Pureflow FILTRATION DIV.

THE REMOVAL OF IRON & MANGANESE FROM DRINKING WATER SUPPLIES

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FOREWORD

This bulletin is offered to provide the reader with general information on the occurrence of iron / manganese in nature, with special emphasis on its effect in potable water, and the various types of iron / manganese removal systems.

Iron / manganese, because they are rather closely related heavy metals are often found together. They give rise to similar problems in water supplies, and fortunately, they generally respond to the same treatment processes for their removal. Therefore, they are usually treated as one subject, although, as will be seen, they differ greatly in their chemistry.

OCCURRENCE AND USES

IRON (Fe), Atomic Number 26, Atomic Weight (most abundant isotope) 56, is found in Group VIII of the Periodic Table of the Elements, right between manganese and cobalt, in Period 4. Iron has valences of +2 and +3, and readily combines with other elements. It is the fourth-most abundant element in the earth's crust, outranked only by aluminum, silicon, and oxygen.

Because of its reactivity, iron is seldom found in its native state. One of the few places on earth where metallic, i.e., "native" iron is found is in Greenland, where it occurs as very small grains or nodules in basalt, an iron-bearing igneous rock.

Early records of human use of metallic iron are around 2000 BC in Egypt, Asia, Assyria and in China. It is almost certain, however, that the first metallic iron to be used was not derived from ores but was obtained from meteorites.

Although gold, silver, copper, brass and bronze were in common use before iron, it was not until man discovered how to extract iron from its ores, about 1300 BC, that civilization began to develop rapidly.

26
Fe
Iron
55.845

MANGANESE (Mn), Atomic Number 25, Atomic Weight 55, is found in Group VII of the Periodic Table of the Elements. The name derives from the Latin Magnes (magnet). The element was discovered by Gahn, a Swedish mineralogist, in 1774. In the first series of transition metals, manganese is the element with the most oxidation states (-3 to +7), with the most important being +2, +4 and +7. It is this abundance of possible oxidation states that account for the rather complicated chemistry of the element.

Manganese is found in most soils at between 200 - 300 mg / kg (ppm). Many rocks contain 800-1400 mg / kg. The main uses of the metal include that of an alloying agent, as a cleaning agent for steel, cast iron and non-ferrous metals, in the manufacture of dry-cell batteries, glass, ceramics, paints and inks.

25
Mn
Manganese
54.938

IRON AND MANGANESE IN THE AQUEOUS ENVIRONMENT

Although many of the ferrous and ferric (+2 and +3) salts, like chlorides or sulfates, are highly soluble in water, the ferrous ions are readily oxidized to the ferric state in natural surface waters, forming insoluble hydroxides. These precipitates tend to agglomerate, flocculate, settle or become adsorbed on surfaces; hence the concentration of iron is rarely high. In ground waters the pH and E_h (Equilibrium Potential - a measure of the oxidation state of a solid / solution) may be such that high concentrations of iron can remain in solution.

Manganese, like iron, forms highly soluble chlorides, sulfates and nitrates, but its oxides, carbonate and hydroxide are only sparingly soluble. For this reason, manganous (+2) and manganic (+4) ions are seldom present above 1 mg / L in natural surface waters. In groundwaters subject to reducing conditions, manganese can be leached from the soil and occur in high concentrations.

The National Inorganic and Radionuclide Survey (NIRS) of Drinking Water Regulators collected data from 989 Public Water Systems between 1984 and 1986 in forty-nine states. Of these samples 68% contained detectable manganese concentrations. The median concentration was 10 µg/L (ppb). This data closely parallels the 1962-67 U.S. occurrence data shown in the table below. Interestingly, very low levels of manganese have also been detected in 97& of Surface Water sites, where the contaminant generally occurs in the benthic deposits.

Casale (2002) reported that 35% of 349 Groundwater Systems in the 1996 AWWA survey reported source water manganese concentrations of greater than 50 µg/L, while approximately 40% of 428 Surface Water Systems in the same survey reported manganese concentrations of greater than 50 µg/L.

The relative abundance of iron and manganese in raw and finished waters in the U.S., based on 1962-1967 data, is as shown in the table below.

		Concentration µg / L (ppb)		
	Frequency of Detection, %	Minimum	Maximum	Mean
		Raw Waters		
Iron	75.6	1.0	4,600	52
Manganese	51.4	0.3	3,230	50
		Finished Waters		
Iron	83.4	2.0	1,920	68.9
Manganese	58.7	0.5	450	25.5

REGULATORY BACKGROUND

The Maximum Contaminant Levels (MCL's) are contained in the National Secondary Drinking Water Regulations (NSDWR) standards of the Safe Drinking Water Act (SDWA). It will be remembered that National Primary Drinking Water Regulations (NPDWR) standards are based upon health considerations, while the NSDWR Secondary Standards are not health related, but predicated upon Consumer Acceptance and Property Protection. Thus, the limits in the SDWA, as well as those of the World Health Organization (WHO) are established on the basis of esthetics and economic considerations, rather than physiological hazards.

HEALTH IMPLICATIONS

IRON

Iron / manganese are essential for the nutrition of plants and animals. The daily nutritional requirement for iron is 1 - 2 mg, and most human diets contain between 7 - 35 mg per day (Average = 16 mg / day). Consequently, drinking water containing iron in concentrations that would render the water unpalatable (1 mg / L or more) would have little effect on total daily iron intake.

