

PHYSICAL-CHEMICAL TREATMENT FOR DISSOLVED CONSTITUENTS

The removal of dissolved constituents in a water, particularly dissolved ions, is often a challenging problem. Chemical precipitation is used with flocculation, sedimentation, and filtration to remove many dissolved components. Adsorption and ion exchange are alternatives that do not require other unit operations.

Another significant physical-chemical treatment is oxidation, which is further discussed in Chapter 16.

15.1 WATER SOFTENING

Water softening is the removal of certain dissolved minerals in water that cause scaling in boilers, form deposits on pipes, and cause excessive consumption of soaps made from natural animal fats. The minerals responsible for these phenomena are referred to as hardness ions. The term hardness arose because of a colloquial reference in earlier times to the difficulty of laundering in waters containing large concentrations of mineral ions. Soaps made from animal fats readily precipitate with hardness ions. Therefore, when water is treated for the removal of hardness ions it is softened and there is a reduction in the consumption of soap as well as the mineral concentration (TDS). Modern synthetic detergents are not affected by the concentration of hardness ions.

Hardness concentration also influences the tendency of a water to protect or corrode distribution pipes. Industries are particularly concerned about the scale formation potential of a water. Hardness ions can also contribute color or influence the taste of products made from the water, which are important considerations for certain industries. Industries often treat water beyond standards for municipal water supplies.

There have been some studies that indicate a link between hardness concentration (particularly calcium and magnesium) and cardiovascular disease (Neri and Johansen, 1978). However, the link is tenuous and many confounding variables existed in studies (Comstock, 1979).

Hardness in water is due to cations such as calcium and magnesium (divalent cations) and to a lesser extent to aluminum, iron, and other divalent and trivalent cations. Calcium and magnesium are the two major cations responsible for hardness in natural waters. Therefore for most waters:

$$\text{TOTAL HARDNESS} = \text{CALCIUM HARDNESS} + \text{MAGNESIUM HARDNESS}$$

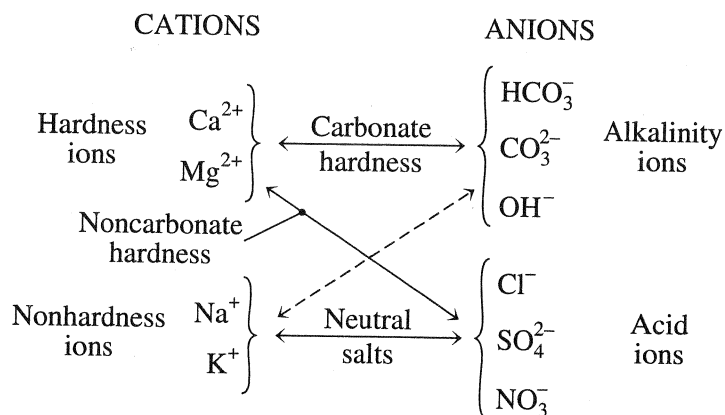


Figure 15.1 Major cations and associated anions in a typical water.

The cations are usually associated with the following anions: HCO_3^- , CO_3^{2-} , and OH^- (these are alkalinity ions), and SO_4^{2-} , NO_3^- , and Cl^- (these are acidity-associated ions). Carbonate hardness is the amount of hardness ions associated with alkalinity ions.

The hydroxyl ion concentration is normally insignificant compared to the hardness ions concentrations. The difference between the equivalents of the hardness ions, calcium and magnesium (and any other significant hardness ions), and the equivalents of bicarbonate and carbonate anions is noncarbonate hardness as indicated on Fig. 15.1. Noncarbonate hardness (also known as permanent hardness) is more costly to remove in precipitation processes as discussed below.

To remove the major ions causing hardness, an examination of solubility products is useful. Table 15.1 provides K_{sp} s and solubilities of various magnesium and calcium salts. It is observed that CaCO_3 and $\text{Mg}(\text{OH})_2$ are relatively insoluble and hardness removal is commonly achieved by formation of these compounds. Furthermore, bicarbonate ion is usually naturally present in significant amounts in water. Because calcium is the most common ion causing hardness and calcium is commonly removed by formation of calcium carbonate with a convenient molecular weight of 100 (equivalent weight of 50), hardness is normally expressed in terms of CaCO_3 .

TABLE 15.1 Solubilities of Possible Compounds Related to Water Hardness

Compound	Solubility, mg/L		K_{sp}
	Cold	Hot (25°C)	
CaCO_3	14	18	5×10^{-9}
CaCl_2		745 000	1 590 000
$\text{Ca}(\text{OH})_2$	1 850	770	8×10^{-6}
CaSO_4	2 090	1 620	2×10^{-5}
MgCO_3	542 500	727 000	—
$\text{Mg}(\text{OH})_2$	9	40	9×10^{-12}
MgSO_4	260 000	738 000	—
$\text{Sr}(\text{OH})_2$	4 100	218 300	—
SrCO_3	11	650	—

TABLE 15.

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TABLE 15.2 Hardness Ranges

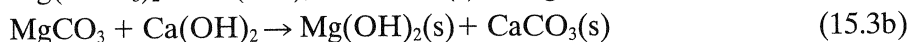
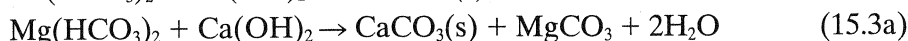
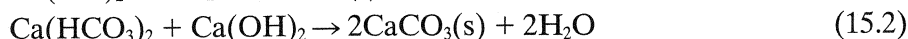
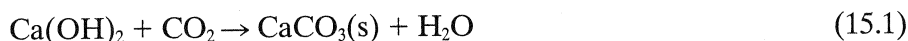
Degree of hardness	Hardness concentration, mg/L as CaCO ₃
Moderately hard	60–120
Hard	120–180
Very hard	180 and over

Water is considered soft when hardness is ≤ 60 mg/L as CaCO₃. Table 15.2 gives qualitative ranges of hardness.

