IRON IN WATER AND
PROCESSES FOR ITS REMOVAL
By
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CONTENTS
I. Iron and Manganese Occurrence and Chemical Forms
     1. Groundwater Supply
     2. Surface Water Supply
II. Problems Associated with Iron and Manganese in Water
III. Processes for the Removal of Iron and Manganese
     1. Oxidation Followed by Filtration
     2. Clarification Followed by Filtration
     3. Ion Exchange
     4. Iron and Manganese Removal by Manganese Greensand
         (a) Continuous Regeneration (CR) Process
         (b) Intermittent Regeneration (IR) Process

The removal of iron and manganese has been the subject of numerous papers over the last 50 years or more. Although this paper is entitled "Iron in Water and Processes for Its Removal", we will also address manganese removal, since both elements frequently occur together and impart similar objectionable characteristics to water.
In this presentation we will attempt to provide an overview of the most common and accepted processes available for the removal of iron and manganese, their various advantages and disadvantages, and some practical advice to guide the choice of one process over another for a particular application.

I   Iron and Manganese Occurrence and Chemical Forms
Iron and manganese, which comprise 5% and 0.1% respectively of the earth's crust, are found widely distributed in both surface and groundwaters in nearly all geographic areas. Dissolution of these elements occurs by various processes and results in a variety of conditions regarding the concentration and chemical forms in which they are found in water.

1.   Groundwater Supply
In groundwaters iron and manganese are found particularly in wells that draw their waters from underground formations comprised of shale, sandstone, and alluvial deposits.

In the reducing environment often found in a deep well supply, that is, one which is devoid of oxygen and which possesses a low pH, the iron and manganese will exist in their divalent soluble forms. The concentration of iron may range from less than 1 mg/L to over 40 mg/L, although the majority of well waters will contain less than 5 mg/L of iron. Manganese generally occurs at concentrations of less than 1 mg/L but has also been found in concentrations as high as 5 mg/L. Occasionally one may encounter even higher concentrations of manganese, and we have on one occasion treated a water containing 15 mg/L of manganese.

Although normally found in their divalent form, iron and manganese may also exist in other forms, thereby complicating the selection of methods for their removal. Complexes of either an organic or mineral nature may occur with both elements. Organic complexes consist of the element sequestered with an organic molecule such as humic, fulvic or tannic acids. Iron and manganese in such a complex may be more difficult to remove due to the protective shell which the organic molecule provides. Complexes of a mineral nature may also occur in the presence of naturally occurring silicates, phosphates, or polyphosphates.

2.   Surface Water Supply

In a surface water supply iron and manganese may be present due to their dissolution from the associated geologic formations and/or from the decomposition of organic materials. For example, anaerobic conditions on a reservoir bottom may cause the dissolution of iron and manganese from the bottom sediments. When seasonal overturns occur due to temperature grad-ients, this dissolved iron and manganese will be distributed throughout the water supply. Although increased levels of iron and manganese may occur during periods associated with overturns, it is also very likely that these elements will be found at objectionable concentrations throughout the year.

Iron occurring in a near-neutral pH surface water supply saturated with oxygen will usually exist in an oxidized state. In this case the insoluble trivalent ferric (Fe^{3+}) iron will predominate. Organic acids are also frequently present so both the iron and manganese may exist as a complex. Manganese in a surface water may exist in either the soluble or insoluble form depending on the conditions found in the water supply. Although iron will almost always be present in the oxidized form, manganese may be found in the reduced form, as oxidation to the insoluble form requires a much more rigorous oxidizing environment than may be found in a typical surface water.

II.   Problems Associated with Iron and Manganese in Water

Iron and manganese are problematic in water due to their tendency to oxidize and precipitate as precipitate as insoluble oxides under a variety of conditions, causing both aesthetic and process water problems. In a potable water system iron and manganese frequently result in consumer complaints due to the metallic taste which they often impart to drinking water and beverages, and staining of laundry and porcelain fixtures. Even very low levels of iron may produce favorable conditions for the growth of what are commonly referred to as iron bacteria. These organisms, the most prevalent of which are Gallionella and Crenothrix, utilize energy obtained from the oxidation of ferrous to ferric

iron to "fix" dissolved carbon dioxide into organic molecular necessary for their existence. The growth of these organisms, which can occur at phenomenal rates, will result in the formation of a gelatinous mat which may cause pipe encrustations and provide an environment for the production of odor- and taste-causing organisms. In addition, corrosion may occur due to the creation of a galvanic cell and the formation of corrosive by-products (e.g., sulfuric acid and hydrogen sulfide) from associated organisms.

Recognizing the problems associated with iron and manganese, the Safe Water Drinking Act established maximum allowable limits of 0.3 mg/L for iron and 0.05 mg/L for manganese. Manganese cause problems at extremely low levels, hence the much lower limit. In practice it is generally desirable to remove iron to a level lower than the 0.3 mg/L standard to prevent some of the associated problems (e.g., growth of iron bacteria) which may occur even at this level. Also the processes discussed here will generally lower the iron concentration to less than the 0.3 mg/L limit.

In industrial applications iron and manganese can present those problems already described as well as other specific problems which may have more serious and costly consequences. Ferrous iron entering a softener or demineralizer may be oxidized on the resin beads, causing fouling and attrition of the ion exchange resins, with a resulting overall loss of operating efficiency and ion-exchange capacity. Process waters used for food or drug production must be iron- and manganese-free to avoid an off-taste and prevent staining of the end product. In textile mills and dye houses, iron and manganese in the wash and dye waters are well noted for causing staining during washing operations, poor dye take-up, and producing off-colors. In just about all processes requiring high purity or ultra-pure water, iron and manganese are two of the first constituents to be considered for removal.

Occasionally iron and manganese can also be removed in processes primarily intended to remove other elements (e.g., hardness by ion exchange or lime softening). However, for the most part iron and manganese removal must be addressed alone and may require removal prior to any additional treatment such as demineralization, reverse osmosis, or carbon filtration.


