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## IRON AND MANGANESE FILTRATION SYSTEMS

### A TECHNICAL DISCUSSION

#### INTRODUCTION

Iron (Fe) and manganese (Mn) are elements that are commonly found in the earth as insoluble forms of ferric oxide and manganese dioxide. Iron and manganese do not dissolve in water that contains oxygen. They do become soluble when water that has no dissolved oxygen percolates through geological formations containing ferric oxides and manganese oxide, manganese carbonate and carbonates.

The occurrence of iron and manganese is commonly found in well water and impounded surface water supplies where anaerobic conditions exist. Biological activity can be a strong factor in dissolving iron and manganese by producing carbon dioxide and lowering the pH. Iron and manganese are reduced to their lower valence states of +2 and form soluble bicarbonates. It is not unusual to find high concentrations of carbon dioxide along with iron and manganese in groundwater supplies. Therefore, in the treatment of iron and manganese the corrosiveness (Langelier Index) should be investigated to assure the treated water will not be aggressive and corrode system and customer piping.

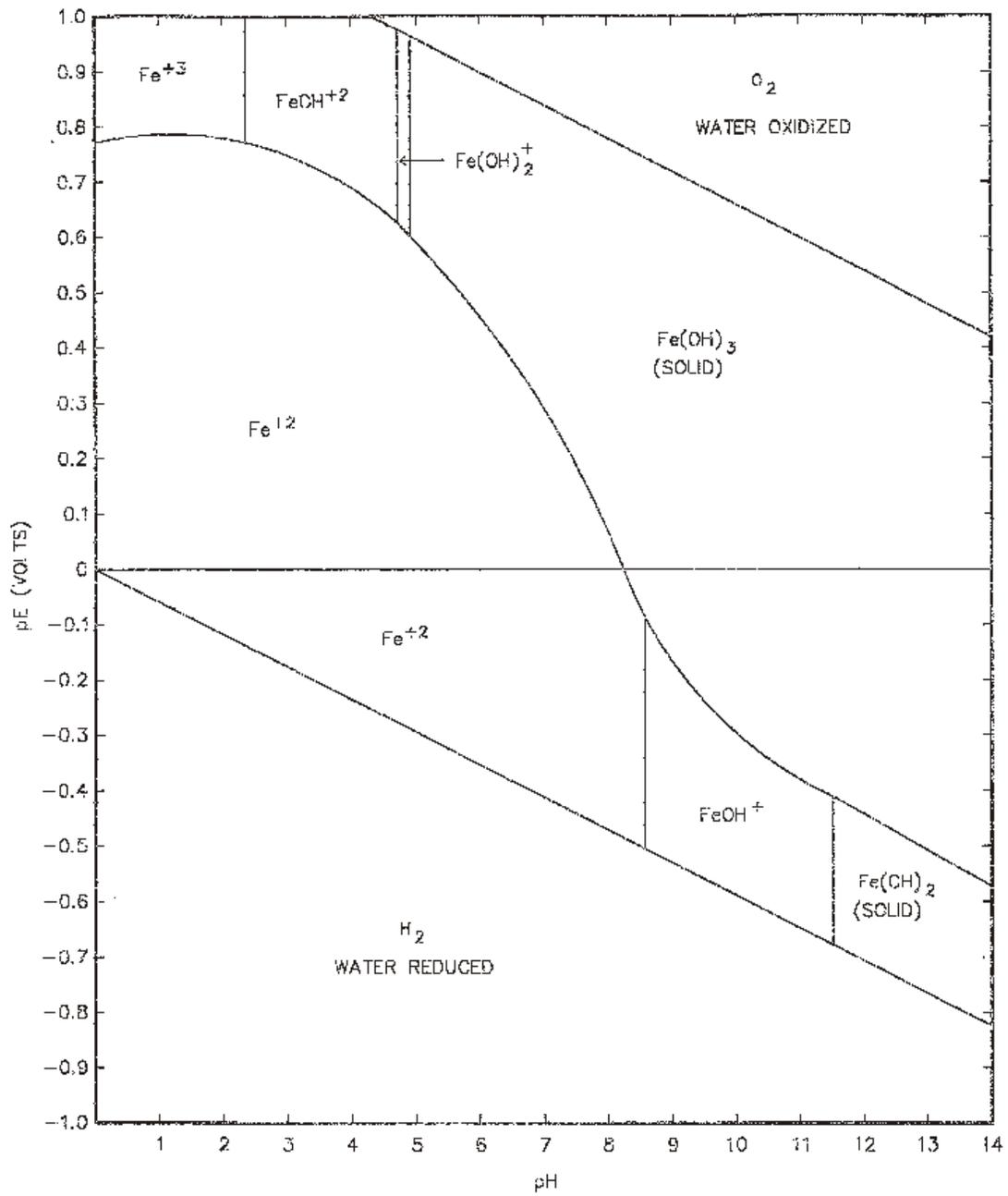


Figure 1 pE-pH DIAGRAM (After Hem & Copper)

Iron in water supplies usually exists in either of the following oxidation states:

- a) Divalent Ferrous Iron ( $\text{Fe}^{+2}$ ) which is the soluble form of iron found in water supplies.
- b) Trivalent Ferric Iron ( $\text{Fe}^{+3}$ ) which is a stable form of iron that is typically insoluble in water. (See Figure 1).

Manganese usually exists in water supplies in the following oxidation states:

- a) In any oxidation state from  $\text{Mn}^0$  to  $\text{Mn}^{+4}$ .
- b) Soluble manganous oxide,  $\text{Mn}^{+2}$ .
- c) Manganic oxide,  $\text{Mn}^{+4}$ , the stable form of manganese that is insoluble in drinking water supplies.

When iron and manganese are found in water that has no dissolved oxygen they exist in the reduced soluble forms. These soluble forms are: divalent ferrous iron, ( $\text{Fe}^{+2}$ ) and manganous oxide, ( $\text{Mn}^{+2}$ ).

Dissolved iron and manganese are removed from water supplies predominately by oxidation and filtration. The soluble ferrous and manganous forms are oxidized to the insoluble ferric and manganic forms. The insoluble ferric and manganic precipitates are then filtered.