MANGANESE

Manganese is a required micronutrient. Typical daily intakes range between 1 – 10 milligrams. Diets deficient in manganese result in impaired or abnormal growth, symptoms of central nervous system disturbance, anemia, and possible interference with reproductive functions. In concentrations not high enough to cause unpleasant tastes, manganese is regarded by most investigators to have no toxicological significance in drinking water. The literature, however, does report some cases of what appears to be manganese poisoning. A small outbreak of an encephalitis-like disease, with early symptoms of lethargy and edema, was traced to manganese in the drinking water of a village outside Tokyo. Excess manganese is also believed to be the cause of a rare disease endemic in Manchukuo. At very high levels, manganese can pose a neurotoxic risk, "Manganism", which appears to be confined to manganese miners, thus due to inhaled, rather than ingested, manganese.

As is the case with iron, manganese is not considered a physiological hazard, in that normal dietary intake is far greater than the amount that would be tolerated aesthetically in drinking water.

Recent research (Spengler and Reid, 2010, Ljung and Vather, 2007) has indicated that manganese from drinking water may contribute adverse health effects, such as neurotoxicity in infants and increased colon and lung cancers in adults at levels below the health advisory concentration of 0.3 mg/L.

Source removal is recommended at ten times the [consumer] notification level. Monitoring for manganese is required within the framework of secondary MCL regulations, but generally not outside that framework. For community systems subject to the secondary MCL monitoring and compliance requirements (22 CCR § 64449), with manganese greater than the notification level, the Division of Drinking Water recommends that information about the health concerns associated with high manganese exposures be provided to consumers as part of the required consumer dissatisfaction determination.

Nevertheless, the California Department of Health Services (CDHS), in 2003, established a "Notification Level" of 0.5 milligrams per liter for manganese. Community water systems that exceed the secondary Maximum Contaminant Level (MCL) of 0.05 mg / L, must notify the Department, and their customers, if the average of four quarterly monitoring results for manganese exceed the notification level.

The primary reasons for the inclusion of iron and manganese in the Secondary Standards, aside from metallic, stringent tastes, is because both elements deposit on foods during cooking, stain laundry and plumbing fixtures, foster the growth of some microorganisms in reservoirs, filters and distribution systems, and are the cause of numerous problems in water-intensive industries ranging from baking through brewing, dyeing, paper-making, photo-finishing, textiles, and many more.

"Legacy" metallic oxide accumulations, especially those of manganese, in distribution systems can and do cause water quality problems for utilities. Most utilities only consider they have manganese problems if customers complain about discoloration of the water, staining of laundry and the water's taste. But, even at very low manganese concentrations, the metallic oxides may accumulate in distribution systems – defined as "legacy" metals. Fortunately, manganese's aesthetic threshold is considerably lower than the health advisory level (0.3 mg/L). Still, Schock, et al, in 2008, and Friedman, et al, in 2010, pointed out that the concern extends beyond manganese itself in that hydrous manganese oxide solids will adsorb other regulated trace metals (i.e., radium, lead, barium, iron and perhaps arsenic), thereby contributing to the accumulation – and their later potential release – of these contaminants into the drinking water system.

Note: Please also refer to BLENDING on *page 16*

"IRON BACTERIA"

Any discussion of iron in water supplies would not be complete without the mention of iron bacteria. These bacteria, Crenothrix polyspora, Sphaerotilus natans, and Gallionella ferruginea, are capable of metabolizing reduced iron present in their aqueous habitat and depositing it in the form of hydrated ferric oxide on or in their mucilaginous secretions. A somewhat similar mechanism is used by bacteria that utilize manganese. The large amount of brown slime so produced will impart a reddish tinge and an unpleasant odor to drinking water and may render the supply unsuitable for domestic or industrial use.

Contrary to popular belief, iron bacteria are not the cause of iron in the water. These bacteria obtain their energy from the oxidation of iron in the Fe^{+2} to the Fe^{+3} state, i.e., from the soluble (thus not visible) form of iron, to the very much apparent slimy-appearing ferric hydroxide, $Fe(OH)_3$.

The divalent (+2) iron may be obtained from the pipe itself, if it is made of iron. More frequently, though, the iron is a natural constituent of an anaerobic aquifer.

Iron bacteria can cause a decline in well water production as follows:

1. Plugging of the aquifer by microorganisms
2. Biofouling of the well screen area by microorganisms

Restoration of well production can be achieved by stimulation or redevelopment. Chlorine is used primarily in conjunction with other chemicals, and methods, involved in the stimulation procedure as a supplement following acid or polyphosphate treatment. (George C. White 1998)

THE CHEMISTRY OF IRON REMOVAL

The basic principles of iron and manganese removal are similar. However, the widely varying chemistry of these elements makes it difficult to discuss the matter in parallel. Thus, the separate discussion of each.

The chemistry of iron in natural water systems involves a number of factors ranging from the Eh / Oxidation Reduction Potential*, to the impact of organic complexing agents. The highly complex nature of the water chemistry of the species serves to complicate the literature on the subject. As a result, the typical phenomenological approach utilized in the water treatment studies, wherein chemicals are added and percent removals are observed, frequently does more to confuse the state of the art than to advance it. A number of factors, such as indicated by Stumm and Lee (1961), increase the rate of ferrous iron oxidation by 100-fold per pH unit. Bicarbonate, sulfate, and dissolved silica, which were indicated by Schenk and Weber (1968), have significant impacts on the rate of oxidation.

