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Chapter 1

Basic Microbiology and Chemistry

Microbiology in Water Treatment

Why might a utility choose to employ the multiple-barrier approach to water treatment? Why not just concentrate on maximizing one approach?

Microorganisms vary greatly in their sizes, shapes, surface charges, surface textures, motilities, and chemical sensitivities. One treatment method is seldom sufficient for surface-water utilities. It is common for one or two species, out of the hundreds that might be present, to evade initial sedimentation or coagulation steps. These few (especially algae and cyanobacteria) can continue to the filtration process where they might cause filtration plugging, or they might also evade filtration and enter the clearwell. Efforts are made to eliminate them by chlorination before they enter the distribution system.

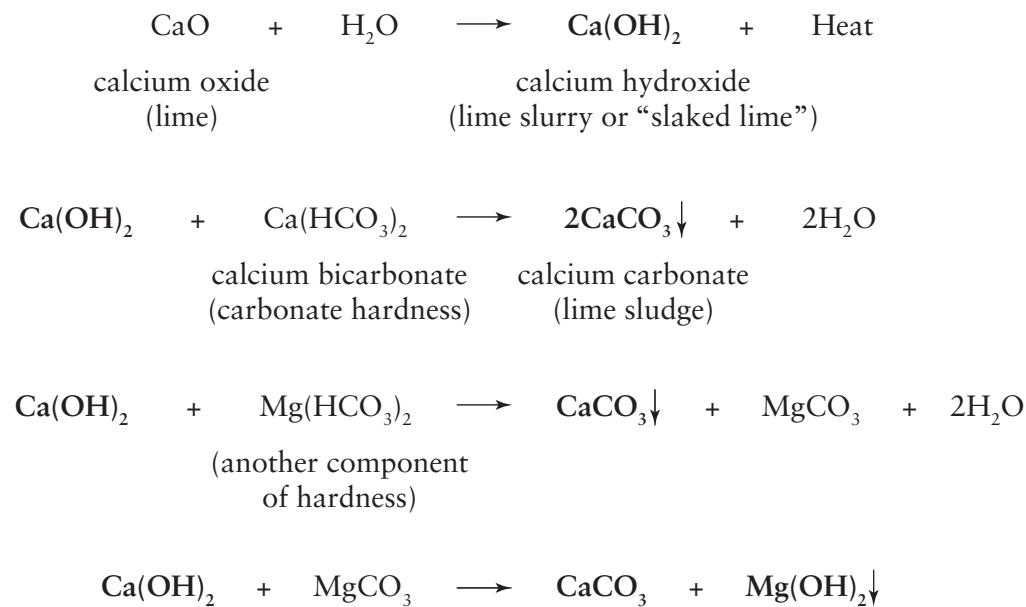
If inadequate treatment barriers precede clearwell chlorination, the removal of *Cryptosporidium* oocysts will be ineffective, since these hardy oocysts are resistant to chlorine, as are other less dangerous microbes.

Surface-water utilities often experience dramatic changes in their source-water rain or snowmelt. The resulting variety in water quality usually necessitates multiple barriers of treatment. Utilities that use groundwater seldom experience these changes and therefore have fewer steps of treatment. If only filtration and chlorination, or only chlorination, are employed, breaches of well casings or the contamination of protected lakes can allow microorganisms to readily pass into the distribution system. In fact, since surface-water utilities have become more vigilant with their treatment for *Cryptosporidium* and other pathogens, groundwater utilities have experienced a greater number of *Cryptosporidium* incidents.

Removing or inactivating microorganisms is an important goal of almost any water treatment process. The addition of lime ($\text{Ca}(\text{OH})_2$) removes suspended solids and dissolved chemicals that cause hardness. This process of softening the water also helps kill or inactivate pathogenic microorganisms. Chlorine or other disinfectants are added to filtered water specifically to prevent the spread of pathogens. Some organisms, notably the parasites *Giardia lamblia* and *Cryptosporidium parvum*, are resistant to disinfection, but effective coagulation and filtration can help to remove them, as can membrane filtration.

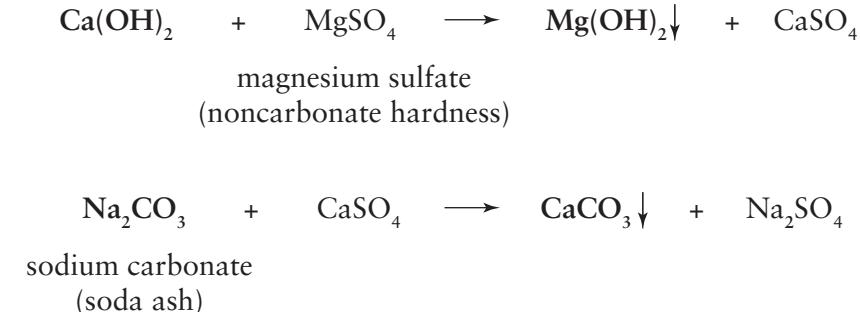
Softening

Water treatment often involves application of chemical principles to remove **calcium bicarbonate**, the cause of carbonate hardness. This is accomplished by adding slaked lime to the water:



Note that the downward-pointing arrows (\downarrow) indicate that the compounds are insoluble and precipitate out of the water.

Addition of slaked lime also aids in the removal of noncarbonated hardness:



These chemical reactions raise the water's pH to between 10 and 11.3. The vast majority of viruses, bacteria, protozoa, and multicellular organisms cannot survive above pH 10.5, so water softening is a powerful disinfectant. Carbon dioxide (CO_2) is added after softening to reduce the water's pH.



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TLS: Lime Softening and Operator Chemistry Made Easy II—Lime Softening (www.awwa.org/wsovideoclips)

calcium bicarbonate

A compound that is controlled through water treatment to prevent the formation of calcium carbonate (hardness).

Disinfection

Water treatment utilities use one of a variety of disinfectants to ensure pathogenic microorganisms are killed in their finished water. Removal of microorganisms actually begins with coagulation and flocculation. As these processes create flocs of suspended solids, some microorganisms are trapped with those particles and removed when the solids settle out during clarification.