III. Processes for the Removal of Iron and Manganese
Nearly all of the available methods for iron and manganese removal, with the exception of ion exchange, rely on the oxidation of the soluble forms to insoluble forms along with or followed by clarification and/or filtration to remove the resulting precipitates. These various processes will be discussed with respect to their mechanisms, applicability, and advantages
and disadvantages.

1. Oxidation Followed by Filtration
When iron and manganese occur in low concentrations in large volumes of water, the removal of iron and possibly manganese from a normal groundwater supply may be

accomplished by oxidation to the insoluble forms followed by either pressure or gravity filtration. Using this method there are so many different flow schemes and variations to achieve the above that it would be impossible to try to include them all in this paper. A typical flow scheme for a plant utilizing this process is shown as Figure 1. Here the raw well water would be aerated with or without pre- or post-pH adjustment. An increased pH would be more favorable for the complete oxidation of iron and if raised high enough might assist the oxidation of manganese as well. For the complete oxidation of soluble manganese (without the addition of a strong oxidant) the pH would have to be increased to 9.5 or above. Iron, if not present as a complex, can usually be oxidized completely by aeration in the 7.0-8.0 pH range. The oxidation reaction for iron as ferrous bicarbonate by aeration is shown below with the reaction theoretically requiring 0.14 milligram of oxygen to oxidize each milligram of ferrous iron.

$$4Fe(HCO_3)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 + 8CO_2$$
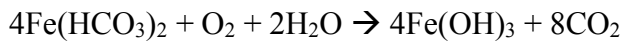
Following aeration a stronger oxidizing agent such as chlorine, potassium permanganate, chlorine dioxide or ozone may be added to oxidize the remaining traces of iron and manganese. Table I contains the stoichiometric amounts of oxidant required for the oxidation of 1 milligram of soluble iron and manganese.

TABLE I
STOICHIOMETRIC AMOUNT OF VARIOUS
OXIDIZING AGENTS REQUIRED FOR THE
OXIDATION OF IRON AND MANGANESE

		Amount to Oxidize 1 mg.
Oxidant	Iron	Manganese
Oxygen (02)	0.14	0.29
Chlorine (C12)	0.62	1.30
Potassium permanganate (KMn04)	0.91	1.92
Chlorine dioxide (CIO2)	1.21	2.45
Ozone (03)	0.86	0.87

In practice the use of a complementary oxidant may not be advisable in such an application. For instance, the efficiency of chlorine as an oxidant for manganese is very dependent upon pH, an excess of chlorine, and mixing conditions. Often actual operating conditions are not optimum for the oxidation of manganese by chlorine. Potassium permanganate is a very effective oxidizing agent but is difficult to control to the exact required dosage. With filtration following aeration as shown on Figure #1, an underfeed of permanganate would result in manganese leakage from the filter and an overfeed would result in the excess permanganate leaking through the filter and causing pink water in the effluent. Chlorine dioxide is an acceptable oxidizing agent but its handling and cost may make it prohibitive. The use of ozone may also be prohibitive due to cost. Also, too large an excess of ozone in the presence of manganese will produce the permanganate ion, resulting in "pink water" in the treated effluent.

Oxidation of the soluble iron and manganese is then followed by filtration using either sand, anthracite, or dual media sand-anthracite filtration to remove the insoluble oxides of iron and manganese. Specially treated manganese greensand which is used in the popular manganese greensand CR process (to be discussed later) may also be employed as the filtration media for the removal of iron and especially manganese. After treating a specific number of gallons the filter will require backwashing to remove the collected products of oxidation. Usually the backwash waste water can be sent directly to the sewer or to a backwash reclamation tank for settling of the contaminants and reuse of the clear supernatant. The very small volume of sludge could then be sent to the city sewer. As the sludge is inert and exerts no biological load on a sewerage system it is generally acceptable to municipal authorities.

The steps discussed above may be altered to provide a variety of treatment schemes as required by the application. For example, if manganese is not present in the raw water, or if manganese can be tolerated in the treated water, the use of a stronger oxidant following aeration could be eliminated. In addition, both pre- and post-pH correction may not be required. Aeration alone followed by chlorination and filtration could provide a clean iron-free water under these circumstances. For the removal of manganese, however, very close control of the process pH and/or additional oxidants may be required.

As the concentration of iron in the raw well water increases, the flow scheme in Figure 1 becomes more and more impracticable due to the increased loading imposed on the filtration bed. As the load increases the service run length will decrease to a point where such a system is very uneconomical due to backwash frequency. Consequently pilot plant testing, which should almost always be a prerequisite for all iron and manganese removal installations, is necessary to provide such information as run length and effluent quality. With pilot plant work the feasibility of such a treatment scheme outlined above could be quite easily and accurately predicted.

2. Clarification Followed by Filtration

When present at very high concentrations, or when existing as either the insoluble oxide or as an organic complex as may be found in a surface water, the removal of iron, and to a lesser degree manganese, may be accomplished by clarification using coagulation and sedimentation processes. Also, when accompanied by either high turbidity or color a clarification step will be required. This may then be followed by high-rate sand or dual media pressure or gravity filtration to insure the complete removal of any fine precipitates of iron and manganese.

When dealing with a groundwater supply there is no hard or fast rule to determine under exactly what circumstances clarification would be recommended over either ion exchange or oxidation followed by either standard filtration or filtration using manganese greensand. The method chosen would depend on a variety of conditions including raw water iron and manganese concentration, the chemical form in which they exist, the plant flow rate, and additional treatment other than iron and manganese removal which may be required (e.g., softening, and turbidity or color removal). Other factors to be considered

would be initial capital cost, operating and chemical costs, ease of operation, requirements for disposal of waste products, and the effluent quality required.

