# Iron and Manganese Removal Handbook

Elmer O. Sommerfeld



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Elmer O. Sommerfeld

Prepared for



Saskatchewan Environment and Resource Management



American Water Works Association
*Dedicated to Safe Drinking Water*

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# Preface

This book is an updated version of the Iron and Manganese Removal Workshop Manual originally created in 1984 by the Saskatchewan Environment and Resource Management Department for water treatment plant operators. In the intervening years, major progress has been made in understanding processes for removing iron and manganese from both groundwater and surface water sources. Also, however, much remains to be learned about (1) how other raw-water constituents interfere with typical treatment methods, (2) how those interferences can be readily and easily identified, and (3) how they can be reduced or eliminated in a cost-effective manner (often a problem in very small communities). Other relevant issues include filter and process auditing and pilot testing, which have made major contributions toward rehabilitating existing iron and manganese removal plants, updating removal processes, and inspiring new plant designs.

Although it was developed as a training tool, this handbook will be a useful reference for anyone interested in removing iron and manganese from potable water, as well as the basic operation of water treatment and filtration plants. The handbook was compiled under the direction of the following individuals from the Municipal Branch, Saskatchewan Environment and Resource Management:

Blaine W. Ganong, Manager, Municipal Assessment and Certification Section

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The personal workshop files of Peter Thiele, Supervisor of Municipal Environment Officers, Municipal Branch, Saskatchewan Environment and Resource Management, offered valuable help in compiling the information in this handbook.
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The authors have taken measures to keep the content of this handbook readily understandable by operators of small water treatment systems. Although highly scientific or technical subject matter has been avoided, all basic concepts of iron and manganese removal have been included. Chapters and sections on mathematics, chemistry, physics, microbiology, hydraulics, and hydrology have been included, as any operator should have a basic understanding of these subjects to maintain efficient operation of a water treatment plant.

In practical activities, an operator may need to use metric, Imperial, and US customary units as interchangeable measures. Operating manuals for new package filtration plants manufactured in the United States use US customary units or varying combinations of US and metric units. Technical data sheets issued currently by North America's only manufacturer of manganese greensand (located in New Jersey), show volumes in US gallons, temperatures in degrees Fahrenheit, and pressures in pounds per square inch (psi).

This handbook emphasizes metric units. It shows the currently accepted standard for each area of the industry will be shown in brackets. A table of common conversions is included at the end of the book.

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# Chapter 1
# Introduction

## The Hydrologic Cycle

Hydrology is the science concerned with the distribution of all the earth's waters and their continual movement from oceans and lakes to the atmosphere, from the atmosphere to the land as surface water, and from the land back to the oceans and lakes (see Figure 1-1). Over 97 percent of all the earth's water is contained in the oceans. The remaining 3 percent is distributed among the atmosphere as water vapor; on land as fresh water, ice, and snow; and as groundwater beneath the earth's surface.

Some 75 percent of all fresh water is held by the polar ice caps and glaciers. Most of the fresh water balance lies in aquifers (water-bearing layers of rock, sand, and gravel). A scant one-third of 1 percent of all fresh water is in lakes and rivers, about 20 percent of this world total in the Great Lakes between Canada and the United

*Source:* A Primer on Fresh Water, *Canada, 1994. Reproduced with the permission of Environment Canada, 1999.*

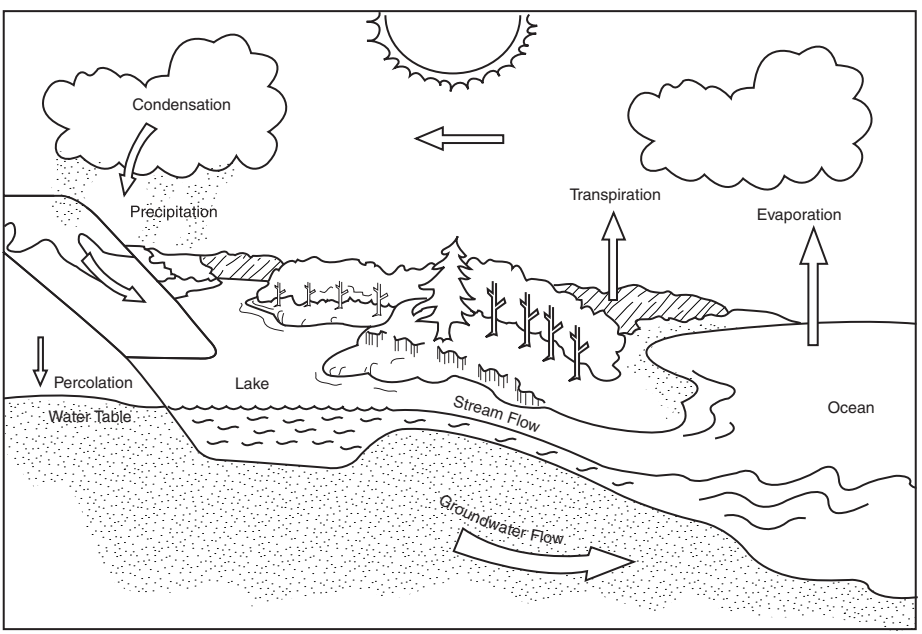



**Figure 1-1** The hydrologic cycle

States. Not all water moves through the hydrologic cycle in the same amount of

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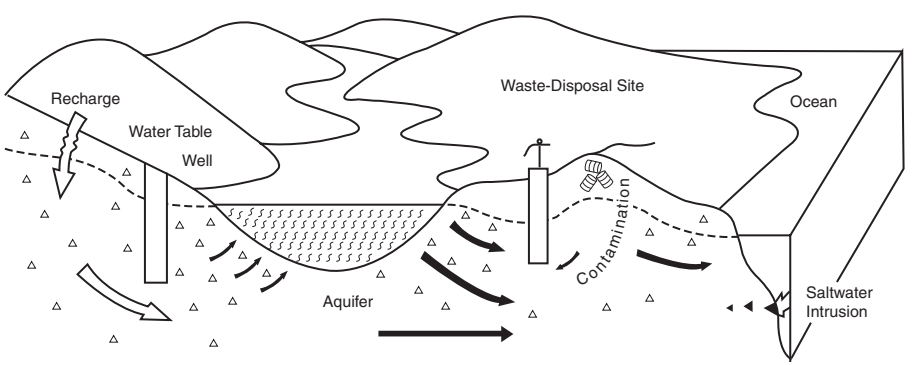
time. Some is evaporated from the oceans, falls as rain on coastal areas, and returns to the oceans within days. Other precipitation takes years to complete the cycle, while still other precipitation never reaches the oceans and lakes, completing its cycle by returning to the atmosphere through evaporation and/or transpiration (movement of water from the soil to the atmosphere through the actions of growing plants).

About 25 percent of the earth's fresh water is stored beneath the planet's surface, where it can spend thousands of years. Of this total, only a small amount is located in easily accessible aquifers that can produce worthwhile volumes of water on an ongoing basis. The important consideration in access to this water, then, is not how much can be drawn from a source, but how quickly the hydrologic cycle can replenish it. Without replenishment, supplies would soon be depleted. Therefore, reservoirs are often constructed to hold adequate supplies for dry seasons, low river flows, and winter months. Good wells, on the other hand, can usually produce reliable, consistent flows day in and day out for years.

Figure 1-2 shows a hypothetical groundwater system. Although water sometimes appears to be at rest, it rarely is. As the figure shows, water is always moving within an aquifer, recharging an aquifer, flowing into a lake, or being contaminated by synthetic products or saltwater. Heavy rainfall, rivers flooding their banks, or drought can all affect raw-water quality in the short term. Often, seemingly small quality changes in raw water significantly affect a treatment or iron (Fe) and manganese (Mn) removal process.

*Source:* A Primer on Fresh Water, *Canada, 1994. Reproduced with the permission of Environment Canada, 1999.*

**Figure 1-2** Groundwater System




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## Iron and Manganese: Nature and Occurrence

These two elements, both relatively abundant in the earth's crust, can cause serious aesthetic problems in potable water systems. If iron were always in the simple form of Fe and manganese were always simple Mn, removal would be a simple process, but such is not the case.

Simple soluble reduced iron is ferrous iron ($Fe^{2+}$), and simple soluble reduced manganese is manganous manganese ($Mn^{2+}$). When oxidized, the iron changes to ferric iron ($Fe^{3+}$), and manganese often (but not always) changes to the insoluble $Mn^{3+}$ or $Mn^{4+}$ forms. These concepts are explained in detail in chapter 2. Both Fe and Mn can form combinations with many other elements and compounds. These other combinations generally do not prevent removal, however, and often they do not inhibit the oxidation/flocculation/sedimentation/filtration process.

Fe and Mn usually occur only in wells and impounded surface supplies (reservoirs). Flowing waters (rivers and streams), even if they normally do not contain significant levels of Fe and Mn, are certain to contain higher levels of these elements and related compounds after being impounded. The amount that goes into solution depends on the character of the soil and the amount of plant life. Decomposition of organic matter (algae, leaves, and other plant material) in the lower sections of a reservoir may result in anaerobic conditions (i.e., near zero oxygen) under which Fe and Mn compounds in those zones are converted to soluble compounds. Groundwaters with intolerable amounts of Fe and Mn contain little or no dissolved oxygen and are often relatively high in carbon dioxide. The absence of dissolved oxygen indicates anaerobic conditions, and high carbon dioxide content suggests extensive bacterial oxidation of organic matter. The presence of hydrogen sulfide is another indicator of the same condition.

Attempts to remove Fe and Mn from impounded surface waters encounter a further challenge at least twice a year in much of North America. Cold water at the top of a reservoir sinks to the bottom, while warmer water at the bottom rises to the top following spring breakup and again just before freeze-up; this sequence is called a water inversion or turnover. The water rising to the top brings with it soluble compounds of Fe and Mn. As wind and wave action mixes oxygen from the air with the water, Fe and Mn are gradually oxidized (an increase in positive valence resulting from the presence of oxygen, as the glossary explains). The oxidized elements precipitate, or separate out of solution. They sink to the bottom again as solids and are brought back into solution where oxygen is absent and carbon dioxide has been formed. While some of the $Mn^{2+}$ is very slowly oxidized in this way, action of certain bacteria causes a much faster rate of oxidation. The scientific name for this process is microbially mediated oxidation. Microbially mediated $Mn^{2+}$ oxidation can make a very important contribution to manganese cycling in a reservoir.