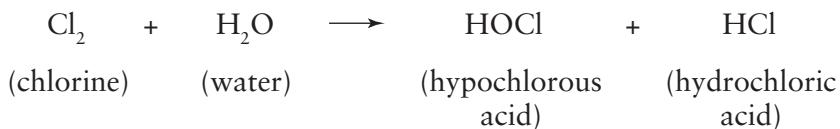
More microorganisms are removed when clarified water passes through granular filters. In rapid sand filters, the first few inches of the granular media trap remaining flocs, algae, and other materials, which in turn capture some microorganisms. The schmutzdecke performs the same function in a slow sand filter.

This physical removal process is very efficient in purifying the water, especially if treatment includes softening. In fact, it may be the most effective way within a conventional treatment plant to remove some pathogens otherwise resistant to disinfection chemicals.

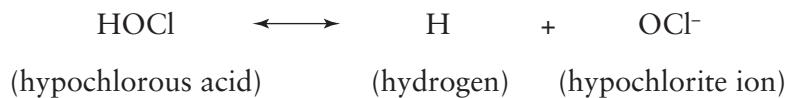
Following filtration, the final stage of treatment usually includes disinfection using chlorine, chlorine dioxide, chloramines, or ozone. Some water treatment plants employ new disinfection processes using ultraviolet light or membrane filtration. Choices among disinfectant practices depend on several factors, such as cost, safety, convenience, effectiveness, and the condition of the water being treated.

Chlorine (Cl_2) is the most widely used disinfectant in water treatment. It is relatively cheap, easy to use, and effective at killing most microorganisms present in the water. In addition, some of the chemical remains in the finished water as a free-chlorine residual that prevents bacterial regrowth in the distribution system.

When chlorine is added to pure water, it reacts as follows:



The chlorine combines with the water to produce hypochlorous acid (HOCl), a weak acid that easily penetrates into and kills bacteria. This action makes chlorine an effective disinfectant. HOCl is also one of two chlorine compounds that act as free available chlorine residual. However, some of the HOCl dissociates as follows:

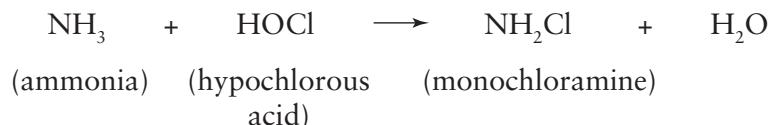


The hydrogen produced in this reaction neutralizes alkalinity and lowers pH, while the hypochlorite ion (OCl^-) is a second type of free available chlorine residual. Its disinfectant action is not as effective as that of HOCl, but it does help to kill microorganisms.

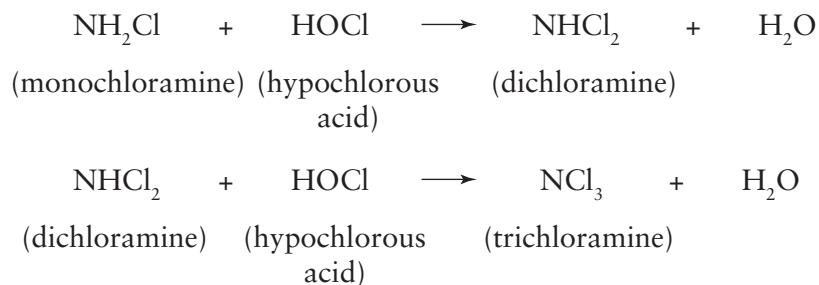
A number of conditions influence the effectiveness of disinfection using chlorine, including pH, water temperature, and contact time. The water's pH, when chlorine is introduced, strongly influences the ratio of HOCl to OCl^- . Low pH values favor formation of HOCl, the more effective free residual, while high pH favors formation of OCl^- . Similarly, low water temperature slightly favors formation of HOCl.

Contact time is important, along with the concentration of chlorine in the water, in determining the effectiveness of these compounds. Either a longer time or a rising concentration increases disinfectant effect.

The chemical reactions that have been described occur when chlorine is added to pure water. Water being treated with disinfectant also contains other substances, however. For example, chlorine reacts with ammonia present in the water to form chloramine compounds:



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The water's pH and the amount of ammonia present determine whether one chloramine compound or more than one are formed.



WATCH THE VIDEO

Operator Chemistry Made Easy II—Disinfection (www.awwa.org/wsovideoclips)

Monochloramine and dichloramine act as disinfectants, although they are not as effective as free available chlorine, such as HOCl. If contact time is sufficient, chloramines can do an acceptable job of disinfection. However, dichloramine and trichloramine compounds may produce taste-and-odor problems.

Disinfection with chlorine requires additional planning for water with high levels of natural organic material. Chlorine reacts with natural organic material to form undesirable disinfection by-products (DBPs). Some of these compounds, especially trihalomethanes (THMs), are regulated as potential carcinogens by the US Environmental Protection Agency (USEPA) under the Disinfectants and Disinfection By-products Rule. To avoid creating these compounds, a utility must minimize residual organic material in the water before disinfection and carefully control chlorine usage. Effective coagulation, flocculation, sedimentation, and filtration remove many organic compounds, so chlorine will not react with the compounds to generate THMs. Chloramine reactions do not produce THMs.

Chlorine dioxide (ClO_2) is another very effective disinfectant, and its reactions produce fewer DBPs than those of chlorine. Chlorine dioxide is also more costly and more hazardous to use, however.

Ozone has become a popular disinfectant, despite its high cost, with utilities that have problems with protozoa. In particular, ozone treatment is one of the few effective methods for inactivating *Cryptosporidium*. After ozonation, however, the water contains no residual disinfectant to protect against regrowth of pathogens in the distribution system. Also, ozone cannot be stored, so it must be generated on-site as needed.

Ultraviolet (UV) disinfection is another technology used by some utilities. Under favorable conditions, it inactivates almost all microorganisms without producing undesirable THMs or other DBPs. Once practical only for small facilities, the technology is now being considered at large water utilities. The primary drawback to this treatment is the potential for the UV light bulbs to become coated with light-obscuring material, which prevents the UV light from reaching and killing the organisms. Careful maintenance is needed to ensure efficient operation. Also, turbidity in the water can shield organisms from the UV light, so this technology is practical only in very clear waters. Finally, UV treatment does not leave any disinfectant residual.