For a well water, the clarification process may be more feasible than either ion exchange or direct oxidation and filtration when the iron and manganese concentrations and the plant flow rate are both high. With low iron and manganese concentrations and a high flow rate, or conversely with a high iron and manganese content and a low plant flow rate, ion exchange or oxidation followed by in-line filtration would probably be more economical.

In the removal of iron and manganese by clarification followed by filtration, the mechanism is the complete oxidation of the elements to the insoluble forms followed by clarification to remove the bulk of the metal oxides and final filtration to remove the remaining precipitated products of oxidation. In a surface water in which the iron and perhaps the manganese are already oxidized, coagulation is required to agglomerate the precipitated oxides and to aid settling. In addition, complementary oxidation using an oxidizing agent may be required if manganese is present in its reduced form. Clarification will then provide for the removal of the bulk of the metal oxides and allow a sufficient detention time for the complete oxidation of iron and manganese. As seen in Figures 2 and 3 this method is also quite adaptable to a variety of conditions, and by manipulating the pH and the addition of oxidants the removal of both iron and manganese to acceptable levels may be accomplished.

Often, however, raw water conditions may be variable, and stringent care in operation of the system must be maintained to achieve a consistently acceptable effluent. Figure 2 represents treatment of a water obtained from a deep well and Figure 3 depicts the same treatment of a surface water supply. Note that the aeration step in Figure 3 has been eliminated, since any iron will probably already exist in the insoluble ferric form although possibly complexed organically. Manganese, however, if present in the soluble form, would require oxidation using one of the stronger oxidants previously mentioned. The coagulation and sedimentation step will remove all but the fine nonsettleable precipitates which would be subsequently removed by a properly designed and operated dual media filter. In some applications the final filtration step has been eliminated but this often results in a non-uniform effluent quality due to upsets in the coagulation-sedimentation basin.

When iron and manganese removal from either a well or surface water supply is required in addition to softening, the cold lime or lime-soda process should be considered. Both iron and manganese, when present as the soluble divalent ion, are more readily converted to the insoluble higher oxides at the high pH present during the softening process. Reduction of the calcium and/or magnesium alkalinity by lime softening will result in an effluent pH of 9.5 to above 10. Since a pH greater than 9.5 is required for the complete removal of manganese the process waters should be stringently controlled to maintain this pH. With high iron concentrations the lime softener will often be preceded by aeration to oxidize the bulk of the iron. With pre-aeration and when operated in the optimum pH range the reactions will be rapid enough to allow for the complete oxidation

of both iron and manganese within the designed detention period of the equipment. Organically bound iron and manganese occasionally present in surface waters may also be removed using this process. Economics, however, usually demand that this process not be considered for iron and manganese removal unless sufficient alkalinity is present for the lime softening reaction and the removal of hardness is desired.

3.   Ion Exchange

Iron and manganese removal by the ion exchange process using a sodium form strong acid cation resin has been used in various applications for a number of years with varying degrees of success. The process should only be considered with clear well waters devoid of oxygen and other oxidizing agents, as the iron and manganese must exist as the soluble divalent ions. In addition, the process should be limited to waters containing small quantities of iron and manganese.

The sodium cycle ion exchange reaction with iron and manganese is similar to that for the exchange of calcium and magnesium in the ion exchange softening process. A typical flow diagram is shown in Figure 4. During service the following reaction will occur with R representing the fixed exchange site on the resin.

$$Fe^{2+} + 2Na•R \rightarrow Fe•R_2 + 2Na^+$$
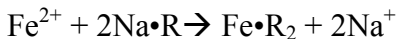
In addition to the removal of iron and manganese the calcium and magnesium hardness will also be exchanged, softening the raw water. Following treatment of a predetermined quantity of water, based on the raw water analysis, resin capacity and volume, the resin will require regeneration to the sodium form as shown by the following reaction:

$$Fe•R_2 + 2NaCl \rightarrow 2Na•R + FeCl_2$$
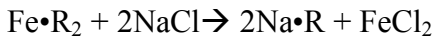
Although this process has been used successfully for iron and manganese removal there are some definite design and operating considerations that should be followed in order to minimize the two main problems frequently encountered—fouling and attrition.
These design and operation considerations include:
• Raw water characteristics (including concentration and form of iron and manganese present);
• Ratio of iron to total divalent cations;
• Resin capacity;
• Regeneration techniques;
• Method for chemical and physical cleaning of the resin.

In general manganese is much more amenable to removal by ion exchange than iron, as the soluble divalent form is much more stable than divalent iron. Manganese therefore behaves much more like calcium and magnesium during the exchange process and does not present the problems generally associated with iron and ion-exchange resins.

As stated previously, for the exchange reactions to occur, the iron and manganese must exist in the soluble form. The raw water must contain no oxidizing agents and should not

be pH corrected prior to treatment. The presence of any oxidizing species or the adjustment of pH could result in the oxidation of the ferrous iron to ferric iron which would then precipitate. The fine particulate iron oxide would not be exchanged on the resin and very little, if any, would be removed by filtration, resulting in iron leakage from the bed. Fouling of the resin beads may occur due to the resin being coated with a sheath-like covering of insoluble ferric hydroxide. This condition occurs due to the iron being in the ferric state either prior to entering the resin bed or by its oxidation on the resin during the service run. Severe fouling may then occur, resulting in a loss of ion exchange capacity, and a decrease .in the kinetics or rate of the ion exchange reaction. In addition, oxidizing conditions in the raw water may oxidize ferrous iron, which has already been exchanged and is within the matrix of the resin, to the ferric form. This particular condition may cause fracturing of the resin due to the increased volume of the precipitated oxide.

The design and operation of the ion exchange process for iron and manganese removal will require a slightly modified approach compared to softening for the removal of calcium and magnesium ions. For example, the normal softening exchange capacity of a gel-type 8% cross-linked strong acid cation resin is approximately 20 kilograins/cu ft using a 6 lb/cu ft salt regenerant level. With softening for hardness removal, the full operating capacity of the resin at a particular regenerant level would be utilized. Therefore, if a 10 lb/cu ft regenerant level was used the resulting ion exchange capacity of the resin would increase to approximately 25 kilo-grains/cu ft. The run length could be extended then by increasing the regeneration level (assuming that the raw water analysis remains the same, of course). In practice, however, the regenerant level and resin capacity are kept at a level which provides the optimum regenerant efficiency.