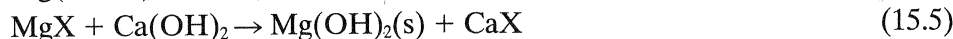
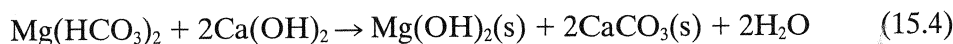
15.2 LIME–SODA SOFTENING

Raising the pH of a water by addition of alkalinity will convert bicarbonates into carbonates and CaCO₃ formation and precipitation will ensue. Also, Mg(OH)₂ will be formed and precipitate. Slaked lime or lime [Ca(OH)₂], which is hydrated calcium oxide (CaO), is usually the least expensive source of alkalinity. Calcium oxide is also known as quicklime. Sodium hydroxide, NaOH (caustic soda), can also be used for alkalinity depending on economics and other factors such as availability and ease of handling. When insufficient bicarbonate concentrations exist, sodium carbonate (Na₂CO₃), known as soda ash, is added to supply both alkalinity and carbonate ions. The stoichiometry of the reactions is straightforward. The reactions involved in the lime–soda process are given below.

Any carbon dioxide present in the raw water consumes lime according to reaction (15.1). As lime is added, the pH rises and HCO₃⁻ is converted to CO₃²⁻ and the reactions in Eqs. (15.2) and (15.3a) occur. As more lime is added, the concentration of OH⁻ ions becomes significant and reactions (15.3b) and (15.5) proceed. Reaction (15.6) applies only when soda ash is added because some of the Ca²⁺ and Mg²⁺ ions are associated with noncarbonate anions. Soda ash is more expensive than lime.



Adding the above two reactions, the net lime requirement for magnesium carbonate hardness is



where

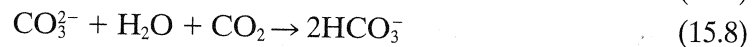
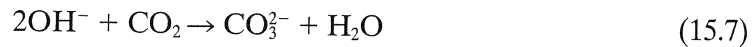
X is a noncarbonate anion such as SO₄²⁻, NO₃⁻, or Cl⁻

Inorganic carbon alkalinity is first associated with Ca²⁺ because of the sequence of reactions that occurs on addition of lime. Bicarbonate is converted to carbonate by the addition of alkalinity and CaCO₃ forms and precipitates. MgCO₃ does not precipitate under normal circumstances but after HCO₃⁻ has been converted to CO₃²⁻, additional OH⁻ does cause the precipitation of Mg(OH)₂. Therefore, when

magnesium removal is desired, an amount of lime sufficient to convert alkalinity to carbonate must be added in addition to the amount of lime required to remove the magnesium.

Although Table 15.1 indicates that calcium concentrations below 20 mg/L as CaCO₃ can be achieved, the practical lower limit of removal is near 30 mg/L as CaCO₃ (0.6 meq/L). When the starting concentrations of Ca²⁺ and CO₃²⁻ are different, precipitation of CaCO₃ occurs until the ion with the lower initial concentration reaches 0.6 meq/L. This assumption is somewhat conservative (see Problem 3). Performance data are required to determine the actual residual calcium hardness. Environmental conditions and residence time in the reactor influence the extent to which equilibrium is achieved. For instance, Cole (1976) found that water treated with lime took 90 min at 1°C to reach the minimum hardness concentration, whereas at room temperature the same water took only 10 min to reach the same concentration.

The practical lower limit for removal of magnesium is 10 mg/L as CaCO₃ (0.2 meq/L). Excess lime at approximately 35 mg/L as CaCO₃ beyond stoichiometric requirements is necessary to raise the pH to levels to ensure Mg(OH)₂ formation. A pH above 10.5 must be achieved in order to precipitate Mg(OH)₂. The actual amount of excess alkalinity required is dependent on the buffering capacity of the water. Carbon dioxide can be added to neutralize the excess lime in the treated water and lower the pH to the desired value as shown by the following equations.



An alternative to remove the Ca²⁺ resulting from excess lime is to add Na₂CO₃. The Na₂CO₃ is added along with the lime to the water entering the basin, where precipitation of CaCO₃ and Mg(OH)₂ will occur. The excess OH⁻ in the effluent from this basin is neutralized by addition of acid to achieve the pH desired for a stable water (Section 15.3). This approach requires only a single basin for hardness removal, in contrast to split recarbonation processes discussed in the next section.

15.2.1 Treatment Methods for Hardness Removal

Softening can be accomplished in conjunction with coagulation, flocculation, and sedimentation of suspended solids as shown in Fig 9.2. There are also a variety of split treatment processes (Fig. 15.2). These processes are often used to control magnesium concentrations in the finished water. Magnesium silicate scale formed at high temperatures is problematic. A split recarbonation process is used to remove magnesium from waters that have high amounts of noncarbonate hardness (Montgomery, 1985). There is no bypass ($x = 0$ in Fig. 15.2). Excess lime is required to precipitate magnesium and recarbonation is required to neutralize the excess lime. If recarbonation is split into two stages where only enough CO₂ is applied in the first stage to react with the excess lime and produce carbonate, at the expense of an additional settling basin more calcium may be precipitated. The second stage recarbonation will be used for final pH adjustment. A single-stage process will produce water with more alkalinity and higher hardness concentrations.

In a split treatment process a portion of the water is treated for hardness (particularly magnesium) removal and recombined with a bypassed stream. The combined flow may be further treated for calcium reduction as shown in Fig. 15.2. Economies are gained by treating smaller volumes of water. Also magnesium concentrations in

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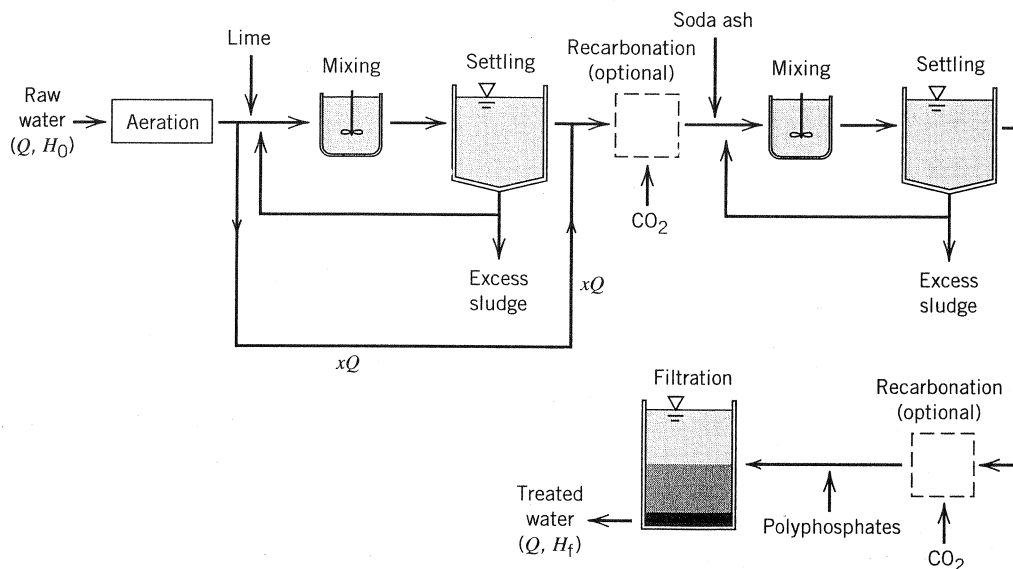