An operator faces the challenge of learning how to read the signs of an inversion and then to adjust the treatment process (usually through a combination of actions,

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such as adding chemicals, shortening filter runs by backwashing more often, etc.) to handle the increased levels of Fe and Mn in the raw water coming into the treatment plant. If time and technology permit, measurements of dissolved oxygen should be taken, and a temperature profile should be developed to assist in identifying stratification. Operating experience helps to position the operator to know just when to prepare for increased levels of Fe and Mn in the raw water. Because these occurrences do not happen at the same time every year, a strong case can be made for historical record keeping. Guided by records showing dissolved oxygen levels, stratification data, weather data, time lapses between events, and dates of events, the operator can respond promptly when the occurrence repeats itself. Gases are usually released as a part of the total water inversion occurrence; however, by the time odors can be detected, Fe and Mn have long ago been released.

During much of the year in temperate climates, water nearest the surface of a reservoir is least likely to contain Fe and Mn. Therefore, the inlet to the water treatment plant feed line should ideally move up and down, so that water can always be taken from a level below surface plant growth, such as algae, but above the zone lacking oxygen.

Amounts of Fe and Mn vary widely across North America, and they can vary widely within a small geographical area, depending on aquifer structure, well depth, surface soils, rock formations, plant types and rates of growth, and many other factors. Some reservoirs accumulate significant amounts of Fe and Mn in short periods of time, while others build up concentrations over many years.

## Effects of Iron and Manganese in Potable Water Systems

The problems resulting from Fe and Mn in potable water addressed in this section are not related to health. Fe and Mn in solution do not commonly rise to amounts considered hazardous to physical well-being in raw-water sources destined for potable use, although some researchers claim that many metals (including manganese) have a negative impact on the body over many years of ingestion.

Instead, these metals cause aesthetic problems. Yellowish to reddish-brown stains result from water containing ferric iron oxides–hydroxides. Manganese-bearing waters with no iron produce dark brown or black stains. Combining the two metals results in stains that range from light brown to black. Initial complaints usually cite stained laundry; later complaints describe brown or dirty water; finally, additional buildup may allow chunks sloughed off in the distribution lines and broken up by the movement of the water to pour from customers' taps.

A treatment and filtration process can control customer complaints of laundry spotting and/or dirty water by producing water with less than 0.3 mg/L iron and less than 0.05 mg/L manganese. Reduction of metals to these levels is not a guarantee the operator will receive no brown-water complaints. Reduction of iron to 0.1 mg/L and manganese to 0.02 mg/L is a positive step, as is maintenance of the dis-

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tribution system in a clean condition. Sporadic complaints or repeated complaints from the same consumer usually result from water heaters that need cleaning, softener beds heavily coated with iron and manganese oxides, and/or overuse of cleaning and laundry products high in chlorine.

Presence of Fe and Mn promote the growth of crenoforms, which are stringy-looking, microscopic organisms. Crenoforms (with scientific names including Crenothrix, Leptothrix, Sphaerotilus, and Gallionella) congregate in piping to form heavy, jelly-like, stringy masses that can impair the hydraulic (water) carrying capacity of an entire system. Allowing the formation of these organisms through inadequate removal of Fe and Mn and inadequate disinfection of filtered water at the water treatment plant is almost sure to result in a substantial cost in time and money to flush and/or swab distribution lines.

According to Cullimore (1993), "It was found during that research phase that 95 percent of the groundwaters tested in Saskatchewan, Canada, were positive for IRB (iron-reducing bacteria). Microscopic examination found that, of the sheathed and stalked IRB, Crenothrix, Leptothrix, Sphaerotilus, and Gallionella were frequently dominant types. Given the universal nature of the presence of IRB it becomes more critical to appreciate their relative aggressivity." For more information on the effects of these and other living creatures on iron and manganese removal, see chapter 4 on microbiology.

Since 1962, the accepted industry standard for maximum allowable limits of Fe and Mn in treated potable water has been 0.3 mg/L (milligrams per litre) iron and 0.05 mg/L manganese. A good general rule, but not a universal one, is to focus on manganese removal, because iron usually falls below 0.3 mg/L when manganese has been reduced below 0.05 mg/L. This tendency was confirmed by a study conducted in 1993 of Fe and Mn removal plants in the province of Alberta, Canada.

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Chapter 2

# Chemistry of Iron and Manganese Removal

This chapter provides an overview of issues related to iron (Fe) and manganese (Mn). The removal of Fe and Mn below targeted levels (i.e., 0.3 mg/L Fe and 0.05 mg/L Mn) can be a difficult objective, because so many factors affect the treatment and removal process. These issues range from other raw-water constituents to flow rates, pH, water temperature, etc. Topics introduced in this section are covered in greater detail in other chapters. If the information presented here is insufficient for your needs, search the index for specific references.

## Water Chemistry

Before iron and manganese can be removed from water by any method, some chemical change must take place. Chemical changes are also usually responsible for any difficulty encountered in removing Fe and Mn.

A treatment plant operator need not memorize the periodic table of the elements, understand atomic structure, or know how to calculate molecular weight, but it is vitally important for an operator to understand some basic changes that take place when certain chemicals come into contact with certain other elements and compounds. For example, the presence of organic carbons, hydrogen sulfide, or ammonia often indicate a potential for interference with Fe and Mn removal processes, thus an operator should have a basic knowledge of organic carbons and ion exchange principles.

A chemical element may be defined as a chemical substance that cannot be broken down into simpler substances by ordinary chemical change. Water, a chemical compound, easily breaks down further into hydrogen and oxygen (which are chemical elements). Hydrogen and oxygen cannot break down into still simpler substances without altering their basic identities.

The smallest part of an element is an atom; it has all the chemical properties of the element in which it exists. Smashing an atom produces new elements of lighter weight and releases a tremendous amount of energy. Atom smashing (fission) is the basis for atomic energy technology.

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## Chemical Symbols, Common Formulae

In the language of chemistry, each element is represented by a symbol. A combination of symbols to characterize a chemical compound is called the formula for that compound. A formula gives all the elements in the chemical compound and the number of atoms of each:

- Symbol for hydrogen: H
- Symbol for oxygen: O
- Formula for water: $H_2O$; the compound water has two atoms of hydrogen combined with 1 atom of oxygen. Note that single atoms are not numbered.
- Symbol for sodium: Na
- Symbol for chlorine: Cl
- Formula for sodium chloride (ordinary table salt): NaCl; the compound has only one atom of each element.
- Symbol for iron: Fe
- Formula for ferric oxide (red rust): $Fe_2O_3$; the compound has two atoms of iron combined with three atoms of oxygen.

## Ionization

Many elements combine with each other on contact. This change can happen slowly, rapidly, or explosively, often under the influence of heat, moisture, or catalytic agents (substances that promote reactions but do not themselves undergo any change during the reactions). Many chemical reactions take place in the presence of water, because water can split some molecules into positively or negatively charged atoms called ions. Naturally, this process is known as ionization. A molecule that produces ions when dissolved in water is said to ionize.

Example: $NaCl \rightarrow Na^+ + Cl^-$. The electrically charged atoms are ions.

Positively charged ions are called cations (pronounced "kat'i'ens"), and negatively charged ions are anions.* The charges must be equal in strength and opposite in sign, otherwise the solution itself would have a charge, which is impossible.

When a molecule ionizes in water, the charges must equalize even when the molecule combines more atoms of one kind than another. For example, $FeCl_3$ (ferric chloride) ionizes like this: $FeCl_3 \rightarrow Fe^{+3} + 3Cl^-$.

Some molecules ionize to yield groups of atoms, consisting of positively charged cations and negatively charged anions. For example, $Na_2SO_4$ (sodium sulfate) ionizes like this: $Na_2SO_4 \rightarrow 2Na^+ + (SO_4)^{-2}$, leaving two sodium cations and one sulfate anion. Combinations of atoms in a unit, such as $(SO_4)^{-2}$ are called radicals.

* These designations are in common use today when referring to the electrical charges carried by polymers, which are used as coagulants and filter aides. To increase their efficiency, many polymers today are either cationic or anionic, and users can specify the strength of the electrical charge each carries.

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## Ion Exchange

A water softener is a common household appliance that removes water hardness, or softens the water, by ion exchange. Hardness is substantially composed of calcium (Ca) and magnesium (Mg). (Note the difference between magnesium and manganese.)

Soap is typically a water-soluble sodium salt of a long-chain organic acid. If the sodium in the soap is exchanged for calcium or magnesium, an insoluble calcium or magnesium soap is formed. Thus, waters high in calcium and/or magnesium are hard to wash with due to the formation of insoluble Ca/Mg soap. That is why the term hardness arose.

So, when calcium and magnesium ions are exchanged for sodium ions, the water is said to be softened. Since each ion has a positive charge, the process is not ionization (as previously described), but ion exchange; a more scientific term would be cation exchange.

Removal of hardness lasts only as long as sodium (Na)* is left on the exchange medium (typically, synthetic zeolite resin beads). Depletion of the sodium requires regeneration of the zeolite bed by passing a strong solution of either salt (NaCl) or potassium chloride (KCl) through it to replace the calcium and magnesium exchanged.

Zeolite softening of potable water has its limitations. The calcium and/or magnesium removed is replaced with sodium. High-sodium water is bad for people with hypertension, however, and poor for plants and lawn watering.

Iron and manganese are removed in a manner similar to this process for calcium and magnesium. Success requires caution to prevent oxidation of iron and manganese ahead of a cation exchange softener, or the precipitates of iron and manganese could foul (or coat) the resin beads.

Ion exchange can also remove all other cations, producing water of almost any quality. By regenerating with hydrogen compounds instead of sodium compounds, cation-free water can be produced. Further, the other ions in the water, anions such as sulfate and chloride, can be replaced by the hydroxyl ion ($OH^-$). In this way, deionized water can be produced, which is ionically the same as distilled water.

## pH Value

Water ionizes to a slight degree, producing both hydrogen and hydroxyl ions, as follows:

$$H_2O \rightleftarrows H^+ + (OH)^-$$

Water may be described as both an acid and a base (alkaline), because it pro-

* In many areas, sodium has been replaced by potassium, so the softened water can be consumed without adverse health effects and without negative effects on natural water and soil environments.

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both hydrogen and hydroxyl ions. Since these ions are present in identical concentrations, however, pure water is neutral—it has no charge. But, when water ionizes, the extent of the ionization depends on the relative concentration of hydrogen and hydroxyl ions. A complicated mathematical formula for this phenomenon produces Table 2-1, which describes the relative acidity or alkalinity of any water sample. The pH scale goes from 0 to 14, neutral water having a pH of 7.

