Manganese & Iron Compliance

Drinking Water Problems: Iron & Manganese

- Iron and manganese control is the most common type of municipal water treatmentment.
- Iron and manganese occur naturally in groundwater.
- Neither element causes adverse heath effects at concentrations typically found in groundwater. These elements are, in fact, essential to the human diet.
- Water containing excessive amounts of iron and manganese can stain clothes, dis-color plumbing fixtures, and sometimes add a "rusty" taste and look to the water.
- Surface water generally does not contain large amounts of iron or manganese, but iron and manganese are found frequently in water systems that use groundwater.
- The Safe Drinking Water Act secondary standards for iron in drinking water is 0.3 parts per million (ppm) and 0.05 ppm for manganese.

Drinking Water Problems: Iron & Manganese

Problems Caused by Iron & Manganese

- 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.

Problems Caused by Iron & 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.

Problems Caused by Iron & Manganese

- Well water from the faucet or tap is usually clear and colorless.
- However, when water containing color-less, 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 water softening equipment.

Problems Caused by Iron & Manganese

Problems Caused by Iron & Manganese

- Iron and manganese can give water an unpleasant taste, odor and color.
- Iron causes reddish-brown stains on laundry, porcelain, dishes, utensils, glassware, sinks, fixtures and concrete.
- Manganese causes brownish-black stains on the same materials.
- These deposits restrict the flow of water and reduce water pressure.
- More energy is required to pump water through clogged pipes and to heat water if heating rods are coated with mineral deposits.
- This raises energy and water costs.

Problems Caused by Iron & Manganese

- Water contaminated with iron and manganese often contains iron or manganese bacteria.
- These bacteria feed on the minerals in the water.
- They do not cause health problems, but do form a reddish-brown (iron) or brownish-black (manganese) slime in toilet tanks and can clog water systems.

Problems Caused by Iron & Manganese

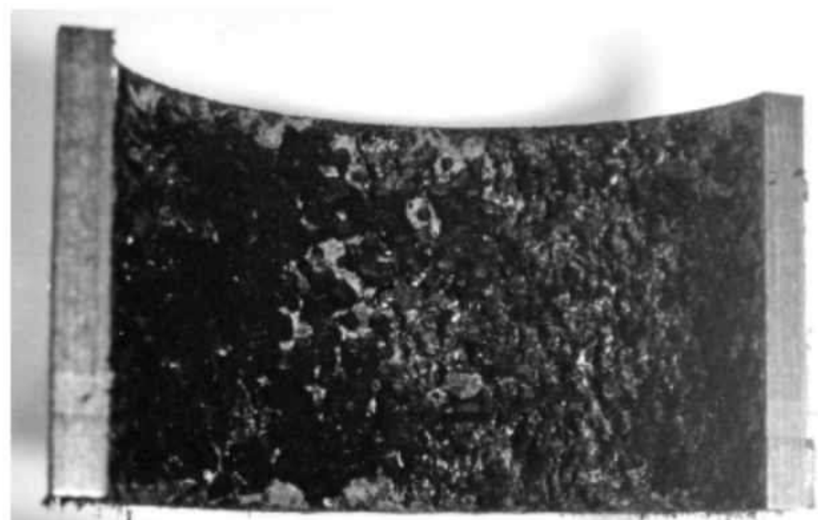
Problems Caused by Iron & Manganese

- Pipelines, 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.

Determination of Iron & Manganese in Water

- The appearance and/or taste of water can indicate the presence of iron and manganese. For example, reddish-brown (iron) or black (manganese) particles may be visible when water is drawn from the tap.
- These particles of iron and/or manganese may come from corroded pipes or from the water supply itself.
- The particles form because the oxygen in the plumbing system is oxidizing the precipitating the iron and manganese.
- If water is clear when it comes from the tap but particles form and settle out after the water has sat for a while, the iron and/or manganese is in the water supply itself.
- It is dissolved in the water and remains invisible until it oxidizes and precipitates.
- Iron does not form particles large enough to precipitate.
- Manganese usually is dissolved in water; although some shallow wells contain colloidal manganese that gives water a black tint.

Determination of Iron & Manganese in Water



Determination of Iron & Manganese in Water

- Reddish-brown or black slime in toilet tanks or faucets is a sign of iron and manganese bacteria.
- Water containing high concentrations of iron and manganese may have an unpleasant metallic flavor.
- The water may react with tannins in coffee, tea and other beverages to produce a black sludge. You may also notice that the water is staining clothing and other items.
- While these systems can indicate that your water contains iron and manganese, you need to test your water to measure how much it contains.