Figure 15.2 Split treatment flow diagram for hardness removal. (H_0 initial total hardness; H_f final total hardness). Adapted from J. L. Cleasby and J. H. Dillingham (1966), "Rational Aspects of Split Treatment," *J. of the Sanitary Engineering Division, ASCE*, 92, SA2, pp. 1-7. Reprinted with permission of ASCE.

the product water can be controlled in a split treatment process. Chemical costs are also reduced in a split treatment process. The bypassed flow can be treated with coagulation agents as required for removal of suspended solids in the settling basin.

A split treatment process is normally applied to a water with a low amount of noncarbonate hardness and magnesium hardness reduction is desired (Montgomery, 1985). In a split treatment process all lime based on the total flow is added to the stream entering the first stage to cause reactions (15.1)–(15.5). There is normally a large excess of lime in the first basin and magnesium concentrations below 0.2 meq/L down to practically zero can be attained in the settled effluent from this stage. Recarbonation of the effluent from the first stage is almost never required because there is sufficient alkalinity and carbon dioxide in the bypassed flow to react with the excess lime. There will be no precipitation of magnesium after the first stage because the pH will be lowered below solubility product values for $Mg(OH)_2$ precipitation.

Mixing the treated and bypassed streams results in more carbonate formation and subsequent precipitation of calcium carbonate. If further reduction of noncarbonate hardness is required the influent to the second stage can be supplemented with Na_2CO_3 to reduce the noncarbonate Ca^{2+} according to reaction (15.6). Another settling basin is required to settle the precipitate formed by these reactions. Finally, CO_2 is added to cause reaction (15.8) to bring the pH to the desired final value.

The final desired magnesium concentration dictates the fraction of flow that is bypassed in a split treatment process. Water heater fouling problems are avoided when magnesium concentrations are 40 mg/L as $CaCO_3$ (0.8 meq/L) or lower (Larson et al., 1959). Because no magnesium is removed in the second stage,

$$(1 - x)Q[Mg]_1 + xQ[Mg]_0 = Q[Mg]_f \quad \text{or} \quad x = \frac{[Mg]_f - [Mg]_1}{[Mg]_0 - [Mg]_1} \quad (15.9)$$

where

x is bypassed fraction of influent flow, Q

$[Mg]_0$, $[Mg]_1$, and $[Mg]_f$ are the influent, first stage, and final magnesium concentrations, respectively

The maximum fraction that can be bypassed occurs when $[Mg]_1 = 0$.

Recycling a portion of the sludge from the clarifier promotes reaction and settling in the process. Doses higher than stoichiometric requirements may be required to achieve desired results.

Carbon dioxide can be supplied in bulk containers or generated by burning a hydrocarbon such as gas or oil or burning coal or coke. Polyphosphates are synthetic phosphate compounds that sequester hardness ions, keeping them in solution. Polyphosphates are often added to treated waters to prevent deposit buildup on pipes.

■ Example 15.1 Lime and Soda Determination for Hardness Removal

Using the river data in Problem 9 in Chapter 9, find the lime and soda requirements to treat the water to a final hardness of (a) 100 mg/L as $CaCO_3$ and (b) the practical limit in a single-stage process. In a single-stage process no CO_2 is added in the hardness precipitation reactor. Assume the excess lime requirement to remove magnesium is 0.75 meq/L. The pertinent data from the problem are as follows:

pH	mg/L as $CaCO_3$		
	Alkalinity	Total hardness	Calcium hardness
7.7	180	215	160

It is assumed that the alkalinity is due totally to inorganic carbon species and the concentrations of iron and manganese are ignored. The concentration of free CO_2 ($H_2CO_3^*$) will be checked to determine whether it is significant. The dissociation constant for $H_2CO_3^*$ (Table 3.2) is 4.3×10^{-7} . $[H^+] = 10^{-pH} = 10^{-7.7} = 2.00 \times 10^{-8} M$.

$$[HCO_3^-] = \left(180 \frac{\text{mg } CaCO_3}{L}\right) \left(\frac{122 \text{ mg } HCO_3^-}{100 \text{ mg } CaCO_3}\right) \left(\frac{1 \text{ mole}}{61\,000 \text{ mg}}\right) = 3.60 \times 10^{-3} M$$

From the equilibrium expression:

$$[H_2CO_3^*] = \frac{[H^+][HCO_3^-]}{K} = \frac{(2.00 \times 10^{-8})(3.60 \times 10^{-3})}{4.3 \times 10^{-7}} = 1.67 \times 10^{-4} M$$

The concentration of $H_2CO_3^*$ in meq/L is

$$[H_2CO_3^*] = (1.67 \times 10^{-4} M)(2\,000 \text{ meq/mole}) = 0.33 \text{ meq/L}$$

$$\begin{aligned} \text{Mg hardness} &= \text{Total hardness} - \text{Ca hardness} = 215 \text{ mg/L} - 160 \text{ mg/L} \\ &= 55 \text{ mg/L as } CaCO_3 \end{aligned}$$

$$[Mg^{2+}] = \left(55 \frac{\text{mg } CaCO_3}{L}\right) \left(\frac{1 \text{ meq}}{50 \text{ mg } CaCO_3}\right) = 1.10 \text{ meq/L}$$

$$[Ca^{2+}] = \left(160 \frac{\text{mg } CaCO_3}{L}\right) \left(\frac{1 \text{ meq}}{50 \text{ mg } CaCO_3}\right) = 3.20 \text{ meq/L}$$

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Because there is 1 meq/mole for HCO_3^- ,

$$[\text{HCO}_3^-] = 3.60 \text{ meq/L}$$

The Ca carbonate hardness is 3.20 meq/L and the Mg carbonate hardness is 0.40 meq/L. There is 0.70 meq/L of Mg noncarbonate hardness. A residual hardness of 100 mg/L as CaCO_3 is equivalent to 2 meq/L.