With the ion exchange process for iron removal, however, the resin should be downrated to prevent loading the resin with iron. As the percentage of iron to total divalent ions increases, this becomes even more critical. Downrating the resin, or using less of the actual operating exchange capacity at a given regenerant level, can be accomplished by maintaining a particular operating capacity and increasing the salt dosage or by decreasing the service run length at a particular regenerant level. Either of these conditions will result in partial use of the total available ex- change capacity, preventing loading the resin with excessively high amounts of iron, therefore minimizing the chances of fouling. This is done at the price of a decreased regenerant efficiency. Although there is no set rule we have rated resin as conservatively as 10 kilograins/cu ft at a 10 lb/cu ft salt regeneration level, or only 40% of the normal operating exchange capacity. This is probably the extreme case, however, and was practiced on an extremely low solids water in which the iron was over 50% of the total divalent cations. With a rating as low as this the resin is of course never fully exhausted. This more frequent regeneration minimizes the chance for iron exchanged on the resin to oxidize, preventing fouling and the previously described problems.

Normally the ion exchange process is used for the removal of iron and manganese from well waters in which the ratio of iron to the total divalent cations is very low, or about 2% or less. At normal design flow rates of 6-12 gpm/sq ft run lengths would be maintained so

that there is no more than 24 hours between regenerations. This would prevent the iron from aging on the resin, minimizing the possibility of fouling.

Even if all of these recommendations are followed, problems may occur during the regeneration of the resin to the sodium form. During regeneration the brine solution will contain at least small amounts of dissolved oxygen. This may cause oxidation of the iron and manganese ions held either in or on the resin or as they are exchanged, probably resulting in both the previously described physical damage to the beads and fouling of the resin. One way in which this situation may be avoided is to maintain a reducing condition in the regenerant by the addition of 0.01 lb. of sodium hydrosulfite per gallon of regenerant. Sodium hexametaphosphate in the regenerant has also been used with some success; however, the mechanism here is different than with the sodium hydrosulfite. The polyphosphate sequesters the iron as it is exchanged off the resin and, even though oxidation of the iron may still occur, the sequestering prevents agglomeration of the iron oxides which would attach to and foul the resin beads.   Since it would be virtually impossible to determine the exact amounts of additive required in the regenerant brine, an excess is often used. This results in traces of the additive in the treated water, which may or may not be objectionable, but should be addressed prior to its use.

When iron and manganese are present at very low or trace levels in a well water that is being softened by the ion exchange process, none of the operational changes discussed here would be required as the fouling problems may be minimal. However, as the iron concentration in the raw water increases, especially when oxidizing conditions are present, separate pretreatment equipment for iron and manganese removal may be required prior to ion exchange softening or demineralization by ion exchange.

When removing iron by the ion exchange process, regardless of the ratio of iron to total exchangeable cations or divalent ions, chemical cleaning of the resin is eventually required. The frequency of cleaning depends on both the type and quantity of iron in the water being treated and the conditions which result in the oxidation of the ferrous iron to ferric iron. The severity of this problem is often unique for a particular installation and often no correlation exists between similar raw water characteristics (e.g., raw water iron concentration) and resulting conditions.

Drastically different water types do of course respond dissimilarly. For example, the type of iron in well waters with high alkalinity and high total dissolved solids, common in the Midwest, oxidizes rapidly and has a tendency to foul ion exchange resins. On the other hand iron in the low total dissolved solids well waters found along the Eastern Seaboard oxidizes much more slowly and fouls the resins to a lesser extent.

Several chemicals are available for treating iron- and/or the less common manganese-fouled resins. The most effective are hydrochloric acid for iron-fouled resins and sodium hydrosulfite for manganese-fouled resins. Many proprietary cleaning compounds are available which claim to clean not only iron- and manganese-fouled resins but also resins contaminated with various organic foulants, slimes, etc.

In general, iron and manganese removal by ion exchange can be practicable under certain stringent conditions. It is, however, expensive considering both capital and operating costs and can be extremely complicated due to the fouling of resins by iron and manganese. Unfortunately the amount of fouling that will occur at a particular installation can be determined only after the unit is in service, making this particular process for iron removal fraught with hazards.

4. Iron and Manganese Removal by Manganese Greensand
Another method for the removal of iron and manganese from groundwaters is the manganese greensand process. This process and variations of this process have been used for over 20 years in the removal of these two contaminants. Today there are two distinct processes (the manganese greensand Intermittent Regeneration (IR) process and the manganese greensand Continuous Regeneration (CR) process) which are standard in the industry and which we will discuss here.

Manganese greensand is processed from what is commonly known as New Jersey greensand but more correctly identified as glauconite, an iron potassium-silicate mineral of marine origin. Glauconite occurs in this area along the East Coast where it was deposited approximately 75-80 million years ago during the geologic time known as the Cretaceous period. Greensand has been used since the 1920's, originally as a natural zeolite for water softening due to its relatively high ion exchange capacity of approximately 3,000 grains/cu ft. Until the development of synthetic gel-type ion exchange resins following World War II, which have a capacity of about 6-7 times that of glauconite, the greensand zeolites were an efficient and reliable part of the softening industry.

For iron and manganese removal the naturally occurring singular nodular grains of glauconite are washed and classified to produce a filtration media having a sieve analysis of 18 by 60 mesh with a resulting effective size of 0.3 to 0.35 mm and a uniformity coefficient of 1.60 or less, giving the media excellent filtering characteristics. The material is processed to stabilize the glauconite which is then coated with manganese oxides in various valence states. It is this coating which provides the glauconite with its special chemical properties for the removal of iron and manganese as well as small quantities of hydrogen sulfide.

