inorganic materials that cause tastes and odors. When it is added to water containing taste-and-odor compounds, the reaction is

2KMnO ₄	+	H_2O	+	taste-	and-c	odor compound \rightarrow	
2MnO ₂ ↓	+	2KOH	+	$3O^{-2}$	+	taste-	(C6–3)
manganese		potassium		oxygen		and-odor	
dioxide		hydroxide				compounds	

This reaction produces oxygen in the water (notice the three Os in the equation above), which oxidizes the organic and inorganic taste-and-odor compounds. The manganese dioxide by-product (insoluble and very finely divided) is removed later, through coagulation, settling, and filtration.

Dosages of KMnO₄ vary from 0.5 to 15 mg/L, although dosages in the range of 0.5– 2.5 mg/L are usually adequate to oxidize most taste-and-odor-producing chemicals. Potassium permanganate should be added very early in the treatment process, perhaps at the intake, in order to allow enough time for oxidation to take place. In most cases, detention times of 1–1.5 hours are adequate, but for some particularly stubborn taste-and-odor compounds, detention times of 4–5 hours may be needed.

Water takes on a pink color when potassium permanganate is first added. Then, as it oxidizes to manganese dioxide (MnO_2), the color begins to change, first to yellow, then orange, and finally brown, which is the color of the manganese dioxide precipitate. By the time the water reaches the filters, the pink color should be gone entirely. If not, oxidation will continue after filtration, giving the water an unacceptable yellow to yellow-brown color. This problem of "color breakthrough" can be controlled by either reducing the KMnO₄ dosage or by moving the point of chemical addition farther upstream.

Chlorine Dioxide

Chlorine dioxide (ClO₂) is a strong oxidizing agent used primarily to control the odors caused by phenolic compounds. It is about 2–2.5 times as powerful as chlorine. Chlorine dioxide is not purchased as a ready-made chemical like most other water treatment chemicals. Instead, it is made at the treatment plant by adding a solution of sodium chlorite (NaClO₂) to a concentrated chlorine solution, as follows:

 $2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$ (C6-4)

The resultant solution should have a pale yellow color. The amount of chlorine and sodium chlorite needed to reach this color usually varies, depending on the strength of the sodium chlorite. The sodium chlorite commonly used is about 80 percent pure. Theoretically, 1.68 lb of sodium chlorite would be mixed with 0.5 lb of chlorine in order to produce 1.0 lb of chlorine dioxide. However, by using more chlorine (at least as much chlorine as

sodium chlorite), operators have shown that the reaction occurs faster and the conversion of the chlorite is more complete.

Ozone

Ozone treatment, called *ozonation*, can be an effective method of taste-and-odor control, although experience shows that results are quite variable, depending on the quality of the water being treated. Although ozonation is not common in the United States, it is widely practiced in Europe. Ozone (O_3) is generated at the treatment plant by releasing an electrical spark into a stream of oxygen under controlled circumstances. Although ozone is a powerful oxidizing agent, the cost to produce it is high.

COAGULATION

In coagulation, colloidal and finely divided suspended matter gather together as a result of the addition of a floc-forming chemical or biological processes. The actual chemical reactions are very complex and are influenced by a variety of factors, including

- type of coagulant used
- amount of coagulant used
- type and length of flash mixing
- type and length of flocculation
- effectiveness of sedimentation
- other chemicals used
- temperature
- pH
- alkalinity
- zeta potential
- raw-water quality

Alum

Because it is effective, inexpensive, and easy to apply, aluminum sulfate (usually called alum) is presently the most widely used coagulant in the field of water treatment.

Alum is available in two forms. Filter alum is the name given to solid or dry alum $[Al_2(SO_4)_3 \cdot 14H_2O]$. (The portion of the equation showing " $\cdot 14H_2O$ " indicates that a certain amount of water is included chemically along with the alum; in this case, 14 molecules of water are included with each molecule of alum. For simplicity, the water portion of the chemical equation is often left off.) Filter alum is ivory-white and is available in lump, ground, rice, or powdered form. Liquid alum $[Al_2(SO_4)_3 \cdot xH_2O]$ is alum already in solution. It is available in three strengths—the strongest being less than half the strength of

dry filter alum. Liquid alum can vary in color, depending on strength, from a slight, white, iridescent-like color to a yellow-brown.

Depending on the form, filter alum varies in density from 48 to 76 lb/ft.³ Liquid alum has a density of approximately 11 lb/gal, considerably more than that of water.