(a) The amount of the total hardness to be removed (ΔTH) is

$$\Delta\text{TH} = 3.20 + 1.10 - 2.00 = 2.30 \text{ meq/L}$$

It will only be necessary to remove calcium hardness. The lime requirement is equal to the CO_2 content and the amount of calcium to be removed, which is increased by 0.6 meq/L to compensate for the residual CO_3^{2-} .

$$[\text{Ca}(\text{OH})_2] = [\text{CO}_2] + [\text{Ca}(\text{HCO}_3)_2] + 0.60 \text{ meq/L} = 0.33 + 2.30 + 0.60 = 3.23 \text{ meq/L}$$

The final concentrations (meq/L) of ions in the water are: $[\text{Ca}^{2+}]$, 0.90; $[\text{Mg}^{2+}]$, 1.10; $[\text{CO}_3^{2-}]$, 0.60; $[\text{HCO}_3^-]$, 0.70

(b) In this case the lime requirement using Eqs. (15.1)–(15.6) is

$$\begin{aligned} [\text{Ca}(\text{OH})_2] &= [\text{CO}_2] + [\text{Ca}(\text{HCO}_3)_2] + 2 \times [\text{Mg}(\text{HCO}_3)_2] + [\text{MgX}] + \text{excess} \\ &= 0.33 + 3.20 + 2 \times 0.40 + 0.70 + 0.75 = 5.78 \text{ meq/L} \end{aligned}$$

If only this amount of lime were added, the amounts of Ca^{2+} and CO_3^{2-} formed would be

$$[\text{CO}_3^{2-}] = 0.33 + 6.40 + 0.80 = 7.53 \text{ meq/L}$$

$$[\text{Ca}^{2+}] = 3.20 + 5.78 = 8.98 \text{ meq/L}$$

The CO_3^{2-} is limiting and the residual Ca^{2+} and CO_3^{2-} concentrations would be

$$[\text{CO}_3^{2-}] = 0.60 \text{ meq/L} \quad [\text{Ca}^{2+}] = 8.98 - 6.93 = 2.05 \text{ meq/L}$$

The residuals for Mg^{2+} and OH^- would be

$$[\text{Mg}^{2+}] = 1.10 - (0.40 + 0.70) + 0.20 = 0.20 \text{ meq/L}$$

$$[\text{OH}^-] = 5.78 - (0.33 + 3.20 + 0.40 + 0.90) = 0.95 \text{ meq/L}$$

The soda ash requirement is

$$[\text{Na}_2\text{CO}_3] = [\text{MgX}] + \text{excess lime} = 0.70 + 0.75 = 1.45 \text{ meq/L}$$

The final composition (meq/L) of the water leaving the settling basin is: $[\text{Ca}^{2+}]$, 0.60; $[\text{Mg}^{2+}]$, 0.20; $[\text{CO}_3^{2-}]$, 0.60; $[\text{OH}^-]$, 0.95; $[\text{Na}^+]$, 1.45.

Acid addition will be required for OH^- neutralization and pH adjustment of the effluent.

■ Example 15.2 Hardness Removal in a Split Treatment Process

Determine the bypassed fraction and doses of lime and soda ash to be applied at each stage in a split treatment process to a groundwater that contains the following softening related constituents:

$[\text{CO}_2]$, 0.40 meq/L; $[\text{Ca}^{2+}]$, 3.60 meq/L; $[\text{Mg}^{2+}]$, 2.00 meq/L; [alkalinity], 5.80 meq/L

The product water should have a magnesium concentration of 50 mg/L as CaCO_3 (1 meq/L) and a total hardness concentration of 100 mg/L as CaCO_3 (2 meq/L) or

lower. Perform the analysis when the concentration of magnesium from the first stage process is 0.2 meq/L. Assume the excess lime required to precipitate $\text{Mg}(\text{OH})_2$ is 0.8 meq/L.

From Eq. (15.9),

$$x = \frac{[\text{Mg}]_f - [\text{Mg}]_i}{[\text{Mg}]_0 - [\text{Mg}]_i} = \frac{1.0 - 0.2}{2.0 - 0.2} = 0.444$$

Because the alkalinity exceeds the sum of the concentrations of the hardness ions, the raw water calcium carbonate hardness (CH) is 3.60 meq/L and the magnesium CH is 2.00 meq/L. There is no need to add Na_2CO_3 because there is no noncarbonate hardness.

The final concentration of calcium is $2.00 - 1.00 = 1.00$ meq/L.

There are two constraints in this problem:

1. To precipitate $\text{Mg}(\text{OH})_2$, lime must be added in excess of the carbon dioxide and alkalinity to result in free hydroxyl ions in the first stage.
2. There must be at least 0.8 meq/L excess OH^- to reduce Mg^{2+} to 0.2 meq/L.

The total equivalents of lime required is the amount required to remove CO_2 , CaCH, and MgCH plus excess.

CO_2 : from Eq. (15.1), 0.40 eq/L

CaCH: from Eq. (15.2), $3.60 - 1.00 = 2.60$ meq/L

MgCH: from Eq. (15.4), $2(2.00 - 1.00) = 2.00$ meq/L

Excess for Ca removal: The usual excess is 0.6 meq/L

The lime requirement is $0.40 + 2.60 + 2.00 + 0.6 = 5.60$ meq/L based on the total flow. The fraction of flow entering the first stage is $1 - 0.444 = 0.556$. The dose of lime (L) to be added to the flow entering the first stage is

$$0.556 L = 5.60 \text{ meq/L} \quad \text{or} \quad L = (5.60 \text{ meq/L})/0.556 = 10.07 \text{ meq/L}$$

Because the CO_2 and HCO_3^- concentrations sum to 6.20 meq/L there is 4.07 meq/L of OH^- , which satisfies constraint 1.