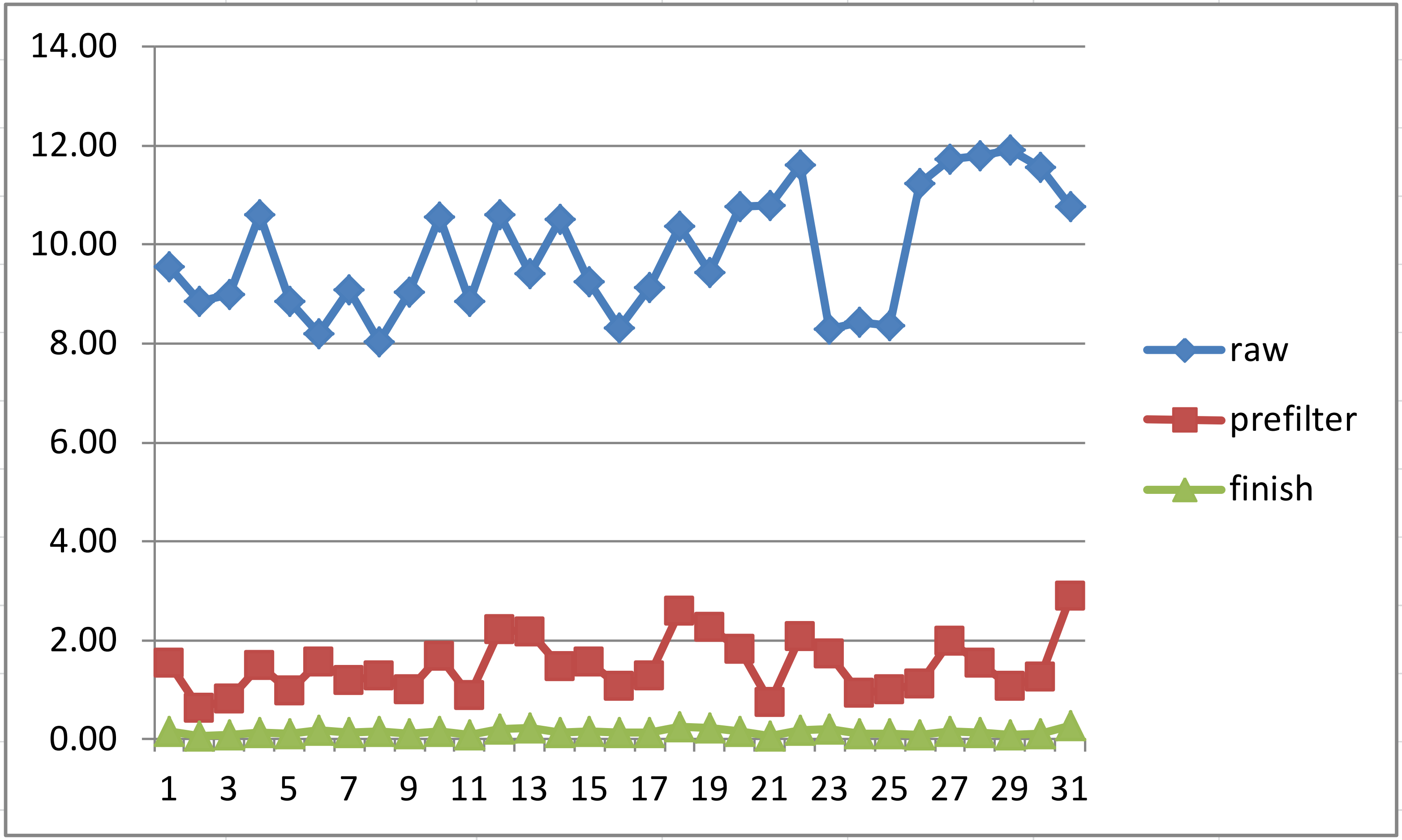
Determination of Iron & Manganese in Water

					chemicals applied		chemical tests			
Date	time	meter	**water**	washwater	chlorine	fluoride	**raw**	**prefilter**	**finish**	
		reading	**treated**	gallons	gallons	gallons	**iron**	**Iron**	**iron**	free cl2
5/1/2009	8.00	874767	**52,200**	2,500	1.1	1.7	**9.56**	**1.53**	**0.16**	0.36
2	8.00	875289	**67,800**	2,900	2.1	2.3	**8.84**	**0.62**	**0.07**	0.19
3	7.40	875967	**72,000**	2,600	1.4	2.4	**9.00**	**0.81**	**0.09**	0.21
4	8.15	876687	**53,600**	2,700	1.8	1.8	**10.60**	**1.48**	**0.14**	0.21
5	7.45	877223	**69,700**	2,500	1.8	2.3	**8.84**	**0.97**	**0.11**	0.16
6	8.00	877920	**70,300**	2,600	2.1	2.4	**8.20**	**1.56**	**0.19**	0.17
7	9.15	878623	**46,300**	2,600	0.7	1.6	**9.08**	**1.18**	**0.13**	0.18
8	7.45	879086	**71,000**	2,700	1.1	2.4	**8.04**	**1.29**	**0.16**	0.14
9	8.25	879796	**75,100**	2,500	2.1	2.5	**9.04**	**0.99**	**0.11**	0.12
10	8.00	880547	**59,800**	2,500	1.4	2.0	**10.56**	**1.69**	**0.16**	0.24
11	8.00	881145	**82,600**	2,800	2.1	2.7	**8.84**	**0.88**	**0.10**	0.19
12	8.00	881971	**86,200**	2,700	2.1	2.9	**10.60**	**2.23**	**0.21**	0.11
13	8.00	882833	**55,100**	2,400	1.4	1.6	**9.40**	**2.16**	**0.23**	0.12
14	8.00	883384	**72,500**	2,400	1.8	2.6	**10.52**	**1.47**	**0.14**	0.15
15	8.30	884109	**47,900**	2,400	0.7	1.6	**9.24**	**1.57**	**0.17**	0.25
16	8.00	884588	**69,400**	2,600	1.4	2.2	**8.32**	**1.08**	**0.13**	0.17
17	8.00	885282	**89,700**	2,800	2.5	2.9	**9.12**	**1.28**	**0.14**	0.11
18	8.00	886179	**83,200**	2,500	2.1	2.7	**10.36**	**2.59**	**0.25**	0.23
19	8.15	887011	**59,800**	2,400	1.8	2.0	**9.44**	**2.27**	**0.24**	0.13
20	7.45	887609	**86,900**	2,600	1.4	0.0	**10.76**	**1.83**	**0.17**	0.18
21	8.10	888478	**87,900**	2,800	2.5	0.0	**10.80**	**0.76**	**0.07**	0.17
22	8.10	889357	**72,400**	2,900	2.5	0.0	**11.60**	**2.09**	**0.18**	0.44
23	8.15	890081	**79,000**	3,100	2.1	0.0	**8.28**	**1.74**	**0.21**	0.78
24	8.00	890871	**80,600**	3,000	1.4	1.9	**8.44**	**0.93**	**0.11**	0.45
25	7.30	891677	**77,500**	3,100	2.1	1.7	**8.36**	**1.00**	**0.12**	0.74
26	7.30	892452	**76,400**	3,000	1.4	1.5	**11.24**	**1.12**	**0.10**	0.75
27	7.30	893216	**68,400**	2,800	1.4	1.4	**11.72**	**1.99**	**0.17**	0.47
28	8.00	893900	**59,000**	3,100	1.8	2.9	**11.80**	**1.53**	**0.13**	0.16
29	8.15	894490	**65,100**	3,000	1.8	2.7	**11.92**	**1.07**	**0.09**	0.18
30	8.00	895141	**68,600**	3,100	2.1	1.6	**11.56**	**1.27**	**0.11**	0.10
31	7.15	895827	**97,200**	3,000	1.4	1.9	**10.76**	**2.91**	**0.27**	0.14
total			**2,203,200**	84,600	53.2	58.2				
maximum			**97,200**	3,100	2.5	2.9	**11.92**	**2.91**	**0.27**	0.78
average			**71,071**	2,729	1.7	1.9	**9.83**	**1.48**	**0.15**	0.26
minimum			**46,300**	2,400	0.7	0.0	**8.04**	**0.62**	**0.07**	0.10