For instance, the fate of iron in oxidative environments is not clearly understood. It is normally assumed that a hydroxide precipitate is formed following oxidation of iron. However, depending on the amount of carbonate alkalinity (less than 250 mg / L as $CaCO_3$, O'Conner, 1969), the chemistry may be such that ferric carbonate is formed, rather than the hydroxide (Cleasby, 1975). Based on Cleasby's analysis, it appears that the more rapidly the iron is oxidized (through the use of strong oxidants such as potassium permanganate, chlorine or ozone) the more likely the end product will be hydroxide. However, when the oxidation is conducted more slowly through the use of aeration, it then appears that the most likely end product would be carbonate in a water with high alkalinity.

Further complicating the reaction for iron oxidation is the impact of organic complexing agents. Various humics and similar materials can act to complex the iron and to slow down the kinetics of the oxidation. As a result, one frequently hears or reads about the failure of a particular removal process in a given situation, when that very same process has been successful in other instances. This is generally due to the inability to break the iron / organics complex at a sufficiently rapid rate to allow the oxidation of the iron within the treatment system. The solution to these problems is to more rapidly and completely oxidize the iron to ensure that the iron is kept at a very high state of E_h. In such a state the complex is broken, and the iron is readily oxidized to the ferric state. Oldham and Gloyna, in 1968, showed that aeration is totally ineffective in complex waters of this nature.

*E_h / Oxidation Reduction Potential (also known as redox potential, oxidation / reduction potential, ORP, pE, ε, or E_h) is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Reduction potential is measured in volts (V), or millivolts (mV). Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced, ORP is a common analytical measurement of raw water quality, and for the control of chemical feed to achieve the required finished water quality.

To ensure the complete and effective removal of iron, it is essential that the right combination of oxidizing agent be utilized in the right pH environment to achieve total oxidation from the ferrous (Fe^{+2}) to the ferric (Fe^{+3}) state. To use an analogy with chlorination, it is essential to achieve a "breakpoint" during the oxidation process, (prior to contact with the filter media) in other words, the oxidant must exceed demand, with a small excess of oxidant remaining.

Note: Refer to the theoretical stoichiometric oxidation chart on *page 18*

THE CHEMISTRY OF MANGANESE REMOVAL

The chemistry of manganese is substantially more complex than that of iron, and only a limited understanding of the oxidation of manganese exists. Kessick and Morado, in 1975, indicated that the most common precipitate formed in manganous oxidation is MnOOH, rather than, as commonly believed, MnO_2.

The oxidation and control of manganese is complicated by factors that range from misunderstanding of the reaction chemistry to the relatively slow kinetics, and the numerous oxidation states that can result. Like iron, manganese precipitation is also affected by the formation of organic complexes, and those complexes must be broken down prior to the oxidation of manganese, just as is the case for iron. In general, the removal of manganese is enhanced by increasing pH and the equilibrium potential.

Note: Refer to the theoretical stoichiometric oxidation chart on *page 18*

IRON AND MANGANESE TREATMENT PROCESSES

There are two major types of processes for the removal of iron and manganese. In the first process group, the object is to oxidize the divalent ferrous and manganous (Fe^{+2}, Mn^{+2}) forms to their higher oxidation states (Fe^{+3} and Mn^{+4}), then remove the insoluble hydroxides. The second process group relies on keeping the iron and manganese in their reduced (ous) forms to facilitate removal by ion-exchange or membrane processes.

Mouchet lists the following available conventional iron and manganese treatment process categories:

IRON AND MANGANESE REMOVAL

- Aeration followed by silica, or garnet, sand filtration (or dual media filtration), often complemented by a contact tank, settling or flotation, and the addition of chemicals
- Chemical oxidation (without pre-aeration) followed by filtration
- Filtration on special catalytic adsorptive media that act as ion or electron exchanges, e.g., manganese dioxide, Manganese Greensands, proprietary media, and zeolites (tecto-silicates)
- Conventional treatment combined with lime softening\

SEQUESTRATION

- Phosphates, polyphosphates, or sodium silicates are used as sequestering agents
  (*Note:* Sequestration is not an iron / manganese removal process. See *page 15* for additional information)

IN-SITU TREATMENT

- Oxygenated water, iron consuming bacteria, and / or proprietary solution is introduced into the aquifer by means of feed wells, creating a treatment area in the aquifer around the main well

Mouchet then proceeds to describe a biological removal scheme in which the usually troublesome iron and manganese bacteria are put to good use in the oxidation of divalent Iron and manganese to their higher oxidation (and insoluble) states, whereupon they, along with the iron and manganese, can be filtered out.

In his list of seven main groups, Mouchet may have touched upon, but did not describe ion exchange or reverse osmosis processes used in the removal of iron and manganese.

PRETREATMENT OXIDATION

Preoxidation of ferrous and manganous materials (and other dissolved contaminants such as organics, sulfides, arsenic, etc.) ahead of iron and manganese removal processes is a commonly practiced pre-treatment concept. Oxidation may be achieved by aeration, or the application of chlorine, ozone, chlorine dioxide, or potassium permanganate, as noted below.

