A NATIONAL DRINKING WATER CLEARINGHOUSE FACT SHEET

Iron and Manganese Removal

Summary

Iron and manganese are common in groundwater supplies used by many small water systems. 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.

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.

Small water plants may choose to either sequestrate or remove iron and manganese. Sequestration only works for combined iron and manganese concentrations up to $1.0\ mg/L$ and only in cases where the treatment is not permanent. Removal is usually achieved through ion exchange or oxidation/filtration. There are a number of chemical oxidants and filtration media available that can be used in various combinations.

What problems are caused by iron and manganese?

Small amounts of iron are often found in water because of the large amount of iron present in the soil and because corrosive water will pick up iron from pipes. Clothing washed in water containing excessive iron may become stained a brownish color. The taste of beverages, such as tea and coffee, may also be affected by iron. Manganese produces a brownish color in laundered clothing, leaves black particles on fixtures, and—as with iron—affects the taste of beverages, including coffee and tea.

Well water from the faucet or tap is usually clear and colorless. However, when water containing colorless, dissolved iron is allowed to stand in a cooking container or comes in contact with a sink or bathtub, the iron combines with oxygen from the air to form reddish-brown particles (commonly called rust). Manganese forms brownish-black particles. These impurities can give a metallic taste to water or to food.

The rusty or brown stains on plumbing fixtures, fabrics, dishes, and utensils cannot be removed by soaps or detergents. Bleaches and alkaline builders (often sodium phosphate) can make the stains worse. Over time, iron deposits can build up in pressure tanks, water heaters, and pipe-

lines, reducing the quantity and pressure of the water supply.

Iron and/or manganese in water creates problems common to many water supply systems. When both are present beyond recommended levels, special attention should be paid to the problem. How iron and manganese are removed depends on the type and concentration and this helps determine the best procedure and (possible) equipment to use.

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 $^{2+}$)
- 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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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), and kills iron bacteria and any other disease-causing bacteria that may be present. The filter then removes the iron or manganese particles.

Oxidation followed by filtration is a relatively simple process. The source water must be monitored to determine proper oxidant dosage, and the treated water should be monitored to determine if the oxidation process was successful.

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 $Fe(OH)_3$. Reduced manganese (Mn^{2+}) is oxidized to (Mn^{4+}), which forms insoluble (MnO_9).

The most common chemical oxidants in water treatment are chlorine, chlorine dioxide, potassium permanganate, and ozone. Oxidation using chlorine or potassium permanganate is frequently applied in small groundwater systems. The dosing is relatively easy, requires simple equipment, and is fairly inexpensive.

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. Chlorine feed rates and contact time requirements can be determined by simple jar tests.

As an oxidant, potassium permanganate ($\rm KMnO_4$) is normally more expensive than chlorine and ozone, but for iron and manganese removal, it has been reported to be 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

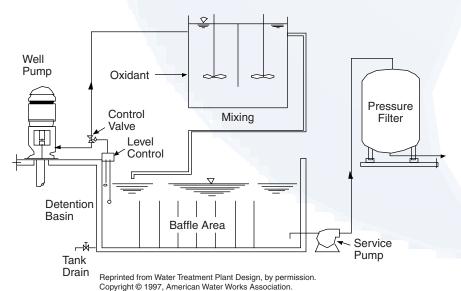
all the iron and manganese, and too much will allow permanganate to enter the distribution system and cause a pink color. Permanganate can also form precipitates that cause mudball formations on filters. These are difficult to remove and compromise filter performance.

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 cagulated to ensure their removal.

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. No chemical dosing is required, which allows for unattended operation. This method is not effective for water in which the iron is complexed with humic materials or other large organic molecules. 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.

The presence of other oxidizable species in water hinders oxidation of the desired reduced compounds. Volatile organic chemicals, other

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



Filtration

In general, manganese oxidation is more difficult than iron oxidation because the reaction rate is slower. A longer detention time (10 to 30 minutes) following chemical addition is needed prior to filtration to allow the reaction to take place.

There are different filtration media for the removal of iron and manganese, including manganese greensand, anthra/sand or iron-man 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 nodular grains of the zeolite mineral glauconite. The material is coated with manganese oxide. The ion exchange properties of the glauconite facilitates the bonding of the coating. This treatment gives the media a catalytic effect in the chemical oxidation-reduction reactions necessary for iron and manganese removal. This coating is maintained through either continuous or intermittent feed of potassium permanganate.

Anthra/sand (also iron-man 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, unlike the other media discussed so far, is not a naturally occurring material which then undergoes processing for iron and manganese removal purposes. It 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.

Each medium has its advantages and disadvantages. Selection of a medium and oxidant should be based on pilot testing in which all

necessary design criteria can be determined. Pressure filtration system manufacturers who offer the indicated media also offer fully automated systems.

Are there 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 ground-water 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.

If the water contains less than 1.0 mg/L iron and less than 0.3 mg/L manganese, using polyphosphates followed by chlorination can be an effective and inexpensive method for mitigating iron and manganese problems. No sludge is generated in this method. Below these concentrations, the polyphosphates combine with the iron and manganese preventing them from being oxidized. Any of the three polyphosphates (pyrophosphate, tripolyphosphate, or metaphosphate) can be used.

To determine the best polyphosphate to use and the correct dosage, a series of samples at different concentrations may be prepared. Chlorine is added, and the samples are observed daily against a white background. The right polyphosphate dose is the lowest dose that does not noticeably discolor the water samples for four days.

Applying sodium silicate and chlorine simultaneously has also been used to sequester iron and manganese. However, while this technique is reliable in the case of iron treatment, it has not been found to be effective in manganese control.

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 (see Ion Exchange and Demineralization Tech Brief #DWBLPE56). 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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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. Oxidation is sometimes a problem because of the presence of organic matter.

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.

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 bituminous linings, or using noncorrosive materials,
- · avoiding dead-end mains,
- · avoiding disturbances in the water flow, and
- flushing periodically.

Where can I find more information?

Information in this fact sheet was primarily obtained from the following sources:

- (1) American Water Works Association. 1998. Water Treatment Plant Design. Third Edition.
- (2) American Water Works Association. 1990. Water Quality 2nd Treatment. Fourth Edition.
- (3) Metcalf, B. M. 1998. "Pressure Filtration for Iron & Manganese Removal," Proceedings of the New England Water Works Association Conference and Exhibition. Marlborough, MA.
- (4) National Research Council. 1997. Safe Water From Every Tap: Improving Water Service to Small Communities. National

- Academy Press. Washington DC.
- (5) Robinson, R. B. 1998. "State-of the-Art: Iron and Manganese Control," Proceedings of the New England Water Works Association Conference and Exhibition. Marlborough, MA.
- (6) U.S. Environmental Protection Agency. 1991. Manual of Small Public Water Supply Systems. EPA 570/9-91-003. Office of Water, Washington, DC.
- (7) Vigneswaran, S., C. Visvanathan. 1995. Water Treatment Processes: Simple Options. CRC Press. New York, NY.