After addition of the lime but before reaction,

$$[\text{Ca}^{2+}] = 10.07 + 3.60 = 13.67 \text{ meq/L} \quad [\text{OH}^-] = 10.07 \text{ meq/L}$$

After reaction of OH^- with CO_2 and HCO_3^- ,

$$[\text{CO}_3^{2-}] = 0.40 + 2(5.80) = 12.00 \text{ meq/L}$$

CaCO_3 is precipitated. CO_3^{2-} is limiting and its concentration is 0.60 meq/L after precipitate formation.

$$[\text{Ca}^{2+}] = 13.67 - (12.00 - 0.60) = 2.27 \text{ meq/L}$$

After reaction of Mg^{2+} with OH^- ,

$$[\text{Mg}^{2+}]_f = 0.20 \text{ meq/L}$$

$$[\text{OH}^-] = 10.07 - 0.40 - 5.80 - (2.00 - 0.20) = 2.07 \text{ meq/L}$$

This is considerably in excess of the 0.8 meq/L constraint. It is probable that more than 1.8 meq/L of Mg^{2+} will be removed but the calculations will be carried on assuming $[\text{Mg}^{2+}]_f = 0.20$ meq/L.

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After mixing the first stage and bypassed flows, the following concentrations result:

$$[\text{OH}^-] = \frac{0.556(2.07) + 0}{1} = 1.15 \text{ meq/L}$$

$$[\text{Ca}^{2+}] = \frac{0.556(2.27) + 0.444(3.60)}{1} = 2.86 \text{ meq/L}$$

$$[\text{HCO}_3^-] = 0.444(5.80) = 2.58 \text{ meq/L} \quad [\text{CO}_2] = 0.444(0.40) = 0.18 \text{ meq/L}$$

$$[\text{Mg}^{2+}] = 0.556(0.2) + 0.444(2.00) = 1.00 \text{ meq/L}$$

$$[\text{CO}_3^{2-}] = 0.556(0.60) = 0.33 \text{ meq/L}$$

OH^- will react with CO_2 and HCO_3^- to produce

$$[\text{CO}_3^{2-}] = 0.33 + 0.18 + 2(1.15 - 0.18) = 2.45 \text{ meq/L}$$

CO_3^{2-} is limiting again. The final concentrations of all species (meq/L) in the water are $[\text{Ca}^{2+}]$, 1.01; $[\text{CO}_3^{2-}]$, 0.60; $[\text{Mg}^{2+}]$, 1.00; $[\text{OH}^-]$, 0.

Because of the operation of the process wherein all of the lime is added to the first stage, a sufficient excess for $\text{Mg}(\text{OH})_2$ removal results and it is not necessary to add the $\text{Mg}(\text{OH})_2$ excess into the lime dose.

If this water were to be treated in a conventional process the lime requirement would be

$$[\text{Ca}(\text{OH})_2] = 0.40 + 5.80 + 2(2.00 - 1.00) + 0.80 = 9.00 \text{ meq/L}$$

to be added to the whole flow to meet the effluent magnesium objective. Calcium would be removed to 0.6 meq/L, which is better than the requirement, but constraint 1 necessitates this condition.

The lime savings is 3.4 meq/L. Also, the effluent from the conventional process would contain 0.8 meq/L of OH^- , requiring CO_2 or other neutralizing agent.

15.2.2 Bar Graphs

The solution of softening problems is conveniently accomplished using bar graphs showing the concentrations of the species involved at various stages during the process. On a bar graph, all concentrations are expressed in meq/L. The first step in a water softening analysis is to measure the concentrations of the major cations and anions. After the concentrations are converted to meq/L, the sums of the cation and anion concentrations should be approximately equal; otherwise there has been an error in analysis or computations, or a significant ion has not been measured.

The use of bar graphs is illustrated by an example. Consider the water with the concentrations of major ions listed in Table 15.3.

Usually only the ions given in Table 15.3 are significant in natural waters. The bar graph corresponding to the raw water is given in Fig. 15.3a. Carbon dioxide is given as the first component. It is not a cation or an anion. The cations are arranged in the order of Ca^{2+} , Sr^{2+} , Mg^{2+} , which is followed by other monovalent cations in any order. The anions are arranged with OH^- , CO_3^{2-} , HCO_3^- , followed by SO_4^{2-} and other monovalent anions in any order. The hypothetical concentrations for $\text{Ca}(\text{HCO}_3)_2$, CaSO_4 , MgSO_4 , and NaCl can be determined easily and are given on the graph for this water. The bar graph provides an easy check on the total cation and anion charge balance. The sum of the positive ions should be within 0.1–0.2 meq/L of the sum of the negative ions.

TABLE 15.3 Water Components

Constituent	Concentration mg/L	Equivalent weight	meq/L
CO ₂	9.5	22	0.43
Ca ²⁺	98	20	4.90
Mg ²⁺	27	12.2	2.20
Na ⁺	6.5	23	0.28
HCO ₃ ⁻	281	61	4.60
SO ₄ ²⁻	120	48	2.50
Cl ⁻	6.1	35.5	0.18

It is desired to attain hardness removal to the practical limits of 30 mg/L of CaCO₃ (0.6 meq/L) and 10 mg/L of MgSO₄ (0.2 meq/L) using a split recarbonation method. The lime requirement is equal to the CO₂, Ca(HCO₃)₂, and Mg²⁺ concentrations plus the excess lime (only when Mg removal is desired). The lime requirement is determined from examination of Eqs. (15.1)–(15.6) and the composition of the water. In this case it is

$$\begin{aligned} \text{Ca(OH)}_2 &= \text{CO}_2 + \text{Ca(HCO}_3)_2 + \text{Mg}^{2+} + \text{excess} \\ &= 0.43 + 4.60 + 2.20 + 1.25 = 8.48 \text{ meq/L} \end{aligned}$$

The excess lime was chosen to be 1.25 meq/L, which is somewhat higher than the more typical value of 0.7 meq/L. The excess lime requirement will be dictated by trial and error for the water and treatment times in each situation.

This amount of lime will remove the CO₂, and Ca²⁺, or CO₃²⁻ will be removed down to the level of 0.60 meq/L, depending on which of these ions is limiting. Likewise, Mg²⁺ is removed only to a level of 0.2 eq/L. The state of the water after addition of the lime is shown in Fig. 15.3b. Figure 15.3c shows the state of the water after reaction of OH⁻ with CO₂ and HCO₃⁻. Note that the total alkalinity has not changed but the forms of alkalinity have changed.

