

14 IRON AND MANGANESE REMOVAL

Iron (Fe) and manganese (Mn) are abundant elements in the earth's crust. They are mostly in the oxidized state (ferric, Fe^{3+} , and Mn^{4+}) and are insoluble in natural waters. However, under reducing conditions (i.e., where dissolved oxygen is lacking and carbon dioxide content is high), appreciable amounts of iron and manganese may occur in groundwater and in water from the anaerobic hypolimnion of stratified lakes and reservoirs. The reduced forms are soluble divalent ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions that are chemically bound with organic matter. Iron and manganese get into natural water from dissolution of rocks and soil, from acid mine drainage, and from corrosion of metals. Typical iron concentrations in ground water are 1.0 to 10 mg/L, and typical concentrations in oxygenated surface waters are 0.05 to 0.2 mg/L. Manganese exists less frequently than iron and in smaller amounts. Typical manganese values in natural water range from 0.1 to 1.0 mg/L (James M. Montgomery Consulting Engineers, 1985). Voelker (1984) reported that iron and manganese levels in groundwaters in the American Bottoms area of southwestern Illinois ranged from < 0.01 to 82.0 mg/L and < 0.01 to 4.70 mg/L, respectively, with mean concentrations of 8.4 mg/L and 0.56 mg/L, respectively.

Generally, iron and manganese in water are not a health risk. However, in public water supplies they may discolor water, stain plumbing fixtures and laundry, and cause tastes and odors. Iron and manganese may also cause problems in water distribution systems because metal depositions may result in pipe encrustation and may promote the growth of iron bacteria which may in turn cause tastes and odors. Iron and manganese may also cause difficulties in household ion exchange units by clogging and coating the exchange medium.

To eliminate the problems caused by iron and manganese, the U.S. Environmental Protection Agency (1987) has established secondary drinking water standards for iron at 0.3 mg/L and for manganese at 0.05 mg/L. The Illinois Pollution Control Board (IPCB, 1990) has set effluent standards of 2.0 mg/L for total iron and 1.0 mg/L for total manganese.

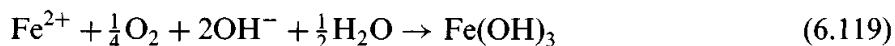
The techniques for removing iron and manganese from water are based on the oxidation of relatively soluble Fe(II) and Mn(II) to the insoluble Fe(III) and Mn(III,IV) and the oxidation of any organic-complex compounds. This is followed by filtration to remove the Fe(III) and processes for iron and manganese removal are discussed elsewhere (Rehfeldt *et al.*, 1992).

Four major techniques for iron and manganese removal from water are: (1) oxidation-precipitation-filtration, (2) manganese zeolite process, (3) lime softening-settling-filtration, and (4) ion exchange. Aeration-filtration, chlorination-filtration, and manganese zeolite process are commonly used for public water supply.

14.1 Oxidation

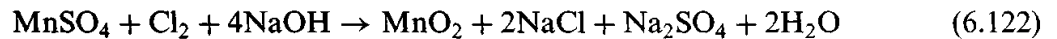
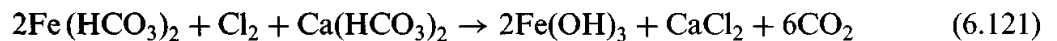
Oxidation of soluble (reduced) iron and manganese can be achieved by aeration, chlorine, chlorine dioxide, ozone, potassium permanganate (KMnO_4) and hydrogen peroxide (H_2O_2). The chemical reactions can be expressed as follows:

For aeration (Jobin and Ghosh, 1972; Dean, 1979)



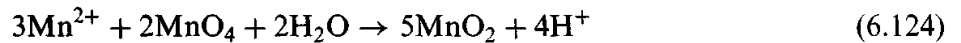
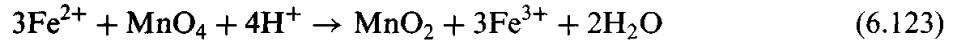
In theory, 0.14 mg/L of oxygen is needed to oxidize 1 mg/L of iron and 0.29 mg/L of oxygen for each mg/L of manganese.