Process Control!

- What are my levels at each treatment:
  - Raw
  - Pre Filter
  - Post Filter
  - Finish
    - Entry Point Into Distribution System
      - Sink? Is it representative?
  - Distribution Sample Site

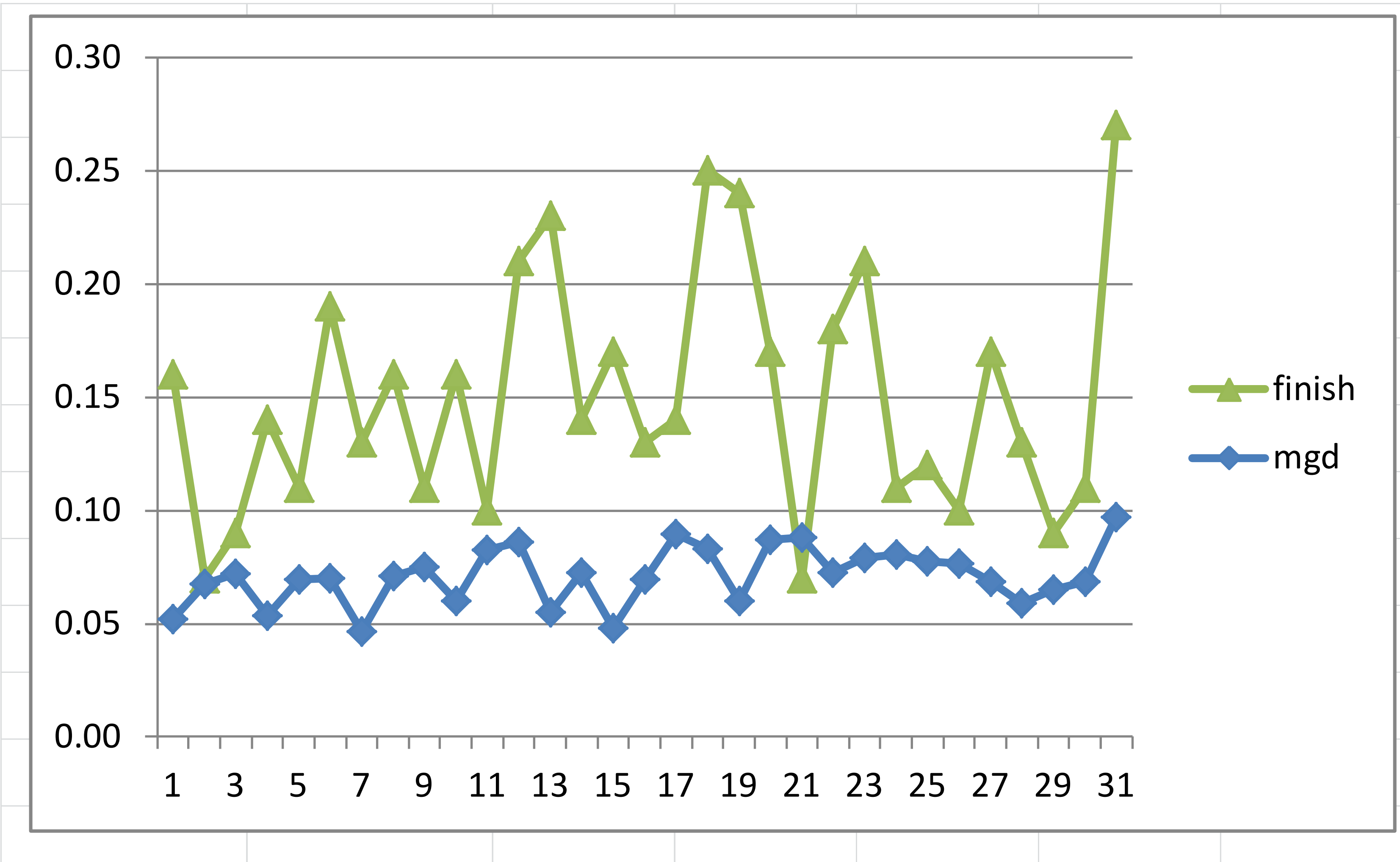
Determination of Iron & Manganese in Water



