are described in *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington, DC. (1992)] or the Colilert™ System [MMO-MUG test, approved *Federal Register*, 57:24744 (1992)].
- The number of monthly samples depends on system size as prescribed in Table 10.6.
- No more than 5% of the monthly samples can test positive if 40 or more samples are analyzed each month.
- No more than one sample can test positive if less than 40 samples are analyzed each month.
- Unfiltered surface water systems must sample the first service connection each day that the final turbidity exceeds 1 NTU, and service connection samples must be included in the positive and negative counts.
- Coliform-positive samples must be analyzed to determine whether fecal coliform are present.
- Repeat samples must be collected within 24 hr of the laboratory report of a coliform-positive result; the number of repeat samples depends on system size as prescribed in Table 10.7.

When the Total Coliform Rule is violated, immediate corrective action is required. The public must be notified of the violation. The method of notification includes the public media and mail. The notification

TABLE 10.5 Principal Waterborne Diseases in the United States

Group/Organism	Disease	Annual Number of Outbreaks	Annual Number of Cases
	Bacteria		
Salmonella typhi	Typhoid fever	1.4	10
Salmonella paratyphi	Paratyphoid fever	—	—
Other *Salmonella*	Salmonellosis	1	171
Shigella	Bacillary dysentery	2	647
Vibrio cholerae	Cholera	—	—
Enteropathogenic *Escherichia coli*	Gastroenteritis	0.1	125
Yersinia enterocolitica	Gastroenteritis	—	—
Campylobacter jejuni	Gastroenteritis	0.1	375
Legionella pneumophilia et al.	Acute respiratory illness	—	—
Mycobacterium tuberculosis et al.	Tuberculosis	—	—
Atypical mycobacteria	Pulmonary illness	—	—
Miscellaneous opportunistic bacteria	Varies	—	—
	Viruses		
Polioviruses	Poliomyelitis	—	—
Coxsackieviruses A	Aseptic meningitis	—	—
Coxsackieviruses B	Aseptic meningitis	—	—
Echoviruses	Aseptic meningitis	—	—
Other Enteroviruses	AHC; encephalitis	—	—
Reoviruses	Mild upper respiratory and gastro-intestinal illness	—	—
Rotaviruses	Gastroenteritis	—	—
Adenoviruses	Mild upper respiratory and gastro-intestinal illness	—	—
Hepatitis A virus	Infectious hepatitis	1.5	50
Norwalk and related G. I. viruses	Gastroenteritis	0.5	154
	Protozoans		
Acanthamoeba castellani	Amebic meningoencephalitis	—	—
Balantidium coli	Balantidiasis (dysentery)	—	—
Cryptosporidium parvum	—	—	—
Entamoeba histolytica	Amebic dysentery	0.3	4
Giardia lamblia	Giardiasis (gastroenteritis)	3.3	2228
Naegleria flowleri	Primary amebic meningoencephalitis	—	—
	Helminths		
Ascaris lumbricoides	Ascariasis	—	—
Trichuris trichiura	Trichuriasis	—	—
Ancylostoma duodenale	Hookworm disease	—	—
Necator americanus	Hookworm disease	—	—
Strongyloides stercoralis	Threadworm disease	—	—
	Cyanobacteria		
Anabaena flos-aquae	Gastroenteritis	—	—
Microcystis aeruginosa	Gastroenteritis	—	—
Aphanizomenon flos-aquae	Gastroenteritis and neurotoxins	—	—
Schizothrix calcicola	Gastroenteritis	—	—
Unknown Etiology	Acute gastroenteritis	16.0	3353

Source: Craun, G.F. and McCabe, L.J. 1973. "Review of the Causes of Water-borne Disease Outbreaks," *Journal of the American Water Works Association*, 65(1): 74.

Sobsey, M. and Olson, B. 1983. "Microbial Agents of Waterborne Disease," in *Assessment of Microbiology and Turbidity Standards for Drinking Water: Proceedings of a Workshop, December 2–4, 1981*, EPA 570–9–83–001, P.S. Berger and Y. Argaman, eds. U.S. Environmental Protection Agency, Office of Drinking Water, Washington, DC.

TABLE 10.6 Sampling Requirements of the Total Coliform Rule

Population Served	Mininum Number of Routine Samples per Month [a]	Population Served	Minimum Number of Routine Samples per Month [a]
25–1000 [b]	1 [c]	59,001–70,000	70
1001–2500	2	70,001–83,000	80
2501–3300	3	83,001–96,000	90
3301–4100	4	96,001–130,000	100
4101–4900	5	130,001–220,000	120
4901–5800	6	220,001–320,000	150
5801–6700	7	320,001–450,000	180
6701–7600	8	450,001–600,000	210
7601–8500	9	600,001–780,000	240
8501–12,900	10	780,001–970,000	270
12,901–17,200	15	970,001–1,230,000	300
17,201–21,500	20	1,230,001–1,520,00	330
21,501–25,000	25	1,520,001–1,850,000	360
25,001–33,000	30	1,850,001–2,270,000	390
33,001–41,000	40	2,270,001–3,020,000	420
41,001–50,000	50	3,020,001–3,960,000	450
50,001–59,000	60	3,960,001 or more	480

[a] In lieu of the frequency specified in this table, a noncommunity water system using groundwater and serving 1000 persons or fewer may monitor at a lesser frequency specified by the state until a sanitary survey is conducted, and the state reviews the results. Thereafter, noncommunity water systems using groundwater and serving 1000 persons or fewer must monitor each calendar quarter during which the system provides water to the public unless the state determines that some other frequency is more appropriate and notifies the system (in writing). Five years after promulgation, noncommunity water systems using groundwater and serving 1000 persons or fewer must monitor at least once per year.

A noncommunity water system using surface water or groundwater under the direct influence of surface water, regardless of the number of persons served, must monitor at the same frequency as a like-sized public water system. A noncommunity water system using groundwater and serving more than 1000 persons during any month must monitor at the same frequency as a like-sized community water system, except that the state may reduce the monitoring frequency for any month the system serves 1000 persons or fewer.

[b] Includes public water systems that have at least 15 service connections but serve fewer than 25 persons.

[c] For a community water system serving 25 to 1000 persons, the state may reduce this sampling frequency, if a sanitary survey conducted in the last 5 years indicates that the water system is supplied solely by a protected groundwater source and is free of sanitary defects. However, in no case, may the state reduce the sampling frequency to less than once per quarter.

Source: Environmental Protection Agency. 1989. “Total Coliforms. Final Rule,” *Federal Register,* 54(124): 27544.