Careful examination of Table 2-1 discloses several important facts:

1. The highest hydrogen ion concentration corresponds to the lowest pH.
2. The lowest hydrogen ion concentration corresponds to the highest pH.
3. Neutrality at pH 7 defines the midpoint in the scale; pH values lower than 7 represent hydrogen ion concentration above neutrality (acidity), and pH values higher than 7 represent hydrogen ion concentration below neutrality (alkalinity).
4. In practice, pH values can fall between whole numbers. For example, one water's pH could be 6.1, another water's pH 6.2, and still another water's pH 9.5.

This variation shows once again the importance of ionization, the major role

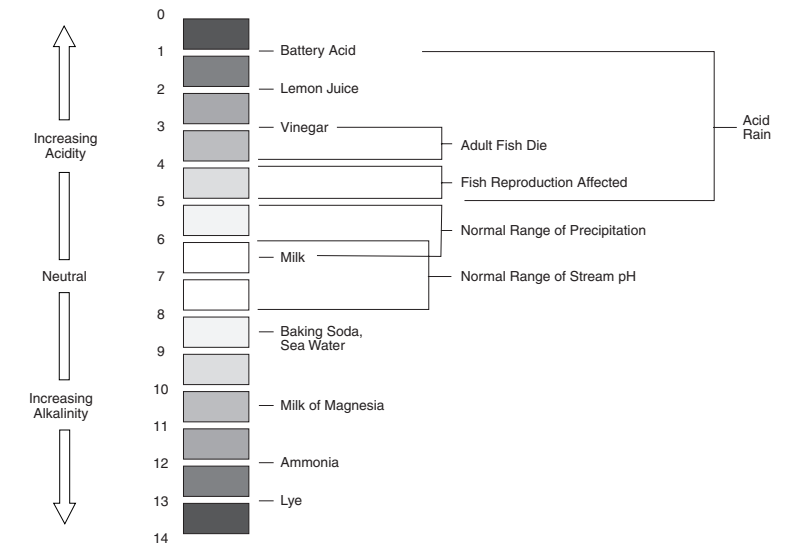
**Table 2-1** Ionization and pH value

| A<br>Grams of $H^+$ ions per litre | B<br>Reciprocal of A | Log B | C<br>(pH) |
|---|---|---|---|
| 1.0 | 1.0 | 0 | |
| 0.1 | 10 | 1 | |
| 0.01 | 100 | 2 | |
| 0.001 | 1,000 | 3 | 0–6: Acid |
| 0.0001 | 10,000 | 4 | |
| 0.00001 | 100,000 | 5 | |
| 0.000001 | 1,000,000 | 6 | |
| 0.0000001 | 10,000,000 | 7 | Neutrality |
| 0.00000001 | 100,000,000 | 8 | |
| 0.000000001 | 1,000,000,000 | 9 | |
| 0.0000000001 | 10,000,000,000 | 10 | |
| 0.00000000001 | 100,000,000,000 | 11 | 8–14: Alkaline |
| 0.000000000001 | 1,000,000,000,000 | 12 | |
| 0.0000000000001 | 10,000,000,000,000 | 13 | |
| 0.00000000000001 | 100,000,000,000,000 | 14 | |

played in chemistry by hydrogen and hydroxyl ions, and the need for an operator

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The acidity of a water sample is measured on a pH scale. This scale ranges from 0 (maximum acidity) to 14 (maximum alkalinity). The middle of the scale, 7, represents the neutral point. The acidity increases from neutral toward 0.

Because the scale is logarithmic, a difference of one unit represents a tenfold change. For example, the acidity of a sample with a pH of 5 is 10 times greater than that of a sample with a pH of 6. A difference of two units, from 6 to 4, would mean that the acidity is 100 times greater, and so on.

Normal rain has a pH of 5.6—slightly acidic because of the carbon dioxide picked up in the earth's atmosphere by the rain.

**Figure 2-1** The pH scale

to know just how acidic or basic (alkaline) a water is.

Figure 2-1 shows the range of the pH scale by identifying values for some common substances. As noted in the figure, "a difference of one pH unit represents a tenfold change." For example, lye with a pH of 13, is 10 times more alkaline than ammonia with a pH of 12. In a water treatment plant, a reading of pH 7 for the raw water and pH 7.5 for the finished water is not just a change of five increments; it would reflect a change from 7 to 35 in equal units. Many chemical reactions are either accelerated or slowed to a crawl by pH adjustments. For example, manganese ($Mn^{+2}$) oxidizes many times more slowly at pH 7 than it does at pH 8.5.

No single finished water pH applies as a standard for all plants. Finished water pH targets should be set by distribution system and consumer issues, including corrosion capabilities. Water with pH 8 may be an answer to a corrosion problem in one plant, while water with pH 7 will do the same in another plant. The Langelier

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Saturation index (LSI) and Aggressive index (AI), discussed in the following section, offer a starting point, but this discussion should not be the final word. An operator concerned about pH is well advised to consult a knowledgeable adviser.

## Langelier and Aggressive Indexes

The Langelier Saturation index (LSI) measures a solution's ability to dissolve or deposit calcium carbonate, and it often serves as an indicator of the corrosivity of water. The index is not related directly to corrosion, but it is related to the formation of deposits of a calcium carbonate film or scale that can insulate pipes, boilers, and other system components from contact with water. This theory assumes even deposits, a situation not likely in the real world. When no protective scale is formed, water is considered to be aggressive, and corrosion can occur. Highly corrosive water can cause system failures or result in health problems from dissolved lead and other heavy metals. On the other hand, too much scale can damage water systems, coat adsorption media (such as manganese greensand and pyrolusite) with scale, or increase the sizes of filter media grains. Media coating is not common in potable water plants (although it occurs from time to time), but scale buildup is regularly seen in industrial boilers.

In developing the LSI, Langelier derived an equation for the pH at which water is saturated with calcium carbonate ($CaCO_3$), assigning this value the symbol $pH_S$. This equation is based on the equilibrium expression for calcium carbonate solubility and bicarbonate dissociation. To improve the approximation of actual conditions, $pH_S$ calculations were modified to include the effects of temperature and ionic strength.

LSI is defined as the difference between actual pH (measured) and the calculated $pH_S$. The magnitude and sign (< or > 0) of the LSI value show a water's tendency to form or dissolve scale and thus inhibit or encourage corrosion.

A water treatment plant operator should exercise great care in applying information developed using the LSI. The Hach Water Analysis Handbook (1992) cautions, "As with L[S]I, the AI [Aggressive index, a similar measure] is not a quantitative measure of corrosion but is a general indicator of the tendency for corrosion to occur and should be used with proper reservation." Neither corrosion nor scale deposition are on–off chemical occurrences of much practical importance, but these processes may interest a plant operator if the water shows a strong tendency.

Current research efforts are examining the basic premises of the Langelier approach. Obtain up-to-date information to resolve any concern about corrosion. Although information obtained from the LSI is not quantitative, it can give useful estimates of water treatment requirements, and it can serve as a general indicator of the corrosivity of water.

The formula and necessary tables of values are included in the Hach Water Analysis Handbook (1992). Several other chemistry handbooks also contain the formula and tables. The calculation requires the following values as input: water

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temperature in °C, total dissolved solids (TDS) in mg/L, calcium hardness, total alkalinity in mg/L $CaCO_3$, and actual pH.

## Chemical Forms of Iron and Manganese

Iron in its simplest soluble form, the form most often encountered in raw well water or raw impounded water, is ferrous iron. Manganese in it simplest soluble form is manganous manganese. Both have a valence (explained in the next section) of 2, i.e., $Fe^{2+}$ and $Mn^{2+}$.

Fe and Mn in surface water are no different chemically from Fe and Mn in water from a well source. Local rain runoff into an impoundment (earthen reservoir) leaches Fe and Mn as it flows toward the impoundment; river water pumped or diverted into an impoundment carries trace amounts of Fe and Mn. Over time, levels of Fe and Mn build up on the bottom of the impoundment. Where inversions take place, as described in chapter 1, both Fe and Mn cycle from bottom to top and back to the bottom again.

Many treatment plants that draw from surface sources do not key on Fe and Mn removal, so they live with some residual levels during periods of impoundment inversions, usually for only several days twice a year. Surface water treatment plants that use lime softening have no difficulty in removing Fe and Mn; an efficient conventional plant (i.e., a coagulation/sedimentation/filtration plant) can usually remove Fe easily if a preoxidation process precedes filtration. Manganese removal is sometimes a challenge for conventional surface-water treatment plants, however. For example, Fe and Mn complexed by low-molecular-weight organics that may not be coagulated (as described later in this chapter) would pass right through a granular media filter. A discussion of molecular weights is too advanced for this handbook, but this possibility emphasizes that the location of the raw-water intake is critical in the control of Fe and Mn levels; an intake too close to the bottom of the impoundment collects high levels of Fe and Mn, while an intake too close to the surface collects high levels of algae.

Some Fe and Mn removal plants draw raw water from both wells and impoundments. Seasonal changes in Fe and Mn levels require additional monitoring and process adjustments.

### Understanding Valence Numbers

Valence, touched upon earlier in the chapter, is the number of electrons that an atom or radical can lose, gain, or share with other atoms or radicals. Valence has the same meaning as combining power. One may say it is the relative worth of an atom of an element in combining with the atoms of other elements to form compounds. A positive or negative whole number ranging from 0 to 7 expresses the valence of an atom or radical.

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If an atom loses electrons from its outermost shell, it has a positive valence. If an atom loses one electron from its outermost shell, it is said to have a valence of 1; similarly, if an atom loses two electrons from its outermost shell, it is said to have a valence of 2. If the outermost shell gains electrons, the atom has a negative valence. An atom that gains one electron has a valence of –1; one that gains two electrons has a valence of –2, and so on.

The manganese in $MnO_2$(s), such as pyrolusite and the artificial coating on manganese greensand, has a valence of 4, expressed as $Mn^{4+}$. The manganese in potassium permanganate ($KMnO_4$) has a 7 valence, expressed as $Mn^{7+}$. In forming the chemical compound $KMnO_4$, the manganese atom lost (or gave up) seven electrons.

An element's valence number states the number of electrons of the element associated with formation of a particular compound. Since this number may differ for different compounds of an element, it follows that any element may have more than one valence number. For example, iron combines with oxygen to form two different compounds: FeO, a black oxide, and $Fe_2O_3$, a red oxide composed of two atoms of iron and three atoms of oxygen. The red oxide is commonly referred to as rust. The black oxide is frequently observed in water plants, particularly underneath the scale of corroded pipe. Iron also forms many compounds with other elements in which it may have a valence number of 2 or 3.