Pre Filter Sampling

Post Filter Sampling

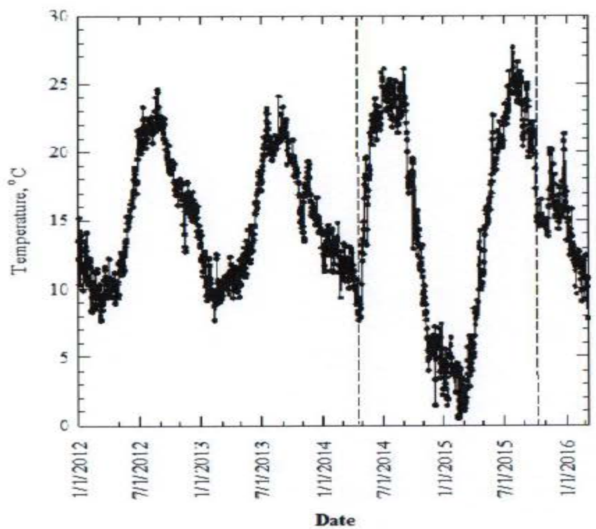
The System Talks



The Systems Talking!

EPA

"Tap" Water Temperature

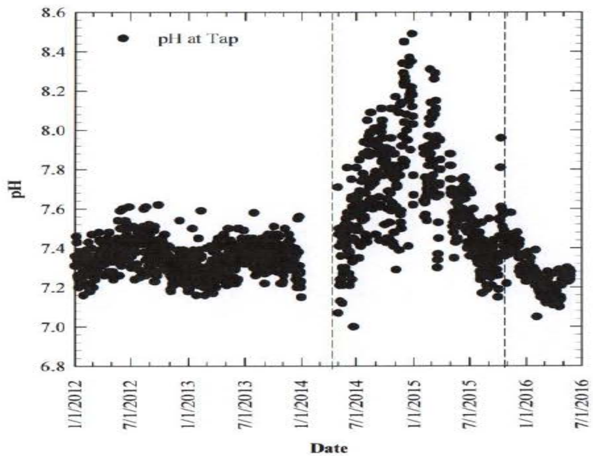


Data Source: http://www.michigan.gov/flintwater

The Systems Talking!