When alum is added to water, it reacts as follows:

Al ₂ (SO ₄) ₃ alum	+	3Ca(HCO ₃) ₂ natural bicarbonate alkalinity	\rightarrow	2A1(OH) ₃ ↓ aluminum hydoxide floc	+	3CaSO ₄ ↓ calcium sulfate	+	6CO ₂ (C6–5) carbon dioxide
Al ₂ (SO ₄) ₃ alum	+	3Na ₂ CO ₃ added carbonate alkalinity	+	3H ₂ O	\rightarrow			
		2A1(OH) ₃ ↓ aluminum hydoxide floc	+	3Na ₂ SO ₄ sodium sulfate	+	3CO ₂ carbon dioxide		(C6–6)
Al ₂ (SO ₄) ₃ alum		3Ca(OH) ₂ added hydroxide alkalinity	\rightarrow	2Al(OH) ₃ ↓ aluminum hydoxide floc		3CaSO₄↓ calcium sulfate		(C6–7)

Notice in each case that alkalinity is absolutely necessary for the reaction to take place. It does not matter whether the alkalinity is present naturally, as in Eq C6–5, or whether it is added prior to coagulation, as in Eq C6–6 and Eq C6–7. The important point is that there must be enough alkaline substances to react with the alum to form aluminum hydroxide $[Al(OH)_3]$, the sticky floc material. About 0.5 mg/L of alkalinity is required for each milligram of alum added per liter. Without an adequate supply of alkalinity, the alum will not precipitate (i.e., will not form aluminum hydroxide floc) and will pass through the filters. If alkalinity is added later, as it might be for corrosion control, the floc will form then and settle out either in the clearwell or in the distribution system, which can cause serious problems.

When alum is added to an alkaline water, as shown in the equations above, coagulation occurs in three steps. First, the positively charged aluminum ions (Al^{+3}) attract the negatively charged particles that cause color and turbidity, then they form tiny particles called microflocs. This marks the beginning of coagulation. Second, because many of these microfloc particles are now positively charged, they begin to attract and hold more negatively charged color-causing and turbidity-causing material. These first two coagulation steps occur very quickly (in microseconds).

Third, the microfloc particles grow into easily visible, "mature" floc particles. This growth occurs partly by the continual attraction of the color and turbidity materials; partly by the adsorption of viruses, bacteria, and algae onto the microfloc; and partly by the random collision of the microflocs that cause particles to stick together. Later, during sedimentation, the large floc particles settle rapidly, leaving the water clear.

The alum dosage to use for best results on a particular water depends on the various factors listed previously. In general, alum dosages range from 15 to 100 mg/L.

The effective pH range for alum dosing is between 5.5 and 8.5. It is often desirable to adjust pH within this range (by increasing alkalinity) so that alum will perform at its best. The pH for best performance can be found by using the jar test technique.

The rate of floc formation varies with temperature. Lower temperature means slower floc formation. Although there is usually no practical way of adjusting water temperature, one can compensate for lower temperatures by increasing the alum dosage.

From time to time, raw-water quality changes, perhaps as a result of changing seasons or possibly because of a high runoff of turbid water from a rainstorm. Routine dosage checks that make use of the jar test will help to ensure adequate coagulation–flocculation results.

Ferric Sulfate

Ferric sulfate is a reddish-gray [commercially called Ferric-floc, $Fe_2(SO_4)_3 \cdot 3H_2O$] or grayish-white [commercially called Ferriclear, $Fe(SO_4)_3 \cdot 2H_2O$] granular material. The densities of the different forms vary. Ferric-floc has a density of 60–74 lb/ft³ and Ferriclear has a density of 78–90 lb/ft³.

When ferric sulfate is added to water it reacts as follows:

$Fe_2(SO_4)_3 +$	$3Ca(HCO_3)_2 \rightarrow$	$2\text{Fe}(\text{OH})_3\downarrow$ +	3CaSO ₄	+	6CO ₂	(C6–8)
ferric	natural	ferric	calcium		carbon	
sulfate	bicarbonate	hydoxide	sulfate		dioxide	
	alkalinity	floc				

The reaction is very similar to that for alum. Notice that as with alum, ferric sulfate requires alkalinity in the water in order to form the floc particle ferric hydroxide $[Fe(OH)_3]$. If natural alkalinity is not sufficient, then alkaline chemicals (soluble salts containing HCO_3^- , CO_3^{-2} , and OH^- ions) must be added.

Ferric sulfate has several advantages compared with alum. The floc particle $[Fe(OH)_3]$ is denser and therefore more easily or quickly removed by sedimentation. Ferric sulfate will react favorably over a much wider range of pH, usually 3.5–9.0, sometimes even greater. However, ferric sulfate can stain equipment; it is difficult to dissolve; its solution is

corrosive; and it may react with organics to form soluble iron (Fe^{+2}) , as discussed later in this chapter. (Soluble iron in water causes red water, as well as staining and taste problems.)

The best ferric sulfate dosage to use in any coagulation application must be decided on a case-by-case basis based on the jar test. However, experience has shown that dosages in water treatment usually run between 5 and 50 mg/L.