## **COMMON EFFECTS**

Soluble iron and manganese cause the following objectionable problems in drinking water supplies. The EPA has established secondary standards of 0.30 mg/l for iron and 0.05 mg/l for manganese to alleviate these objectionable affects to water consumers and purveyors.

## **WATER CONSUMER**

- Metallic and bitter taste and odors.
- Staining of porcelain household fixtures, clothing and swimming pool plaster. Iron causes a reddish color. Manganese causes a blackish color. Iron and manganese in combination cause reddish black color.
- Fouling of water softener resins. Water quality decreases and regeneration costs are significantly increased
- Fouling of cooling water systems. Deposition in water heaters.
- Industrial process water contamination such as food, beverage and textile processing and silicon chip manufacturing.

## **WATER PURVEYOR**

- Deposits in pipelines, service laterals and reservoirs.
- Clogging of water meters.
- Constant water main flushing required.
- Reduction in pipe diameter resulting in higher energy costs.
- Varying water velocities and direction can cause high concentrations of iron and manganese to break free from the pipe.
- Responding to numerous consumer complaints regarding tastes, odor and color.
- Ferrous iron provides a food supply for the growth of bacteria in the distribution system.

## **FACTORS AFFECTING IRON AND MANGANESE REMOVAL**

The removal of iron and manganese from potable water supplies is affected by various chemical and physical characteristics of the water. These characteristics are interrelated and an accurate and complete water analysis is essential to identifying potential problems. Proper design of the required pretreatment and filtration systems depend on a complete and accurate water analysis. Those factors are:

### **TIME**

The reactions are not instantaneous. Detention time following oxidation will determine the completeness of the chemical reactions. Five to twenty minutes may be required for the oxidation and precipitation of iron. Up to two hours may be required for the oxidation and precipitation of manganese.

### **pH**

The oxidation rates are slower at low pH values than at high pH values. Oxidation by aeration requires a pH greater than 6.4 for iron and greater than 9.3 for manganese.