The reasons for some facts of chemical life are unknown. Manganese can have valence numbers 2, 3, 4, 6, and 7:

- $Mn^0$ is manganese metal.
- $Mn^{2+}$, pale pink in color, is the manganous ion $Mn^{+2}$.
- $Mn^{3+}$, red–violet in color, is the manganic ion $Mn^{+3}$.
- $Mn^{4+}$, brown–black in color, is the valence of the Mn in solid pyrolusite, $MnO_2$(s).
- $Mn^{6+}$, dark bottle-green in color, is the manganate ion in $MnO_4^{2-}$.
- $Mn^{7+}$, intense purple in color, is the permanganate ion in $MnO_4$ (as in $KMnO_4$).

Why manganese can't have a 5 valence is a puzzler.

## Compounds of Fe and Mn

Some waters contain many Fe and Mn compounds. The following compounds are sometimes found in groundwaters, although Fe and Mn compounds don't usually prevent removal of the metals: Fe and Mn hydroxides, $Fe(OH)_2$ and $Mn(OH)_2$; Fe and Mn bicarbonates, $Fe(HCO_3)_2$ and $Mn(HCO_3)_2$; Fe and Mn sulfates, $FeSO_4$ and $MnSO_4$; and others.

It is difficult to establish whether or not the Fe and Mn in a raw water is organically bound, as described later in the chapter, and, if so, in what percentage. Determination of organic complexing in a specific water is often just speculation. If organic carbons are found in the water to be treated, but Fe and Mn can be

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removed to low levels, then the levels of organic carbons do not affect the removal process and are of no concern, except as they may contribute to potential trihalomethane (THM) formation. However, difficulty in removing Fe and Mn to low levels using the preoxidation/sedimentation/filtration process suggests a need for investigation. The presence of more than 2.0 to 2.5 mg/L organic carbons and/or hydrogen sulfide and/or ammonia is sufficient reason to conduct a pilot study to determine the process needed to yield water meeting quality requirements.

## Oxidation of Fe and Mn

The three most common forms of water treatment oxidants are oxygen (from the air), chlorine, and potassium permanganate. Other oxidants in use today include ozone, chlorine dioxide, ultraviolet light, and hydrogen peroxide. All have legitimate applications.

Iron in solution, as mentioned earlier, is known as ferrous iron, $Fe^{2+}$. Following oxidation it is ferric iron, $Fe^{3+}$. Manganese in solution is known as manganous manganese, $Mn^{2+}$. Following oxidation, it is manganic manganese, $Mn^{4+}$, although it may also take the form $Mn^{3+}$.

Oxidized Fe and Mn most often form iron hydroxide and manganic dioxide. Iron hydroxide can form a relatively large, sticky floc, which is very visible and easy to filter out of treated water. A coarse coal layer is often sufficient to filter out the iron hydroxide, though this is not true in every case. Some oxidized Fe precipitates require the addition of a polymer before removal. Manganic dioxide forms a far finer floc, so fine at times that a granular media filter will not remove it. The sticky iron hydroxide often traps or sticks to some of the oxidized manganese and aids in its removal.

## Background on Organic Chemistry

This field is the specific branch of chemistry concerned with compounds of carbon. Carbon is unique among all other elements, not only because of its great reactivity, but also because of its ability to combine with itself in various ways to form a very large number of compounds. Many thousands of carbon compounds are known, and more are being discovered. The possibilities seem endless, especially as chemists design synthetic compounds for special purposes. All plant and animal tissue is composed of numerous carbon atoms in combination chiefly with hydrogen and oxygen and less commonly with nitrogen, phosphorus, sulfur, and metals.

Not all carbon compounds, by any means, are good for people, though. For example, some by-products resulting from combinations of chlorine and organic carbons are known as trihalomethanes, or THMs. Under laboratory conditions, THMs have caused cancer in animals. Trihalomethanes are therefore known as carcinogens. Obviously, every water treatment plant operator should recognize the dangers of producing chemical by-products harmful to humans. The old anaes-

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thetic, chloroform, is trichloromethane ($CHCl_3$), one member of the THM grouping of undesirable by-products.

Carbon has a valence of +4. To understand this characteristic, picture the carbon atom as having four hooks. A hydrogen atom has one hook, oxygen has two hooks, nitrogen has three hooks, ferrous iron has two hooks, and ferric iron has three hooks. The concept gets more complicated with some other elements, like manganese, which has two-, three-, four, six-, and seven-hook variations. The "hooks" are called bonds or valence, as explained earlier in the chapter.

## Organic Complexing of Fe and Mn

The whole question of organic complexing of Fe and Mn is difficult to address in a meaningful way for a small-plant operator. Studies of Fe and Mn organic complexing are few, no service offers on-site determination of organic complexing, and few laboratories are capable of identifying and quantifying troublesome organic acids. Still, recurring phenomena may display almost identical early warning signs, indicating at the very least the presence of organic compounds. Such a condition suggests a need to depart from preoxidation/sedimentation/filtration processes.

Experience with trouble calls from operators experiencing difficulty in removing Fe and Mn (especially manganese) below targeted levels has uncovered some common factors:

1. Well water is being drawn from shallow wells adjacent to flowing water, lakes, or sloughs.
2. A level of organic carbons over 2 mg/L is identified.
3. Some level of ammonia is quantified.
4. Some level of hydrogen sulfide is detected.

If the preoxidation/sedimentation/filtration process cannot remove Fe and Mn below target levels in a situation marked by these four warning flags, perhaps they can be removed to acceptable levels by treating them as organically complexed. If so, what practical need does an operator have to determine whether or not organic complexing is established beyond a shadow of a doubt? Also, does the operator need to know why the Fe and Mn are in a colloidal state or go to a colloidal state when an oxidant is applied? Few people would demand these explanations.

A treatment plant operator is expected to find a practical, safe, effective, affordable way of meeting Fe and Mn removal objectives. At the same time, the operator should have some knowledge of organic chemistry to allow identification of certain characteristics of the raw water being treated, without expending great amounts of time and money conducting exhaustive scientific determinations. At the very least, an operator needs to know the information presented in this section.

The most troublesome of organic compounds in Fe and Mn removal processes are the organic acids, which contain one or more carboxylic groups (COOH). In this carboxyl group, the hydrogen (H) is "active," i.e., it will ionize slightly to give acidic

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$H^+$ ions. More importantly, the active hydrogen will exchange for ions such as calcium, magnesium, sodium, iron, manganese, nickel, etc., exactly as occurs in zeolite softening. The common, naturally occurring organics encountered in water result from decomposition of organic materials (e.g., plants, leaves, and algae). A common organic compound is humic acid, which has the approximate formula:

$$C_{140}H_{126}O_5(COOH)_{17}(OH)_7(CO)_{10}OCH_3$$

Chemists have defined no exact formula for this acid. A molecule of humic acid contains about 17 carboxylic groups, so it shares some characteristics with a water-soluble, ion exchange resin.

Some ion exchange "zeolites," or more accurately resins, are water insoluble and contain thousands of carboxylic sites. Called weak acid cation exchange resins, they are used widely in the water industry.

Anionic polymers also contain the carboxyl as their active sites. As H ionizes to $H^+$, the rest of the carboxyl group has a negative charge.

This discussion relates to Fe and Mn removal because hydrogen of the carboxyl group will exchange with $Fe^{+2}$ and $Mn^{+2}$ ions, each of these soluble, two-valent ions exchanging with two hydrogens. This process is commonly described as organic binding or complexing.

An attempt to oxidize the bound $Fe^{+2}$ or $Mn^{+2}$ may or may not succeed. If oxidation occurs, creating insoluble ferric iron ($Fe^{+3}$) or changing $Mn^{+2}$ to insoluble $Mn^{+3}$ or $Mn^{+4}$, the iron or manganese may still be held by the ion exchange bonding. In such a case, the process may yield complexed, oxidized Fe/Mn forming a tiny organics/Fe/Mn clump or colloid, which carries an overall negative charge and is very difficult to remove, as it does not settle and passes through filters. A nonionic or anionic polymer may help to agglomerate colloids to form units large enough to settle out or become trapped in filters. Organic complexing can result from ion exchange, although not all chemical binding works this way.

Attempts to identify precisely the organics present in a raw water require extremely difficult and costly methods seldom justifiable as a routine control measure. Instead, operators monitor total organic carbon (TOC) as an indicator to warn of a potential for organic complexing. Total organic carbon levels greater than 2.0 to 2.5 mg/L indicate a potential removal problem using the preoxidation/direct filtration process.

In carbon compounds, hydrogen ions may have been exchanged for iron ions, creating difficulties in oxidizing the iron. When iron can be oxidized, it still may remain bound to its host carbon rather than agglomerating with other oxidized iron ions to form a particle big enough to be removed by conventional granular filters (i.e., the particles remain very fine or colloidal in size). Knocke et al. (1990, pp. 3, 5) reported:

> In many surface waters, a significant amount of the iron exists in a complexed form with organic matter. This complexation effect has been noted for decades; for example, Weston (1909) observed that certain

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waters containing organic matter were able to hold iron in solution for indefinite periods of time after aeration. Weston believed that organic compounds were involved in an attachment with the iron that prevented subsequent iron precipitation.

The impact of such complexation of iron oxidation by organic matter has been reported by several authors. For example, Hem (1960) demonstrated that tannic acid had the ability to form complexes with ferrous iron and significantly retard its subsequent oxidation by oxygen. Jobin and Ghosh (1972) showed that both humic acids and tannic acids have the ability to complex iron and retard its oxidation upon exposure to $O_2$(aq), allowing essentially no iron oxidation to take place.

Theis and Singer (1973, 1974) presented excellent research results aimed at elucidating the ability of various organic compounds to complex iron and retard its removal by contact with $O_2$(aq). The authors showed that tannic acid, gallic acid, pyrogallol, and other products of natural vegetative decay can effectively retard the oxidation of Fe(II) for several days, even in waters saturated with $O_2$(aq).

Fe and Mn that are organically complexed can usually be oxidized using chlorine or $KMnO_4$, given the appropriate dosage, pH, and detention time. Organically complexed iron can sometimes be oxidized by oxygen from simple aeration. In this state, its size is usually very fine or colloidal, so it is too small to be removed by a granular media filter. One removal option is to neutralize the surface charge using coagulants like alum, iron salts, poly aluminum compounds, or cationic polymers, followed by settling and/or direct filtration.

Oxidized Fe and Mn species not organically complexed, and their compounds, can remain colloidal following oxidation. Again, the removal method described in the last paragraph is one option. In some cases, however, the raw water contains elements and compounds that interfere with the action of certain coagulants.