IRON AND MANGANESE REMOVAL

Iron and manganese, two troublesome constituents affecting water quality, are found predominantly in groundwater supplies and occasionally in the anaerobic bottom waters of deep lakes. In nature, iron and manganese exist in stable forms—the ferric (Fe⁺³) form and the manganic (Mn⁺⁴) form; these forms are insoluble. Under anaerobic conditions, which can develop in groundwater aquifers and at the bottom of deep lakes, these forms are reduced to the soluble forms—ferrous (Fe⁺²) and manganous (Mn⁺²). The objective of most iron and manganese removal processes is to oxidize the reduced forms back into their insoluble forms so they will settle out.

Chlorine

When iron is present in the form of ferrous bicarbonate $[Fe(HCO_3)_2]$, it is easily treated for removal by chlorine, as shown in the following reaction:

$$2Fe(HCO_3)_2 + Cl_2 + Ca(HCO_3)_2 \rightarrow (C6-9)$$

$$2Fe(OH)_3 \downarrow + CaCl_2 + 6CO_2$$

This reaction, which is almost instantaneous, works in a pH range of 4–10, working best at pH 7. Removing 1 mg/L of iron (Fe⁺²) requires 0.64 mg/L of chlorine. The resulting precipitate, ferric hydroxide, is easily recognized as a fluffy, rust-colored sediment. The calcium bicarbonate [Ca(HCO₃)₂] in the reaction represents the bicarbonate alkalinity of the water. The reaction works using either free or combined chlorine residual (free and combined chlorine are discussed later in this chapter).

The reaction with manganese works similarly. The manganese may begin as a salt, such as manganous sulfate $(MnSO_4)$.

$$\begin{array}{rcrcrc} MnSO_4 & + & Cl_2 & + & 4NaOH & \rightarrow & (C6-10) \\ & & & MnO_2 \downarrow & NaCl & + & Na_2SO_4 & + & 2H_2O \end{array}$$

Then, with the addition of chlorine and sodium hydroxide, oxidized manganese produces the precipitate manganese dioxide (MnO_2). In order for the reaction to work, 1.3 mg/L of free available chlorine must be added per 1 mg/L of manganese to be removed. Chloramines (combined chlorine residuals) have little effect on manganese.

Sodium hydroxide, NaOH, causes the hydroxyl alkalinity in the sample. The reaction works best in the pH range of 6–10. The speed with which manganese oxidizes varies from a few minutes at pH 10, to 2–3 hours at pH 8, to as much as 12 hours at pH 6.

Aeration

Both ferrous iron (Fe^{+2}) and manganous manganese (Mn^{+2}) can be removed by aeration.

				aeratio	n			
4Fe(HCO ₃) ₂ ferrous bicarbonate	+	10H ₂ O	+	$O_2 \rightarrow$	4Fe(OF ferric hydrox	$I)_3 \downarrow +$ c ide	8H ₂ CO ₃	(C6–11)
				8	aeration			
$2MnSO_4$	+	O ₂	+	4NaOH	\rightarrow			(C6–12)
manganous sulfate				sodium hydroxide				
		2MnO ₂ manganese dioxide		2Na ₂ SO ₄ ↓ sodium sulfate	+	2H ₂ O		

The removal of iron is actually a two-step reaction. First, the soluble ferrous bicarbonate $[Fe(HCO_3)_2]$ is converted to the less soluble form, ferrous hydroxide $[Fe(OH)_2]$. Then, under further aeration, the ferrous hydroxide is converted to the insoluble form, ferric hydroxide $[Fe(OH)_3]$, which will filter out or settle out of solution as a fluffy, rust-colored sludge. The reaction works best in the pH range 7.5–8.0. It takes about 15 minutes to complete. To remove 1 mg/L of iron (Fe^{+2}) requires about 0.14 mg/L of oxygen.

The soluble salt of manganese, in this case manganous sulfate ($MnSO_4$), is oxidized to the insoluble form manganese dioxide (MnO_2), which filters out or settles out of solution. The reaction works best at a high pH, normally greater than 10. Sodium hydroxide (NaOH), shown as part of the reaction, raises the pH to the desired level and provides the hydroxide alkalinity (hydroxyl ions, OH⁻) necessary to raise the pH for the reaction. To remove 1 mg/L of manganese (Mn^{+2}) requires about 0.27 mg/L of oxygen. The manganese removal reaction takes place in about 15 minutes.