**_Note:_ Refer to _page 18_ for the theoretical reaction stoichiometry to oxidize iron (Fe^{+2}) and manganese (Mn^{+2}).

AERATION

Aeration of iron and manganese-bearing waters has two purposes: (1) to transfer oxygen to the water for iron and manganese oxidation, and (2) to remove any volatile organics that may be present that would reduce the efficiency of subsequent processes due to their oxidant demand. State, or local, air quality control regulations may require additional treatment of any off-gassing such as hydrogen sulfide. It should be noted that the oxidation of manganese-bearing water by aeration is generally not effective below a pH of 9.5.

Depending upon raw water quality parameters such as pH, temperature, hydrogen sulfide and organic loading, the post aeration detention time required may take from several minutes, to hours, to form a filterable iron hydroxide floc.

CHLORINATION

Chlorination is widely used for the oxidation of divalent iron and manganese. The use of chlorine (chlorine gas, sodium hypochlorite or calcium hypochlorite), provides a much more rapid oxidation process than aeration, especially under conditions of organic interference with the oxidation process.

The insoluble formed may be highly dispersed, and when very high levels (5-10 mg / L or more) of iron and manganese are present, coagulation and clarification may be required prior to filtration. Chlorine demand can be determined by a simple jar test, or, by the preferred method of field pilot testing.

For effective oxidation of iron and manganese, however, the filter effluent should contain about 0.5 mg / L of free chlorine. Field pilot testing must include a break point chlorination curve that is run by treating the raw water prior to filtration. The potential formation of trihalomethanes should be considered if precursors such as humic and / or fulvic acids are present in the raw water. Potassium permanganate ($KMnO_4$) or chlorine dioxide (ClO_2) can be fed as an oxidant if the trihalomethane formation exceeds the MCL, and if State Health Department regulations allow the use of ClO_2 in potable water.

OZONATION

While ozonation can be utilized for iron and manganese oxidation, it is rarely used for these purposes unless other contaminants in the raw water (such as hydrogen sulfide) are better treated with ozone. Ozone may not be effective for oxidation in the presence of humic or fulvic (naturally occurring) organic materials. When ozone is applied to water, excess air or oxygen is also applied in sufficient quantities to supersaturate the dissolved oxygen content of the water. The excess oxygen is of concern due to its effect on accelerated corrosion and outgassing. Care must also be taken to prevent overdosing due to the ozone's ability to oxidize Mn^{+2} to Mn^{+7} (permanganate), resulting in a pink coloration of the water, with resultant consumer complaints.

CHLORINE DIOXIDE

Chlorine dioxide is generated on site by various methods (e.g., chlorine gas and sodium chlorite) and is a more powerful oxidant than all of the above except ozone and fluorine. It reacts more rapidly than standard oxidants, does not produce trihalomethanes and is especially effective in ground waters with humic constituents.

POTASSIUM PERMANGANATE

Potassium permanganate ($KMnO_4$) is a strong oxidant and is commonly fed ahead of Greensand iron and manganese filters both as an oxidizing agent (iron, manganese, organics, etc.) and as a regenerant to replace the manganese oxide coating on the media that is removed during backwashing. As noted above, permanganate imparts a pink color to the water (if overdosed in the 0.05 mg / L range), thus the dosage rate is critical, if pink water complaints are to be avoided.

OXIDATION FILTRATION PROCESSES

SILICA SAND / GARNET SAND AND ANTHRACITE

Standard silica sand / garnet sand and anthracite media have been used to remove iron and manganese from drinking water supplies since the earliest days of water treatment. Aeration, followed by storage, to give the iron / manganese time to oxidize / flocculate, preceded slow silica / garnet sand filters that rely on the iron / manganese in the raw water to naturally coat the media on site. Current silica / garnet sand and anthracite filter designs include pretreatment with chlorine to oxidize the iron / manganese (and other contaminants such as hydrogen sulfide, organics, etc.). This process eliminates aeration and storage and relies on the chlorine to oxidize contaminants. The time required to condition the silica sand with a complete coating of iron / manganese is site specific, depending on water quality. It can take weeks or months, in some cases, to complete the sand coating process required to achieve an effluent water quality that meets USEPA / DHS standards.

ANTHRASAND

Anthrasand is a filter media that is similar to Greensand. A base material of standard silica sand is capped with anthracite in a conventional dual media configuration. The sand and anthracite are placed in the filter vessel where they are soaked in a manganous salt solution for a prescribed period of time. Potassium permanganate ($KMnO_4$) is then added to oxidize the manganous ion to the MnO_2 form(s). This process applies a thin layer of MnO_2 on the media and is referred to as in-situ generated manganese dioxide (MnO_2).

The suggested pretreatment for the Anthrasand process includes dosing the raw water (ahead of the filter) with $KMnO_4$ to oxidize the iron and manganese. Sufficient (excess) $KMnO_4$ is fed to maintain the MnO_2 coating on the silica sand in a regenerated condition. Chlorine can also be fed as a pretreatment chemical to oxidize other contaminants, as well as the iron / manganese, and to provide a disinfection residual. Feeding chlorine does not eliminate the requirement to feed potassium permanganate.