The advantages of the manganese greensand process over aeration and filtration are single pumping (as the process generally employs pressure filtration), reliability, flexibility, a high quality effluent and ease of operation. Both the CR and IR processes are relatively uncomplicated in both their design and operation but result in an efficient, reliable method for iron and manganese removal. In general, iron and manganese removal with manganese greensand is cost-effective when the iron and manganese concentrations are relatively low and the plant flow rates high. At low plant flow rates and high iron and manganese concentrations, the process should also be investigated. As with the previously discussed aeration followed by direct filtration process, the filter run length will decrease as the iron concentration increases due to the increased loading on the filter. Normally, high concentrations of iron (10-15 ppm) coupled with high flow

rates (over 5-8 mgd) require coagulation. However, there can be circumstances for considering this process and the parameters such as run length, pressure drops, chemical dosage, etc., should be investigated by a pilot plant study.

The mechanism for iron and manganese removal by manganese greensand in both the CR and IR method is oxidation followed by physical removal of the resulting precipitates by filtration using a manganese greensand or manganese greensand-anthracite bed. Generally the continuous regeneration or CR process is recommended for waters where iron predominates with only small amounts of manganese. The IR process is used for water where manganese removal with or without the presence of iron is required.

(a) Continuous Regeneration (CR) Process
The manganese greensand CR process, as previously mentioned, is applicable on well waters where iron removal is the main objective with or without the presence of manganese. In theory, this process can remove iron from water in concentrations up to 15 mg/L or more. However, with such high concentrations the run length between backwashing would be as little as 4-6 hours, based on a service flow rate of 1.5-2.5 gpm/sq ft. With a high iron concentration such as this, low flow rates are required to produce an acceptable run length. Waters having iron concentrations in the lower range of 0.5-3 mg/L would have run lengths of 18-36 hours at a more acceptable design flow rate of 3-5 gpm/sq ft.
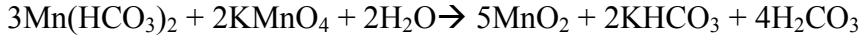
The CR process involves the feeding of an oxidant or combination of oxidants such as potassium permanganate and chlorine to the raw water prior to contact with the manganese greensand bed. A typical flow diagram is shown as Figure 5. Chlorine, which is recommended, should be fed prior to the permanganate injection point. The chlorine will oxidize the bulk of the iron. Potassium permanganate will then complete the oxidation of trace amounts of iron and soluble manganese. Since permanganate is a strong oxidant, manganese can be completely oxidized even at the minimum recommended pH of 6.2.
The manganese greensand bed performs a dual function to complete the removal of iron and manganese. First, correct operation of a CR filter requires that a slight excess of permanganate, indicated by the influent water having a slight pink color, will insure that the oxidant demand, whether using permanganate alone or in combination with chlorine, has been met. The excess permanganate will be reduced to a manganese oxide by the manganese greensand. The manganese oxides will then precipitate on the grains, maintaining them in a continually regenerated state. Conversely, a momentary underfeed of oxidant would utilize the oxidizing capacity of the regenerated manganese greensand to complete the oxidation of iron and manga-nese as required. In the CR process then the manganese greensand acts as a redox buffer with capabilities of both reactions as required by influent water conditions. Second, it is a well-known fact that in iron and manganese removal by oxidation, the presence of manganese oxide will act as a catalyst whether phe oxidizing agent be oxygen, chlorine, ozone, or permanganate, insuring that the reaction goes rapidly to completion.

Reactions involved in iron and manganese removal by potassium permanganate and manganese greensand include the oxidation of iron by chlorine (if used) and permanganate:
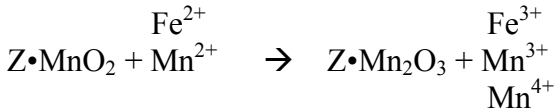
$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl$

$3Fe(HCO_3)_2 + KMnO_4 + 7H_2O \rightarrow MnO_2 + 3Fe(OH)_3 + KHCO_3 + 5H_2CO_3$

the oxidation of manganese by permanganate:

$3Mn(HCO_3)_2 + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + 2KHCO_3 + 4H_2CO_3$

and the reduction of any excess potassium permanganate by the manganese greensand (where Z represents manganese greensand "zeolite") to manganese dioxide:

$3Z\bullet MnO + 2KMnO_4 + H_2O \rightarrow 3Z\bullet MnO_2 + 2KOH + 2MnO_2$
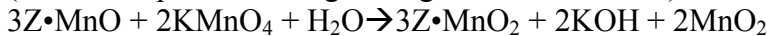
Conversely, the oxidation of soluble iron or manganese by the manganese greensand when the oxidant demand on the raw water has not been fully met:

$$\begin{array}{ccc} & Fe^{2+} & Fe^{3+} \\ Z\bullet MnO_2 + Mn^{2+} & \rightarrow & Z\bullet Mn_2O_3 + Mn^{3+} \\ & & Mn^{4+} \end{array}$$

Extended service with an underfeed of permanganate prior to the CR filter will result in the eventual exhaustion of the oxidative capacity of the media with resultant iron and manganese leakage into the treated water. The media must therefore remain in a continually regenerated form at all times. This is easily accomplished by a visual check for the "just-pink" color in the filter influent.

The closed pressure filter normally contains a gravel support bed for the proper distribution of backwash waters, a manganese greensand bed and an anthracite bed. As a run progresses pressure drop increases as the filter bed becomes contaminated with the insoluble products of oxidation. After either a predetermined number of gallons, or when the head loss reaches10 psi, the bed must be backwashed to remove the filtered particulates. In addition it is also beneficial (although not necessary) to provide some means of air washing on a weekly basis to thoroughly clean the manganese greensand grains. Naturally, no regeneration of the media is required prior to placing the unit back in service due to the continuous regeneration during service. As with oxidation by aeration followed by filtration, the backwash waste water can be collected for reuse and the settled precipitates sent to a sanitary sewer or drying bed.