Membrane filtration is an effective technology for physical removal of microorganisms from water. During membrane filtration, water is fed through membranes with pores of a specific size. Membrane-based water treatment processes

ultraviolet (UV) disinfection

Disinfection using an ultraviolet light.

membrane filtration

Water treatment processes in which relatively pure water passes through a porous membrane while particles, molecules, or ions of unwanted matter are excluded.

(listed in order from larger to smaller pore sizes) include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Each removes a progressively finer particle. Ultrafiltration is usually sufficient to remove all microorganisms. No disinfectant residual remains in the water after membrane treatment.

Chemistry of Lime–Soda Ash Softening

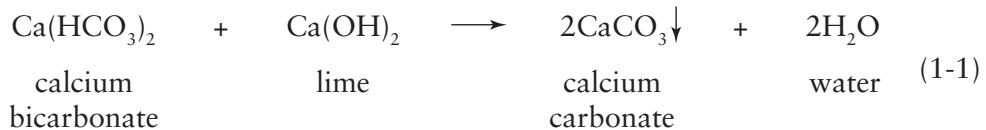
The two ions most commonly associated with **hardness** in water are calcium (Ca^{+2}) and magnesium (Mg^{+2}). Although aluminum, strontium, iron, manganese, and zinc ions can also cause hardness, they are not usually present in large enough concentrations to produce a hardness problem. Chemical precipitation is one of the more common methods used to soften water. The chemicals normally used are lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$) and soda ash (sodium carbonate, Na_2CO_3).

There are two types of hardness: (1) **carbonate hardness**, caused primarily by calcium bicarbonate, and (2) **noncarbonate hardness**, caused by the salts of calcium and magnesium, such as calcium sulfate (CaSO_4), calcium chloride (CaCl_2), magnesium chloride (MgCl_2), and magnesium sulfate (MgSO_4). Lime is used to remove the chemicals that cause carbonate hardness. Soda ash is used to remove the chemicals that cause noncarbonate hardness.

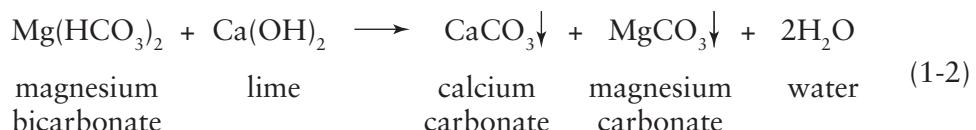
Carbonate Hardness

During treatment for carbonate hardness, lime is the only softening chemical needed, as illustrated in the following reactions:

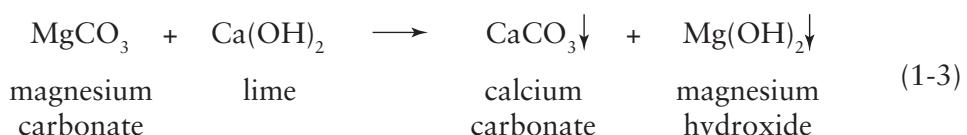
To remove calcium bicarbonate:



To remove magnesium bicarbonate:



then



To remove the magnesium bicarbonate, it takes two separate reactions and twice the lime needed to remove calcium bicarbonate. In Equation 1-1, lime reacts with calcium bicarbonate to form **calcium carbonate**. Calcium carbonate is relatively insoluble and precipitates.

In Equation 1-2, lime reacts with magnesium bicarbonate to form calcium carbonate, which precipitates, and magnesium carbonate, which does not. In addition to being soluble, magnesium carbonate is a form of carbonate hardness. Therefore, the same amount of lime added in Equation 1-2 is called for in Equation 1-3. Thus, twice the lime required to remove calcium bicarbonate is necessary to remove magnesium bicarbonate and carbonate. In Equation 1-3, the additional lime reacts with magnesium carbonate to form calcium carbonate (CaCO_3) and

hardness

A characteristic of water, caused primarily by the salts of calcium and magnesium. Causes deposition of scale in boilers, damage in some industrial processes, and sometimes objectionable taste. May also decrease the effectiveness of soap.

carbonate hardness

Hardness caused primarily by bicarbonate.

noncarbonate hardness

Hardness caused by the salts of calcium and magnesium.

calcium carbonate

The principal hardness- and scale-causing compound in water.

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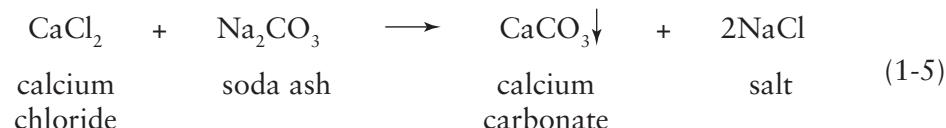
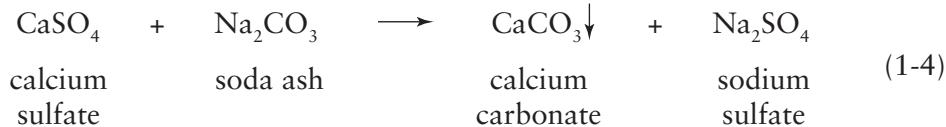
magnesium hydroxide (Mg(OH)_2), both relatively insoluble materials that will settle out.

If the water originally had no noncarbonate hardness, then further softening would not be needed. However, because CaCO_3 and Mg(OH)_2 are very slightly soluble, a small amount of hardness remains, usually at least 35 mg/L.