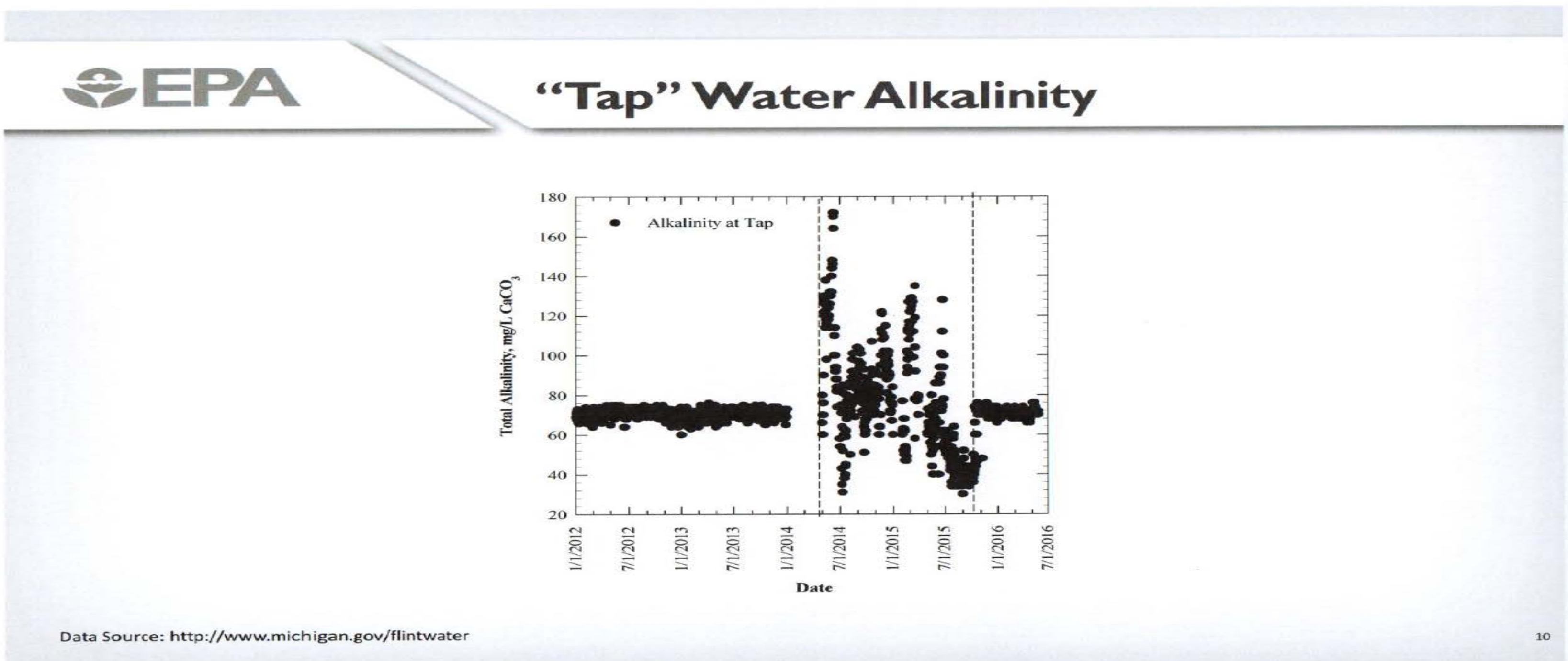
EPA

"Tap" Water pH

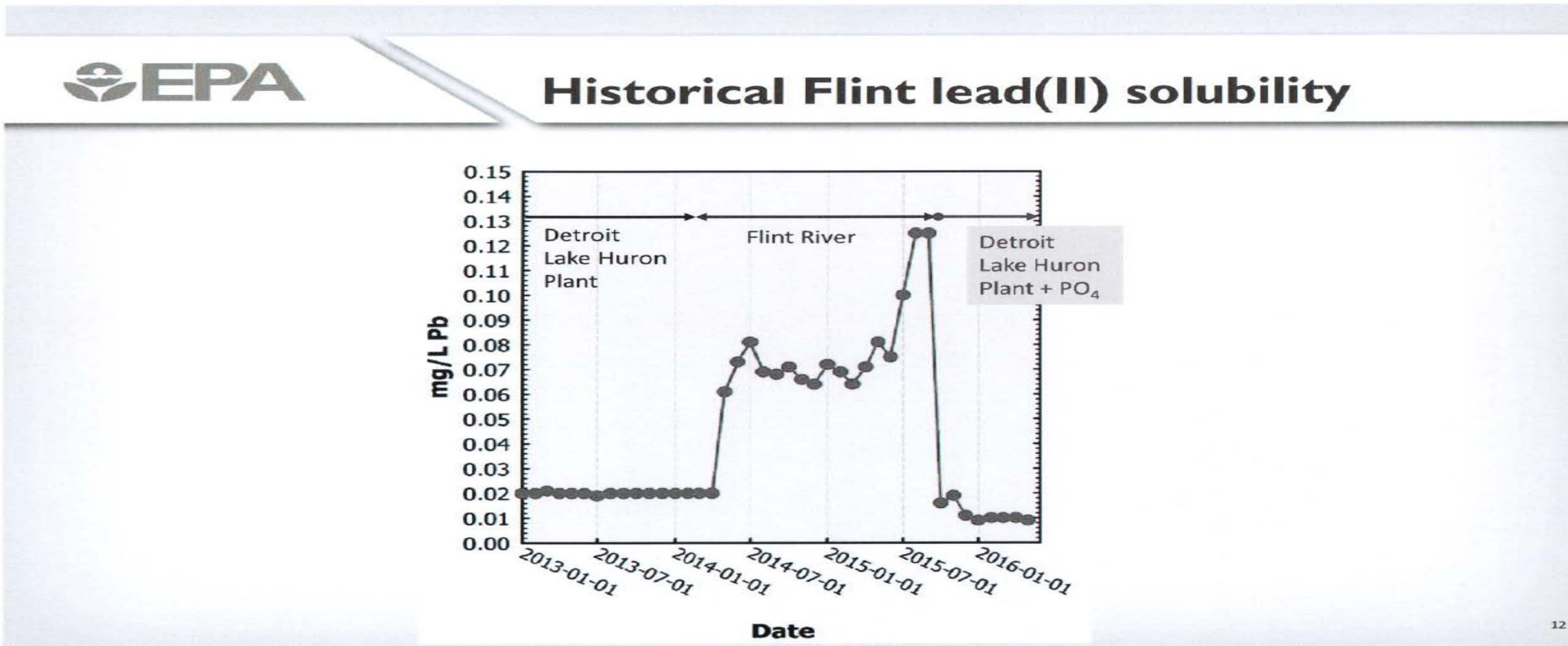


Data Source: http://www.michigan.gov/flintwater

The Systems Talking!



Was Anyone Listening?

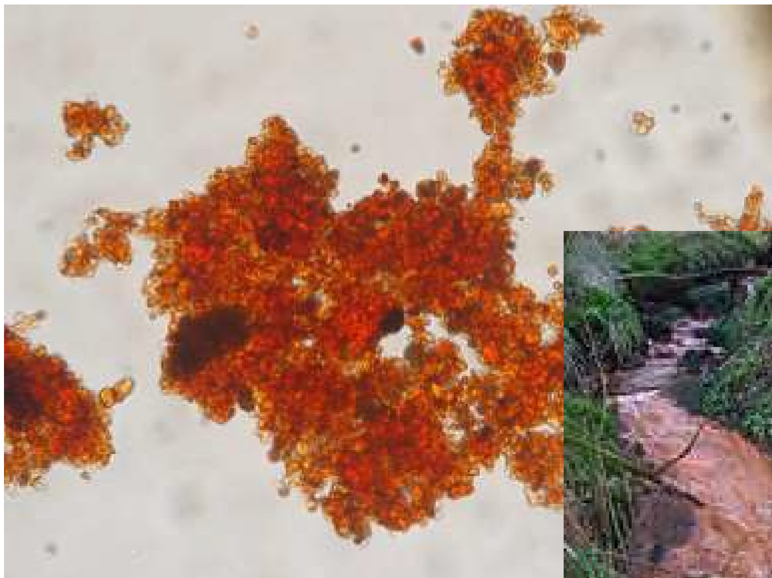


Bacteria & Iron & Manganese

- Iron and manganese in water also promote the growth of bacteria (including iron bacteria).
- These organisms obtain energy for growth from the chemical reaction that occurs when iron and manganese mix with dissolved oxygen.
- These bacteria form thick slime growths on the walls of the piping system and on well screens.
- These shines tend to be are rust-colored from iron and black-colored from manganese.
- Variations in flow can cause these slime growths to separate from pipe walls, resulting in dirty water in the system.

