

CE 370

Iron and Manganese Removal

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Iron and Manganese Removal; Overview

- Iron and Manganese are natural constituents of soil and rocks.
- Usually natural waters have an iron content which is greater than manganese content.
- Waters are seldom found which have iron levels greater than 10 mg/l or manganese levels greater than 2 mg/l.
- Iron exists in the +2 or +3 oxidation states, whereas manganese exists in either the +2, +3, +4, +6, or +7 oxidation states. However, iron (III) and manganese (IV) are the only stable oxidation states found in waters containing oxygen.

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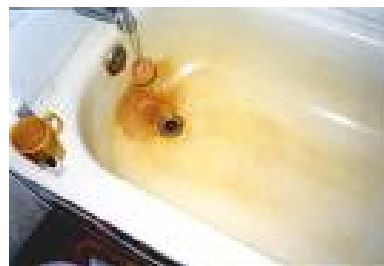
What problems are caused by iron and manganese?

The presence of significant amounts of either or both of these metals in a water supply can create several problems for the consumers. The problems caused by the presence of iron including:

- Large concentration of iron impart a metallic taste to the water.
- Industrial products such as paper, textiles, or leather may be discolored.
- Household fixtures such as porcelain basins, bathtubs, glassware, and dishes are stained.
- Clothes may stain a yellow or brown-yellow color.
- Iron precipitates clog pipes and promote the growth of gelatinous masses of iron bacteria. These bacteria slough off and create “red water”
- Iron bacteria may cause odor and taste problems, particularly, when the flow in pipes is low.

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What problems are caused by iron and manganese?



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What problems are caused by iron and manganese?

The problems caused by the presence of manganese are similar to those of iron:

- High concentrations of manganese may produce taste problems.
- Manganese may cause a discoloration of industrial products similar to that caused by iron.
- Household fixtures may be stained a brown or black color.
- Clothes may be stained and become dingy or grayish.

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What is the chemistry of iron and manganese in water systems?

- Iron (Fe) and manganese (Mn) can be present in water in one of three basic forms:
 1. Dissolved: ferrous (Fe^{2+}) and manganous (Mn^{2+}) states
 2. Particulate: ferric (Fe^{3+}) and manganic (Mn^{4+}) states
 3. Colloidal: very small particles (difficult to settle and filter).
- The predominance of one form over another is dependent on the pH, Eh (redox potential), and temperature of the water. Knowledge of the forms or states of iron and manganese can help fine-tune a given treatment practice for these metals.

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Drinking water standards for Iron and Manganese?

- Iron and manganese are common in groundwater supplies and their presence in drinking water do not pose health hazard.
- There are secondary standards set for iron and manganese, but these are not health related and are not enforceable. The secondary (aesthetic) MCLs for iron and manganese are 0.3 milligrams per liter (mg/l) and 0.05 mg/l, respectively
- Exceeding the suggested maximum contaminant levels (MCL) usually results in discolored water, laundry, and plumbing fixtures. This, in turn, results in consumer complaints and a general dissatisfaction with the water utility.
- Any water containing iron and manganese above the recommended levels should be treated to reduce the levels below the standards.

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What are the most common treatment processes?

- The majority of iron and manganese treatment systems employ the processes of oxidation/filtration.
- The oxidant chemically oxidizes the iron or manganese (forming a particle).
- The filter then removes the iron or manganese particles.
- Oxidation followed by filtration is a relatively simple process.

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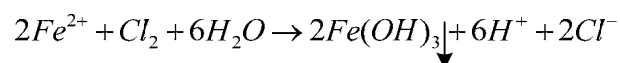
Oxidation

- Before iron and manganese can be filtered, they need to be oxidized to a state in which they can form insoluble complexes.
- Oxidation involves the transfer of electrons from the iron, manganese, or other chemicals being treated to the oxidizing agent.
- Ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which readily forms the insoluble iron hydroxide complex $\text{Fe}(\text{OH})_3$.
- Manganese (Mn^{2+}) is oxidized to (Mn^{4+}), which forms insoluble (MnO_2).

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Oxidation

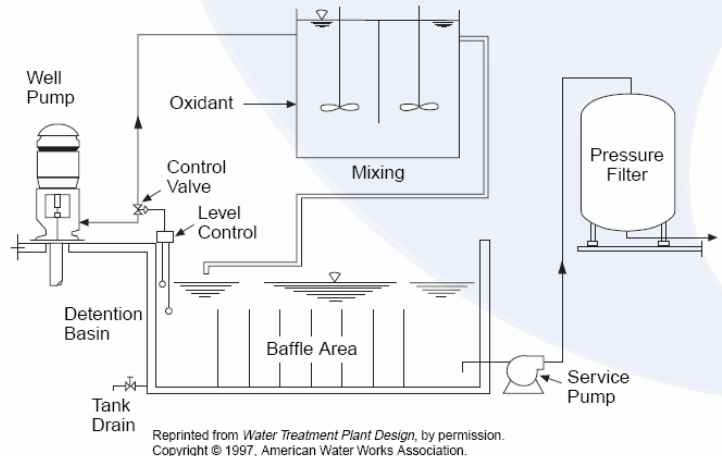
- The most common chemical oxidants in water treatment are chlorine, chlorine dioxide, potassium permanganate, ozone, and oxygen.
- **Chlorination** is widely used for oxidation of divalent iron and manganese. However, the formation of trihalomethanes (THMs) in highly colored waters may be a problem.
- Following is the oxidation reaction of chlorine:



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Oxidation

Table 1: Chlorination, detention, and filtration (iron and manganese removal)