Noncarbonate Hardness

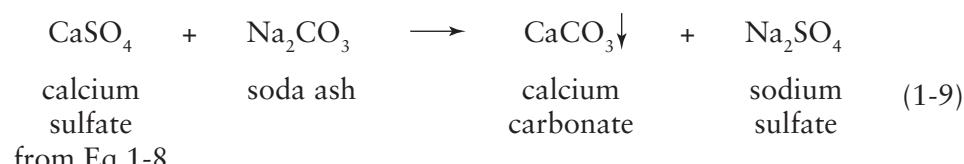
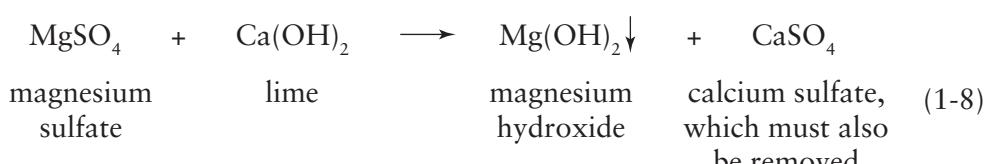
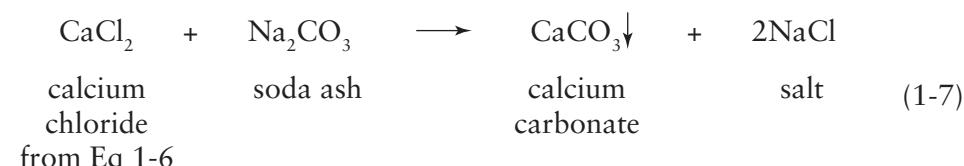
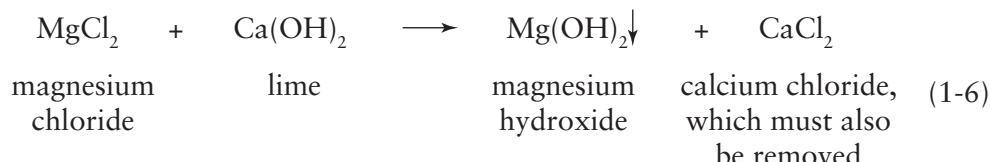
For noncarbonate hardness to be removed, soda ash must be added to remove the noncarbonated calcium compounds, and soda ash together with lime must be added to remove the noncarbonate magnesium compounds.

To remove calcium noncarbonate hardness:



In both cases, the calcium noncarbonate hardness is removed by soda ash. The calcium sulfate and the calcium chloride acquire CO_3 from soda ash and precipitate as CaCO_3 . The compounds that remain after softening, Na_2SO_4 in Equation 1-4 and NaCl in Equation 1-5, are salts and do not cause hardness.

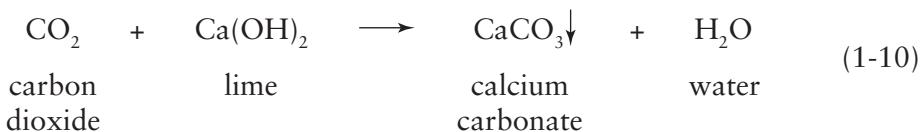
To remove magnesium noncarbonate hardness:



The removal of magnesium noncarbonate hardness with lime forms calcium non-carbonated hardness, which must then be removed with soda ash.

The final reaction related to softening involves carbon dioxide (CO_2), a gas that is found in dissolved form in most natural waters. Unless CO_2 is removed

prior to softening (for example, by aeration), it will consume some of the lime added.

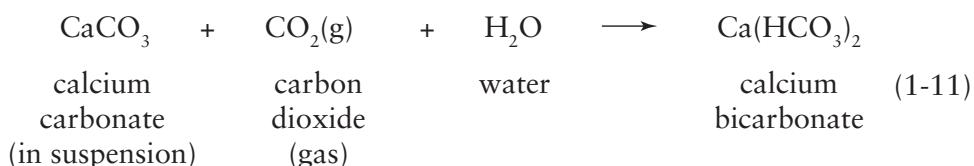


If CO_2 is present, then enough lime must be added at the beginning of softening to allow this reaction to take place and still leave enough lime to complete the softening reactions. Whenever CO_2 is present, the CO_2 reaction occurs before the softening reactions take place.

Chemical softening takes place at a high pH. To precipitate calcium carbonate, a pH of about 9.4 is necessary; the precipitation of magnesium hydroxide requires a pH of 10.6. In both cases, the necessary pH is achieved by adding the proper amount of lime.

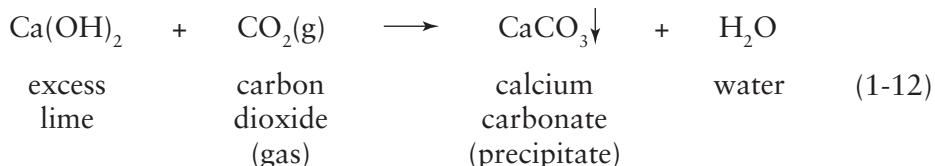
Recarbonation

Recarbonation is the reintroduction of carbon dioxide into the water either during or after lime-soda ash softening. When hard water is treated by conventional lime softening, the water becomes supersaturated with calcium carbonate and may have a pH of 10.4 or higher. This very fine, suspended calcium carbonate can deposit on filter media, cementing together the individual media grains (encrustation) and depositing a scale in the transmission and distribution system piping (postprecipitation). To prevent these problems, carbon dioxide is bubbled into the water, lowering the pH and removing calcium carbonate as follows:



This type of recarbonation is usually performed after the coagulated and flocculated waters are settled but before they are filtered, thereby preventing the suspended CaCO_3 from being carried out of the sedimentation basin and cementing the filter media.

When the excess-lime technique is used to remove magnesium, a considerable amount of lime remains in the water. The result is a water that is undesirably caustic and high in pH. Carbon dioxide introduced into the water reacts as follows:

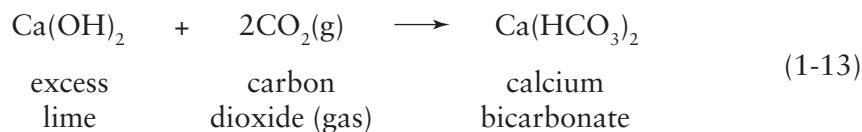


This form of recarbonation is performed after coagulation and flocculation but before final settling. Carbon dioxide reacts with the excess lime, removing the cause of the caustic, high-pH condition and, incidentally, removing the calcium that added to the hardness. The product, calcium carbonate, is removed by the filtration process.

recarbonation

The reintroduction of carbon dioxide into the water, either during or after lime-soda ash softening.