TABLE 10.7 Monitoring and Repeat-Sample Frequency After a Total-Coliform-Positive Routine Sample

Number of Routine Samples per Month	Number of Repeat Samples [a]	Number of Routine Samples Next Month [b]
1 or fewer	4	5
2	3	5
3	3	5
4	3	5
5 or greater	3	Table 47

[a] Number of repeat samples in the same month for each total-coliform-positive routine sample.

[b] Except where the state has invalidated the original routine sample, substitutes an on-site evaluation of the problem, or waives the requirement on a case-by-case basis.

Source: Environmental Protection Agency. 1989. “Total Coliforms. Final Rule,” *Federal Register*, 54(124): 27544.

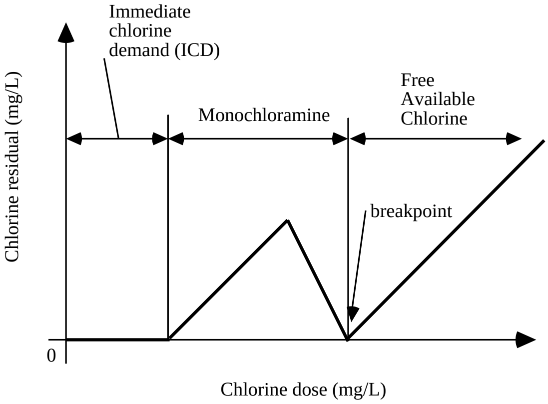


FIGURE 10.5 The chlorine breakpoint curve.

must conform to federal regulations regarding language and must include a description of the Total Coliform Rule, the public health significance of the violation, precautions consumers should take, a description of the corrective actions being taken by the utility, and telephone numbers for additional information. Corrective measures include flushing mains, increasing disinfectant doses, and improving filtration performance.

Community water systems collecting fewer than five samples per month are required to conduct a sanitary survey within 5 years of the promulgation of the rule and every 5 years thereafter. Noncommunity water systems are required to conduct a sanitary survey within 10 years after the rule is promulgated and every 5 years thereafter. If the noncommunity water system uses protected and disinfected groundwater, the sanitary survey may be repeated every 10 years instead of every 5 years.

Disinfectants

Although chlorine has been primarily used throughout the U.S., other chemical oxidants are becoming more popular. These include chlorine dioxide, chloramines, and ozone. In addition, ultraviolet irradiation is rapidly gaining acceptance, particularly in smaller treatment facilities (Parrotta and Bekdash, 1998). The chemistry of the disinfectants is discussed above. The solubilities of the gaseous disinfectants and pH effects on their forms are discussed in a previous chapter.

Chlorine

Generally, the disinfecting power of hypochlorous acid is greater than that of hypochlorite. In addition, the presence of ammonia in water results in the formation of chloramines. Thus, the form of chlorine present in the water is critical in determining the extent of disinfection.

The Breakpoint Curve

The breakpoint curve is a plot of the measured chlorine residual vs. the chlorine dose. It consists of three regions (see Fig. 10.5):

- An initial region at low chlorine dosages where there is no measurable residual [This represents the immediate chlorine demand (ICD) due to the oxidation of reactive substances like ferrous iron and sulfide.]
- A second region at higher doses in which the measured residual first increases with chlorine dose and then decreases (This region occurs when the raw water contains ammonia or organic nitrogen. The measured residual consists mostly of monochloramine, and it is called the combined residual. Combined residual rises as ammonia is converted to monochloramine, and it declines as

monochloramine is converted to nitrogen gas and nitrate. The minimum point of the falling limb of the curve is the "breakpoint," which marks the elimination of the combined residual.)

- A final region in which the measured residual increases linearly 1:1 with chlorine dose [The measured residual is a mixture of molecular chlorine, hypochlorous acid, and hypochlorite, and it is called the free available chlorine (FAC) residual. (See Chapter 9, Section 9.8, "Aeration and Gas Exchange.")]

The existence of an ICD and a combined residual depends on raw water composition, and either or both may be absent. Ferrous iron and sulfide are common in groundwater but rare in surface water. Unless it has been nitrified, wastewater contains significant amounts of ammonia, but surface waters do not.

Monochloramine, hypochlorite, and hypochlorous acid differ greatly in their disinfecting power, and determination of the breakpoint curve is needed to know which form is present.

Combined Residual Chlorine (Chloramines)

Hypochlorous acid reacts with ammonia to form monochloramine (Palin, 1977; Wei and Morris, 1974; Saunier and Selleck, 1979):

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \tag{10.95}$$

This is the only product formed until the ammonia is nearly exhausted. Then, hypochlorous acid reacts with monochloramine to form dichloramine. Small amounts of nitrogen trichloride may also be formed:

$$HOCl + NH_2Cl \rightarrow NHCl_2 \tag{10.96}$$

$$HOCl + NHCl_2 \rightarrow NCl_3 \tag{10.97}$$

Saunier and Selleck (1979) propose that mono- and dichloramine react with water and/or hydroxide to form hydroxylamine:

$$NH_2Cl + OH^- \rightarrow NH_2OH + Cl^- \tag{10.98}$$

$$NHCl_2 + H_2O + OH^- \rightarrow NH_2OH + HOCl + Cl^- \tag{10.99}$$

They further propose that the hydroxylamine is oxidized by hypochlorous acid to nitrosyl hydride. This intermediate was also suggested by Wei and Morris (1974). However, nitrosyl hydride has never been observed, and its existence may be impossible (Sidgwick, 1950).

$$HOCl + NH_2OH \rightarrow NOH + H_2O + H^+ + Cl^- \tag{10.100}$$

If nitrosyl hydride exists, it would react with mono- and dichloramine to form nitrogen gas or with hypochlorous acid to form nitrate:

$$NOH + NHCl_2 \rightarrow N_2 + HOCl + H^+ + Cl^- \tag{10.101}$$

$$NOH + NH_2Cl \rightarrow N_2 + H_2O + H^+ + Cl^- \tag{10.102}$$

$$NOH + HOCl \rightarrow HNO_2 + H^+ + Cl^- \tag{10.103}$$

$$HNO_2 + HOCl \rightarrow HNO_3 + H^+ + Cl^- \tag{10.104}$$

The net stoichiometry would be a mixture of Eqs. (10.105) and (10.106):

$$3\ \mathrm{HOCl} + 2\ \mathrm{NH_3} \rightarrow \mathrm{N_2} + 3\ \mathrm{H_2O} + 3\ \mathrm{H^+} + 3\ \mathrm{Cl^-} \tag{10.105}$$

$$4\ \mathrm{HOCl} + \mathrm{NH_3} \rightarrow \mathrm{HNO_3} + \mathrm{H_2O} + 4\ \mathrm{H^+} + 4\ \mathrm{Cl^-} \tag{10.106}$$

It appears that the formation of nitrogen gas predominates, and the molar ratio of hypochlorous acid to ammonia at the breakpoint is about 1.6 to 1.7 (Wei and Morris, 1974). This amounts to about 8.1 to 8.6 kg chlorine per kg of total kjeldahl nitrogen (TKN).