Determination of Iron & Manganese in Water

Bacteria & Iron & Manganese

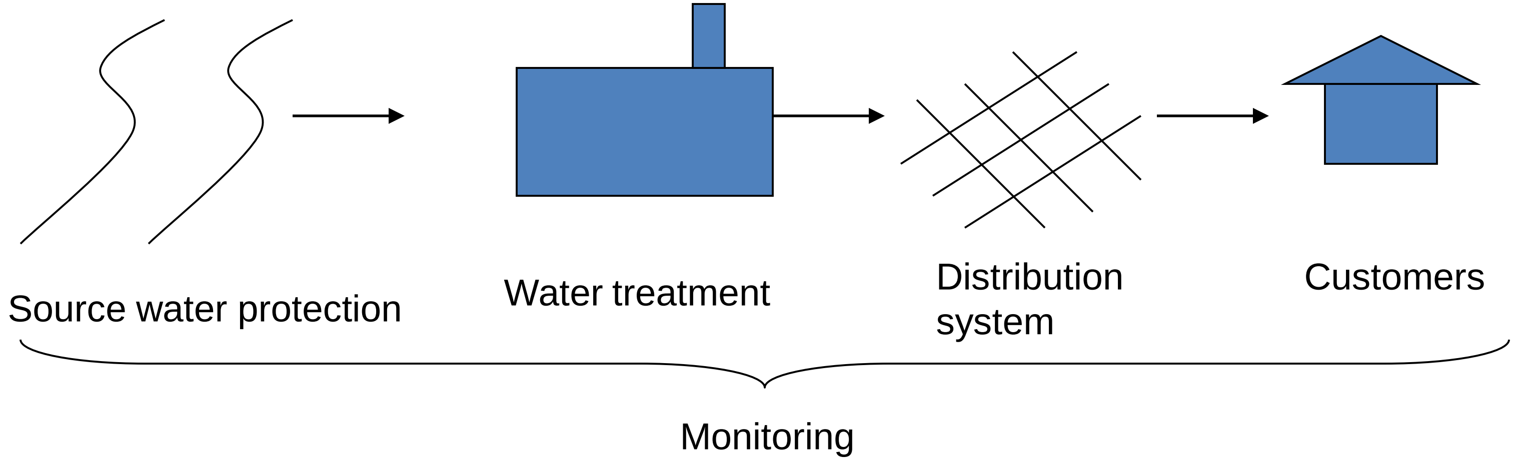


Bacteria & Iron & Manganese

- The growth of iron bacteria can be controlled by chlorination. However, when water containing iron is chlorinated, the iron is converted from the ferrous state to the ferric state--in other words, rust--and manganese is converted into black manganese dioxide.
- These materials form a coating on the inside of the water main and, when they break loose, a customer will sometimes complain of “dirty” water.
- Iron bacteria will use even small amounts of iron present in the ferrous state, oxidize it, and then use the energy.
- Manganese is also used by other bacteria to form organics, which contribute to the iron bacteria slime in the well and/or water system.
- Iron bacteria are found any where a food source of iron is available.
- The presence of one bacterium is all that is needed to start an infestation in a well or a distribution system.

Multi-Barrier Approach

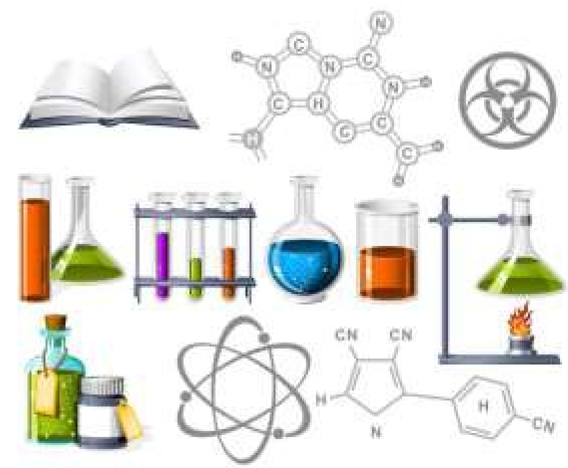
- “Multi-barriers” are needed to reliably provide high quality, safe drinking water



Chemistry of Iron & 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).



Chemistry of Iron & Manganese in Water Systems

- The predominance of one form over another is dependent on pH, 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 of these metals.

Testing of Iron & Manganese

- It is important to have a laboratory test to measure how much of these substances is in the water, and to measure for other conditions and substances (pH, oxygen, hardness and sulfur) that can determine the most suitable treatment method.

Testing of Iron & Manganese

- Your test results probably will be reported as mg/L (milligrams per liter).
- The U.S. Environmental Protection Agency has set Secondary Maximum Contaminant Levels (SMCL) for iron and manganese at 0.3 mg/L and 0.05 mg/L.
- Water that contains less than 0.3 mg/L of iron and 0.05 mg/L of manganese should not have an unpleasant odor, taste or appearance and should not require treatment.

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_x)

Oxidation

- The most common oxidants in the water industry 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.