For chlorine (White, 1972)

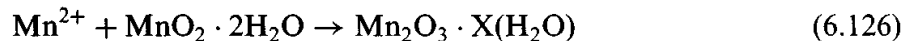


The stoichiometric amounts of chlorine needed to oxidize each mg/L of iron and manganese are 0.62 and 1.3 mg/L, respectively.

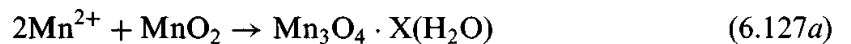
For potassium permanganate (Ficek 1980)



In theory, 0.94 mg/L of KMnO_4 is required for each mg/L of soluble iron and 1.92 mg/L for one mg/L of soluble manganese. In practice, a 1 to 4 percent solution of KMnO_4 is fed in at the low-lift pump station or at the rapid-mix point. It should be totally consumed prior to filtration. However, the required KMnO_4 dosage is generally less than the theoretical values (Humphrey and Eikleberry 1962, Wong 1984). Secondary oxidation reactions occur as

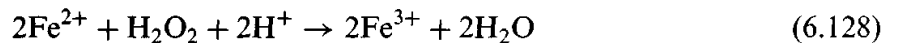


and



For hydrogen peroxide (Kreuz, 1962)

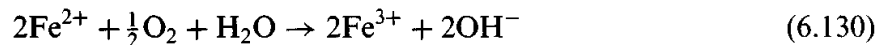
1. Direct oxidation



2. Decomposition to oxygen

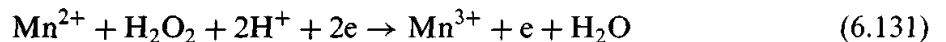


followd by oxidation



In either case, two moles of ferrous iron are oxidized per mole of hydrogen peroxide, or 0.61 mg/L of 50 percent H_2O_2 oxidizes 1 mg/L of ferrous iron.

For oxidation of manganese by hydrogen peroxide, the following reaction applies (H.M. Castrantas, FMC Corporation, Princeton, NJ, personal communication).



To oxidize 1 mg/L of soluble manganese, 1.24 mg/L of 50 percent H_2O_2 is required.

Studies on ground water by Rehfeldt *et al.* (1992) reported that oxidant dosage required to meet the Illinois recommended total iron standard follow the order of $\text{NaOCl} > \text{KMnO}_4 > \text{H}_2\text{O}_2$. The amount of residues generated by oxidants at the critical dosages follow the order of $\text{KMnO}_4 > \text{NaOCl} > \text{H}_2\text{O}_2$, with KMnO_4 producing the largest, strongest, and most dense flocs.

For ozone: It is one of the strongest oxidants used in the water industry for disinfection purposes. The oxidation potential of common oxidants relative to chlorine is as follows (Peroxidation Systems, 1990):

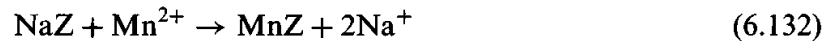
Fluoride	2.32
Hydroxyl radical	2.06
Ozone	1.52
Hydrogen peroxide	1.31
Potassium permanganate	1.24
Chlorine	1.00

Ozone can be very effective for iron and manganese removal. Because of its relatively high capital costs and operation and maintenance costs, the ozonation process is rarely employed for the primary purpose of oxidizing iron and manganese. Since ozone is effective in oxidizing trace toxic organic matter in water, pre-ozonation instead of pre-chlorination is becoming popular. In addition, many water utilities are using ozone for disinfection purposes. Ozonation can be used for two purposes: disinfection and metal removal.