It is important to select the correct carbon dioxide dosage. If too much CO_2 is added, the following can happen:

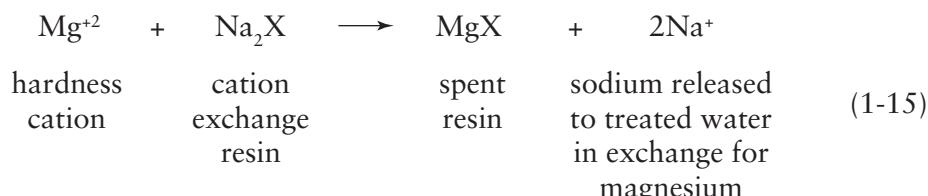
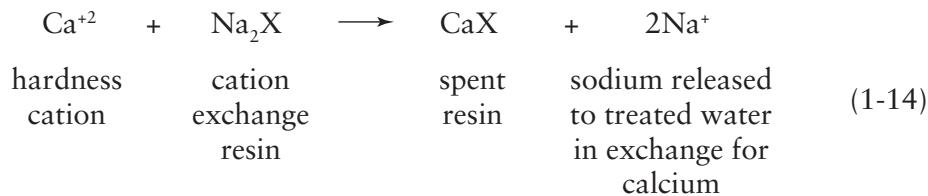


Notice that the excess lime combines with the excessive CO_2 to form carbonate hardness. In the excess-lime method, there is too much calcium hydroxide present, and the reaction in Equation 1-13 would significantly increase water hardness. In the methods using lower lime doses, the conversion to calcium bicarbonate may not significantly increase water hardness.

Chemistry of Ion Exchange Softening

The **ion exchange process** of water softening uses the properties of certain materials (termed *cation exchange materials*) to exchange the hardness-causing cations of calcium and magnesium for nonhardness-causing cations of sodium. The most common cation exchange materials are synthetic polystyrene resins. Each resin particle is a BB-sized, transparent, amber-colored sphere. Each of these insoluble resin spheres contains sodium ions that are released into the water in exchange for hardness ions of calcium and magnesium. When properly operated, ion exchange is completely effective in removing all hardness, whether carbonate or noncarbonate.

The two reactions involved in the cation exchange softening process are as follows:



The letter X is used to represent the exchange resin. Before softening, the resin with the nonhardness cations of sodium appears in the equations as Na_2X . Although this is not a chemical compound, it does behave somewhat like one. The sodium cations ("Na₂" in the resin, "2Na⁺" after release) are released into the water just as the sodium in Na_2SO_4 would be released when that compound is dissolved in water. Although the resin "X" acts similarly to an anion such as the sulfate ion (SO_4^{2-}), the resin is actually an insoluble organic material that does not react chemically as SO_4^{2-} would. Instead, it functions more like a "parking lot" for exchangeable cations. The terms CaX and MgX represent the same resin after the exchange has been made.

As shown in the equations, calcium and magnesium hardness ions are removed from the water onto the surface of the resin. In exchange, the resin releases sodium ions. Note that one hardness ion (Mg^{+2} or Ca^{+2}) with a charge of +2 is exchanged for two sodium ions, each having a charge of +1, a total charge of +2. Hence, a +2 charge is exchanged for a +2 charge, an electrically equivalent exchange.

ion exchange process

A process used to remove hardness from water that depends on special materials known as resins. The resins trade nonhardness-causing ions (usually sodium) for the hardness-causing ions, calcium and magnesium. The process removes practically all the hardness from water.

Equations 1-14 and 1-15 can be expanded to show the reactions of the specific hardness-causing compounds (similar to the equations shown for lime–soda ash softening):



In each reaction, the anion originally associated with the hardness cation stays in the softened water; after softening, these anions are associated with the sodium cations released by the resin. Hence, the softened water contains sodium bicarbonate (NaCHO_3), sodium sulfate (Na_2SO_4), and sodium chloride (NaCl). These compounds do not cause hardness and are present in such small concentrations that they do not cause tastes. Unlike lime–soda ash softening, ion exchange softening operates the same for both carbonate and noncarbonate hardness. Both types are removed by the same exchange reactions.

After most of the sodium ions are removed from the exchange resin in the softening process, the resin must be **regenerated** in order to restore its softening capacity. That is, the exchange process must be reversed, with the hardness cations of calcium and magnesium being forced out of the resin and replaced by cations of sodium. This reverse exchange is achieved by passing a strong brine solution (a concentrated solution of common table salt) through the resin bed. The two ion exchange regeneration reactions are shown below:



When sodium is taken back into the exchange resin, the resin is again ready to be used for softening. The calcium and magnesium, released during regeneration, are carried to disposal by the spent brine solution.

Properly maintained and operated, cation exchange removes *all* hardness. Water of zero hardness is corrosive, so the final step in ion exchange softening is to mix a portion of the unsoftened water with the softened effluent to provide water that is still relatively soft, but that contains enough hardness to be noncorrosive (stable).

regeneration

The process of reversing the ion exchange softening reaction of ion exchange materials. Hardness ions are removed from the used materials and replaced with nontroublesome ions, thus restoring the exchange capacity of the resin for further softening.

Scaling and Corrosion Control

Scaling and corrosion are closely related problems in water treatment. They may be thought of as being at opposite ends of a hypothetical stability scale, as shown in Figure 1-1.

The objective of scale and corrosion control is to stabilize the water, thus preventing both scale formation and corrosion. The stable range is relatively narrow,

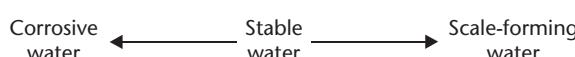


Figure 1-1 Hypothetical stability scale

requiring careful monitoring during treatment in order to avoid under- or overshooting the stable range.

Scaling and Corrosion

Scale is the familiar chalky-white deposit frequently found at the bottom of a tea kettle. It is caused by carbonate and noncarbonate hardness constituents in water.