Establishing, and maintaining, a complete and fully oxidized MnO_2 coating in-situ can be difficult, depending on the raw water chemistry. Silica sand does not generally have the same ion exchange properties as the glauconite sand that is used to process Manganese Greensand, nor does it have surface areas increased by pockets or caves as is the case with glauconite sand.

GREENSAND PLUS

Greensand Plus is a filter media that is similar to Manganese Greensand. The difference between Manganese Greensand and Greensand Plus is in the substrate that forms the core of the media, and the method by which the manganese dioxide (MnO_2) coating is attached to that substrate. The substrate of Manganese Greensand is glauconite, and the substrate of Greensand Plus is silica sand. The manganese dioxide coating is ionically bound to the Manganese Greensand, while the manganese dioxide coating is fused to the silica sand core of Greensand Plus. Regeneration of the manganese dioxide coating on Greensand Plus is recommended to extend the life cycle of the media and is accomplished by either feeding potassium permanganate ($KMnO_4$) continuously, at relatively low dosage rates, (CR / Continuous Regeneration) or intermittently at higher dosage rates (IR / Intermittent Regeneration).

Greensand Plus is an exact replacement for Manganese Greensand and requires no changes in backwash rate, duration, or chemical feeds.

MANGANESE GREENSAND FILTRATION

Manganese Greensand / Greensand is manufactured by coating various minerals (glauconite, silica sand etc.) with manganese dioxide (MnO_2). These media operate on the chemical principles of oxidation and reduction, and the catalytic effect of the manganese dioxide (MnO_2) coating. Pretreatment chemical oxidation is required. The most common chemicals used are potassium permanganate ($KMnO_4$), and chlorine, or a combination of chlorine and potassium permanganate ($KMnO_4$), fed in series.

Regeneration of the manganese dioxide (MnO_2) coating is required to extend the life cycle of the media and is accomplished by two (2) distinct methods of operation; either Continuous Regeneration (CR) or Intermittent Regeneration (IR) depending upon raw water characteristics. The CR method uses a continuous feed of potassium permanganate, or a combination of chlorine and $KMnO_4$ at stoichiometric dosage rates. The IR method uses KMnO4 (at a higher dosage rate) to regenerate the media during backwash cycles.

Greensand media will remove arsenic, iron and manganese without regeneration, however, if it is not regenerated the manganese dioxide coating will either wear off or may become permanently fouled (with iron or manganese) which will result in media blinding. These conditions will cause the Greensand media to gradually lose its effectiveness and the media may require replacement before the end of its expected life cycle.

CATALYTIC / ADSORPTIVE MEDIA FILTERS

In these, sometimes proprietary, filtration systems (Pureflow Filtration Div.© is one), the iron and manganese, along with other dissolved contaminants such as hydrogen sulfide, organic carbon, and arsenic, etc. are oxidized by chemical pretreatment, usually followed by an inline static mixer (contact time after oxidation is not required for iron, manganese, sulfides, ammonia or arsenic). The iron and manganese are then precipitated as hydroxides and filtered on a catalytic / adsorptive filter medium where another adsorptive reaction occurs at the water / medium interface. There, localized zones of high pH assure not only the formation, but the maintenance of an active, adsorbent, hydroxide floc. The mechanism is not unlike what occurs on, or in, a bed of activated alumina, with the notable exception that adsorptive media, unlike alumina, requires no re-generation and can be backwashed like any conventional filter. Typical examples of catalytic / adsorptive media are Pureflow PM-100 (proprietary) and PM-200 (manganese dioxide*) media that are selected according to raw well water quality parameters.

*MANGANESE DIOXIDE MEDIA

Manganese dioxide (MnO_2) is a natural manganese ore that is selected for its capacity to attract heavy metals, such as iron and manganese, and for the co-precipitation of arsenic, along with other contaminants, such as hydrogen sulfide (H_2S). Manganese dioxide does not affect the alkalinity, or the pH, of the filtered water, and does not add any extraneous species during treatment.

Sometimes referred to as pyrolusite, manganese dioxide is a catalytic adsorptive media that can operate at high flux and loading rates, depending on the raw water contaminant levels, and the reactivity of the manganese dioxide media.

Contaminants in the raw water (arsenic, iron, manganese, hydrogen sulfide, etc.) are first oxidized (usually with chlorine) and are then adsorbed onto the filter media. Manganese dioxide is a permanent media that is backwashed with filtered water and does not require chemical regeneration.

Some proprietary blends of high manganese content manganese dioxide have elevated catalytic activity. The increased catalytic activity results in the removal of contaminants such as arsenic, iron, manganese, sulfides, etc. without chemical oxidation. These media also do not affect the alkalinity of the water and can be used as a disposable media. Manganese dioxide media can also be regenerated periodically with sodium hypochlorite if manganese is being removed, or, in the case of arsenic removal, the adsorbed arsenic may be removed with a dilute solution of sodium hydroxide or nitric acid, followed by thorough backwashing.

BACKWASH WATER RECLAIM / RESIDUAL SOLIDS DISPOSAL

Backwash water from iron / manganese oxidation-filtration processes is non-hazardous and can be drained directly into a sanitary sewer if permitted by the local sewer authority. The backwash water can also be piped to a storage tank, decanted and reclaimed, allowing more than 99.9% recovery and water recycle. The collected iron / manganese residual solids can also be drained to a sewer or can be dewatered with a filter press and hauled to a land fill. The use of a filter press to dewater the solids will result in a zero-discharge process by returning the water from the press back to the solids holding tank.