Required Chlorine Dose

Generally, it is desirable to produce a free available chlorine residual consisting of hypochlorous acid, because this is the most effective form of chlorine for inactivation of microorganisms. The free residual is related to the chlorine dose by,

$$D_{Cl_2} = \mathrm{ICD} + 8.6\ \mathrm{TKN} + C_{FAC} \tag{10.107}$$

where C_{FAC} = the free, available chlorine consisting of a mixture of dissolved chlorine, hypochlorous acid, and hypochlorite in mg/L
D_{Cl_2} = the required chlorine dose in mg/L
ICD = the immediate chlorine demand in mg/L
TKN = the total kjeldahl nitrogen concentration in mg/L

The pH dependency of the distribution of hypochlorous acid and hypochlorite is discussed in Chapter 9, Section 9.8 “Aeration and Gas Exchange.”

Dechlorination

Chlorine is highly toxic to fish: the 96-hr-LC_{50} is about 10 μg/L for most freshwater fish and about 2 μg/L for salmonids (Criteria Branch, 1976). High concentrations are also undesirable in drinking water for aesthetic reasons.

The usual method of dechlorination is reaction with sulfur dioxide. Sulfur dioxide reacts with hypochlorous acid and monochloramine:

$$\mathrm{SO_2} + \mathrm{HOCl} + \mathrm{H_2O} \rightarrow 3\ \mathrm{H^+} + \mathrm{Cl^-} + \mathrm{SO_4^{2-}} \tag{10.108}$$

$$\mathrm{SO_2} + \mathrm{NH_2\ Cl} + 2\mathrm{H_2O} \rightarrow \mathrm{NH_4^+} + 2\ \mathrm{H^+} + \mathrm{Cl^-} + \mathrm{SO_4^{2-}} \tag{10.109}$$

Chlorine can also be removed by reaction with activated carbon. The initial reaction with fresh carbon (R) results in the formation of carbon-oxides (R = O) on the carbon surfaces (Stover et al., 1986):

$$\mathrm{R} + \mathrm{HOCl} \rightarrow \mathrm{R{=}O} + \mathrm{H^+} + \mathrm{Cl^-} \tag{10.110}$$

The surface oxides may eventually evolve into carbon monoxide or carbon dioxide. Monochloramine undergoes a similar reaction:

$$\mathrm{R} + \mathrm{NH_2\ Cl} + \mathrm{H_2O} \rightarrow \mathrm{R{=}O} + \mathrm{NH_4^+} + \mathrm{Cl^-} \tag{10.111}$$

Chlorine Dioxide

The relative advantages and disadvantages of chlorine dioxide as a disinfectant are as follows (Katz, 1980):

- It destroys phenols rather than chlorinating them, and reducing taste and odor products compared to free chlorine.
- It destroys some algal taste and odor compounds.

TABLE 10.8 Specific Lethality Coefficients for 5°C

	K (L/mg min)			
Disinfectant	Amoebic Cysts	Enteric Bacteria	Spores	Viruses
Hypochlorite, OCl^-	0.0005	0.2	<0.0005	<0.02
Hypochlorous Acid, HOCl	0.05	20	0.05	≥1
Monochloramine, NH_2Cl	0.02	0.1	0.001	0.005
Ozone, O_3	0.5	500	2	5

Source: Morris, J.C. 1975. "Aspects of the Quantitative Assessment of Germicidal Efficiency," p. 1 in *Disinfection: Water and Wastewater*, J.D. Johnson, ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

- It does not hydrolyze, so its disinfecting power is not affected by pH.
- Because it does not hydrolyze, it can be removed from water by air-stripping.
- It does not react with ammonia.

Chlorine dioxide does not form trihalomethanes (Rav-Acha, 1984). However, the excess chlorine used to make it will form THMs. Also, some chlorine is released during chlorine dioxide reactions, and this chlorine may form trace amounts of THMs.

Disinfection Kinetics

The Chick–Watson Law

In batch disinfection systems, the die-away of microbes is often exponential, which implies a first-order decay law called the Chick (1908)–Watson (1908) Law:

$$\frac{dN}{dt} = kC^n N \tag{10.112}$$

$$N(t) = N_o e^{-kC^n t} \tag{10.113}$$

where C = the disinfectant concentration (kg/m^3 or lb/ft^3)
k = the coefficient of specific lethality (m^{3n}/kg$^{n}\cdot$s or ft^{3n}/lb$^{n}\cdot$sec)
N = the number concentration of microbes (number/m^3 or number/ft^3)
n = the coefficient of dilution (dimensionless)
t = elapsed time (sec)

The coefficient of dilution is frequently near 1, and Morris (1975) argues that quality of the data typically obtained does not warrant any other value. Some specific lethality coefficients reported by Morris are given in Table 10.8.

Effect of Microbial Clusters

Microorganisms frequently exist clustered together or with other suspended solids. This offers protection for those organisms imbedded within the cluster and changes the pattern of inactivation. Die-away curves may exhibit an initial lag (called a "shoulder") and/or a sharp reduction in slope as the contacting time increases (called a "tail"). This situation can be modeled as a multi-Poisson process in which microorganisms in individiual clusters are inactivated sequentially (Wei and Chang, 1975):

$$S_t = \sum_{i=1}^{n}\left[X_i^o e^{-kt}\sum_{r=0}^{i-1}\frac{(kt)^r}{r!}\right] \tag{10.114}$$

where i = the number of viable microorganisms in a cluster (dimensionless)
k = the inactivation rate for a single microorganism (per sec)
n = the maximum number of microorganisms in a cluster (dimensionless)
S_t = the concentration of clusters containing viable microorganisms at time t (number/m^3 or number/ft^3);
X_i^o = the initial concentration of clusters containing i viable microorganisms (dimensionless)
t = the contacting time (sec)

Equation (10.114) fits all of the observed die-away patterns.

Ct Products

The results of disinfection studies are frequently reported as *Ct* products. These products can be derived directly from the Chick–Watson Law. Their use implies that the Chick–Watson Law accurately describes the die-away curve, and that the dilution coefficient is 1:

$$Ct = \frac{\ln N_o/N(t)}{k} \tag{10.115}$$

The value of *Ct* depends on the ratio of initial to final microorganism concentrations. Generally, the products are reported for ratios that are multiples of 10, and the reduction in microbial counts is referred to as one-log (10:1 ratio), two-log (100:1 ratio), three-log (1000:1), etc. Alternatively, one speaks of viable count reductions of 90, 99, 99.9%, etc., respectively.