Oxidation

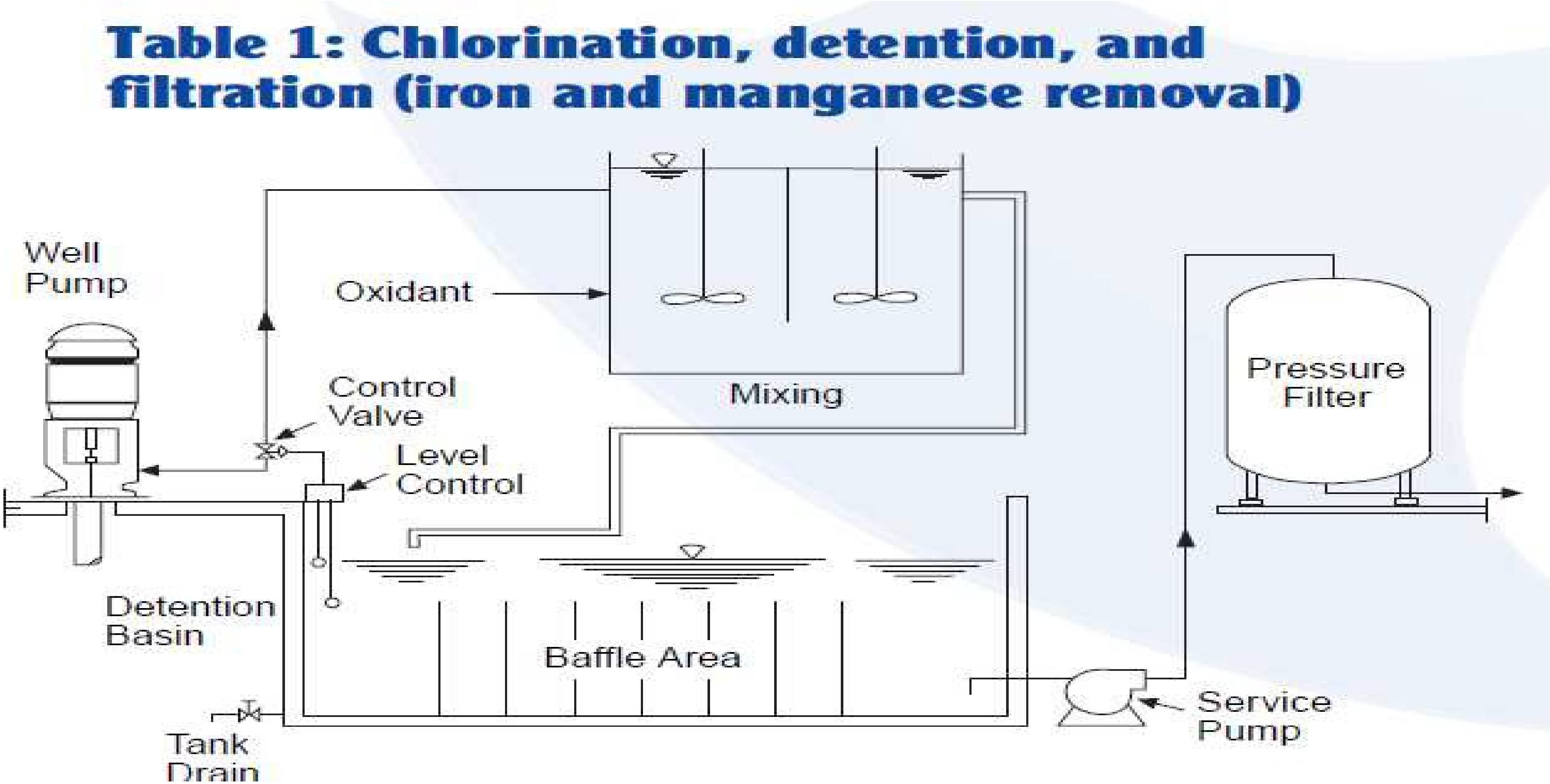


Table 1: Chlorination, detention, and filtration (iron and manganese removal)
Well Pump
Oxidant
Mixing
Control Valve
Level Control
Pressure Filter
Detention Basin
Baffle Area
Service Pump
Tank Drain

Oxidation

- Chlorination is widely used for oxidation of divalent iron and manganese.
- However, the formation of disinfection byproducts (DBPs) 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 ($KMnO_4$) is normally more expensive than chlorine , 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

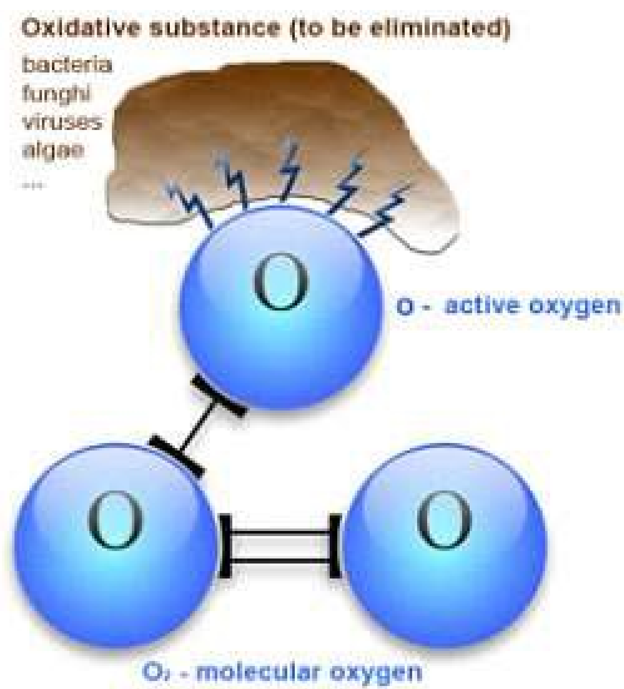
Oxidation

- Too much will allow permanganate to enter the distribution system and cause a pink color.
- Permanganate can also form precipitates that cause mud-ball formations on filters. These are difficult to remove and compromise filter performance.
- Ozone may be used for iron and manganese oxidation.
- 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 oxidization of reduced manganese, must be carefully coagulated to ensure their removal.
- Ozone may not be effective for oxidation in the presence of humic or fulvic materials.