Although every treatment plant operator should display scientific curiosity, the complexation of manganese (or lack of it) is well beyond the research capabilities of operators with limited training and inadequate laboratory equipment. Priorities focus, not on confirming manganese/organic complexing, but on finding the process that will remove the manganese. Analysis should determine how the raw-water manganese behaves, but scientific terminology for defining that behavior is not important to the operator. With these limitations in mind, one basis for organic complexing is ion exchange.

## Adsorption Removal Methods

In most cases, an adsorption process works well for the removal of manganese. For optimum chemical cost and simplicity of operations, use of the adsorption process often makes the most sense, especially in small plants. Pyrolusite, manganese greensand, or any medium coated with $MnO_2$(s) has the capacity to adsorb $Mn^{2+}$.

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Regeneration is accomplished by exposing the medium to a chlorine solution or a solution containing $KMnO_4$. The amount of regenerant can be calculated based on the volume of water treated, amount of Fe and Mn in the raw water (milligrams per litre), and theoretical oxidant demand.

The major risk in using an adsorption process to remove iron results from gradual coating of the $MnO_2(s)$ surfaces with oxidized iron, which can result in media blinding. To prevent or minimize this problem, a pilot test is usually undertaken to evaluate a system to oxidize the iron and remove it by filtration in a top coal layer. The Mn is then removed by adsorption. Iron oxidation/filtration combined with manganese adsorption is a dual process practiced successfully in many small plants.

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# Chapter 3
# Physics and Mathematics of Iron and Manganese Removal

## Hydraulics and Applicable Water Physics

Hydraulics is the name given to the branch of science concerned with fluids at rest and in motion. Hydrostatics refers to fluids at rest, and hydrodynamics refers to fluids in motion. The fluid dealt with in this handbook is water, but many of the same principles apply to air and individual gases.

Quantitative descriptions of hydraulic events can become very complicated, using many coefficients, rates, mathematical descriptions of friction, flow curves, and diverse other factors. This part of the discussion will cover only the basics of hydraulic heads and the effects of heads and pressure differentials on certain granular filter media.

### Types of Heads

Head is the amount of energy exerted by a unit quantity of water at its given location. Ordinarily, the energy is expressed in metre-kilograms (m-kg)(pound feet), and the unit quantity of water considered is 1 kg (2.2 lb). The head, then, is expressed in metre-kilograms of energy per kilogram of water, or

$$\frac{m \times kg}{kg} = m \qquad (3\text{-}1)$$

For this reason, all heads can be expressed in metres. Energy in water can result from its elevation, pressure, or velocity. These energies are called static (elevation) head, pressure head, and velocity head. Other heads are pump head, which equals the metre-kilograms of energy given to each kilogram of water passing through a pump, and friction head, which is the energy lost due to friction within the fluid and against the walls of a pipe or channel.

Static (or elevation) head. Elevations are expressed as the vertical distance from some base level (known point or reference plane), such as sea level, the surface of the ground, the bottom of a filter, or some other arbitrarily chosen level. See Figure 3-1.



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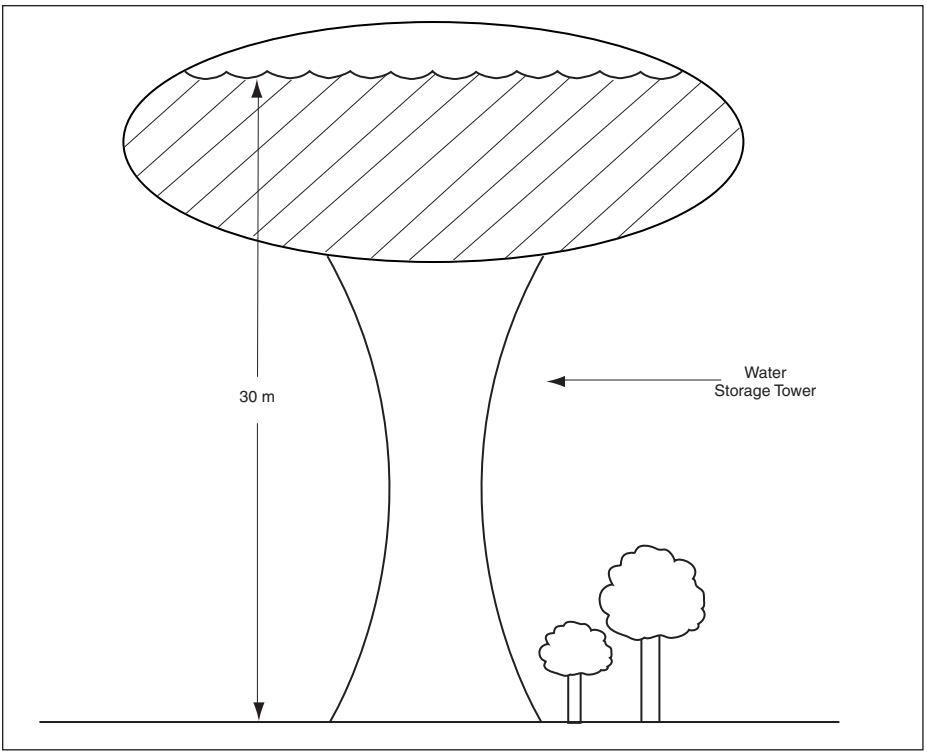



**Figure 3-1** Static head

For example, water that is 3 m (9.8 ft) above the bottom of a filter exerts 3 m-kg of energy, and its static (or elevation) head is 3 m (9.8 ft).

Pressure head. Pressures are expressed in terms of force per unit area, such as kilopascals (kPa) or pounds per square inch (psi). So, 1 kPa is the unit of force that will give a mass of 1 kg of water an acceleration of 1 metre per second per second ($m/s^2$). If water could be piled up to exert a pressure of 10 kPa (1.5 psi), the pressure head would be l m, since all heads can be expressed in metres.

Conversion. Some common conversion formulas follow; refer to appendix A for other conversions.

- To convert psi to kPa, multiply psi by 6.895.
- To convert kPa to psi, multiply kPa by 0.14504.
- To convert $lb/ft^2$ (pounds per square foot) to kPa, multiply $lb/ft^2$ by 0.0479.

## Pressure Differential and Head Loss

Many plants remove Fe and Mn using pressure filters with manganese greensand as the principle filtering medium. Manganese greensand is a glauconite sand coated with manganese dioxide, $MnO_2(s)$. At pressure differentials exceeding 55.2

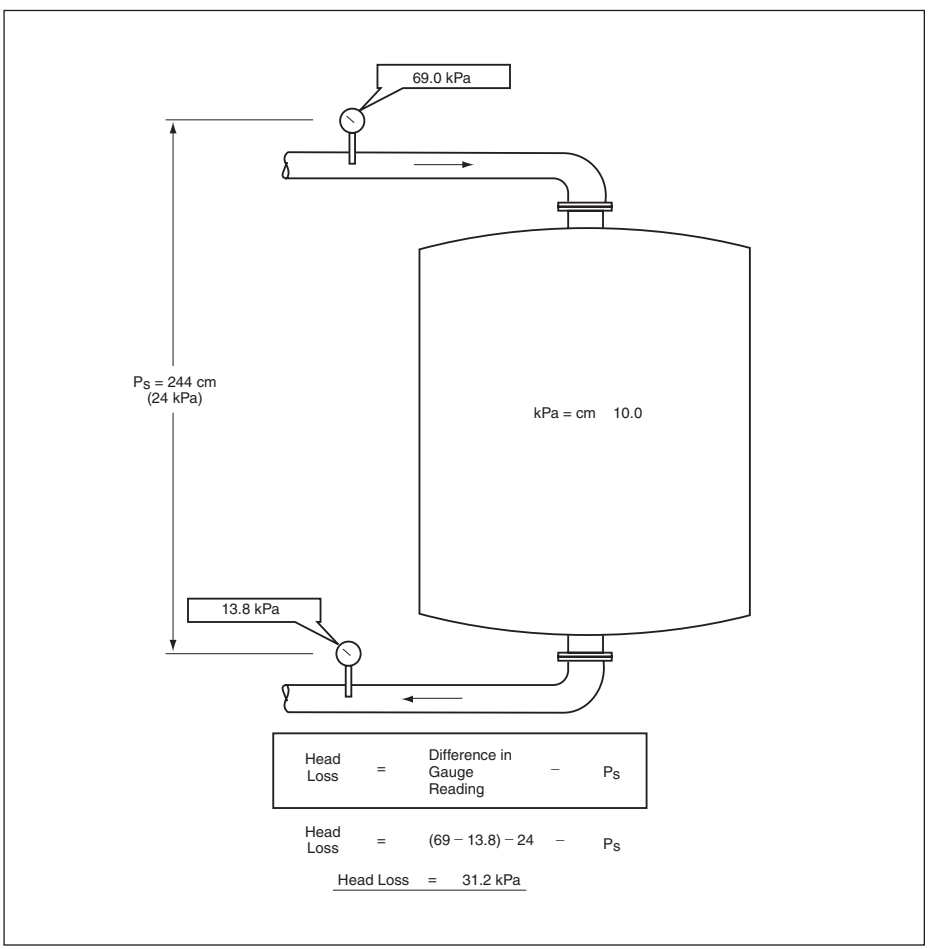
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kPa (8 psi) the $MnO_2$(s) coating can undergo fracturing that could reduce the medium's adsorptive/exchange capacity for Fe and Mn. Repeated exposure to pressure differentials exceeding 55.2 kPa (8 psi) could also result in the breakdown of some of the base glauconite particles.

Figure 3-2 shows the top gauge reading 69.0 kPa (10 psi) and the bottom gauge reading 13.8 kPa (2 psi). The pressure drop (or differential), therefore, is 55.2 kPa (8 psi).

Applying the information on static and pressure head presented earlier to Figure 3-2, the distance from the top gauge to the bottom gauge equals 244 cm (8 ft). The static head is 244 cm, or 2.44 m (8 ft), but the pressure head, referred to as $P_s$, is 244 (8) divided by 10 (2.3), as calculated earlier, or 24 kPa (3.5 psi).




*Source: Antratech Western Inc.*

**Figure 3-2** Head loss example

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The formula for calculating head loss in kPa is:

$$\begin{aligned} \text{head loss} &= \text{difference in gauge readings minus } P_s \\ &= (69 - 13.8)\ \text{kPa} - 24\ \text{kPa} \\ &= 55.2 - 24 \\ &= 31.2\ \text{kPa} \end{aligned} \qquad (3\text{-}2)$$

Manganese greensand performs in the same way regardless of the source of pressure. If a filter bed is plugged with particles (manganese, iron, silt, fines, etc.), pressure builds up regardless of the type of filter (closed pressure filter or open gravity filter). If the pressure differential builds to a point that it exceeds the strength of the particles, the glauconite and its $MnO_2$(s) coating could be fractured, eliminating some $MnO_2$(s) coating and ultimately reducing the bed's adsorptive capacity. The manufacturer of manganese greensand specifies a maximum pressure differential of 69 kPa (10 psi); some authors of this book have observed particle/coating fracturing at 55 kPa (8 psi). Although documentation of this phenomenon could not be found, the operator is well-advised to heed these maximum pressure differential figures.