Strictly speaking, the concept of the *Ct* product does not apply if the dilution coefficient is not 1. When this situation occurs, reported *Ct* products vary with the disinfectant concentration, and the applicable concentration must be specified. The result is a specification of the required contacting time.

Ct products also do not apply when there is microbial clustering. However, this situation may be handled by estimating the initial lag period. The die-away curve is plotted semilogarithmically, and the linear portion is extrapolated back to the initial microorganism concentration. The initial lag period is then read off the time axis. During the lag period, there is no inactivation, so any disinfection system must provide a contacting time longer than this lag period.

Finally, it must be remembered that *Ct* products are obtained from batch disinfection experiments. If they are to be used in the design of continuous flow systems, the systems must achieve nearly ideal plug flow. In this regard, the U.S. Environmental Protection Agency requires that the contacting time for any system be calculated as the time that at least 90% of the water is held (EPA, 1989). This can be determined by tracer studies.

Ct products can be determined for any microorganism, but as a practical matter, only those microbes most resistant to disinfection are of interest. For design purposes, the critical organisms are the cysts of the protozoan *Giardia lamblia* and viruses. The U.S. Environmental Protection Agency (1989) requires that water treatment plants achieve an overall reduction of 99.9% (3-log) of *G. lamblia* cysts and 99.99% (4-log) of viruses. The Agency credits coagulation-flocculation-settling-filtration with most of the removal of these indicator organisms and requires chemical disinfection for the remainder of the 3-log and 4-log removals. Their requirements are shown in Table 10.9. Some *Ct* products for chemical disinfection of *G. lamblia* and viruses are given in Tables 10.10 and 10.11, respectively. See the EPA website for conditions other than those listed in these tables.

Chlorine

Because chlorine forms a weak acid in water and forms weak oxidants with ammonia, chlorination kinetics exhibit special features.

pH Effects

As Table 10.8 shows, the hypochlorite ion is a poor disinfectant compared to undissociated hypochlorous acid. Consequently, in a mixture of hypochlorite and hypochlorous acid, nearly all the inactivation is

TABLE 10.9 Pathogen Inactivation Requirements of the Surface Water Treatment Rule

	Removal Credited to Process (logs)		Additional Removal by Disinfection (logs)	
Process	*G. lamblia*	Virus	*G. lamblia*	Virus
Conventional treatment	2.5	2.0	0.5	2.0
Direct filtration	2.0	1.0	1.0	3.0
Slow sand filters	2.0	2.0	1.0	2.0
Diatomaceous earth filters	2.0	1.0	1.0	3.0

Source: Environmental Protection Agency. 1989. "Drinking Water; National Primary Drinking Water Regulations; Filtration, Disinfection, Turbidity, *Giardia lamblia*, Viruses, *Legionella*, and Heterotrophic Bacteria. Final Rule," *Federal Register*, 54(124): 27485.

TABLE 10.10 *Ct* Products for One-Log *Giardia lamblia* Inactivation

		Ct Product (L/mg·min)			
		Temperature (°C)			
Disinfectant	pH	0.5	5	10	15
Free available chlorine	6	49	35	26	19
(at 2 mg/L)	7	70	50	37	28
	8	101	72	54	36
	9	146	146	78	59
Ozone	—	0.97	0.63	0.48	0.32
Chlorine dioxide	—	21	8.4	7.4	6.3
Chloramine (preformed)	—	1270	730	620	500

Source: Environmental Protection Agency. 1989. "Drinking Water; National Primary Drinking Water Regulations; Filtration Disinfection, Turbidity, *Giardia lamblia*, Viruses, *Legionella*, and Heterotrophic Bacteria. Final Rule," *Federal Register*, 54(124):27485.

TABLE 10.11 *Ct* Products for Virus Inactivation Between pH 6 and 9

		Ct Product (L/mg·min)			
		Temperature (°C)			
Disinfectant	log Inactivation	0.5	5	10	15
Free available chlorine	2	6	4	3	2
	3	9	6	4	3
Ozone	2	0.9	0.6	0.5	0.3
	3	1.4	0.9	0.8	0.5
Chlorine dioxide	2	8.4	5.6	4.2	2.8
	3	25.6	17.1	12.8	8.6
Chloramine	2	1243	857	843	428
	3	2063	1423	1067	712

Source: Environmental Protection Agency. 1989. "Drinking Water; National Primary Drinking Water Regulations; Filtration, Disinfection, Turbidity, *Giardia lamblia*, Viruses, *Legionella*, and Heterotrophic Bacteria. Final Rule," *Federal Register*, 54(124): 27485.

achieved by the undissociated acid. This means that the specific lethality coefficient reported for FAC will depend on pH.

A pH-independent specific lethality coefficient based on HOCl can be calculated from,

$$k_{FAC}C_{FAC}^{n} = k_{HOCl}C_{HOCl}^{n} \tag{10.116}$$

where C_{FAC} = the free available chlorine concentration (kg/m^3 or lb/ft^3)
C_{HOCl} = the hypochlorous acid concentration (kg/m^3 or lb/ft^3)
k_{FAC} = the coefficient of specific lethality based on the free available chlorine concentration (m^{3n}/kg$^{n}\cdot$s or ft^{3n}/lb$^{n}\cdot$sec)
k_{HOCl} = the coefficient of specific lethality based on the hypochlorous acid concentration (m^{3n}/kg$^{n}\cdot$s or ft^{3n}/lb$^{n}\cdot$sec)
n = the dilution coefficient (dimensionless)

The molar fraction of hypochlorous acid depends strongly on pH and can be estimated from the following (see Chapter 9, Section 9.8 "Aeration and Gas Exchange"):

$$pK_a = -10.069 + 0.025T - \frac{3000}{T} \tag{10.117}$$

$$f = \frac{[\mathrm{HOCl}]}{[\mathrm{HOCl}] + [\mathrm{OCl}^-]} = \frac{1}{1 + \dfrac{K_a}{[\mathrm{H}^+]}} \tag{10.118}$$

where T = Kelvin.