The exact combination of pH and alkalinity that will result in scale (or corrosion) depends on the overall chemical characteristics of the water. Under conditions of pH 7.0–9.5, with corresponding alkalinites of 300–1,500 mg/L, calcium carbonate (CaCO_3) will precipitate and form a scale on interior surfaces of pipes and tanks. One of two chemical reactions will occur:



or



In controlled amounts, this scale is beneficial, forming a protective coating inside pipelines and tanks. However, excessive scaling can reduce the capacity of pipelines and the efficiency of heat transfer in boilers.

Corrosion is the oxidation of unprotected metal surfaces. In water treatment, a primary concern is the corrosion of iron and its alloys. Corrosion of iron and steel products is easily identified by the familiar red rust that forms. Iron is an important element in many metallic pipe materials and process equipment. It exists naturally as iron ore, in stable forms such as hematite (Fe_2O_3), magnetite (Fe_3O_4), iron pyrite (FeS_2), and siderite (FeCO_3). Smelting converts this ore to elemental iron, which is then used in the manufacture of pipeline materials and treatment equipment. Elemental iron is unstable and has a strong tendency to return by the oxidation or corrosion process to the more stable ore forms noted above. Advanced cases of iron corrosion create the problem of “red water.”

There are various theories on how iron corrosion occurs and several factors known to affect corrosion. The following simplified discussion of corrosion chemistry highlights the influence of pH, alkalinity, dissolved oxygen, and carbon dioxide in the corrosion process. Remember that corrosion is a complex process that can be influenced by other factors as well. For example, iron bacteria (*Crenothrix* and *Leptothrix*) and sulfate-reducing bacteria can be major causes of corrosion. Increases in water temperature and velocity of flow can accelerate corrosion. The softening process can convert a noncorrosive water to a corrosive one. However, certain constituents in water, such as silica, are believed to protect exposed metal surfaces from corrosion.

When iron corrodes, it is converted from elemental iron (Fe) to ferrous ion (Fe^{+2}):



The electrons that come from the elemental iron build up on metal surfaces and inhibit corrosion. If the water has a very low pH (lower than that of potable water), then hydrogen ions (H^+) in solution will react with electrons to form hydrogen gas ($\text{H}_2 \uparrow$):



The hydrogen gas coats the metal surface and could reduce corrosion; however, the coating is removed, partly by the scrubbing action of moving water and partly by combination with oxygen (O_2) normally dissolved in the water:



The metal surface is exposed again and corrosion continues. Failure to protect the metal surface or remove corrosion-causing elements will result in destruction of pipes or equipment.

Once the reaction in Equation 1-26 has occurred, subsequent reactions depend on the chemical characteristics of the water. If water is low in pH, is low in alkalinity, and contains dissolved oxygen, then the ferrous ion reacts with water to form ferrous hydroxide, Fe(OH)_2 :



The insoluble ferrous hydroxide immediately reacts with CO_2 present in low-alkalinity water to form soluble ferrous bicarbonate, $\text{Fe(HCO}_3)_2$:



Since ferrous bicarbonate is soluble, it detaches from the metal surface and is mixed throughout the water. The dissolved oxygen in the water then reacts with the ferrous bicarbonate to form insoluble ferric hydroxide, Fe(OH)_3 :



Because this reaction occurs throughout water, ferric hydroxide does not form a protective coating on the metal surface. The ferric hydroxide appears as suspended particles that cause red water.

If water begins with a higher pH and alkalinity (where CO_2 is not present), then the corrosion reaction can be controlled. The ferrous ion shown in Equation 1-26 combines with the hydroxyl alkalinity that is present naturally or induced by lime treatment, forming an insoluble film of ferrous hydroxide on the metal surface:



If dissolved oxygen is present in the water, it will react with the ferrous hydroxide to form an insoluble ferric hydroxide coating:



Both ferrous and ferric hydroxide are somewhat porous, and although their coatings retard corrosion, they cannot fully protect the pipe. However, the same high-pH and high-alkalinity conditions that cause the rust coating to form also favor the formation of a calcium carbonate coating. Together these coatings protect the pipe from further corrosion.

Chemical Methods for Scale and Corrosion Control

Table 1-1 shows common methods used to control scale and corrosion. The following paragraphs contain brief discussions of each method. Lime, soda ash, and caustic soda are typically used to raise pH and alkalinity. Carbon dioxide and

Table 1-1 Scale and corrosion control methods

Method	For Control of:	
	Scale	Corrosion
pH and alkalinity adjustment with lime	X	X
Chelation	X	
Sequestering	X	
Controlled calcium carbonate scaling		X
Other protective chemical coatings		X
Softening	X	

sulfuric acid are used to lower pH and alkalinity. However, in situations where stabilization is achieved by pH and alkalinity adjustment, the effects of all chemicals used in water treatment must be taken into account. Alum and ferric sulfate (discussed previously) lower pH and alkalinity, as do chlorine (discussed later) and fluorosilicic acid (used in fluoridation).

pH and Alkalinity Adjustment With Lime

For each milligram per liter of lime added, approximately 0.56 mg/L of carbon dioxide is removed. Carbon dioxide is in the form of carbonic acid (H_2CO_3) when dissolved in water. The following equation indicates the chemical reaction that takes place:



As carbon dioxide (carbonic acid) is removed, pH increases.

For each milligram per liter of lime added, the alkalinity of the treated water will increase by about 1.28 mg/L. The reaction is



If the lime dosage is too high, excessive scale will form. If it is too low, the water will be corrosive. The **Langelier saturation index** is one measure used to determine the tendency of water to scale or corrode piping and tanks. The index is based on the assumption that every water has a particular pH value for which the water will neither deposit scale nor cause corrosion. This stable condition is termed **saturation**. The pH value, called saturation pH and abbreviated pH_s , varies, depending on calcium hardness, alkalinity, and temperature. Once the pH_s is calculated, the Langelier saturation index is found as follows:

$$\text{Langelier saturation index} = \text{pH} - \text{pH}_s$$

If the actual pH of the water is less than the calculated pH_s , then the water has a negative Langelier index and may be corrosive. If the actual pH is greater than the calculated pH_s , then the Langelier index is positive and the water is likely to form scale. In either case, the water is unstable. The greater the difference between pH and pH_s , the stronger the tendency for the water to either form scale or cause corrosion. Thus, water with a Langelier index of +0.4 has a stronger scaling tendency than water with an index of +0.1. Similarly, water with a Langelier index of -0.4 has a stronger corrosion tendency than water with an index of -0.2. If the pH and pH_s are equal, then the Langelier saturation index is zero and water is stable. Neither scale formation nor corrosion should occur.