Figure 3-2 can be a very misleading introduction to head loss. The formula and calculation are correct, assuming that no water is flowing. However, if water were flowing through the lines and filter, depending on the amount of resistance of the filter bed and the underdrain, the static head (shown as $P_s$) might be only 60 to 120 cm (24 to 48 in.), a calculation best left to someone familiar with the process. Many other factors can affect an actual head loss calculation. If a pump located in the effluent line is actually pulling water through the filter, that's another factor to consider, and results could vary with others.

In many water treatment plants (WTPs), automatic devices trigger backwash cycles based on head loss. A number of different devices can be used for this purpose, but how does information about head loss help a plant operator? The operator simply needs to recognize the big difference between head loss and pressure differential. Head loss is very important to a plant designer, while pressure differential is important to the operator. If, for example, an operator sees a pressure differential near 55 kPa (8 psi) on a manganese greensand filter, this condition can signal the need for a backwash, regardless of any other sensing equipment on the filter.

## Flow Rates

Flow rates can be expressed in metres per hour (m/h); in filtration, m/h is actually an expression for cubic metres per square metre per hour ($m^3/m^2/h$).

Most often, flow rates for both filtration and backwash are expressed in gallons per minute per square foot ($gpm/ft^2$). In this system, a filtration flow rate of 2–3 $gpm/ft^2$ is considered appropriate for a manganese greensand pressure or gravity filter. Greensand backwashing requires 10–12 $gpm/ft^2$ depending on water temperature. To convert $gpm/ft^2$ to m/h, multiply $gpm/ft^2$ by 2.4476.

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Water treatment plant gauges often record mixtures of pounds per square inch, feet of water, and kilopascals. Training manuals and reference books use either US customary measurements or a combination of customary and metric units. For practical functioning, an operator should keep a metric converter pocket calculator handy, along with the common conversion factor tables at the back of this handbook.

# Mathematics

## Calculating Chemical Dosages

Optimum chemical dosages can critically affect any Fe and Mn removal process. As an example, manganous manganese is the simplest form of soluble reduced manganese; its symbol is $Mn^{2+}$. When fully oxidized, it changes to manganic manganese, with the symbol $Mn^{4+}$. In order to reach that 4+ valence, each mg/L of manganese requires 1.3 mg/L of chlorine (in the form of hypochlorous acid, HOCl), or 1.92 mg/L of potassium permanganate ($KMnO_4$). Actual chemical oxidant demand of a raw water often exceeds the theoretical demand for treatment of Fe and Mn alone, because other constituents, such as organic carbons and ammonia, contribute to oxidant demand, as well.

The most commonly used oxidants in water treatment applications include

- air (atmospheric oxygen) as $O_2$ aq (meaning oxygen in a water solution, or aqueous oxygen)
- ozone as $O_3$ aq
- chlorine ($Cl_2$) in the form of hypochlorous acid as HOCl
- chlorine dioxide as $ClO_2$
- potassium permanganate as $KMnO_4$

Table 3-1 details the reactions that result.

The amount of chemical required depends on the actual form and strength of the product used. For example, chlorine gas is 100 percent chlorine, calcium hypochlorite is 65% available chlorine, and commercial sodium hypochlorite is 12 percent available chlorine. (Ordinary household bleach is about 5–6 percent available chlorine.) Available chlorine in calcium and sodium hypochlorite is taken as the percentage of OCl present. Depending on the brand name, potassium permanganate is 97–99 percent strength. Potassium permanganate normally comes as solid crystals, calcium hypochlorite in granular or pellet form, and sodium hypochlorite in liquid form. Both solid products require mixing with water to make a solution, which is then fed into the process flow. Sodium hypochlorite liquid can be fed neat (i.e., full strength as it comes from the supplier) or diluted with water.

Caution: When preparing solutions of water and sodium hypochlorite, the two-tank method should always be used to avoid the potential for plugging chemical pumps or chemical feed lines with precipitates. Following batch mixing, the solu-

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**Table 3-1** Theoretical reaction stoichiometry, $Fe^{2+}$ and $Mn^{2+}$

| Metal/Oxidant | Reaction | Stoichiometry mg/L Oxidant Versus Metal |
|---|---|---|
| Iron | | |
| $O_2$ (aq) | $2Fe^{2+} + {}^1/_2O_2 + 5H_2O \rightarrow 2Fe(OH)_3(s) + 4H^+$ | 0.14 mg : 1 mg Fe |
| $O_3$ (aq) | $2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3(s) + O_2 + 4H^+$ | 0.43 mg : 1 mg Fe |
| HOCl | $2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_3(s) + Cl^- 5H^+$ | 0.64 mg : 1 mg Fe |
| $KMnO_4$ | $3Fe^{2+} + MnO_4 + 7H_2O \rightarrow 3Fe(OH)_3(s) + MnO_2 + 5H^+$ | 0.94 mg : 1 mg Fe |
| $ClO_2$ | $5Fe^{2+} + ClO_2 + 13H_2O \rightarrow 5Fe(OH)_3(s) + Cl^- + 11H^+$ | 0.24 mg : 1 mg Fe |
| Manganese | | |
| $O_2$ (aq) | $Mn^{2+} + {}^1/_2O_2 + H_2O \rightarrow MnO_2(s) + 2H^+$ | 0.29 mg : 1 mg Mn |
| $O_3$ (aq) | $Mn^{2+} + O_3 + H_2O \rightarrow MnO_2(s) + O_2 + 2H^+$ | 0.88 mg : 1 mg Mn |
| HOCl | $Mn^{2+} + HOCl + H_2O \rightarrow MnO_2(s) + Cl^- + 3H^+$ | 1.30 mg : 1 mg Mn |
| $KMnO_4$ | $3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$ | 1.92 mg : 1 mg Mn |
| $ClO_2$ | $Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow MnO_2(s) + 2ClO^{2-} + 4H^+$ | 2.45 mg : 1 mg Mn |

tion should be allowed to settle and stabilize. The stable solution should then be drawn off into a second container into which the chemical pump's suction end is placed.

The combination of water and sodium hypochlorite forms caustic, which reacts chemically with calcium and magnesium, producing softened water and precipitates. The volume of precipitates can be substantial enough to be a very bothersome problem. The choice whether or not to use treated water from the clear well in making the solutions doesn't matter much when comparing hardness that may reach 400 mg/L to 2–5 mg/L iron and less than 1 mg/L manganese.

Depending on the quantity of solution required daily and the chemical used to make it, solution strengths typically range from 0.5 to 4 percent. Potassium permanganate does not dissolve easily or rapidly in cold water, so solution strengths should not exceed 4 percent when using cold water (see Figure 5-2 later in the handbook). Also, the mixer should run for 30 minutes or more.

Solution strength in percentage is equivalent to the weight of the chemical divided by the weight of the water in which it is mixed, assuming the chemical product is made up 100 percent of the active ingredient. If not, the following formula is used: (3-3)

$$\text{percentage solution strength} = \frac{\text{weight of chemical added} \times \text{percentage available active ingredient}}{\text{weight of water in solution}}$$

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Using Eq 3-3, find the solution strength produced by adding 1,000 grams of $KMnO_4$ to 50 L of water.

$$\text{percentage solution strength} = \frac{\text{1,000 g } KMnO_4 \text{ x 99 percent}^*}{\text{50,000 g (same as mL) water}}$$

$$\text{solution strength} = 1.98 \text{ percent}$$

Equivalents:

- When weighing water in metric units, 1 L = 1,000 g
- In Imperial units, 1 gal = 10 lb
- In US customary units, 1 gal = 8.34 lb

(3-4)

To make a solution of a specified strength, calculate the weight of the chemical required as:

$$\text{weight of chemical} = \frac{\text{percentage strength x weight of water}}{\text{percentage active ingredient}}$$

Example 1: To prepare 75 L of 2 percent $KMnO_4$ solution, the calculation is:

$$KMnO_4 = \frac{2\% \times 75 \times 1{,}000}{99\%^\dagger}$$

$$= 1{,}515 \text{ g} = 1.52 \text{ kg}$$

Example 2: To prepare 45 Imperial gal of 3 percent $KMnO_4$ solution, the calculation is:

$$KMnO_4 = \frac{3 \times 45 \times 10}{99\%}$$

$$= 13.64 \text{ lb, or } 13 \text{ lb } 10 \text{ oz}$$

The information needed to calculate the amount of chemical required includes the desired concentration, the amount of water to be treated, and the solution strength of the chemical product. The formulas in the remainder of this chapter are used for various dosage and concentration calculations.

(3-5)

## 1. Dosage: How Much Chemical Is Needed?

*Potassium permanganate active ingredient expressed as a percentage.

†The $KMnO_4$ product has 99 percent active ingredient in this example.

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$$\text{weight of chemical} = \frac{\text{dosage (in mg/L)} \times \text{weight of water treated} \times 100\%}{1{,}000{,}000 \times \text{percentage active ingredient}} \quad (3\text{-}6)$$

Same formula in metric units:

$$\text{grams of chemical} = \frac{\text{dosage (in mg/L)} \times \text{litres treated} \times 1{,}000 \times 100\%}{1{,}000{,}000 \times \text{percentage active ingredient}} \quad (3\text{-}7)$$

Same formula in Imperial units:

$$\text{pounds of chemical} = \frac{\text{dosage (in mg/L)} \times \text{gallons treated} \times 10 \times 100\%}{1{,}000{,}000 \times \text{percentage active ingredient}} \quad (3\text{-}8)$$

To calculate the volume of a treatment solution, use the following formula for both metric and Imperial units:

$$\text{volume of solution} = \frac{\text{weight of chemical required} \times \text{percentage active ingredient}}{\text{percentage solution strength} \times \text{weight of water (litres or gallons)}} \quad (3\text{-}9)$$

## 2. Dosage: How Many Milligrams per Litre Need to Be Fed?

$$\text{dosage (in mg/L)} = \frac{\text{weight of chemical used} \times 1{,}000{,}000 \times \text{percentage active ingredient}}{\text{weight of water treated} \times 100\%} \quad (3\text{-}10)$$

Same formula in metric units:

$$\text{dosage (in mg/L)} = \frac{\text{grams of chemical used} \times 1{,}000{,}000 \times \text{percentage active ingredient}}{\text{litres treated} \times 1{,}000 \times 100\%} \quad (3\text{-}11)$$

For solutions:

dosage percentage litres of

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$$\text{(in mg/L)} = \frac{\text{solution strength x solution used x 1,000,000}}{\text{litres treated x 100\%}}$$

Same formula in Imperial units: (3-12)

$$\text{dosage (in mg/L)} = \frac{\text{pounds of chemical used x 1,000,000 x percentage active ingredient}}{\text{gallons treated x 10 x 100\%}}$$

For solutions: (3-13)

$$\text{dosage (in mg/L)} = \frac{\text{percentage solution strength x gallons of solution used x 1,000,000}}{\text{gallons treated x 100\%}}$$

Example Dosage Calculations: Metric

Assumptions:

Treatment handles 450,000 L per day.
Chlorine demand is 7.5 mg/L.
Potassium permanganate demand is 1.5 mg/L.
Actual daily usage is 92 L of 3.5 percent calcium hypochlorite solution, and 33 L of 1.75 percent $KMnO_4$ solution.