(b) Intermittent Regeneration (IR) Process
When the well water contains all manganese, or mostly manganese with lesser quantities of iron, the intermittent regeneration process is preferred. This process involves passage of the raw water through a manganese greensand bed where oxidation of manganese occurs directly onto the grains utilizing the oxidative capacity of the treated greensands. The flow diagram of a typical IR application is shown in Figure 6. Although manganese greensand will oxidize appreciable amounts of iron directly on the grains as well, iron has a tendency, depending on the concentration, to coat or foul the media with iron oxides which then inhibit the oxidation properties and permanganate regeneration reactions of

the manganese greensand. For this reason waters being treated by the IR process for manganese removal, which also contain appreciable concentrations of iron, should have a pre-oxidation step, either in the form of chlorine injection or aeration to convert the iron to its insoluble form. Precipitates of iron are then filtered out and manganese is oxidized on the individual grains, becoming an integral part of the manganese oxide coating with a capacity equal to the original coating.

After treating a specified number of gallons the oxidation capacity of the media will be consumed and regeneration is required. Prior to regeneration the media should be backwashed to remove collected precipitates and to restratify the media. Again, with an appreciable iron concentration, a high loading of filterable material indicated by a high pressure drop across the bed, will require that the filter be backwashed possibly before the oxidation capacity of the media has been fully utilized. In such a case as this the filter can be backwashed without regeneration and then placed back in service.

Regeneration consists of the downflow passage of a potassium permanganate solution through the bed with a regenerant level of 1.5 oz potassium permanganate/cu ft of media. Following regeneration the filter will require rinsing until all the excess permanganate is gone. The IR method may also be very flexible with regard to regeneration, as the excess regenerant can be recycled to use for the next regeneration. In this way there, are no permanganate disposal problems and chemical costs are minimized.

There are certain limitations with the use of manganese greensand in either the CR or IR/process. The minimum pH with either process is 6.0. At a raw water pH of less than 6.0, pre-pH adjustment would be required. With the CR process, however, pre-pH correction should not exceed 6.8-7.0 to prevent formation of a nonfilterable iron colloid. With the IR, process in the absence of iron, the maximum pH would be 8.5. Also as with ion exchange resins, the media should not experience high pressure drops as fracturing of the material may occur.

Summary

Processes for the removal of iron and manganese must be approached with an understanding of the water source, iron and manganese concentration, chemical form, and any additional contaminants or species that require removal. In addition, the end use of the water must be considered to determine what level of treatment is required and whether iron and manganese removal should be considered as a treatment step preceding other water purification methods.

As previously mentioned we cannot stress enough the need for a pilot plant study of a water source requiring iron or manganese removal. With a groundwater this can be accomplished in an easily set up and operated pilot plant filter. A surface water may require jar testing followed by gravity filtration to determine the resultant water quality. With pilot testing those unusual waters with complexed iron and manganese will be identified and a treatment waters with complexed iron and manganese will be identified

and a treatment scheme developed. Following a thorough investigation, including pilot work, a treatment process can be recommended for iron and manganese removal.
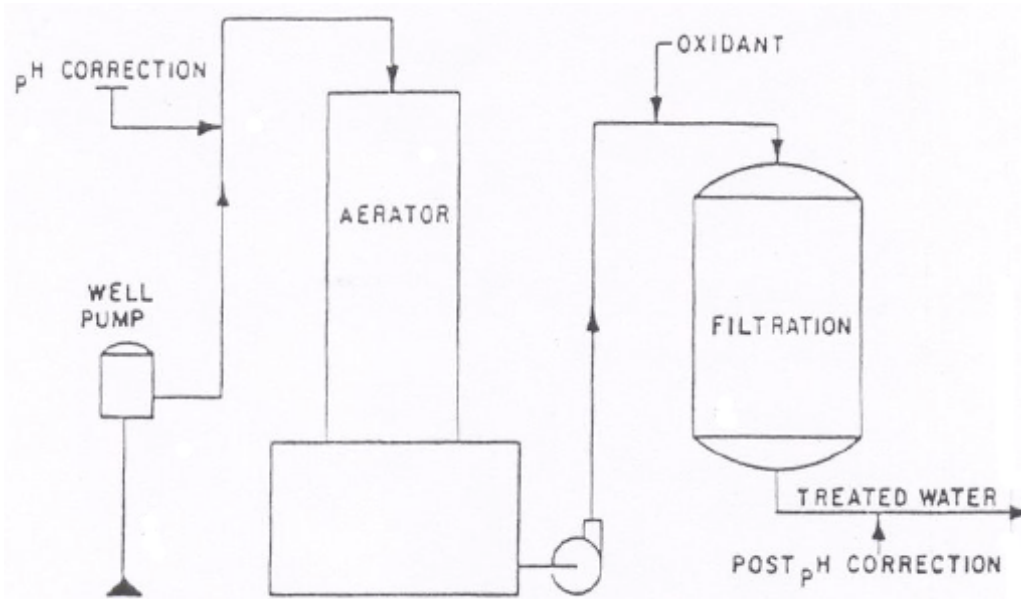