Consequently, the relationship of the HOCl-based coefficient to the pH-dependent FAC-based coefficient is,

$$k_{HOCl} = k_{FAC}\left\{\frac{K_a + [\mathrm{H}^+]}{[\mathrm{H}^+]}\right\}^n \tag{10.119}$$

Temperature Effects

The analysis of Fair and Geyer (1954) indicates that the Streeter–Phelps theta value for coliform inactivation by free available chlorine is approximately 1.04 at pH values below 8.5 and is 1.08 at pH values above 9:

$$k_{HOCl}(T_1) = k_{HOCl}(T_o)\cdot\theta^{T_1 - T_o} \tag{10.120}$$

where $k_{HOCl}(T_0)$ = the specific lethality coefficient at the reference temperature T_0 (m^{3n}/kg$^{n}\cdot$s or ft^{3n}/lb$^{n}\cdot$sec)
$k_{HOCl}(T_1)$ = the specific lethality coefficient at the chlorine contactor temperature T_1 (m^{3n}/kg$^{n}\cdot$s or ft^{3n}/lb$^{n}\cdot$sec)
T_0 = the reference temperature, frequently 5°C (K or °R)
T_1 = the chlorine contactor temperature (K or °R)
θ = the Streeter–Phelps temperature coefficient (dimensionless)
= 1.04, for pH less than 8.5
= 1.08, for pH greater than 9

Chloramines

Monochloramine occurs naturally in the disinfection of many wastewaters, because the wastewaters contain substantial amounts of ammonia. In water treatment, monochloramines are formed when anhydrous ammonia is added along with chlorine. Monochloramine, dichloramine, and nitrogen trichloride are oxidants, and they are usually reported as equivalent molecular chlorine and called the "combined available chlorine" or "combined residual chlorine."

Monochloramine is a relatively poor disinfectant. However, disinfection with monochloramine is sometimes practiced in order to reduce trihalomethane and phenolic odor formation. Best results are obtained with low pH values around 6 and rather low ammonia-to-chlorine weight ratios (around 2:1), which enhance the formation of dichloramine (Haas, 1990).

The Streeter–Phelps theta value for monochloramine inactivation is about 1.08.

Contactor Design

The Surface Water Treatment Rule requires that the specified inactivation of cysts and viruses be completed by the time the water reaches the first customary service at the peak hourly flow. The *Ct* product may be calculated using the detention times of all the tanks and piping between the point of application of the disinfectant and the first service. For the purpose of the calculation, the disinfectant residuals are measured at tank outlets and the downstream end of pipeline sections. The hydraulic detention time of pipe sections can be estimated by assuming ideal plug flow. The hydraulic detention of tanks is estimated as the time required for 10% of a tracer applied to the tank inlet to reach the outlet, T_{10}. In the case of cysts, the calculation is,

$$\frac{\sum_{i=1}^{n}\left(C_{eff}T_{10}\right)_i}{(Ct)_{99.9}} \geq 1 \qquad (10.121)$$

where C_{eff} = the disinfectant concentration at the effluent end of the *i*-th sequential unit (kg/m^3 or lb/ft^3)

$(Ct)_{99.9}$ = the *Ct* product for 99.9% inactivation (m^3·s/kg or ft^3·sec/lb)

T_{10} = the detention time for 90% of the flow entering the *i*-th sequential unit (sec)

The detention should be determined by tracer studies. The best method of tracer application is step-input, because pulse-input tests require more work (Teefy and Singer, 1990). Suitable tracers are chloride (at drinking water concentrations less than 250 mg/L), fluoride (at drinking water concentrations less than 2 mg/L), and Rhodamine WT (at drinking water concentrations less than 0.1 μg/L). Fluoride adsorbs to aluminum hydroxide and ferric hydroxide flocs, reducing its usefulness. Rhodamine B is a suspected carcinogen and should not be used.

Mixed-Cells-in-Series

In the past, little attention has been paid to the hydraulic design of disinfectant contactors, and the residence time distributions of existing contactors are generally unknown. In this situation, tracer studies are mandatory in order to satisfy the requirements of the Surface Water Treatment Rule.

It is possible, however, to produce contactor designs that have predictable residence distributions and achieve predictable degrees of inactivation. The easiest way to do this is to build contactors as mixed-cells-in-series. Each cell should have a mixer and a disinfectant dosing device so that both the hydraulic regime and the disinfectant concentration are controllable.

For a contactor consisting of *n* completely-mixed-cells-in-series, each cell having the same volume V_1, the ratio of the outlet to inlet microorganism concentrations is,

$$\frac{N}{N_o} = \left[\frac{1}{1 + kC\left(V_1/Q\right)}\right]^n \qquad (10.122)$$

where C = the disinfectant concentration (kg/m^3 or lb/ft^3)

k = the specific lethality coefficient (m^3/kg·s or ft^3/lb·sec)

N = the required effluent microbial concentration (number/m^3 or number/ft^3)

N_0 = the influent microbial concentration (number/m^3 or number/ft^3)

n = the number of mixed-cells-in-series (dimensionless)

Q = the flow rate through the contactor (m^3/s or ft^3/sec)
V_1 = the volume of one cell (m^3 or ft^3)

It is assumed that the coefficient of dilution is 1, and that the cells are equivolume.

The ratio N/N_0 is determined by the required log inactivation: the ratio is 0.10 for a one-log inactivation, 0.01 for a two-log inactivation, etc. The specific lethality coefficient can be calculated from Ct product data by Eq. (10.115). In the case of chlorine, if the disinfectant concentration is reported in terms of free available chlorine $\{[Cl_2]+[HOCl]+[OCl^-]\}$, the specific lethality coefficient for the contactor pH must be used. If the concentration of the undissociated hypochlorous acid is reported, no pH correction is needed, but the specific lethality coefficient for HOCl is needed. The fraction of hypochlorous acid in the free available chlorine is given by Eq. (10.117). In any case, the specific lethality coefficient must be corrected for temperature using Eq. (10.118).

For a reactor consisting of mixed-cells-in-series, the value of T_{10} can be calculated theoretically. The exit age distribution for n mixed-cells-in-series is given by Eq. (10.123) (Wen and Fan, 1975):

$$E = \frac{n^n}{(n-1)!}\left(\frac{t}{nV_1/Q}\right)^{n-1} \exp\left(-\frac{t}{V_1/Q}\right) = \frac{C(t)nV_1}{M} \tag{10.123}$$

In a pulse input tracer test, E is also the ratio of the tracer concentration in the effluent times the tank volume to the mass of tracer injected. The cumulative exit age distribution is given by Eq. (10.124) (Wen and Fan, 1975):

$$F = 1 - \exp\left(-\frac{t}{V_1/Q}\right)\sum_{i=1}^{n}\frac{1}{(i-1)!}\left(\frac{t}{V_1/Q}\right)^{i-1} = \frac{C(t)}{C_o} \tag{10.124}$$

This is also the dimensionless tracer response obtained in a step-input tracer test. In either equation, the value of T_{10} is the time for the first 10% of the tracer to appear in the effluent.

The computation recommended by the Surface Water Treatment Rule underestimates the inactivation actually achieved by mixed-cells-in-series if the dimensionless contacting number $KC(nV_1/Q)$ is less than 14, and the number of compartments is four or more (Lawler and Singer, 1993). For larger values of the parameter or fewer compartments, the SWTR overestimates the inactivation achieved.