The concentrated residual solids collected in the reclaim tank must be removed periodically to prevent the solids from interfering with the decanted supernatant water reclaim process, and to prevent mounding / hardening of the residual solids. A skid mounted residual solids fluidization and transfer system, with automatic controls, can be included as part of the backwash water reclaim process.

A centrifugal pump will recirculate the settled solids / water to provide a homogenous mixture that will be transferred to either the sewer, or, to a solids thickening tank for storage prior to the filter press dewatering system. The solids fluidization and transfer system also eliminates the manual labor, and confined space entry issues, associated with the problem of removing hardened residual solids from iron and manganese backwash water storage tanks. Field pilot test protocol should include testing of the backwash water. Standard Imhoff cone procedures should be used to develop residual solids settling rate, volume, recovery percentage and supernatant clarity.

FILTER MEDIA CONDITIONING

Iron and manganese removal filter media (including sand, Greensand, GreensandPlus, anthrasand, garnet, manganese dioxide and proprietary media), unlike filter media for the removal of turbidity, sometimes require a conditioning period before the media produces water that meets all optimum effluent parameters. Due to this requirement, filter manufacturers often use conditioned media in their pilot filters to determine the optimum performance of the full-scale filter process. Media conditioning time (and alternate media conditioning techniques) can be established with a pilot filter study using new (unconditioned) filter media, in addition to conditioned media. The use of different types of media should also be considered as part of the pilot test protocol to determine if media conditioning can be optimized or eliminated.

The time required to condition the filter media (sometimes referred to as “Filter Ripening Time”) varies from one installation to another and can be affected by multiple parameters including the following:

Raw water quality	**Chemical pretreatment scheme**
Filter flow rate (gpm)	**Filter loading rate (gpm/ft^2)**
Contaminant concentration	**pH**
Iron and manganese concentration	**Filter run time (continuous daily operation)**
Type of filter media	**Langelier index**

Some filter installations require very little or no media conditioning. For example, media conditioning could be as simple as performing multiple backwashes to remove fine media. Excess fines in the media cause high differential pressure and shortened filter runs. Filter media containing excessive fines requires “skimming” of the fines from the media bed surface after each of the initial series of backwashes, using tools and manual labor.

If filter effluent water cannot be discharged into the water distribution system, unless all water quality parameters are achieved, the filtered water must be run-to-waste until the effluent water quality is acceptable. When planning for disposal of the filtered water during the media conditioning period, parameters such as flow rate, continuous run time, volume of water, pH, chlorine residual, etc. must be considered. An alternative to long-term operation of the filter system to “waste” (until the media is conditioned), is soaking the media in-situ in a ferric or manganous salt solution to coat the media, thereby reducing conditioning time. If the problem is only a pH issue, a chemical feed pump can be temporarily installed downstream of the filter(s) to adjust the pH until the media is conditioned and the pH returns to normal.

Filter installations that require media conditioning can take from a few days to several weeks before the optimum effluent water quality is achieved. The filter(s) must be operated at the maximum design flow rate in order to condition the media within the shortest possible time frame. Operating the filter vessels at lower than maximum design flow rate can result in extended conditioning time that may be considerably longer than expected.

If an extended conditioning period is unacceptable, an alternate media should be tested during the pilot filter study.

Notes: 1. For additional information refer to AWWA "Iron and Manganese Removal Handbook" by E.O. Sommerfield

2. Refer to pilot testing on page 17

ION EXCHANGE PROCESS

LIME (SOFTENING) TREATMENT

Lime ($Ca[OH]_2$) or excess lime softening processes are very effective in the removal of iron and manganese. If the water is pre-aerated, and if the pH is maintained above 9.5, essentially total removals are possible. Due to high capital and operating costs, however, this process is feasible only if there also is a demonstrated need for softening of the water.

ZEOLITE SOFTENING

Reduced iron and manganese are readily removed in a cation exchange softening system, i.e., zeolites et al. Great care must be taken to prevent the water from contacting air ahead of the softener. Likewise, any oxidative disinfection must be applied after the softener to assure the iron and manganese remain in their divalent (+2) states. Since the cation exchange resins are not iron and / or manganese selective, this relatively expensive process (like lime softening, above) would only be warranted for the removal of iron and manganese if there is a need for hardness removal as well.

An example is the City of Santa Monica, California, where a 7.5 MGD plant removes approximately 1 mg / L of iron from groundwater by a process of aeration, followed by filtration through about 30 inches of ion exchange media which also provides the desired softening action.

MEMBRANE PROCESSES

REVERSE OSMOSIS

This membrane process is primarily designed for the desalting of saline or brackish waters by the application of hydrostatic pressure (Montgomery). This overcomes osmotic pressure and drives the water to be treated through a semi-permeable membrane designed to allow passage of water, but not of dissolved contaminants. The process requires expensive and fragile membrane stacks, either cellulose-acetate or thin film composite. Cellulose-acetate membranes can be operated up to 400 psi, or more, but are subject to biological attack and hydrolysis. They also allow the salt passage to double after a service life of about 3 years. The more expensive thin film composite membranes are capable of the same, or greater, flux rate, but at half the applied pressure. These allow only a less than 30% increase in salt passage after 3 years. Both require considerable pre-treatment to prevent scaling, plugging, and colloidal or biological fouling, in addition to fouling caused by iron / manganese.