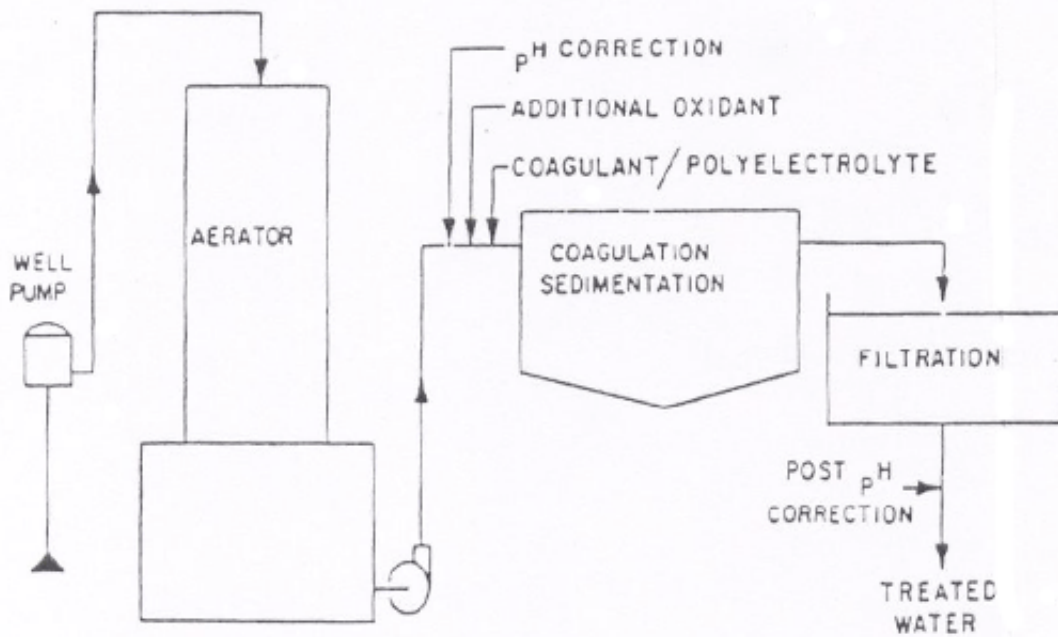Fig 1 – Aeration, Additional Oxidation Followed by Filtration

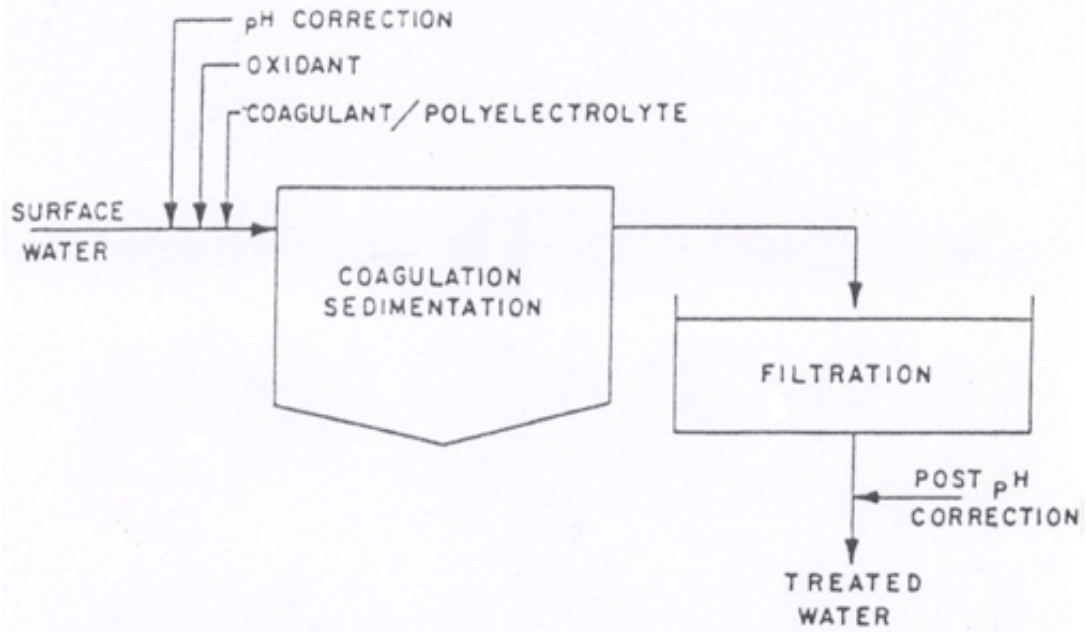Fig 2 – Aeration, Additional Oxidation, Coagulation and Sedimentation Followed by Filtration