Ultraviolet Irradiator Design

Ultraviolet radiation destroys nucleic acids, which inactivates mircroorganisms (Stover et al., 1986). Optimum disinfection occurs at UV wavelengths about 254 nm, and most commercial lamps are designed to emit near the optimum.

Ultraviolet disinfection units consist of parallel arrays of long emission lamps. The lamps are generally 0.9 m to 1.6 m long and 1.5 to 1.9 cm in diameter. They are usually spaced several cm apart (center line to center line), and are operated submerged. The liquid flow may be parallel to the lamp axes or normal to them. The tanks containing the arrays are designed with inlet and outlet baffles to control flow distribution.

The inactivation rate is directly proportional to the UV light intensity, generally expressed as $\mu W/cm^2$. However, water and suspended solids absorb UV light, so in any real reactor, the light intensity declines with distance from the lamp. Inactivation rates are expressed in terms of the average intensity, $\bar{I}$. Because the details of the intensity distribution vary from one design to the next, different designs achieve different inactivation rates even if they produce the same average intensity.

For batch systems, the inactivation rate would be represented by (Stover et al., 1986),

$$\frac{dN}{dt} = -a\bar{I}^b N \tag{10.125}$$

where a = an empirical rate coefficient ($cm^{2b}/\mu W^{b}\cdot s$)
b = an empirical exponent (dimensionless)
$\bar{I}$ = the volume-averaged light intensity ($\mu W/cm^2$)
N = the number concentration of microbes ($number/m^3$)
t = exposure time (sec)

Values of a are strongly dependent on the suspended solids content of the water being irradiated. Reported wastewater treatment plant values vary from 40×10^{-9} $(cm^2/\mu W)^{-b}\cdot s^{-1}$ to 0.10×10^{-3} $(cm^2/\mu W)^{-b}\cdot s^{-1}$. Reported values of b are less variable and range from 1.09 to 2.2.

Typical average UV light intensities are on the order of several thousand $\mu W/cm^2$, which corresponds to a UV power density of several W/L. Tubular arrays of lamps generally produce lower average intensities for the same power density than do uniform arrays.

The disinfection units may be analyzed as plug flow reactors with dispersion (Stover et al., 1986):

$$N = N_o \exp\left[\frac{UL}{2E}\left(1-\sqrt{1+\frac{4a\bar{I}^bE}{U^2}}\right)\right]+0.26X_{SS}^{1.96} \qquad (10.126)$$

where a = an empirical rate coefficient ($cm^{2b}/\mu W^{b}\cdot s$)
b = an empirical exponent (dimensionless)
E = longitudinal shear dispersion coefficient (m^2/s)
$\bar{I}$ = the volume-averaged light intensity ($\mu W/cm^2$)
L = the length of the irradiation chamber (m)
N = the effluent number concentration of microbes (coli/100 mL)
N_o = the influent number concentration of microbes (coli/mL)
U = the mean velocity in the irradiator (m/s)
X_{ss} = the suspended solids concentration (mg/L)

The first term on the right-hand side represents the residual microbial concentration that would be in the irradiator effluent if all the microorganisms were dispersed as single cells or cysts. The second term represents the microorganisms that are incorporated into suspended solids and that escape irradiation.

The coefficient and exponent on the suspended solids concentration X_{ss} represent the experience at the Port Richmond Water Pollution Control Plant on Staten Island, New York, for the disinfection of coliform bacteria. If the suspended solids concentration is given as mg/L, the resulting fecal coliform count is given as cells per 100 mL. Fecal coliform data from other wastewater treatment facilities are scattered widely around the Port Richmond correlation. Correlations for water treatment plants are not available.

Disinfection By-Products

A current challenge of water treatment facilities is to balance adequate disinfection with minimal disinfection by-product (DBP) formation. Disinfection by-products are formed from the reaction of disinfection oxidants with natural organic and inorganic matter in source water. Many of these DBPs are probable or possible human carcinogens (AWWA, 1999). Thus, these DBPs are regulated under the Total Trihalomethane Rule and Stage 1 Disinfectants and Disinfection By-products (D/DBP) Rule (EPA, 2001a). The Total Trihalomethane Rule, applying to water systems serving at least 10,000 people using a disinfectant, set an interim MCL for total trihalomethanes of 0.10 mg/L as an annual average.

In 1998, the U.S. EPA finalized Stage 1 of the Disinfectants/Disinfection By-products (D/DBP) Rule to regulate maximum residual concentrations of disinfectants; lower the MCL for total trihalomethanes (TTHMs); and establish a new MCL for 5 haloacetic acids (HAAs), chlorite, and bromate. This rule applies to community water supplies using disinfectants regardless of size (EPA, 2001b). In addition, this rule specifies removal requirements for DBP precursor compounds. The removal requirements increase with increasing raw water total organic carbon (TOC) and decreasing alkalinity. Note that the Stage 1 DBP Rule supersedes the 1979 TTHM standard.

Halogenated DBPs

The chlorination of natural waters containing humic and fulvic acids results in the formation of chloroform and other halogenated methane derivatives. In test animals, chloroform causes central nervous system depression, hepatotoxicity, nephrotoxicity, teratogenicity. and carcinogenicity (Symons, et al., 1981). Chloroform in drinking water is suspected to cause cancer in humans.

Halogenated by-product formation may be minimized by removing the organic precursors with activated carbon prior to chlorination or by switching to an alternative disinfectant such as chlorine dioxide or ozone for primary disinfection (Symons et al., 1981).

The substances that comprise total trihalomethanes include chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHCl_2Br$), and dibromochloromethane ($CHClBr_2$). Haloacetic acids included in Stage 1 DBP Rule include dichloroacetic acid ($Cl_2CHCOOH$), trichloroacetic acid ($Cl_3CHCOOH$), monochloroacetic acid ($ClCH_2COOH$), monobromoacetic acid ($BrCH_2COOH$), and dibromoacetic acid ($Br_2CHCOOH$).