Since the recovery of product water, as a percentage of feed water, is a function of applied hydrostatic pressure (up to 400 psi, or more), the process tends to be quite energy intensive. Most reverse osmosis plants are designed for 75-80% recovery, i.e., up to 25% of the flow must be disposed as a concentrated waste (Montgomery).

Reverse osmosis is quite capable of the removal of iron and manganese to very low levels. Process operation, routine maintenance, brine disposal and membrane replacement costs; as well as labor intensity, will tend to rule out its application for all but small volume treatment systems.

NANO-FILTRATION

This process, also known as “Membrane Softening” uses an ultra-low-pressure membrane designed to allow only passage of particles less than 1 nanometer (10 Angstroms) in size. It is, thus, very efficient (more so than Reverse Osmosis) in the removal of dissolved matter, but is, of course, not selective for iron and manganese only. Like all other membrane processes, extensive pretreatment is necessary to prevent fouling of the delicate and expensive membranes caused by particulate matter, scaling, or biofouling.

MICRO-FILTRATION AND ULTRA-FILTRATION

Each of these low-pressure membrane processes is considered to be a promising technology for dissolved solids removal. They can be applied over a wide range of water quality that contains high turbidity, iron, manganese, sulfate and nitrate. The use of low-pressure membranes eliminates the breakthrough of iron / manganese laden coagulant flocs (a typical occurrence with conventional granular media filters) by taking advantage of the membranes’ particle barrier. As with all membrane processes, provision for adequate pretreatment to control feed water quality should be taken to protect the membrane from fouling caused by particulate matter, scaling and biofouling to optimize membrane performance and life. Disposal of the reject water (which is not considered to be a hazardous waste) can be to a sanitary sewer if permitted by the local sewer authority.

OTHER PROCESSES SEQUESTRATION

Sequestration is NOT a removal process. Rather, it accomplishes the opposite of oxidation by keeping iron and manganese in solution. The term "to sequester" means to remove from further chemical reaction (such as oxidation and precipitation), to "bind up" or to "complex". A chemical used for this purpose is sodium hexametaphosphate, commonly known as polyphosphate, and sold under a number of trade names.

When polyphosphates are used to sequester iron and / or manganese, it is of the utmost importance to feed the phosphate ahead of any contact of the water with an oxidant, including air. Sequestration can only occur with iron and manganese in their divalent states, thus, if used in a well, phosphates must be fed at the bottom of the well to allow time for the sequestration reaction before chlorine and air contact the iron / manganese in the water.

Great care must be taken with phosphate feeds. These chemicals tend to be aggressive to metals, and in older systems will preferentially react with precipitated iron (such as corrosion products) sometimes leading to pipe failures due to perforation.

Phosphates are biological stimulants and should therefore be used with caution if the treated water is to be stored in open reservoirs, because algal blooms may result. In some areas of the USA discharge limitations severely restrict the use of phosphates.

In the European Common Market countries phosphate addition is limited and controlled. The effectiveness of sequestration appears to diminish with increased temperature. It is not unusual for a utility practicing sequestration to deliver perfectly acceptable, aesthetically pleasing, cold water, only to have customers complain of iron and manganese staining in their hot water systems.

MAGNETITE

Another process which has been demonstrated, at least in the pilot stage, is a proprietary process, in which about 1% (10,000 mg / L) of fine (1 - 2 micron) magnetite particles, a naturally occurring iron oxide, (Fe_3O_4) with a specific gravity of about 5.0, is fed to the water to be treated. Before feeding, the magnetite is activated with caustic soda. After addition and mixing, colloidal materials attach to the surface of the magnetite particles, and the magnetic floc settles rapidly because of its high specific gravity. The settled magnetite is collected, washed clean of iron and manganese on magnetic plates, before reactivation and reuse. Multiple manipulations tend to make this reactive media process rather awkward and expensive for large-scale application.

BLENDING

While dilution (i.e., blending of a source water high in contaminants with a source low or free of such contaminants) is not a treatment process, it can be successfully used to bring waters into MCL compliance for certain contaminants (example: nitrate) – but not for iron and manganese. This is because, even though the blending with a low Fe/Mn source may bring the water into MCL compliance, the "finished water" will still contain the metals in various oxidation states. And these metals will tend to deposit in distribution lines, on valves, in storage facilities, (creation of "Legacy Manganese")* and in water heater and boiler systems where they frequently become the cause of destructive and expensive under-deposit corrosion.

**Note:* Please also refer to Legacy Metallic Oxide Accumulations on *page 6*

OTHER PRETREATMENT ADDITIVES

FILTER AIDS

When iron is associated with organics, or if there is significant color of an organic nature present, large doses of coagulants may be required for the removal of iron, manganese, and color after oxidation. Different processes use different coagulant aids. Activated silica has been shown effective in such conditions. For this purpose, 1.5% sodium silicate (Na_2SiO_3), is activated with chlorine. The chemical is difficult to handle, to activate, and to feed; therefore, maintenance and operating costs may be high.