### **TEMPERATURE**

The oxidation rate is faster at higher water temperatures than at lower water temperature. The rate of reaction doubles for every 10EC increase in temperature.

## **TOC**

The oxidation of iron and manganese is slower in the presence of organic matter that forms complexes. Chelation can occur which severely inhibits the oxidation of iron and manganese.

## **DISSOLVED OXYGEN**

The presence of dissolved oxygen accelerates the oxidation of iron and manganese.

## **AMMONIA**

Ammonia exerts a significant oxidant demand and interferes with the oxidation of iron and manganese.

## **CARBON DIOXIDE**

Carbon dioxide lowers the pH of the water through the formation of carbonic acid and reduces the rate of oxidation.

## **LANGELIER INDEX**

Corrosive water with a negative Langelier Index dissolves iron and manganese in proportion to their solubility product at the observed pH. It also constitutes the reason for many "red water" complaints when the raw water iron and manganese values may even be at or below MCL levels. The treatment for corrosive water should be addressed as a pre-treatment requisite for iron and manganese.

## **HYDROGEN SULFIDE** (H<sub>2</sub>S)

This gas is often found in groundwater that contains iron and manganese. It is easily identified by its "rotten egg" odor. In addition to causing serious taste and odor problems, sulfide also promotes the growth of sulfur bacteria. Hydrogen sulfide can cause corrosion problems with iron and concrete pipes and reservoirs.

Sulfides are formed by the anaerobic reduction of sulfates and organic matter into sulfides and bisulfides. This reaction is pH dependent.

- Hydrogen sulfide predominates at a pH of less than 7.
- Hydrogen bisulfide predominates in a pH range between 7 and 9.5.
- Sulfide is predominant at a pH above 9.5.

Standard treatment for hydrogen sulfide has been aeration and degasification or oxidation with chlorine to elemental sulfur. Hydrogen sulfide reacts with oxidants such as  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{ClO}_2$  and  $\text{H}_2\text{O}_2$  to form polysulfides ( $\text{HS}_m$ ) and hydrogen polysulfide ( $\text{H}_2\text{S}_m$ ). These compounds cause a milky blue suspension of colloidal sulfur getting a "musty or earthy" taste or an odor similar to a rubber tire and a taste similar to drinking from a rubber garden hose. This odor may not become apparent until the water is heated and the polysulfide odor is released.

Polysulfides are treated by oxidation and the addition of sulfur dioxide ( $\text{SO}_2$ ). The sulfur dioxide promotes the conversion of polysulfides and elemental sulfur to thiosulfate.

Oxidation of sulfides in the treatment process is extremely important in the removal of iron and manganese. The following factors affect water quality:

- Treatment of all other substances that have an oxidation demand must be completed before the oxidant can effectively oxidize iron and manganese.
- Organic complexes must be oxidized before the oxidant can effectively oxidize iron and manganese.
- An excess of 0.5 mg/l of oxidant (chlorine) is required in this reservoir/distribution system to inhibit any growth of sulfur bacteria.
- Sulfide oxidation must be complete or taste and odor problems will persist in the distribution system even though iron and manganese has been removed.

## **IRON BACTERIA**

Iron bacteria occur naturally in the soil, shallow aquifers and cool surface waters. The two most common forms of iron bacteria found in water are *Callionella* and *Crenothrix*. They use soluble ferrous iron ( $\text{Fe}^{+2}$ ) as an energy source by oxidizing it to insoluble ferric iron ( $\text{Fe}^{+3}$ ). This process precipitates the iron which results in the formation of rusty red slime masses that can cause numerous operational problems.

Most iron bacteria prefer a pH range from 6 to 10. Their tolerance range for dissolved iron is 0.01 to 4.0 mg/l. They are aerobic bacteria and require oxygen in the range of 0.5 to 4.0 mg/l. They prefer water in the 40E F to 60E F temperature range.

The problems caused by iron and bacteria activity are independent from those problems associated with dissolved mineral iron. Although they do not cause health problems, iron bacteria cause the following problems in well piping and casing and throughout the distribution system.

- Reduced well capacity and service life.
- Well redevelopment expense.