Predictive, empirical models for the resulting THM or HAA have been developed by Watson (1993). In these models, the concentration of the DBP is given in μg/L; all other concentrations are in mg/L; the extinction coefficient for UV light at 254 nm is given in reciprocal cm; the contacting time is in hours:

Chloroform:

$$\begin{aligned} CHCl_3 = 0.064(TOC)^{0.329}(pH)^{1.161}(°C)^{1.018}(Cl_2\ Dose)^{0.561} \times \\ \times\left(Br^- + 0.01\right)^{-0.404}\left(k_{ext,254}\right)^{0.874}(hr)^{0.269} \end{aligned} \tag{10.127}$$

Bromodichloromethane, for $Cl_2/Br^- < 75$:

$$CHCl_2Br = 0.0098(pH)^{2.550}(°C)^{0.519}(Cl_2Dose)^{0.497}\left(Br^-\right)^{0.181}(hr)^{0.256} \tag{10.128}$$

Bromodichloromethane, for $Cl_2/Br^- > 75$:

$$CHCl_2Br = 1.325(TOC)^{-0.725}(°C)^{1.441}(Cl_2\ Dose)^{0.632}\left(Br^-\right)^{0.794}(hr)^{0.204} \tag{10.129}$$

Dibromochloromethane, for $Cl_2/Br^- < 50$:

$$CHClBr_2 = 14.998(TOC)^{-1.665}(°C)^{0.989}(Cl_2\ Dose)^{0.729}\left(Br^-\right)^{1.241}(hr)^{0.261} \tag{10.130}$$

Dibromochloromethane, for $Cl_2/Br^- >50$:

$$\begin{aligned} CHClBr_2 = 0.028(TOC)^{-1.078}(pH)^{1.956}(°C)^{0.596}(Cl_2\ Dose)^{1.072} \times\ldots \\ \ldots\times\left(Br^-\right)^{1.573}\left(k_{ext,254}\right)^{-1.175}(hr)^{0.200} \end{aligned} \tag{10.131}$$

Bromoform:

$$CHBr_3 = 6.533(TOC)^{-2.031}(pH)^{1.603}(Cl_2\ Dose)^{1.057}\left(Br^-\right)^{1.388}(hr)^{0.136} \tag{10.132}$$

Monochloroacetic acid, for hr > 12:

$$\begin{gathered}\mathrm{ClCH_2COOH} = 1.634(\mathrm{TOC})^{0.753}(\mathrm{pH})^{-1.124}(\mathrm{Cl_2\ Dose})^{0.509}\times\ldots\\ \ldots\times\left(\mathrm{Br}^- + 0.01\right)^{-0.085}(\mathrm{hr})^{0.300}\end{gathered}\tag{10.133}$$

Dichloroacetic acid:

$$\begin{gathered}\mathrm{Cl_2CHCOOH} = 0.605(\mathrm{TOC})^{0.291}(^\circ\mathrm{C})^{0.665}(\mathrm{Cl_2\ Dose})^{0.480}\times\ldots\\ \ldots\times\left(\mathrm{Br}^- + 0.01\right)^{-0.568}\left(\mathrm{k}_{\mathrm{ext},254}\right)^{0.726}(\mathrm{hr})^{0.239}\end{gathered}\tag{10.134}$$

Trichloroacetic acid:

$$\begin{gathered}\mathrm{Cl_3CCOOH} = 87.182(\mathrm{TOC})^{0.355}(\mathrm{pH})^{-1.732}(\mathrm{Cl_2\ Dose})^{0.881}\times\ldots\\ \ldots\times\left(\mathrm{Br}^- + 0.01\right)^{-0.679}\left(\mathrm{k}_{\mathrm{ext},254}\right)^{0.901}(\mathrm{hr})^{0.264}\end{gathered}\tag{10.135}$$

Monobromoacetic acid:

$$\begin{gathered}\mathrm{BrCH_2COOH} = 0.176(\mathrm{TOC})^{1.664}(\mathrm{pH})^{-0.927}(^\circ\mathrm{C})^{0.450}\left(\mathrm{Br}^-\right)^{0.795}\times\ldots\\ \ldots\times\left(\mathrm{k}_{\mathrm{ext},254}\right)^{-0.624}(\mathrm{hr})^{0.145}\end{gathered}\tag{10.136}$$

Dibromoacetic acid:

$$\begin{gathered}\mathrm{Br_2CHCOOH} = 84.945(\mathrm{TOC})^{-0.620}(^\circ\mathrm{C})^{0.657}(\mathrm{Cl_2\ Dose})^{-0.200}\times\ldots\\ \ldots\times\left(\mathrm{Br}^-\right)^{1.073}\left(\mathrm{k}_{\mathrm{ext},254}\right)^{0.651}(\mathrm{hr})^{0.120}\end{gathered}\tag{10.137}$$

where Br^- = the bromide concentration in mg/L
°C = the reaction temperature in °C
$\mathrm{Cl_2}$ Dose = the chlorine dose in mg/L
DBP = the disinfection by-product in μg/L
hr = the contacting time in hours
$\mathrm{k}_{\mathrm{ext},254}$ = the extinction coefficient for ultraviolet light at 254 nm in cm^{-1}
pH = the contacting pH
TOC = the total organic carbon concentration in mg/L

Inorganic By-products

Bromate and hypobromate are formed from the reaction of ozone or hydroxyl radicals with bromide naturally occurring in source water (von Gunten and Hoigne, 1994). To date, this by-product is the only ozonation by-product to be regulated (Richardson et al., 1998). The level of bromate produced increases with increasing bromide concentration in the source water. However, lowering the pH or ozone exposure time reduces bromate formation (von Gunten and Hoigne, 1994).

Both chlorite and chlorate have been identified as DPBs from chlorine dioxide. Chlorite is the predominant product of $\mathrm{ClO_2}$ disinfection [see Eq. (10.86)]. However, it can be minimized by the addition of a reducing agent such as ferric chloride to reduce $\mathrm{ClO_2^-}$ to $\mathrm{Cl^-}$ as shown in Eq. (10.87). Granular activated carbon filtration has also been shown to be effective in the removal of chlorite. Health risks associated with chlorate are unclear; thus, it is not regulated, but formation may be minimized by optimizing ClO_2 generation (Richardson et al., 1998).

Other inorganic by-products of concern but not regulated include iodate, hydrogen peroxide, and ammonia. Iodate is formed from the oxidation of iodide in source water. Hydrogen peroxide may result from its direct addition as used with certain AOPs or from its formation *in situ* from the decomposition of ozone. Ammonia would be expected in conjunction with chloramine use.

Organic Oxidation By-products

Although not regulated, organic oxidation by-products are of growing concern. These by-products are formed from reactions between natural organic matter and any of the oxidizing agents (EPA, 1999). This would include compounds such as aldehydes, ketones, and organic acids.

References

American Water Works Association. 1999. *Water Quality and Treatment: A Handbook of Community Water Supplies*, 5th edition, McGraw-Hill, New York.

Chick, H. 1908. "An Investigation of the Laws of Disinfection," *Journal of Hygiene*, 8: 92.

Craun, G.F. 1988. "Surfacewater Supplies and Health," *Journal of the American Water Works Association*, 80(2): 40.

Craun, G.F. and McCabe, L.J. 1973. "Review of the Causes of Water-borne Disease Outbreaks," *Journal of the American Water Works Association,* 65(1): 74.