Questions:

1. How much sodium hypochlorite is needed each day?
2. How much potassium permanganate is needed each day?
3. If calcium hypochlorite is mixed to a 3.5 percent chlorine solution, how much would be used in a day?
4. If potassium permanganate is mixed to a 1.75 percent solution, how much would be used in a day?
5. What average $Cl_2$ and $KMnO_4$ dosages result?

Answers:

Question 1

$$\text{grams of chemical} = \frac{\text{dosage x litres x 1,000 x 100}}{\text{1,000,000 x percentage active ingredient}}$$

$$= \frac{7.5 \times 450{,}000 \times 1{,}000 \times 100}{1{,}000{,}000 \times 12}$$

$$= \frac{7.5 \times 450 \times 100}{12}$$

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= 28,125

Remember, 1 L equals 1,000 g, so 28,125 g or 28.125 L of sodium hypochlorite is needed.

Question 2

$$\text{grams} = \frac{1.5 \times 450{,}000 \times 1{,}000 \times 100}{1{,}000{,}000 \times 99}$$

$$= \frac{67{,}500}{99}$$

$$= 681.8 \text{ g}$$

Since 1,000 g equals 1 kg, 682 g equals about 0.7 kg, the amount of $KMnO_4$ needed each day.

Question 3 The first half of this two-part problem is the same as question 2.

$$\text{grams} = \frac{7.5 \times 450{,}000 \times 1{,}000 \times 100}{1{,}000{,}000 \times 65}$$

= 5,192 g = 5.2 kg calcium hypochlorite needed

The second half of question 3 asks:

$$\text{litres} = \frac{\text{grams of chemical} \times \text{percentage active ingredient}}{\text{percentage solution strength} \times 1{,}000}$$

$$= \frac{5{,}192 \times 65}{3.5 \times 1{,}000} = \frac{337{,}480}{3{,}500}$$

= 96.4 L used daily

Question 4

$$\text{litres} = \frac{682 \times 99}{1.75 \times 100} = \frac{67{,}518}{1{,}750}$$

= 38.58, or about 39 L used daily

Question 5

$$Cl_2 \text{ dosage} = \frac{\text{percentage solution strength} \times \text{litres of solution} \times 1{,}000{,}000}{\text{litres treated} \times 100}$$

$$= \frac{3.5 \times 92 \times 1{,}000{,}000}{450{,}000 \times 100}$$

= 7.2 mg/L

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$$KMnO_4 \text{ dosage} = \frac{1.75 \times 33 \times 1{,}000{,}000}{450{,}000 \times 100}$$

$$= 1.3 \text{ mg/L}$$

## Metric Formula Summary

1. chemical required = chemical demand + residual (or excess)

To calculate:

2. Solution strength

$$\text{percentage strength ent} = \frac{\text{kilograms of chemical added} \times \text{percentage active ingredi-}}{\text{litres of water in solution} \times 1{,}000}$$

3. Chemical needed for a dilute solution

$$\text{grams of chemical} = \frac{\text{percentage strength} \times \text{litres of water in solution} \times 1{,}000}{\text{percentage active ingredient}}$$

4. Chemical needed for a particular dosage

$$\text{grams of chemical} = \frac{\text{dosage} \times \text{litres treated} \times 1{,}000 \times 100\%}{1{,}000{,}000 \times \text{percentage active ingredient}}$$

5. Volume of solution to be fed

$$\text{litres of solution} = \frac{\text{grams of chemical needed} \times \text{percentage active ingredient}}{\text{percentage solution strength} \times 1{,}000}$$

6. Dosage applied—dry chemical feed

$$\text{dosage (mg/L)} = \frac{\text{grams of chemical} \times 1{,}000{,}000 \times \text{percentage active ingredient}}{\text{litres treated} \times 1{,}000 \times 100\%}$$

7. Dosage applied—solution feed*

$$\text{dosage (mg/L)} = \frac{\text{percentage solution strength} \times \text{litres of solution used} \times 1{,}000{,}000}{\text{litres treated} \times 1{,}000 \times 100\%}$$

## Imperial Formula Summary

*This formula applies to dilute solutions of about 5 percent or lower strength.

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1. chemical required = chemical demand + residual (or excess)

To calculate:

2. Solution strength

$$\text{percentage solution strength} = \frac{\text{pounds of chemical added} \times \text{percentage active ingredient}}{\text{weight of water in solution}}$$

3. Chemical needed for a dilute solution

$$\text{pounds of chemical} = \frac{\text{percentage strength} \times \text{weight of water in solution}}{\text{percentage active ingredient}}$$

4. Chemical needed for a particular dosage

$$\text{pounds of chemical} = \frac{\text{dosage} \times \text{gallons treated} \times 10 \times 100\%}{1{,}000{,}000 \times \text{percentage active ingredient}}$$

5. Volume of solution to be fed

$$\text{gallons of solution} = \frac{\text{pounds of chemical needed} \times \text{percentage active ingredient}}{\text{percentage solution strength} \times 10}$$

6. Dosage applied—dry chemical feed

$$\text{dosage (lb/gal)} = \frac{\text{pounds of chemical used} \times 1{,}000{,}000 \times \text{percentage active ingredient}}{\text{gallons treated} \times 10 \times 100\%}$$

7. Dosage applied—solution feed*

$$\text{dosage (lb/gal)} = \frac{\text{percentage solution strength} \times \text{gallons of solution used} \times 1{,}000{,}000}{\text{gallons treated} \times 100\%}$$

## Practical Math

Detention and fill time calculations. Removal of Fe and Mn almost always requires the addition of an oxidant to the raw water to bring about a chemical transformation of the iron and manganese in solution to a filterable form. Raw-water pH and temperature as well as chemicals or compounds naturally present in the raw water

*This formula applies to dilute solutions of about 5 percent or lower strength.

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determine the time needed to complete oxidation and formation of a filterable floc.

Detention time is the time required for a particular flow to travel through a tank. Another way to think of detention time is the time required for a given flow to fill a tank. The tank in this definition may be an actual tank designed to hold water over time (a detention or holding tank or vessel); it may also include part of a pressure filter vessel above the filter media, the piping from the dosing point to the filter entry, or a combination of all three. Typically, detention time as used in chemical pretreatment is equivalent to contact time, not to be confused with the C x T value, which describes the residual concentration of a disinfectant over time. (3-14)

Two variables affect detention time: the flow rate through the tank and the volume of the tank. Use this formula to determine detention time:

$$\text{detention time} = \frac{\text{volume of tank}}{\text{flow rate}}$$

Two other considerations influence detention time calculations.

1. Flow rate and volume must be expressed in the same terms. If the tank's volume is stated in cubic metres, then the flow rate must be stated in cubic metres per unit of time. Likewise, a volume in gallons requires a flow rate in gallons per unit of time (i.e., gpm, gph, gpd, and so forth).
2. The time frame of the flow rate determines the time frame of the detention time calculation. For example, if the flow rate is stated as cubic metres per hour, the detention time is in hours; if the flow rate is stated in gallons per minute, the detention time is in minutes.

Example calculation:

A detention tank is 3 m long, 2 m wide, and 2.5 m deep to the full line. If the flow rate is 30 $m^3/h$, what is the detention time? First, the standard geometric formula (l x w x d) gives a tank volume of 15 $m^3$.

detention time = 15/30, or 0.5 h (30 min)

Calculating media surface area. For a square or rectangular filter, surface area is the product of the length multiplied by the width:

A (area) = l (length) x w (width)

In the previous example, the area equals 3 x 2, or 6 $m^2$.

For a round filter, apply the formula:

A = pi x r squared, or $A = \pi r^2$

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The symbol for pi is π (π = 22 divided by 7, or 3.142; r refers to radius, i.e., one-half the diameter of a circle).

Example:
What is the surface area of the media in a cylindrical, vertical pressure filter with a diameter of 1.83 m (6 ft)? Since radius is half the diameter, r = 1.83/2 = 0.915; $r^2$ = r x r = 0.915 x 0.915 = 0.837. Therefore,

$$\begin{aligned} A &= 3.142 \times 0.837 \\ &= 2.630\ m^2 \end{aligned}$$

In Imperial measurements, the calculation would be:

$$\begin{aligned} A &= 3.142 \times (3\ ft \times 3\ ft) \\ &= 3.142 \times 9\ ft^2 \\ &= 28.278\ ft^2 \end{aligned} \qquad (3\text{-}15)$$

Rounded to the first decimal place, the surface area is 28.3 $ft^2$.

Flow rate calculation. The round filter receives unfiltered water at the rate of 16 $m^3$ (cubic metres) per hour. What is the rate of filtration per square metre of filter surface area?

$$\text{filtration rate} = \frac{\text{flow rate}}{\text{area}}$$

The example's filtration rate equals 16 $m^3$/h divided by 2.63 $m^2$, or 6.08 $m^3/h/m^2$, which reduces to 6.1 m/h.

In Imperial measurements, the calculation would begin by converting 16 $m^3$ to gallons; multiplying by 220 gives 3,520 Imp gph. Since filtration rates in Imperial units are usually given in gallons per minute, divide 3,520 by 60 to get 58.67 Imp gpm.

$$\text{filtration rate} = 58.67/28.3 = 2.07, \text{ or } 2.1 \text{ Imp gpm/ft}^2$$

In US measurements, the calculation would first, convert 16 $m^3$ to gallons; multiplying by 264.2 gives 4,227.2 gph divided by 60 equals 70.453 gpm.

$$\text{filtration rate} = 70.453/28.3 = 2.49, \text{ or about } 2.5 \text{ gpm/ft}^2$$

An operator unfamiliar with conversions of metric values to Imperial or US customary units should refer to the conversion factors available in appendix A.