- Formation of a reddish brown or white gelatinous slime and stringy masses that can slough off causing a variety of problems.
- Taste and odor problems.
- Staining.
- Reduction in pipe diameter.

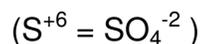
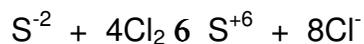
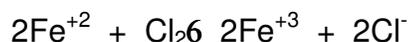
Although iron bacteria do not corrode well casing or steel pipe, they aid the processes that do. They contribute to galvanic corrosion and provide an environment for the growth of other bacteria that generate corrosive sulfuric acid and hydrogen sulfide.

Presentation and treatment of iron bacteria consists of disinfection of all materials which contact the well. This includes: tools, circulating fluids, gravel pack, pump and all other equipment. Chlorine is the most commonly used disinfectant. However, chlorine cannot penetrate incrustation and other chemicals may be required for proper treatment.

### **REACTION VESSEL I**

Water is received from the well source and treated with chlorine to oxidize the iron, manganese and sulfides present. **Electromedia® I may be used with any number of oxidants.** The iron is oxidized to ferric iron. The manganese to the manganic form and sulfides are oxidized to sulfate. Sulfate is common in water supplies and does not contribute objectionable taste or odor. A sufficient amount of chlorine is added to the water to meet the chemical demand and reach the chlorine breakpoint. A minimum free chlorine residual of 0.5 mg/l is provided to the distribution system. A higher residual may be carried if desired.

The oxidation reduction reactions are:



The stoichiometric requirements for the above reactions are:

0.63 mg/l of chlorine per mg/l of iron

1.29 mg/l of chlorine per mg/l of manganese  
8.33 mg/l of chlorine per mg/l of sulfide

The chemistry of sulfur is quite complex. In the equation given above the sulfur is oxidized from sulfide with a valence of -2 to sulfate ( $\text{SO}_4$ )<sup>-2</sup> with a valence of +6. This reaction proceeds through intermediate complex forms of sulfur as discussed in the section on hydrogen sulfide. Typically "rubber tire" taste and odor complaints are the result of polysulfide formation. "Earthy" or "musty" taste and odor complaints are from the formation of colloidal elemental sulfur. To preclude the formation of these products, a small dose of sulfur dioxide is added in the presence of excess oxidant. The sulfur dioxide carries the reaction through these intermediate products to sulfate. The same mechanism is used in the production of sulfuric acid. The dosage of sulfur dioxide depends on the chemistry of the water and is determined from the general mineral analysis. It is typically 0.25 mg/l to 0.50 mg/l.

## **REACTION VESSEL II**

The water is received from reaction vessel number one and injected with a small dose of sulfur dioxide ( $\text{SO}_2$ ). The sulfur dioxide injection point is in the cross-over pipe between the reaction vessels. Sulfur compounds are similar to carbon compounds in that they both tend to link with one another. When sulfides are oxidized this tendency is prevalent.

If the sulfur does link together, polysulfides are formed. Their presence is identified by the characteristic "musty rubber tire" taste and odor.

The introduction of 0.25 mg/l to 0.50 mg/l of sulfur dioxide accelerates the oxidation of the sulfides to sulfates and precludes the formation of intermediate objectionable products.

## **FILTRATION**

The filter vessel contains ***Electromedia***<sup>®</sup> I. A media specifically designed for iron and manganese removal. Its adsorptive surface attracts iron and manganese ions and holds them in the bed. The oxidation of iron and manganese is quite rapid. The reaction with water to form hydroxides or precipitates (filterable substances) requires significant times. Iron requires approximately 20 minutes for a complete reaction to a filterable precipitate at pH of 7 to 8. Manganese requires an hour or more to complete the reaction. The adsorptive qualities of ***Electromedia***<sup>®</sup> I hold the iron and manganese ions in the filter bed and permit this reaction to occur as the water passes through the filter.

The adsorptive qualities of the media or any media cannot be effectively explained. Some of the theories proposed to explain the effects of adsorption include:

- Van der Waals forces
- Hydrogen bonding
- Coulombic bonding

- Chemical bonding

Chemical bonding is known to play a role in "greensand" because of the regeneration requirement and the oxidation-reduction reactions which occur within the bed.