Criteria Branch, ed. 1976. *Quality Criteria for Water*. U.S. Environmental Protection Agency, Office of Water Planning and Standards, Division of Criteria and Standards, Washington, DC.

Environmental Protection Agency. 1989a. "Drinking Water; National Primary Drinking Water Regulations; Filtration, Disinfection, Turbidity, *Giardia lamblia*, Viruses, *Legionella*, and Heterotrophic Bacteria. Final Rule," *Federal Register*, 54(124): 27485.

Environmental Protection Agency. 1989b. "Total Coliforms. Final Rule," *Federal Register*, 54(124): 27544.

Environmental Protection Agency. 1993. "Standards for the Use or Disposal of Sewage Sludge," *Federal Register*, 58(32): 9248.

Environmental Protection Agency. 1999. "Alternative Disinfectants and Oxidants Guidance Manual," *EPA 815-R-99–014.* (*http://www.epa.gov/safewater/mdbp/mdbptg.html#disinfect*).

Environmental Protection Agency. 2001b. "The Stage 1 Disinfection and Disinfection Byproducts Rule: What Does it Mean to You?" *EPA 816-R-01–014.* (*http://www.epa.gov/safewater/mdbp/stage1dbprwhatdoesitmeantoyou.pdf*).

Fair, G.M. and Geyer, J.C. 1954. *Water Supply and Wastewater Disposal*. John Wiley & Sons, Inc., New York.

Haas, C.N. 1990. "Disinfection," p. 877 in *Water Quality and Treatment: A Handbook of Community Water Supplies*, 4th ed., F.W. Pontius, ed. McGraw-Hill, Inc., New York.

Hazen and Sawyer. 1992. *Disinfection Alternatives for Safe Drinking Water*. Van Nostrand Reinhold, New York.

Herwaldt, B.L., Craun, G.F., Stokes, S.L., and Juranek, D.D. 1992. "Outbreaks of Waterborne Disease in the United States: 1989–1990," *Journal of the American Waterworks Association*, 84(4): 129.

Joint Task Force American Society of Civil Engineers and American Water Works Association. 1990. *Water Treatment Plant Design*, 2nd ed. McGraw-Hill, Inc., New York.

Joint Task Force of the Water Environment Federation and the American Society of Civil Engineers. 1992. *Design of Municipal Wastewater Treatment Plants: Volume II — Chapters 13–20*. Water Environment Federation, Alexandria, VA; American Society of Civil Engineers, New York.

Lawler, D.F. and Singer, P.C. 1993. "Analyzing Disinfection Kinetics and Reactor Design: A Conceptual Approach Versus the SWTR," *Journal of the American Water Works Association*, 85(11): 67.

Morris, J.C. 1975. "Aspects of the Quantitative Assessment of Germicidal Efficiency," p. 1 in *Disinfection: Water and Wastewater*, J.D. Johnson, ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Palin, A.T. 1977. "Water Disinfection: Chemical Aspects and Analytical Control," p. 67 in *Disinfection: Water and Wastewater*, J.D. Johnson, ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Parrota, M.J. and Bekdash, F. 1998. "UV Disinfection of Small Groundwater Supplies," *Journal of the American Water Works Association,* 90(2): 71–81.

Pontius, F.W. 1990. "New Regulations for Total Coliforms," *Journal of the American Water Works Association*, 82(8): 16.

Pontius, F.W. 1993. "Protecting the Public Against Cryptosporidium," *Journal of the American Water Works Association*, 85(8): 18.

Rav-Acha, C. 1984. "The Reactions of Chlorine Dioxide with Aquatic Organic Materials and Their Health Effects," *Water Research*, 18(11): 1329.

Richardson, S.D. 1998. "Drinking Water Disinfection By-products," p. 1398 in *Encyclopedia of Environmental Analysis and Remediation,* R.A. Meyers, ed., John Wiley & Sons, New York.

Rose, J.B. 1988. "Occurrence and Significance of *Cryptosporidium* in Water," *Journal of the American Water Works Association*, 80(2): 53.

Rowan, J. and Behm, D. 1993. "Fatal Neglect," *The Milwaukee Journal*, September 19–26.

Saunier, B.M. and Selleck, R.E. 1979. "The Kinetics of Breakpoint Chlorination in Continuous Flow Systems," *Journal of the American Water Works Association*, 71(3): 164.

Sidgwick, N.V. 1950. *The Chemical Elements and Their Compounds, Volume I.* Oxford University Press, London.

Sobsey, M. and Olson, B. 1983. "Microbial Agents of Waterborne Disease," in *Assessment of Microbiology and Turbidity Standards for Drinking Water: Proceedings of a Workshop, December 2–4, 1981*, EPA 570–9–83–001, P.S. Berger and Y. Argaman, eds., U.S. Environmental Protection Agency, Office of Drinking Water, Washington, DC.

Stover, E.L., Haas, C.N., Rakness, K.L., and Scheible, O.K. 1986. *Design Manual: Municipal Wastewater Disinfection*, EPA/625/1–86–021. U.S. Environmental Protection Agency, Office of Research and Development, Water Engineering Research Laboratory, Center for Environmental Research Information, Cincinnati, OH.

Symons, J.M., Stevens, A.A., Clark, R.M., Geldreich, E.E., Love, O.T., Jr., and DeMarco, J. 1981. *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*, EPA-600/2–81–156. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory, Drinking Water Research Division, Cincinnati, OH.

Teefy, S.M. and Singer, P.C. 1990. "Performance and Analysis of Tracer Tests to Determine Compliance of a Disinfection Scheme with the SWTR," *Journal of the American Water Works Association*, 82(12): 88.

von Gunten, U. and Hoigne, J. 1994. "Bromate Formation During Ozonation of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions," *Environmental Science and Technology,* 28: 1234.

Watson, H.E. 1908. "A Note on the Variation of the Rate of Disinfection with Change in the Concentration of the Disinfectant," *Journal of Hygiene*, 8: 536.

Watson, M. 1993. *Final Report: Mathematical Modeling of the Formation of THMs and HAAs in Chlorinated Natural Waters.* American Water Works Association, Denver, CO.

Wei, I.W. and Morris, J.C. 1974. "Dynamics of Breakpoint Chlorination," p. 297 in *Chemistry of Water Supply, Treatment, and Distribution,* A.J. Rubin, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Wei, J. and Chang, S.L. 1975. "A Multi-Poisson Distribution Model for Treating Disinfection Data," p. 11 in *Disinfection: Water and Wastewater*, J.D. Johnson, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Wen, C.Y. and Fan, L.T. 1975. *Models for Flow Systems and Chemical Reactors*. Marcel Dekker, Inc., New York.