Oxidation

FULVIC ACID

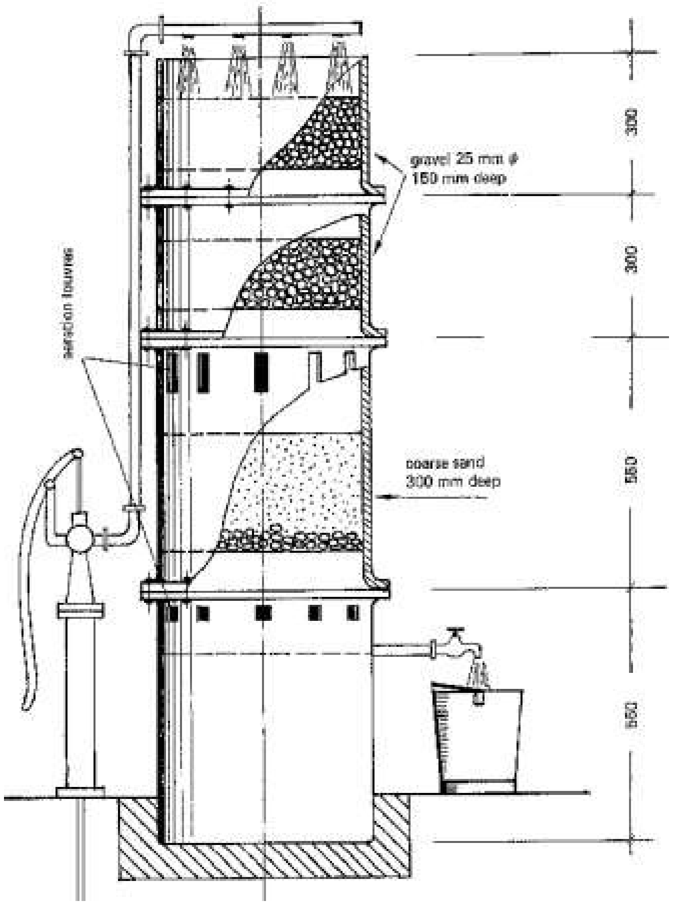
HUMIC ACID

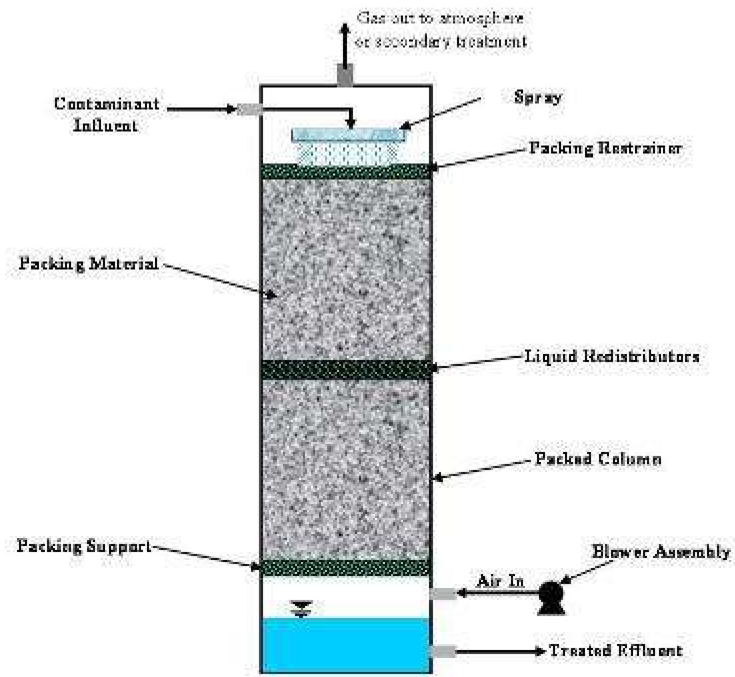


Oxidation

- 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.
- 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.

Oxidation


gravel 25 mm ϕ
150 mm deep
aeration louvres
coarse sand
300 mm deep
300
300
550
550


Gas out to atmosphere
or secondary treatment
Contaminant
Influent
Spray
Packing Restrainer
Packing Material
Liquid Redistributors
Packed Column
Packing Support
Blower Assembly
Air In
Treated Effluent

Oxidation

- Organic compounds, or taste- and odor-causing compounds may result in an oxidant demand.
- This additional oxidant demand must be accounted for when dosing the oxidant.
- The expense of operation derives from the chemical use in most cases, and therefore is directly related to the source water quality.

Aeration/Filtration

- High concentrations of iron and manganese can be treated with an aeration/filtration system.
- In this system, air is pulled in and mixed with the passing stream of water.
- The air-saturated water then enters a precipitator/aerator vessel where air separates from the water.
- The water then flows through a filter where various filter media screen out oxidized particles of iron, manganese, and some carbonate or sulfate.
- Backwashing the filter periodically is a very important maintenance step.
- Aeration is not recommended for water containing iron/manganese bacteria or colloidal (organic complexes of) iron/manganese because they can clog the aspirator and filter.

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 ironman sand, electro media, and ceramic.

Greensand (Gluconite)

Filtration

- Manganese green sand 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.

Filtration

- 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.
- Electro-media provides a slightly different option from the manganese oxide coated media.
- This is a priorietary multi-media formulation which uses a naturally occurring zeolite and does not require potassium permanganate regeneration.

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.
- 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 taphosphate) can be used.

Other Treatment Options

- 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 remove iron and manganese, as long as they make certain that they are oxidized.
- Oxidation is sometimes a problem due to the presence of organic matter.

Reminders

- The Safe Drinking Water Act secondary standards for iron in drinking water is 0.3 parts per million (ppm) and 0.05 ppm for manganese.
- Why should we be concerned about iron and manganese in drinking water?
  - Staining of fixtures, clothing
  - Promote growth of iron bacteria
  - Bacteria form thick slimes on walls of pipe (rust colored)
  - Variations in water flow in mains can cause riled water
  - Slimes cause foul tastes and odors
  - **Because it is important to OEPA!**

Thanks