The ***Electromedia***<sup>®</sup> I system does not require regeneration. The nature and size of the media and the vigorous backwash characteristic of the system achieve a mechanical cleaning of the media surface. This system is so effective there is no requirement for "air scouring" or "surface wash" as is needed by other systems.

At the end of the filtration cycle the iron and manganese are backwashed from the media and the surfaces are thoroughly scrubbed. The backwash rate is 20 gallons per minute per square foot with a duration of 4 minutes.

### **PROCESS ANALYZER**

At the discharge of the filter a continuously monitoring analyzer samples the effluent. The process signal is displayed on a color coded chart recorder. The operator must adjust the chlorine dosage to maintain the recording in the green area to affect proper chemical dosage. No calculations or separate analysis is required. This system has a positive response to the oxidant dosage. Five minutes after adjustment the trend is displayed on the recorder and equilibrium is reached within 10 minutes. Therefore, the operator can quickly establish the proper dosage without guessing.

### **SYSTEM ADVANTAGES**

1. Oxidant dosage is dedicated to the source water quality by separate meter panels and rate valves. The valves are operated by solenoid valves. This feature permits setting the dosage for both the flow and the chemical demand for the source.
2. No pink water complaints. Since the system utilizes only chlorine as the oxidant pink water complaints from excess potassium permanganate are not possible.
3. Positive indication of the proper chemical dosage through the process recorder. This feature provides the operator with a simple and direct method for control of the system.
4. Continuous stand-by reserve of chemicals. Automatic switchover is provided for both chlorine and sulfur dioxide. This gives maximum assurance of continued uninterrupted service.
5. Safe. The ***Electromedia***<sup>®</sup> I system utilizes an all vacuum distribution of chemicals from cylinder mounted regulators to the point of injection. The only

pressure point is at the cylinder. A failure in a vacuum line automatically shuts down the chlorine supply.

6. Efficient. Chemical injection is accomplished by gas at the point of application. This utilizes the maximum chemical oxidation-reduction potential possible and a minimum cost. There are no errors in measuring or dilution of chemicals. Approximately 30% less chlorine is required to perform the same oxidation task performed by potassium permanganate. The filter loading is reduced since potassium permanganate is not present to be removed by the filter.
7. Operator friendly. The system is designed for unattended automatic operation. The operator checks chlorine dosage by ensuring that the pen arm on the recorder stays in the green band area. This is done by the operator, if necessary by adjusting the chlorine feed and waiting 10 minutes to insure equilibrium in the "green".
8. When the raw water is relatively corrosive a pH adjustment will be required. The final pH will be a function of the Langelier Index and may be determined by a general mineral analysis. A variety of chemicals may be used for this purpose: sodium carbonate, lime or sodium hydroxide.

## **OPERATION AND DESIGN SPECIFICATIONS**

- Filter flux rate: Up to 15 gpm/ft<sup>2</sup>
- Backwash duration: 4 minutes regardless of loading
- Backwash initiation: 8 to 12 hours, started by a timer with a differential pressure override at 10 psi
- Purge: 1 minute, after each backwash
- Internal distribution system: Hub and lateral/manifold and lateral
- Valving: Pneumatic/butterfly
- Chlorine feed: Gas feed system injected before the first one minute reaction vessel
- Chlorine feed rate: Shall be that which must stoichiometrically oxidize: 0.63 mg/l of chlorine per mg/l of iron 1.29 mg/l of chlorine per mg/l of manganese 8.33 mg/l of chlorine per mg/l of sulfide Plus organic demands which may be present
- Sulfur dioxide: Feed rate of 0.25 mg/l to 0.50 mg/l between the first and second one minute reaction vessel
- Media: Filtronics ***Electromedia***<sup>®</sup> I

## POTASSIUM PERMANGANATE

The use of potassium permanganate for the removal of iron and manganese is attractive because the reactions are complete and rapid. When iron and manganese are organically bound or complexed they are more difficult to remove. This requires a higher oxidation-reduction potential to initiate the reactions. The reactions for oxidizing iron, manganese and sulfides with potassium permanganate are:



The stoichiometric requirements for the above reactions are:

0.94 mg/l of potassium permanganate per mg/l of iron

1.92 mg/l of potassium permanganate per mg/l of manganese

12.37 mg/l of potassium permanganate per mg/l of sulfide

The resultant product in every equation is  $\text{MnO}_2$ , a precipitate that must be removed by the filter. Most manganese greensand filters are capped with a layer of anthracite to help remove the bulk of the solids so as not to blind the greensand. The filters are equipped with an air scour step to ensure the greensand is scrubbed clean during backwash.

Manganese greensand is a zeolite possessing adsorptive qualities when properly treated with an excess of potassium permanganate.

The manganese resident in the greensand complexes with the excess permanganate to form manganese in the +5 and +6 valence forms. The adsorptive qualities provide the greensand with two features. One, it will attract soluble iron, manganese and sulfide compounds to the surface of the media and retain them in the bed. Two, since energy is stored in the bed through the regeneration process, the bed can oxidize these compounds/elements to form the required precipitates or non-objectionable compounds (such as sulfide to sulfate). The sulfate is a soluble compound and passes through the filter. The iron and manganese form precipitates which are eventually backwashed from filter.

Regeneration may be accomplished by two methods: continuous regeneration or intermittent regeneration (regeneration at backwash). Regeneration at backwash would occur after a normal backwash sequence consisting of:

- 1) Drain down

- 2) Air scour
- 3) Fill
- 4) Backwash at 12 to 15 gpm per square foot for a period of 15 minutes.
- 5) Reduce backwash rate to 1 gpm per square foot and inject a concentrated solution of potassium permanganate, 2% is recommended, until the pink color of the solution is detected in the backwash water.

Continuous regeneration is more efficient but more difficult to control. An excess of permanganate must be carried to the filter to accomplish the regeneration. Should the demand vary, an over feed or under feed condition will occur. Continuous over feed conditions result in permanganate remaining in solution and passing through the filter resulting in the classic "pink" water complaint. Under feed eventually depletes the bed and the soluble manganese from the well passes through the filter resulting in the brown or black water complaints. Demand variances from varying hydrogen sulfide concentrations can be particularly troublesome because of the high ratio of permanganate to sulfide required to achieve the oxidation of sulfide to sulfate. It requires 12.37 mg/l of potassium permanganate to oxidize 1.0 mg/l of sulfide. Therefore, a small change in sulfide concentration can result in a large change in the permanganate requirement resulting in "pink" water going to the distribution system if overdosed or rotten egg odor complaints if under dosed.

#### SUMMARY:

- Filtronics **Electromedia**<sup>®</sup> I systems are easier to operate and produce consistently high quality filtrate.
- Filtronics **Electromedia**<sup>®</sup> I systems save money. Chlorine is much less expensive than potassium permanganate.
- Filtronics **Electromedia**<sup>®</sup> I systems use low chemical feeds. For every part per million of:

|           | Cl <sub>2</sub> |     | KMnO <sub>4</sub> |
|-----------|-----------------|-----|-------------------|
| Iron      | 0.64 ppm        | vs. | 0.94              |
| Manganese | 1.29 ppm        | vs. | 1.92              |
| Sulfide   | 8.33 ppm        | vs. | 12.37             |

- **Electromedia**<sup>®</sup> I systems don't burden the process by introducing a chemical

compound that ultimately must be removed by the filter.

- Reliable and built to last.
- Efficient - use less backwash water, reclaim backwash systems optional to recover 99.9% backwash water.
- Less manpower to maintain and operate.

### **WHAT TO DO NEXT?**

1. Complete a general mineral analysis form for each water source. The form is in this catalog section.
2. Return the completed general mineral analysis to us. We will review the chemical nature of the water and hydraulic considerations.
3. We will discuss possible options with you and prepare a budget proposal covering the equipment required for this application. We approach it from a "system responsibility" point of view. We will also provide a cost comparison.
4. Fax us your information now to (714) 630-1160.