SULFUR DIOXIDE

Sulfur dioxide (SO_2), or sodium bisulfite ($NaHSO_3$), can be fed downstream of the oxidant (e.g., chlorine), when sulfides are present, to prevent the formation of polysulfides. Organic contaminants which are not completely oxidized can cause complexing which may require additional sulfur ions. (Journal AWWA 1974).

Oxidation with breakpoint chlorination alone will convert sulfides to sulfates, without the formation of polysulfides, eliminating the requirement for sulfur dioxide or sodium bisulfite. If water contains a high concentration of sulfide, and / or the sulfide is complexed with organics, a stronger oxidant such as ozone (O3) should be considered. As with any chemical feed, mixing of the chemical oxidant is critical to complete the reaction and must be considered in the process design. Inline static mixers are recommended.

REACTION VESSELS

Reaction vessels are not required in the pretreatment process to remove iron, manganese, sulfides, or a low level of color. The chemical reaction required to oxidize these contaminants requires complete, homogenous mixing that can be provided with inline static mixers, or by feeding the chemical ahead of water main appurtenances such as pumps, sand separators, valves, etc. that cause the required mixing.

Reaction vessels may be required when high levels of organic carbon compounds cause the iron / manganese to be chelated and / or cause a significant color problem. High chlorine dosage rates, or a stronger oxidant such as ozone, may be required to break an organic chelation bond. A filter aid such as an organic / inorganic coagulant may be added ahead of the reaction vessel (s) to assist in color particulate removal.

PILOT TESTING

Pilot testing at each well site is highly recommended due to varying ground water quality that can significantly affect iron and manganese removal processes. Raw water quality analyses should be made prior to pilot testing to determine all of the constituents in the water that can affect iron and manganese removal processes. The pilot filter system should be designed to treat all of the constituents in the raw water that will affect the efficiency of the treatment process. On-site testing should be verified by taking raw and treated water samples that are tested by an independent certified laboratory. The pilot test process should include pretreatment equipment as dictated by the raw water quality analysis to assure continued treatment to below USEPA standards, and to maximize process runs and optimize media / membrane life. Both conditioned and new media should be tested in the pilot study.

The pilot filter treatment system must verify removal of iron and manganese throughout the process run cycle, as well as determine pretreatment chemical dosage requirements, and the following costs: pre and post treatment chemicals, operation / maintenance, media (or membrane) disposal and replacement, backwash water or brine treatment / disposal. Pilot filter studies should also include testing for disinfectant by-products (e.g., trihalomethanes, bromates, etc.) that can result from feeding pre-treatment oxidants such as chlorine, ozone, etc. when organic carbons are present in the raw water. The pilot test protocol should also include filter media conditioning.

CONCLUSION

Neither iron nor manganese, at levels commonly found in well / surface water, have any known adverse health effects, which accounts for the inclusion of both elements in the secondary (NSDWR) rather than the primary (NPDWR) drinking water regulations. Both elements are essential to the growth of many plants and animals, including humans. However, the iron / manganese found in drinking water have no nutrient value for humans. Even if iron / manganese were present in beneficial amounts, their presence in drinking water would still be objectionable.

Pilot testing of each well is recommended to verify contaminant concentration, oxidation demand, process design and operational costs.

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*OXIDATION - FILTRATION PROCESS FOR IRON & MANGANESE REMOVAL

TYPICAL INSTALLATION

**THEORETICAL REACTION STOICHIOMETRY IRON (FE) AND MANGANESE (MN) OXIDATION

Metal / Oxidant	Reaction	Stoichiometry mg / L Oxidant versus Metal
	Iron	
O_2 (aq)	$2Fe^{2+} + {}^{1}/_{2}O_2 + 5H_2O \rightarrow 2Fe(OH)_3(s) + 4H^+$	0.14 mg : 1 mg Fe
O_3 (aq)	$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3(s) + O_2 + 4H^+$	0.43 mg : 1 mg Fe
HOCl	$2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_3(s) + Cl^- + 5H^+$	0.64 mg : 1 mg Fe
$KMnO_4$	$3Fe^{2+} + MnO_4 + 7H_2O \rightarrow 3Fe(OH)_3(s) + MnO_2 + 5H^+$	0.94 mg : 1 mg Fe
ClO_2	$5Fe^{2+} + ClO_2 + 13H_2O \rightarrow 5Fe(OH)_3(s) + Cl^- + 11H^+$	0.24 mg : 1 mg Fe
	Manganese	
O_2 (aq)	$Mn^{2+} + {}^{1}/_{2}O_2 + H_2O \rightarrow MnO_2(s) + 2H^+$	0.29 mg : 1 mg Mn
O_3 (aq)	$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2(s) + O_2 + 2H^+$	0.88 mg : 1 mg Mn
HOCl	$Mn^{2+} + HOCl + H_2O \rightarrow MnO_2(s) + Cl^- + 3H^+$	1.30 mg : 1 mg Mn
$KMnO_4$	$3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$	1.92 mg : 1 mg Mn
ClO_2	$Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow MnO_2(s) + 2ClO^{2-} + 4H^+$	2.45 mg : 1 mg Mn

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info@waterbypureflow.com

(800) 926-3426

(562) 945-3425

6739 Washington Ave.

Whittier, CA 90601

www.waterbypureflow.com

Pureflow® FILTRATION DIV.