Potassium Permanganate

Potassium permanganate ($KMnO_4$) is a powerful oxidizing agent and can be used successfully to remove both iron and manganese, as shown by the following equations. This form of chemical treatment is preferable for manganese removal.

$$Fe(HCO_3)_2 + KMnO_4 + H_2O + 2H^+ \rightarrow MnO_2\downarrow + Fe(OH)_3\downarrow + KHCO_3 + H_2CO_3 \quad (C6-13)$$

$$3Mn(HCO_3) + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2\downarrow + 2KHCO_3 + 4H_2CO_3$$
(C6–14)

$$3MnSO_4 + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2\downarrow + K_2SO_4 + 2H_2SO_4$$
(C6–15)

Experience has shown that about 0.6 mg/L of KMnO₄ is adequate to remove 1 mg/L of iron (Fe⁺²). Similarly, it takes about 2.5 mg/L of KMnO₄ to remove 1 mg/L of manganese (Mn⁺²).

Softening

The lime-softening process operates normally at a pH in the range 10–11. Contingent removal of iron and manganese occurs within this range. Iron is eliminated in the form of ferrous hydroxide $Fe(OH)_2$, instead of the familiar ferric hydroxide $Fe(OH)_3$ shown in previous reactions.

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, Ca(OH)₂] and soda ash [sodium carbonate, Na₂CO₃].

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 [CaSO₄], calcium chloride [CaCl₂], magnesium chloride [MgCl₂], and magnesium sulfate [MgSO₄]. 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:

$$\begin{array}{cccc} Ca(HCO_3)_2 &+ & Ca(OH)_2 &\rightarrow & 2CaCO_3 \downarrow &+ & 2H_2O \\ calcium & lime & calcium & water \\ bicarbonate & & carbonate \end{array}$$
(C6–16)

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 Eq C6–16, lime reacts with calcium bicarbonate to form calcium carbonate (CaCO₃). Calcium carbonate is relatively insoluble and precipitates.

In Eq C6–17, 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 Eq C6–17 is called for in Eq C6–18. Thus, twice the lime required to remove calcium bicarbonate is necessary to remove magnesium bicarbonate and carbonate. In Eq C6–18, the additional lime reacts with magnesium carbonate to form calcium carbonate [CaCO₃] and 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 noncarbonate calcium compounds, and soda ash together with lime must be added to remove the noncarbonate magnesium compounds.

To remove calcium noncarbonate hardness:

CaSO ₄ calcium sulfate	+	Na ₂ CO ₃ soda ash	\rightarrow	CaCO ₃ ↓ calcium carbonate	+	Na ₂ SO ₄ sodium sulfate	(C6–19)
CaCl ₂ calcium chloride	+	Na ₂ CO ₃ soda ash	\rightarrow	CaCO ₃ ↓ calcium carbonate	+	2NaCl salt	(C6–20)

* Chemistry 7, Chemical Dosage Problems.

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 Eq C6–19 and NaCl in Eq C6–20, are salts and do not cause hardness.

To remove magnesium noncarbonate hardness:

MgCl ₂ magnesium chloride	+	Ca(OH) ₂ lime	\rightarrow	(Mg(OH) ₂ ↓ magnesium hydroxide	+ calo wh	CaCl ₂ cium chloride, ich must also be removed	(C6–21)
CaCl ₂ calcium chloride from Eq C6–2	+ 1	Na ₂ CO ₃ soda ash	\rightarrow	CaCO ₃ ↓ calcium carbonate	+	2NaCl salt	(C6–22)
MgSO ₄ magnesium sulfate	+	Ca(OH) ₂ lime	\rightarrow	(Mg(OH) ₂ ↓ magnesium hydroxide	+ cal wh	CaSO ₄ lcium sulfate, ich must also be removed	(C6–23)
CaSO ₄ calcium sulfate from Eq C6–2:	+ 3	Na ₂ CO ₃ soda ash	\rightarrow	CaCO ₃ ↓ calcium carbonate	+	Na ₂ SO ₄ sodium sulfate	(C6–24)

The removal of magnesium noncarbonate hardness with lime forms calcium noncarbonate 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.

CO_2	+	$Ca(OH)_2$	\rightarrow	CaCO ₃ ↓	+	H_2O	(C6–25)
calcium		lime		calcium		water	
dioxide				carbonate			

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 (CaCO₃), 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:

CaCO ₃ +	$CO_2(g)$	+	H_2O	\rightarrow Ca(HCO ₃) ₂	(C6–26)
calcium	carbon		water	calcium	
carbonate	dioxide			bicarbonate	
(in suspension)	(gas)				

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. This creates a water that is undesirably caustic and high in pH. Carbon dioxide introduced into the water reacts as follows:

$Ca(OH)_2$	+	$CO_2(g)$	\rightarrow CaCO ₃ +	- H ₂ О	(C6–27)
excess		carbon	calcium	water	
lime		dioxide	carbonate		
		(gas)	(precipitate)		

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.

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

Ca(OH) ₂	+	2CO ₂ (g)	\rightarrow Ca(HCO ₃) ₂	(C6–28)
excess		carbon	calcium	
lime		dioxide	bicarbonate	
		(gas)		

^{*} Chemistry 7, Chemical Dosage Problems.