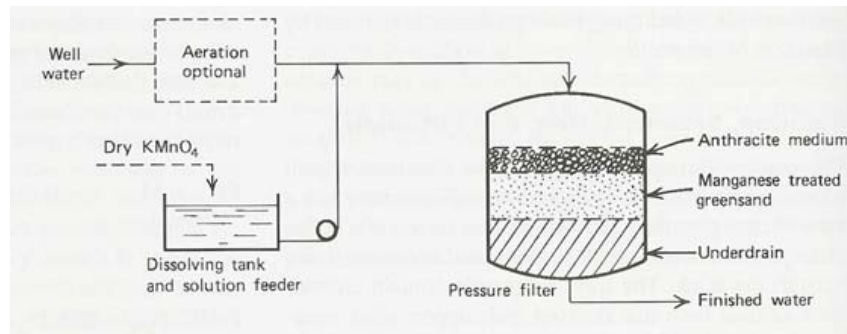
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Oxidation

- **Potassium permanganate (KMnO_4)** is normally more expensive than chlorine and ozone.
- For iron and manganese removal, it is as efficient and it requires considerably less equipment and capital investment.
- The dose of potassium permanganate, however, must be carefully controlled. Too little permanganate will not oxidize all the iron and manganese, and too much will allow permanganate to enter the distribution system and cause a pink color.
- Permanganate can also form precipitates that cause mudball formations on filters. These are difficult to remove and compromise filter performance.

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Removal of iron and manganese from groundwater



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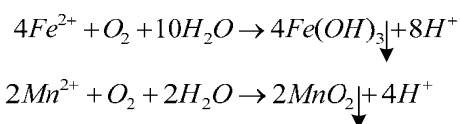
Oxidation

- **Ozone** may be used for iron and manganese oxidation.
- Ozone may not be effective for oxidation in the presence of humic or fulvic materials.
- If not dosed carefully, ozone can oxidize reduced manganese to permanganate and result in pink water formation as well.
- Manganese dioxide particles, also formed by oxidation of reduced manganese, must be carefully coagulated to ensure their removal.

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Oxidation

- A low-cost method of providing oxidation is to use the oxygen in air as the oxidizing agent in a tray aerator.
- Water is simply passed down a series of porous trays to provide contact between air and water.
- Oxygen is not a strong enough oxidizing agent to break the strong complexes formed between iron and manganese and large organic molecules.
- Furthermore, the rate of reaction between oxygen and manganese is very slow below pH values of 9.5.



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Filtration

- After oxidation of iron and manganese, the water is filtered to remove insoluble (particulate) ferric hydroxides and manganese oxides.
- There are different filtration media for the removal of iron and manganese, including manganese greensand, anthra/sand, electromedia, and ceramic.
- Manganese greensand is by far the most common medium in use for removal of iron and manganese through pressure filtration. Greensand is a processed material consisting of grains of the zeolite mineral glauconite. The material is coated with manganese oxide. This coating is maintained through either continuous or intermittent feed of potassium permanganate.

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Filtration

- Anthra/sand are other types of media available for removal of iron and manganese. They consist of select anthracite and sand with a chemically bonded manganese oxide coating. Unlike manganese greensand, these media are conditioned in the filter after media installation.
- Electromedia provides a slightly different option from the manganese oxide coated media. This is a proprietary multi-media formulation which uses a naturally occurring zeolite and does not require potassium permanganate regeneration.
- Finally, macrolite is a manufactured ceramic material with a spherical shape and a rough, textured surface. The principal removal mechanism is physical straining rather than contact oxidation or adsorption.

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Filtration; media



Manganese greensand



anthracite

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Alternative Treatments

➤ Sequestration

- Sequestration is the addition of chemicals to groundwater aimed at controlling problems caused by iron and manganese without removing them. These chemicals are added to groundwater at the well head or at the pump intake before the water has a chance to come in contact with air or chlorine. This ensures that the iron and manganese stays in a soluble form.
- Adding polyphosphates followed by chlorination can be an effective and inexpensive method for mitigating iron and manganese problems. No sludge is generated in this method. The polyphosphates combine with the iron and manganese preventing them from being oxidized.
- Also, sodium silicate and chlorine simultaneously has also been used to sequester iron and manganese.

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Alternative Treatments

➤ Ion Exchange

- Ion exchange should be considered only for the removal of small quantities of iron and manganese because there is a risk of rapid clogging.
- Ion exchange involves the use of synthetic resins where a pre-saturant ion on the solid phase (the “adsorbent,” usually sodium) is exchanged for the unwanted ions in the water
- One of the major difficulties in using this method for controlling iron and manganese is that if any oxidation occurs during the process, the resulting precipitate can coat and foul the media. Cleaning would then be required using acid or sodium bisulfate.

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Alternative Treatments

➤ Other

- Systems that have a lime-soda ash softening plant do not need a separate iron and manganese removal plant. The high pH during softening allows rapid oxidation and precipitation of the iron and manganese as well as incorporation in the calcium and magnesium precipitates.
- Similarly, surface water treatment plants using coagulation, flocculation, sedimentation, and filtration also will remove iron and manganese as long as they make certain the iron and manganese get oxidized.
- Finally, biological treatment methods are being pilot tested at different locations. Biological treatment methods are used extensively in European countries, such as the Netherlands, France, and Germany, and are advantageous primarily when water simultaneously contains iron, manganese, and ammonia.

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How can iron and manganese problems be minimized in distribution mains?

➤ Problems due to iron and manganese in distribution mains may be minimized by:

- prior removal by appropriate treatment,
- protecting iron/steel mains with proper linings, or using noncorrosive materials,
- avoiding dead-end mains,
- avoiding disturbances in the water flow, and
- flushing periodically.

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