Manganese zeolite process. In the manganese zeolite process, iron and manganese are oxidized to the insoluble form and filtered out, all in one unit, by a combination of sorption and oxidation. The filter medium can be manganese greensand, which is a purple-black granular material processed from glauconitic greens, and/or a synthetic formulated product. Both of these compositions are sodium compounds treated with a manganous solution to exchange manganese for sodium and then oxidized by KMnO_4 to produce an active manganese dioxide. The greensand grains in the filter become coated with the oxidation products. The oxidized form of greensand then adsorbs soluble iron and manganese, which are subsequently oxidized with KMnO_4 . One advantage is that the greensand will adsorb the excess KMnO_4 and any discoloration of the water.

Regenerative-Batch Process. The regenerative-batch process uses manganese treated greensand as both the oxidant source and the filter medium. The manganese zeolite is made from KMnO_4 -treated greensand zeolite. The chemical reactions can be expressed as follows (Humphrey and Eikleberry, 1962; Wilmarth, 1968):

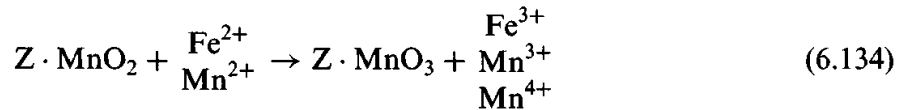
Exchange:



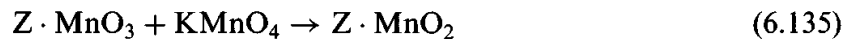
Generation:



Degeneration:



Regeneration:



where NaZ is greensand zeolite and $\text{Z} \cdot \text{MnO}_2$ is manganese zeolite. As the water passes through the mineral bed, the soluble iron and manganese are oxidized (degeneration). Regeneration is required after the manganese zeolite is exhausted.

One of the serious problems with the regenerative-batch process is the possibility of soluble manganese leakage. In addition, excess amounts of KMnO_4 are wasted, and the process is not economical for water high in metal content. Manganese zeolite has an exchange capacity of 0.09 lb of iron or manganese per cubic foot of material, and the flow rate to the exchanger is usually 3.0 gpm/ft³. Regeneration needs approximately 0.18 lb KMnO_4 per cubic foot of zeolite.

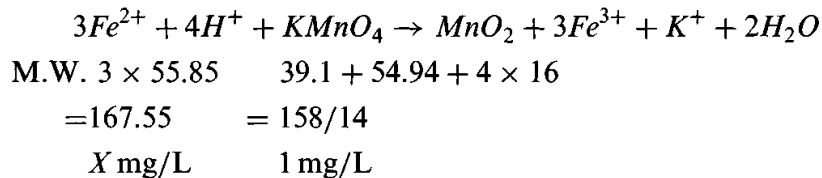
Continuous Process. For the continuous process, 1–4% KMnO_4 solution is continuously fed ahead of a filter containing anthracite (6–9 in. thick), manganese-treated greensand (24–30 in.), and gravel. The system takes full advantage of the higher oxidation potential of KMnO_4 as compared to manganese dioxide. In addition, the greensand can act as a buffer. The KMnO_4 oxidizes iron, manganese, and hydrogen sulfide to the insoluble state before the water reaches the manganese zeolite bed.

Greensand grain has a smaller effective size than silica sand used in filters and can result in comparatively higher head loss. Therefore, a layer of anthracite is placed above the greensand to prolong filter runs by filtering out the precipitate. The upper layer of anthracite operates basically as a filter medium. When iron and manganese deposits build up, the system is backwashed like an ordinary sand filter. The manganese zeolite not only serves as a filter medium but also as a buffer to oxidize any residual soluble iron and manganese and to remove any excess unreacted KMnO_4 . Thus a KMnO_4 demand test should be performed. The continuous system is recommended for waters where iron predominates, and the intermittent regeneration system is recommended for groundwater where manganese predominates (Inversand Co., 1987).