After precipitation of the remaining CaCO₃ and Mg(OH)₂ the water is in the state shown in Fig. 15.3d. Note that the cation and anion orders given previously are maintained throughout all of the bar graphs. The water in Fig. 15.3d is the effluent from the first stage of the process.

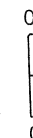
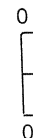
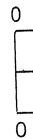
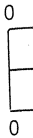
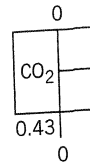
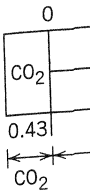
Now CO₂ is added to convert the excess OH⁻ (1.45 meq/L from excess lime and Mg²⁺ that was not precipitated) to CO₃²⁻, and Na₂CO₃ is added before the second mixing (reaction) vessel to precipitate the remaining Ca²⁺ as CaCO₃ in the second settling basin. The Na₂CO₃ requirement is

$$\text{Na}_2\text{CO}_3 = 4.35 - 1.45 - 0.60 = 2.30 \text{ meq/L}$$

Figure 15.3e shows the water after recarbonation and addition of Na₂CO₃. After final precipitation of CaCO₃ the water is in the state shown in Fig. 15.3f. Recarbonation or acid addition to achieve the desired pH for stabilization of the water may now be performed.

Lime Recovery and Sludge Reduction

Softening sludges, generated in basins that are separate from primary sedimentation basins, contain only CaCO₃ and Mg(OH)₂. Softening processes may be operated to



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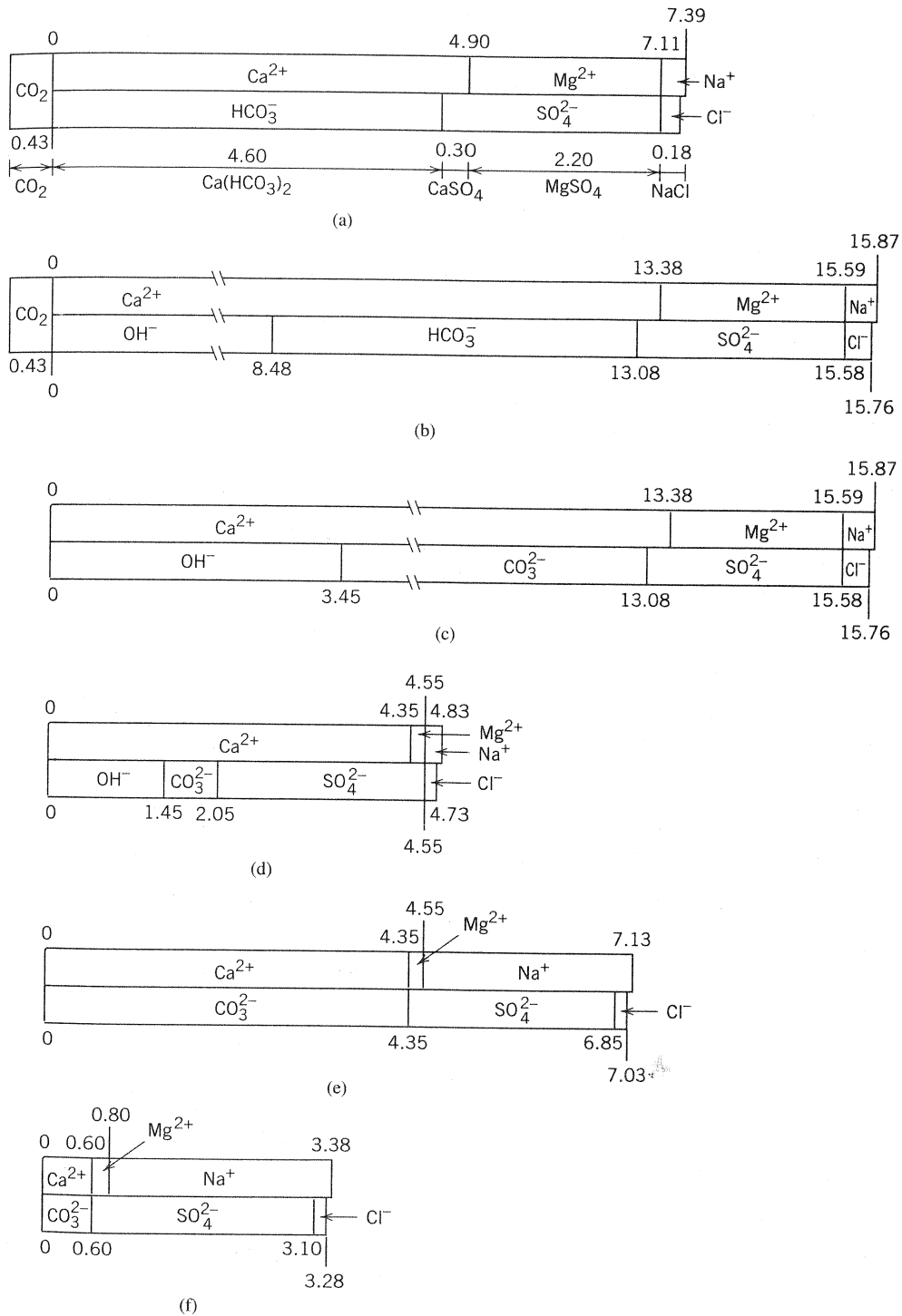


Figure 15.3 State of the water at stages during treatment.

exclusively remove CaCO_3 in one basin. Lime is readily recovered from calcium carbonate sludge by heating it to drive off CO_2 .



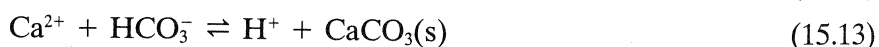
Lime recovery reduces the amount of lime required as well as decreases the quantity of sludge. For waters with a high alkalinity content, each mole of calcium removed produces 2 moles of calcium carbonate as shown in reaction (15.2). Not all sludge will need to be treated for lime recovery to sustain the process.

15.3 CHEMICAL STABILIZATION OF WATER

Water leaving the treatment plant should not be corrosive to the pipes in the distribution system or in households. To protect pipes from corrosive agents in the water, the pH, $[Ca^{2+}]$, and alkalinity content of the water are adjusted to the calcium carbonate saturation equilibrium value at the temperature of the water. Normally a slight tendency to precipitate calcium carbonate is maintained. This preserves a film of calcium carbonate in distribution pipes and retards corrosion of the pipes (see Section 2.3.2). This process is referred to as chemical stabilization of the water.