The value of pH_s can be calculated mathematically, but it is simpler to use a graph, as illustrated in Figure 1-2. To find pH_s , the calcium hardness in milligrams per liter as CaCO_3 , alkalinity in milligrams per liter as CaCO_3 , pH, and water temperature must be determined. For example, the following information may be used to demonstrate reading the graph:

$$\text{calcium hardness} = 240 \text{ mg/L as CaCO}_3$$

$$\text{alkalinity} = 200 \text{ mg/L as CaCO}_3$$

$$\text{pH} = 6.8$$

$$\text{water temperature} = 70^\circ\text{F}$$

Enter the graph at a calcium hardness of 240 mg/L, as shown by the dotted line in Figure 1-2. Proceed upward to the 200-mg/L alkalinity curve. Travel across to locate the temperature of 70°F (estimate the temperature location between the

Langelier saturation index

A measure of the tendency of water to scale or corrode pipes, based on pH, conductivity, hardness, alkalinity, and water temperature.

saturation

A stable condition of water in which the water will neither deposit scale nor cause corrosion.

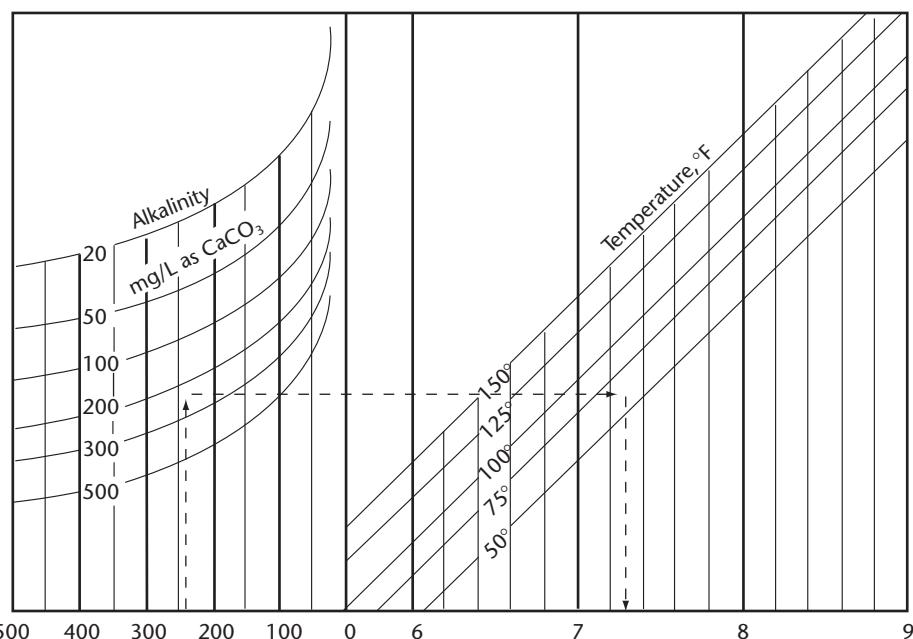


Figure 1-2 Determination of pHs for the Langelier saturation index, given hardness, alkalinity, and temperature (assuming average total dissolved solids of about 500 mg/L)

Courtesy of Ondeo Nalco, Ondeo Nalco Center, Naperville, Illinois, from *Water: The Universal Solvent*.

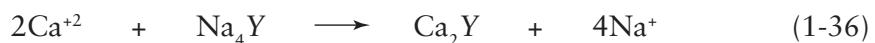
50°F and 75°F lines). Move downward from the temperature point to the bottom of the graph and identify the pH_s value as 7.3. Finally, calculate the Langelier saturation index as follows:

$$\begin{aligned}
 \text{Langelier saturation index} &= \text{pH} - \text{pH}_s \\
 &= 6.8 - 7.3 \\
 &= -0.5
 \end{aligned}$$

Since the index is negative, the water is corrosive.

Chelation

Chelation is a chemical treatment process used to control scale formation. The chemical added is known as a chelating agent. It is a water-soluble compound that captures scale-causing ions in solution, preventing precipitation and scale formation. There are several natural organic materials in water that have chelating ability, including humic acid and lignin. When added to water, the chelating agent reacts with calcium ions to keep them in solution and prevent the formation of calcium carbonate scale. In the following equation, the Y represents the chelating agent:



Sequestration

Sequestration is a chemical addition treatment process that controls scale. The chemical added to the water *sequesters*, or holds in solution, scale-causing ions such as calcium, iron, and manganese, thus preventing them from precipitating and forming scale. Any one of several polyphosphates may be used in this process. The most commonly used is sodium hexametaphosphate, $(\text{NaPO}_3)_6$. A common dosage for scale prevention is approximately 0.5 mg/L. Note that sequestration is often related to the deliberate process of adding chemicals to drinking water. Chelation, on the other hand, is often considered a natural process.

chelation

A chemical process used to control scale formation, in which a chelating agent "captures" scale-causing ions and holds them in solution, thus preventing them from precipitating out and forming scale.

sequestration

A chemical process used to control scale formation, in which a sequestering agent holds scale-causing ions in solution, preventing them from precipitating out and forming scale.

Controlled Calcium Carbonate Scaling

One commonly practiced form of corrosion management is controlled calcium carbonate scaling. As stated at the beginning of this section, there are three conditions water can have relative to scale formation and corrosion. Water may be corrosive, stable, or scale-forming. By careful control of the pH and alkalinity adjustment, the condition of water can be altered so that it is slightly scale-forming. Eventually the scale will build up beyond the desired thickness. Adjusting pH and alkalinity to a point that is slightly corrosive will then dissolve the excess scale.

Controlled scaling requires careful and continuous laboratory monitoring because the slightest change in the quality of water may require a change in the amount of lime needed. It is also necessary to monitor the thickness of the calcium carbonate coating developed in the transmission and distribution system pipeline. The coating should be thick enough to prevent corrosion without obstructing the flow of water.