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# Chapter 4
# Microbiology of Iron and Manganese Removal

"Groundwater is an important source of water, especially in rural areas. This resource is of increasing concern to microbiologists" (Prescott, Harley, and Klein 1990).

The science of biology is concerned with the study of living organisms, including their habits, food requirements, and general life processes. The living organisms covered in this chapter are too small to be seen with the unaided eye; some can be seen with light microscopes that magnify up to 2,000 diameters. Hence, the name microbiology.

Every water treatment plant operator needs to monitor the impact of the common forms of groundwater bacteria on water treatment and finished water quality. This impact highlights the importance of adequate disinfection in the plant's clear well and distribution system.

Rust bubbles of corrosion appear on pipes, for example, due to microbially induced corrosion by specific bacteria. Certain bacteria form slimes that bioaccumulate (hold onto and build up) iron and manganese. These slimes are often evident in toilet tanks in areas where Fe and Mn abound in the raw water and those where raw well water does not undergo any treatment before use. These same slimes have been known to foul well pumps to the point that they force shutdowns. Other bacteria, known as sulfur bacteria, can generate unpleasant tastes and odors in finished water already in the clear well, reservoir, or distribution system. Some bacteria types are much more aggressive than others, perhaps even causing unwanted events in less than a day after their introduction.

An operator needs to know that active, growing, and dying organisms generate much of the material seen accumulating on pipes, filter walls, and clear well ladders, as well as that floating on the surface of the clear well and moving in distribution pipes.

## Potential Effects of Microbiological Organisms

According to Cullimore (1993, pp. 12–13),

> Microbial events can include corrosion initiation, bioimpedance of hydraulic or gaseous flows (e.g., plugging, clogging), bioaccumulation of chemicals (e.g., localized concentration of heavy metals, hydrocarbons and/or radionu-

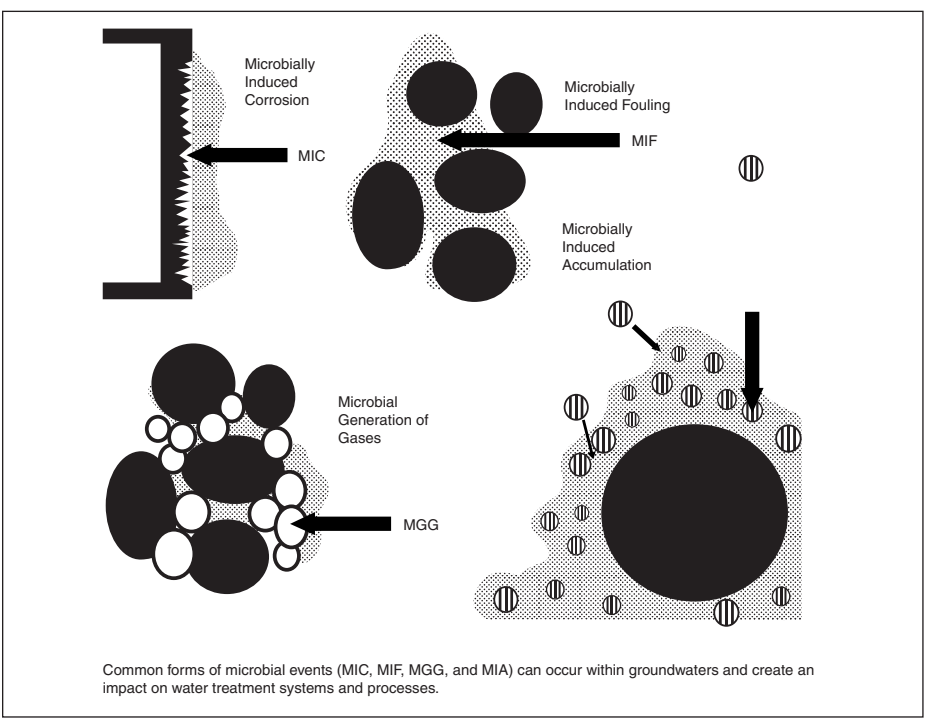


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clides within a groundwater system), biodegradation (e.g., catabolism of potentially harmful organic compounds), biogenesis of gases (including methane, hydrogen, carbon dioxide, or nitrogen, which can lead to such events as the fracturing of clays, displacement of water tables, and differential movement of soil particles), and water retention within biofilms (which, in turn, can influence the rates of desiccation and/or freezing of solids). These events occur naturally within the biosphere as microbiologically driven functions within and upon the crust of the planet.

This paragraph introduces many uncommon terms and big words, but it does reinforce the point that microbiological activity can have major influences on groundwater sources and raw-water quality. As the operator gains knowledge of the water to be treated, the likelihood increases of choosing the appropriate treatment process. Figure 4-1 illustrates some of the events described in the quoted paragraph and in the following definitions:

- Microbially induced fouling (MIF) This term refers to rust bubbles, layer after layer of corrosion inside piping, and buildups of microbiological slimes, along with any other accumulation that reduces the flow volume. In other words, it describes events that result in gradual plugging.




Common forms of microbial events (MIC, MIF, MGG, and MIA) can occur within groundwaters and create an impact on water treatment systems and processes.

*Source: Reprinted with permission from D.R. Cullimore. 1993.* Practical Manual of Groundwater Microbiology. *Chelsea, Mich.: Lewis. Copyright CRC Press, Boca Raton, Florida.*

**Figure 4-1** Microbes in action

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- Microbially induced accumulation (MIA) As MIF takes place, a bioaccumulation also concentrates various ions, such as metallic elements (iron, manganese, etc.) in the form of dissolved or insoluble salts and organic complexes.
- Microbial generation of gases (MGG) As groups of microorganisms mature in primarily anaerobic conditions, gases are likely to form. Corrosion bubbles, for example, can be filled with carbon dioxide, methane, hydrogen, and nitrogen. Such gases in their dissolved states can be parts of other slime groups. Under the right conditions, sufficient volumes of gases can form within biological growths to expand their sizes and reduce the diameter of a pipe, thus reducing the volume of water that the pipe can carry, despite the porous appearance of biological growth.
- Microbially induced corrosion (MIC) Commonly called rusting, this process occurs when microbes attach themselves to a surface, for example, the wall of a steel pipe. They cover themselves up, creating anaerobic environments. Within their self-built homes, they may generate hydrogen sulfide (which promotes electrolytic corrosion) and/or organic acids (which can transform metals into solution). The results appear as surface pitting and/or rusting out (corrosion that extends through a metal wall of a pipe, filter, or filter false bottom).
- Microbially induced relocation (MIR) As microorganisms live their lives, they consume nutrients and use oxygen until a change in the oxidation–reduction potential takes place. Under the right conditions, flowing water begins to rip apart the biofilm. Small pieces (or colonies) find new locations where nutrients and oxygen are available, and new colonies are created and grow until they too get ripped apart and flow to new homes.

## The Importance of Oxidation–Reduction (redox)

As Figure 4-2 illustrates, much of the microbial growth that affects groundwater sources, and hence treatment of those groundwaters for removal of Fe and Mn, takes place in the zone where aerobic and anaerobic conditions meet.

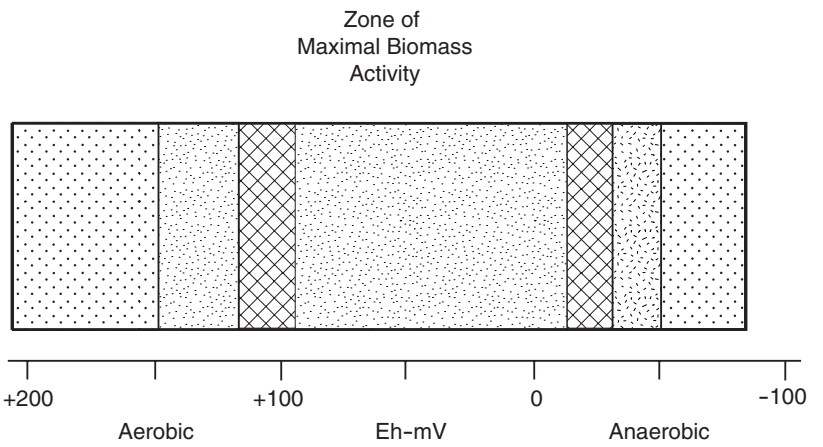
According to Cullimore (1993, pp. 17–18),

> Redox has a major controlling impact on microorganisms through the oxidation-reduction state of the environment. Generally, an oxidative state (+Eh values) will support aerobic microbial activities while a reductive state (–Eh values) will encourage anaerobic activities which, in general, may produce a slower rate of biomass generation, a downward shift in pH where organic acids are produced, and a greater production potential for gas generation (e.g., methane, hydrogen sulfide, nitrogen, hydrogen, carbon dioxide). Aerobic microbial activities forming sessile growths are often noted to occur most extensively over the transitional redox fringe of –50 to +150 Mv.

(The glossary provides a definition of sessile.)

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In groundwater systems, the microbial growth (biomass) often focuses at the reduction-oxidation (redox) interface at Eh values +150 to -50 V.

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**Figure 4-2** Where aerobic and anaerobic meet

## Effect of Microbiological Activity on Fe and Mn Levels

When microbiological organisms (i.e., biofilms) join together to form a colony by attaching themselves to a surface, they simply grab their food from the passing water. (They may also use iron from certain pipe materials under some circumstances.) Obviously, any increase in the nutrient (i.e., food) level in the passing water speeds the colony's growth to maturity. At the same time, the biofilm can draw into itself such metals as iron, manganese, aluminum, copper, and zinc. Figure 4-3 shows this process.

The abundance of food is not the only influence on how a biofilm behaves. Figure 4-4 shows how a biofilm grows, compresses to allow increased flows to pass (thereby bringing more food), and then pulses as the phases repeat. The importance to iron and manganese treatment is the sloughing stage of phase four, referred to as MIR (microbially induced relocation), in which passing water rips pieces from the biofilm. Depending on the extent of biofilm concentrations, slugs of Fe and Mn they carry may hit the treatment process in bunches, perhaps allowing them to pass through the treatment and filtration process.

Figure 4-4 also serves as a reminder of what can happen if Fe and Mn are not removed in the plant, so they can accumulate as biofilms in distribution lines. Such events are often the causes of brown water complaints from consumers. When complaints are received, plant operators naturally consider what changes they can

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