Water is considered to be stable when it will neither dissolve nor deposit calcium carbonate, i.e., it is just saturated with calcium carbonate. A water that has a tendency to dissolve calcium carbonate is an aggressive water. An aggressive water is not necessarily innately more corrosive than a stable water. But because of its ability to remove the protective $CaCO_3$ barrier, an aggressive water will indirectly enhance the corrosion of the pipes.

The chemical reactions involved are the solubility product relation for calcium carbonate and a carbonate equilibrium expression. Bicarbonate alkalinity will be the predominant form of alkalinity at pHs of treated water. The two equations can be added to find a single equation relating $[Ca^{2+}]$, pH ($[H^+]$), and alkalinity as follows:



To accurately determine the pH required to precipitate $CaCO_3$, activity coefficients must be incorporated into the equilibrium expressions (see Eq. 2.10). The equilibrium expressions for the above equations are

$$\text{For Eq. (15.11):} \quad K_{sp} = \gamma_{Ca^{2+}}[Ca^{2+}]\gamma_{CO_3^{2-}}[CO_3^{2-}]$$

$$\text{For Eq. (15.12):} \quad K_2 = \frac{\gamma_{CO_3^{2-}}[CO_3^{2-}]\gamma_{H^+}[H^+]}{\gamma_{HCO_3^-}[HCO_3^-]}$$

Therefore the equilibrium expression for Eq. (15.13) is

$$K = \frac{K_{sp}}{K_2} = \frac{\gamma_{Ca^{2+}}[Ca^{2+}]\gamma_{HCO_3^-}[HCO_3^-]}{\gamma_{H^+}[H^+]} \quad (15.14)$$

A pH meter actually measures the activity of the hydrogen ion.

$$pH_{\text{meter}} = -\log \gamma_{H^+}[H^+]$$

Defining the pH corresponding to the saturation condition as pH_s , from Eq. (15.14),

$$\begin{aligned} pH_s &= -\log \gamma_{H^+}[H^+] = \log K - \log \gamma_{Ca^{2+}}[Ca^{2+}] - \log \gamma_{HCO_3^-}[HCO_3^-] \\ &= \log K_{sp} - \log K_2 - \log [Ca^{2+}] - \log [HCO_3^-] - \log \gamma_{Ca^{2+}}\gamma_{HCO_3^-} \end{aligned}$$

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Equilibrium Table 14 range. N is one c aragonit differen factor in out that

The also possible $CaCO_3$ the pH,

TABLE

Temperature °C
5
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15
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25
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35
40
45
50
60
70
80
90

^aAdapted
^bFrom Pl
^cFor calc
^dBased o

Using the “p” notation, the definition of alkalinity given by Eq. (3.25), and assuming that the carbonate ion concentration is negligible,

$$\text{pH}_s = \text{p}K_2 - \text{p}K_{\text{sp}} - \log [\text{Ca}^{2+}] + S - \log [\text{Alkalinity}] \quad (15.15)$$

where

S is a salinity correction factor equal to $-\log \gamma_{\text{Ca}^{2+}}\gamma_{\text{HCO}_3^-}$

(Note that $[\text{Ca}^{2+}]$ and $[\text{Alkalinity}]$ are in mole/L and alkalinity is assumed to be $[\text{HCO}_3^-]$.)

The factor S adjusts the equation for the true activities of the ions in the equilibrium expressions. Equation (15.15) is valid in the pH range of 6.0–8.5 in which most treated waters fall (AWWA Joint Task Group, 1990). This equation is based on the assumption that bicarbonate ion is the only significant alkalinity ion.

Equation (15.15) should be applied at the temperature of the treated water. The equilibrium constants, K_{sp} and K_2 , and activity coefficients are functions of temperature. Table 15.4 gives values of S and the equilibrium constants over a broad temperature range. Note that $\text{p}K_{\text{sp}}$ values in Table 15.4 are based on the formation of calcite, which is one crystalline form of CaCO_3 . Other isomorphs of CaCO_3 that may form are aragonite and vaterite. The solubility products for these other forms are slightly different from that for calcite and their formation changes pH_s . This is a complicating factor in any pH_s calculation. However, the AWWA Joint Task Group (1990) points out that the most common form of CaCO_3 in fresh waters is calcite.

The parameters involved are all readily assessed by simple lab procedures. It is also possible to determine pH_s for a water by keeping the water in contact with pure CaCO_3 overnight which is sufficient time to establish equilibrium conditions. Then the pH, which will be pH_s , should be measured.

TABLE 15.4 Equilibrium Constants and Salinity Factors for Saturation Index^a

Temperature, °C	$\text{p}K_2^b$	$\text{p}K_{\text{sp}}^{b,c}$	S^d				
			TDS, mg/L				
			50	150	400	1 000	1 500
5	10.55	8.39	0.082 5	0.137	0.210	0.300	0.345
10	10.49	8.41	0.083 2	0.138	0.211	0.303	0.348
15	10.43	8.43	0.083 8	0.139	0.213	0.305	0.351
20	10.38	8.45	0.084 5	0.140	0.215	0.308	0.354
25	10.33	8.48	0.085 4	0.142	0.217	0.311	0.358
30	10.29	8.51	0.086 1	0.143	0.219	0.314	0.362
35	10.25	8.54	0.086 9	0.144	0.221	0.318	0.366
40	10.22	8.58	0.087 9	0.146	0.224	0.322	0.370
45	10.20	8.62	0.088 8	0.148	0.226	0.325	0.375
50	10.17	8.66	0.089 8	0.149	0.229	0.329	0.379
60	10.14	8.76	0.091 9	0.153	0.235	0.337	0.389
70	10.13	8.87	0.094 1	0.157	0.241	0.346	0.400
80	10.13	8.99	0.096 5	0.161	0.247	0.356	0.411
90	10.14	9.12	0.099 0	0.165	0.254	0.366	0.423

^aAdapted from AWWA Joint Task Group (1990).

^bFrom Plummer and Busenberg (1982).

^cFor calcite as recommended by AWWA Joint Task Group (1990).

^dBased on Eq. (1.10) for ionic strength and the activity expression given by AWWA Joint Task Group (1990).