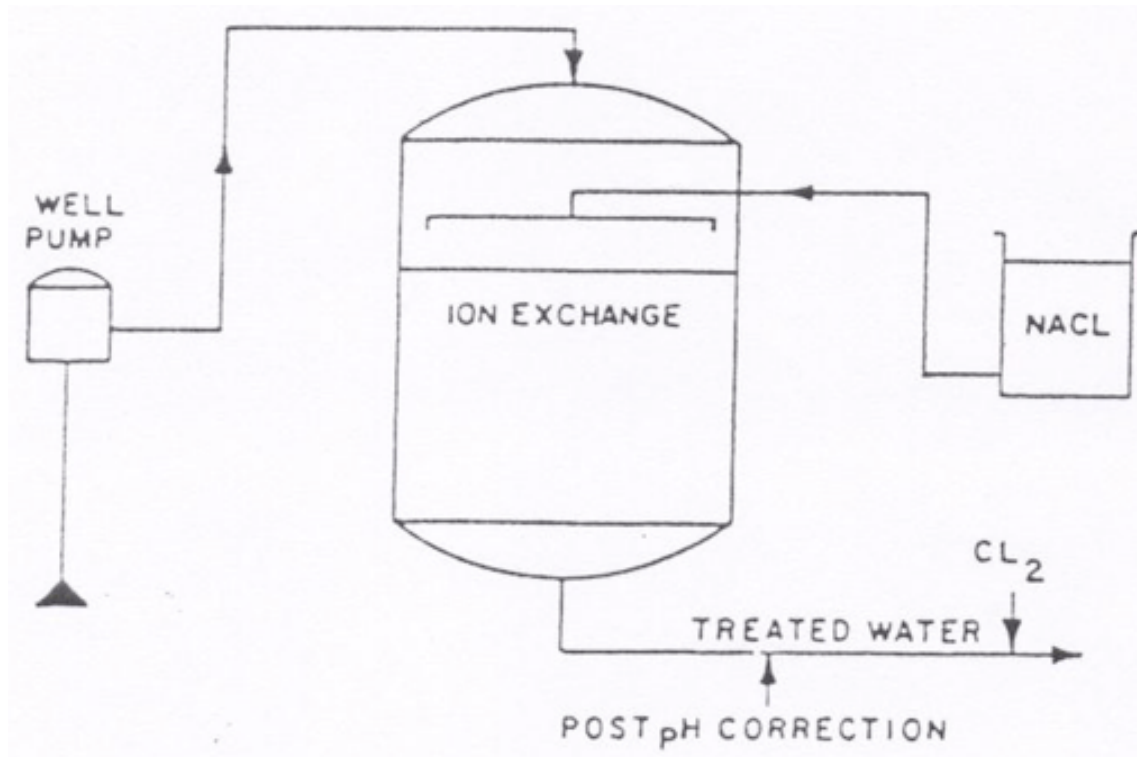Fig 3 – Oxidation, Coagulation and Sedimentation Followed by Filtration
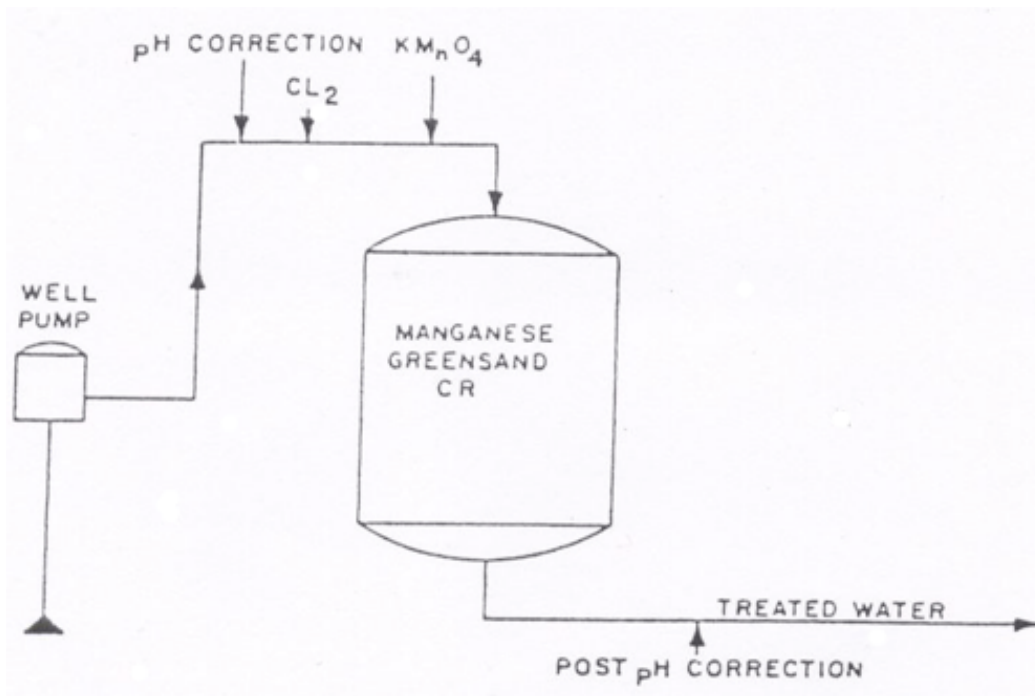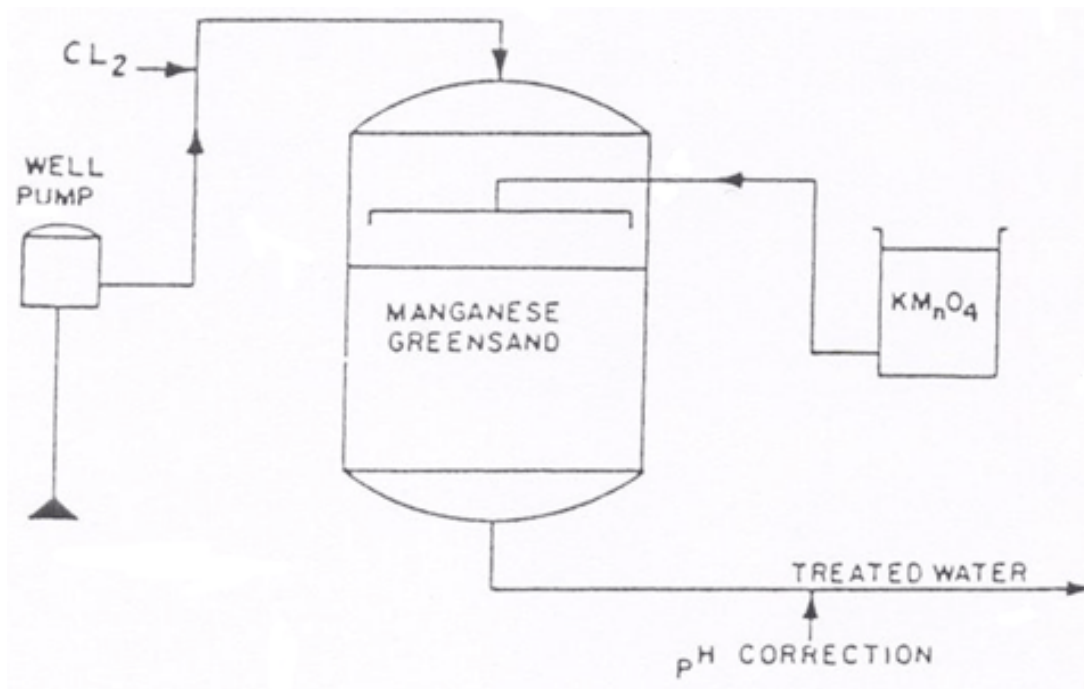

Fig 4 – Ion Exchange

Fig 5 – Manganese Greensand CR Process

Fig 6 – Manganese Greensand IR Process