EXAMPLE 1: Theoretically, how many mg/L each of ferrous iron and soluble manganese can be oxidized by 1 mg/L of potassium permanganate?

Solution:

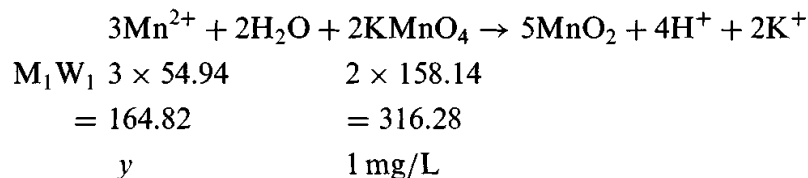
Step 1. For Fe^{2+} , using Eq. (6.123)



By proportion

$$\begin{array}{l}
 \frac{X}{1} = \frac{167.55}{158.14} \\
 X = 1.06 \text{ mg/L}
 \end{array}$$

Step 2. For Mn^{2+} , using Eq. (6.124)



then

$$y = \frac{164.82}{316.28} = 0.52 \text{ mg/L}$$

EXAMPLE 2: A groundwater contains 3.6 mg/L of soluble iron and 0.78 mg/L of manganese. Find the dosage of potassium permanganate required to oxidize the soluble iron and manganese.

Solution:

From Example 1 the theoretical potassium permanganate dosage are 1.0 mg/L per 1.06 mg/L of ferrous iron and 1.0 mg/L per 0.52 mg/L of manganese. Thus

$$\begin{aligned} \text{KMnO}_4 \text{ dosage} &= \frac{1.0 \times 3.6 \text{ mg/L}}{1.06} + \frac{1.0 \times 0.78 \text{ mg/L}}{0.52} \\ &= 4.9 \text{ mg/L} \end{aligned}$$

15 ACTIVATED CARBON ADSORPTION

15.1 Adsorption Isotherm Equations

The Freundlich isotherm equation is an empirical equation which gives an accurate description of adsorption of organic adsorbate in water. The equation under constant temperature equilibrium is (U.S. EPA, 1976; Brown and LeMay, 1981; Lide, 1996)

$$q_e = KC_e^{1/n} \quad (6.136)$$

or

$$\log q_e = \log K + (1/n) \log C_e \quad (6.136a)$$

where q_e = quantity of adsorbate per unit of adsorbent, mg/g
 C_e = equilibrium concentration of adsorbate in solution, mg/L
 K = Freundlich adsorption coefficient, (mg/g) (L/mg)^{1/n}
 n = empirical coefficient

The constant K is related to the capacity of the adsorbent for the adsorbate. $1/n$ is a function of the strength of adsorption. The molecule that accumulates, or adsorbs, at the surface is called an *adsorbate*; and the solids on which adsorption occurs is called *adsorbent*. Snoeyink (1990) compiled the values of K and $1/n$ for various organic compounds from the literature which is listed in Appendix D.

From the adsorption isotherm, it can be seen that, for fixed values of K and C_e , the smaller the value of $1/n$, the stronger the adsorption capacity. When $1/n$ becomes very small, the adsorption tends to be independent to C_e . For fixed values of C_e and $1/n$, the larger the K value, the greater the adsorption capacity q_e .

Another adsorption isotherm developed by Langmuir assumed that the adsorption surface is saturated when a monolayer has been absorbed. The Langmuir adsorption model is

$$q_e = \frac{abC_e}{1 + bC_e} \quad (6.137)$$

or

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{a} \quad (6.138)$$

where a = empirical coefficient
 b = saturation coefficient, m³/g

Other terms are the same as defined in the Freundlich model. The coefficient a and b can be obtained by plotting C_e/q_e versus C_e on arithmetic paper from the results of a batch adsorption test with Eq. (6.138).

Adsorption isotherm can be used to roughly estimate the granular activated carbon (GAC) loading rate and its GAC bed life. The bed life Z can be computed as