If the pH of the water is less than pH_s , there will be no deposition of $CaCO_3$ and hence the possibility of corrosion is enhanced. If the pH of the water is greater than pH_s then $CaCO_3$ can be deposited in pipes.

Langelier (1936) performed the development just described and the value of $pH - pH_s$ (pH is the actual pH of the water being tested) is called the Langelier index or saturation index (SI).

$$SI = pH - pH_s \quad (15.16)$$

It is common practice to adjust waters to an SI value of 0.2 by addition of the appropriate alkalinity or acidity agent. Lime changes both calcium and alkalinity concentrations. Other agents that can be used to adjust the water to the desired conditions are Na_2CO_3 , CO_2 , and strong acids or bases such as HCl and NaOH. These agents will change the ratio of $H_2CO_3^*$ and HCO_3^- from which the new pH of the water can be calculated with Eq. (3.22b).

The SI, although widely used, is only a qualitative indication of the amount of potential $CaCO_3$ deposition. A larger value of the index does not necessarily mean that more $CaCO_3$ will deposit and, at the extreme case of a pH greater than pK_2 for carbonic acid, an undersaturated solution will yield a positive index value. Snoeyink and Jenkins (1980) and Rossum and Merrill (1983) offer a comprehensive discussion of the index, pointing out other deficiencies.

There are a number of other indexes of a similar nature to the SI (Rossum and Merrill, 1983; AWWA Joint Task Group, 1990). The modified Caldwell-Lawrence approach (Caldwell and Lawrence, 1953; Merrill, 1978), which is beyond the scope of this text, offers a relatively easy approach to quantitatively estimating the extent of potential precipitation. Other indexes or methods to quantify the deposition potential of $CaCO_3$ require computer code or extensive calculations. These indexes usually consider more chemical equilibria, particularly the formation of complexes, and so produce more accurate results. The programs for calculating the indexes are readily run on a personal computer with a relatively small amount of memory.

■ Example 15.3 Saturation Index

The calcium concentration of a water is 42 mg/L and the alkalinity concentration is 60 mg/L as $CaCO_3$. TDS have been measured at 120 mg/L. The pH of the water is 7.73 and its temperature is 12°C. Find the SI of this water.

Equation (15.15) is required to calculate pH_s . The values for pK_2 , pK_{sp} , and S are obtained from Table 15.4. At the given values of temperature and TDS it will be necessary to interpolate for each parameter. The values for pK_2 , pK_{sp} , and S are

$$pK_2 = 10.49 + \frac{(12 - 10)}{(15 - 10)}(10.43 - 10.49) = 10.47$$

$$pK_{sp} = 8.41 + \frac{(12 - 10)}{(15 - 10)}(8.43 - 8.41) = 8.42$$

$$S_{12,50} = 0.0832 + \frac{(12 - 10)}{(15 - 10)}(0.0838 - 0.0832) = 0.08344$$

$$S_{12,150} = \frac{(12 - 10)}{(15 - 10)}(0.139 - 0.138) = 0.1384$$

$$S_{12,120} = S_{12,50} + \frac{(120 - 50)}{(150 - 50)}(S_{12,150} - S_{12,50}) = 0.08344 + \frac{(70)}{(100)}(0.1384 - 0.08344) = 0.122$$

Converting the calcium and alkalinity concentrations to M :

$$[\text{Ca}^{2+}] = \left(42 \frac{\text{mg}}{\text{L}}\right) \left(\frac{1 \text{ mole}}{40 \text{ g}}\right) \left(\frac{1 \text{ g}}{1000 \text{ mg}}\right) = 1.05 \times 10^{-3} M$$

$$[\text{Alkalinity}] = \left(60 \frac{\text{mg CaCO}_3}{\text{L}}\right) \left(\frac{61 \text{ g HCO}_3^-}{50 \text{ g CaCO}_3}\right) \left(\frac{1 \text{ mole}}{61 \text{ g HCO}_3^-}\right) \left(\frac{1 \text{ g}}{1000 \text{ mg}}\right)$$

$$= 1.20 \times 10^{-3} M$$

Substituting these values into Eq. (15.15),

$$\text{pH}_s = 10.47 - 8.42 - \log(1.05 \times 10^{-3}) + 0.122 - \log(1.20 \times 10^{-3}) = 8.07$$

and

$$\text{SI} = 7.73 - 8.07 = -0.34$$

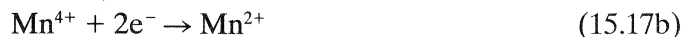
The water is undersaturated and it will be necessary to add strong base or Ca^{2+} [$\text{Ca}(\text{OH})_2$ accomplishes both] to raise the SI.

Corrosion results in the addition of metals to the water and wastewater. The bulk of metals in a wastewater is removed with the sludge in a wastewater treatment process. Another benefit of water stabilization is reduction in the metal content of sludges, which improves the reusability of the sludge from the wastewater treatment plant (Kuchenrither et al., 1992).

15.4 IRON AND MANGANESE REMOVAL

Iron and manganese are discussed together because they commonly occur together in raw waters and the problems resulting from them and their methods of treatment are similar. Iron and manganese are minerals that cause staining of plumbing fixtures and laundered clothes as well as produce distinct tastes and odors in a drinking water. Iron and manganese also contribute to the hardness of a water. These are aesthetic problems; there is no health risk associated with excessive amounts of iron and manganese. The WHO standards for acceptable concentrations of iron and manganese are 0.3 and 0.1 mg/L, respectively.

The solubilities of iron and manganese are primarily controlled by their oxidation state. The redox reactions are



The higher oxidation states of both iron and manganese are soluble to an insignificant degree in waters in normal pH ranges. At these oxidation states, the precipitates of Fe_2O_3 and MnO_2 form. The iron oxide (rust) has a reddish-brown color and the manganese dioxide has a brown to brownish-black appearance.

In the presence of dissolved oxygen, iron and manganese are oxidized to their insoluble oxidation states of Fe(III) and Mn(IV) according to redox reactions (15.17a) and (15.17b). Reducing (anaerobic) conditions cause the dissolution of these minerals. Therefore, groundwaters are particularly susceptible to excess concentrations of these minerals when soil contains these minerals. Also, in the bottom sediments of streams and lakes, anaerobic conditions exist and precipitated organic matter releases iron and manganese to the water. Redox reactions are slower than acid-base reactions.