Other Chemical Protective Coatings

There are two other types of chemicals used to create protective coatings in pipelines: (1) polyphosphates and (2) sodium silicate. Polyphosphates include sodium hexametaphosphate, $(NaPO_3)_6$; sodium pyrophosphate, $Na_4P_2O_7$; and a group known as bimetallic glassy phosphates. After being fed into the water, polyphosphates form a phosphate film on interior metal surfaces, protecting them from corrosion. Polyphosphates are also effective as sequestering agents for preventing calcium carbonate scale and for stabilizing dissolved iron and manganese. Dosages of 5–10 mg/L are recommended when treatment is initiated. After 1–2 months' worth of protective film is established, the dosages are reduced and maintained at approximately 1 mg/L.

Sodium silicate ($Na_2Si_4O_9$), or water-glass, can also be used to control corrosion in water systems. Sodium silicate combines with calcium to form a hard, dense calcium silicate film ($CaSiO_3$). Dosages vary widely depending on water quality.

Softening

A major problem caused by water hardness is scale formation. Hard waters form calcium carbonate scales in pipelines and boilers. These scales reduce pipeline capacities, lower boiler heat transfer efficiencies, and cause heat exchange tube failures because excessive heating is required to overcome the insulating effects of scale. The results are higher pumping and maintenance costs, longer repair times, shortened equipment life, and higher fuel and power costs.

There are four major water characteristics that control hardness. The tendency to form scale is greater when the hardness, alkalinity, pH, or temperature is increased. Figures 1-3, 1-4, and 1-5 demonstrate how these characteristics are

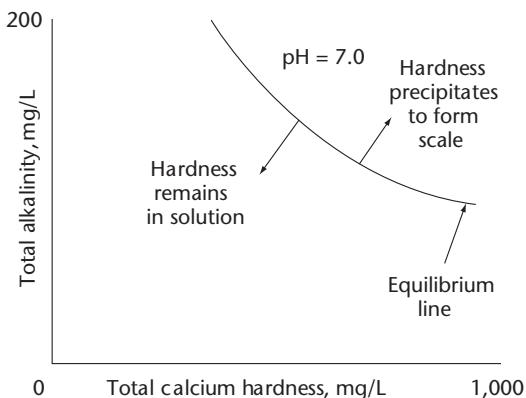


Figure 1-3 Total alkalinity versus total calcium hardness at 77°F (25°C)

Note: Data were computed for one water sample and are not generally applicable.

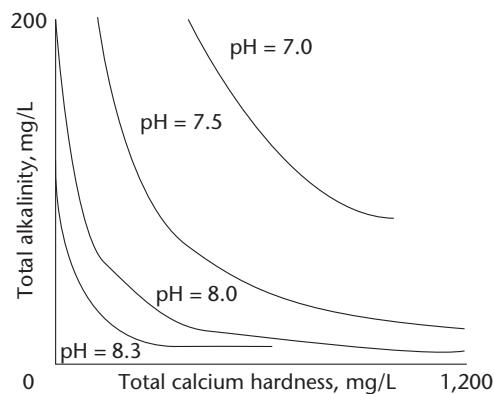


Figure 1-4 Effect of total alkalinity and pH on the amount of total calcium hardness that can be kept in solution

Note: Data were calculated for one water sample and are not generally applicable.

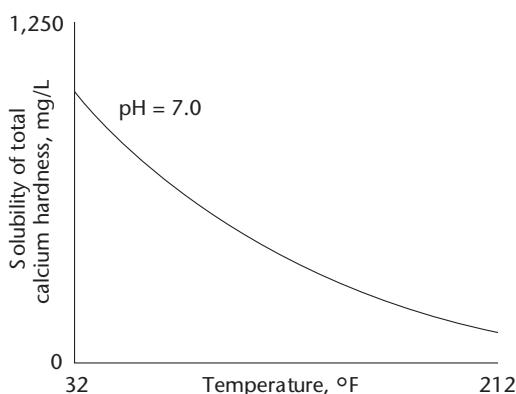


Figure 1-5 Effect of temperature on the amount of calcium that will stay in solution

Note: Data were calculated for one water sample and are not generally applicable.

interrelated. The graphs in the figures were determined for one water sample; they should not be applied in general, but they do illustrate the interaction between the indicated variables.

The 10 chemical reactions involved in water softening were presented earlier in the discussion of lime–soda ash softening. Refer to that material to review hardness removal using lime and soda ash.

Study Questions

1. Which disinfectant would work best against *Cryptosporidium*?
 - Ozone
 - Dichloramine
 - Hypochlorite ion
 - Hypochlorous acid
2. The pH of a water sample is greater than the pH_s so the Langlier index?
 - Indicates that the water is corrosive.
 - Is negative.
 - Indicates the water is scale forming.
 - Indicates the water is stable.
3. When water high in calcium bicarbonate is softened by ion exchange _____.
 - All cations and anions are removed.
 - Regeneration is usually accomplished by an acid.
 - Lime is used at a pH of 9.5
 - Sodium bicarbonate remains in the product water.

4. Lime softening can effectively disinfect water because:
 - a. Particles containing microorganisms are settled out in the process.
 - b. The pH level is higher than 10.5.
 - c. The pH level is below 10.5.
 - d. Microorganisms are sensitive to calcium level.
5. A noncarbonate hardness compound is
 - a. CaCO_3
 - b. MgCO_3
 - c. $\text{Ca}(\text{HCO}_3)_2$
 - d. MgSO_4
6. What term refers to the reintroduction of carbon dioxide into water either during or after lime–soda ash softening?
 - a. Regeneration
 - b. Recarbonation
 - c. Replenishment
 - d. Recycling
7. _____ is the oxidation of unprotected metal surfaces.
 - a. Corrosion
 - b. Saturation
 - c. Softening
 - d. Chelation
8. What is the cause of carbonate hardness?
9. Which two ions are most commonly associated with water hardness?
10. For noncarbonate hardness to be removed, what must be added to remove the noncarbonated calcium compounds?

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