

Tech Brief – June 2020

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Iron and Manganese Removal – Options and Cautions

Iron, manganese, and hydrogen sulfide gas are all nuisance actors in water. They exist in various forms and they complex with other waterborne contaminants to create difficult compounds to control. Because of this, there cannot be a single source solution for controlling these common water issues. The tools required to combat problem-water nuisance vary with the form these metals and gases present themselves in a specific water supply. While science and theory abound on this topic, it sometimes helps to just look at working solutions - discuss how they work and what pitfalls exist with a particular technology. This article will concentrate on iron and manganese, but hydrogen sulfide plays a role in managing these metals – read on....

The simplest forms of iron are ferrous (Fe^{2+}) and ferric (Fe^{3+}). Iron that is in solution (Fe^{2+}), and remains in solution, is simply removed through ion exchange. Ferrous iron is divalent and will exchange for sodium using cation resin. Ion exchange is also effective in controlling manganous manganese (the divalent form of Mn^{2+} .) It is also possible, and more environmentally responsible, to strip Fe^{2+} using catalytic collection. Catalytic collection allows the iron in solution to temporarily bond to the catalyst supported by the media substrate. During the service cycle, this form of iron is captured and held until backwash. The air scour and backwash cycle clean the media of the iron solids and send it to drain. This method of removing ferrous iron uses no chemicals or regenerants. It simply uses ambient air and O_2 to recharge the media during the scour and backwash cycles to recharge the media.

When iron is oxidized into its ferric state Fe^{3+} , it requires mechanical separation for removal. Mechanical straining differs depending on the particle size of the iron floc. A smaller floc requires tighter filtration; conversely a larger floc allows for larger micron solutions. Iron particles that are submicron and colloidal usually require a flocculant to increase the size of the floc or dead-end process filtration to control.

Dead-end filtration is a batch process where water is forced through a separation (filter) media. Retained particles stay behind on the filter surface, and in the case of a depth filter, within the media while water flows through. Accumulated particles will eventually block or plug the filter requiring its replacement. Process filtration allows for both nominal (approximate) and absolute (exact) micron filtration – an advantage when targeting a particular particle size. If 99.9% removal is not critical, nominal filters offer a less expensive option. If the targeted particle “must” come out, one uses absolute process filtration solutions.

Backwashing filter solutions range from natural zeolite (Clinoptilolite) that captures particulates in the 5 to 12 Micron (μm) range. There is a large variety of media and mixed media available for particulates (Fe^{3+}) larger than 12 μm . Multi-media filters generally trap particles down to 12-20 microns. Traditional commercially available filter medias are effective on particles $> 20 \mu\text{m}$. (Chart 1.)

All of these applications, ion exchange and mechanical straining are simple technologies and easily accomplished with standard equipment.

Ion Exchange for Ferrous (Clear Water) Iron and Mn^{2+}

Ion Exchange for divalent cations is just another way to say, “water softener.” Cautions with this application include limiting iron loading. Use compensated hardness calculations by adding four grains for every mg/l of Fe^{2+} and Mn^{2+} . Being conservative with NaCl (salt) and attempting to maximize capacity throughput is fine for regular water softening applications. This practice may result in damage to the resin bed in water with high iron and manganese content. Be generous with the NaCl and conservative with the capacities in problem water.

Note: Softening resin prefers calcium (predominant hardness mineral) to iron to 1.7 in selectivity respectively. This means the resin is 1.8 more times select for hardness over divalent ferrous iron. Why is this important? Iron leakage occur if the hardness penetrates too far into the resin column – thus driving off the iron and releasing it into the soft water. This is why a softener installed for Fe^{2+} and Mn^{2+} needs to regenerate more often and use more NaCl.

Do an iron speciation test to ensure that the Fe^{3+} is $\leq 0.3 \text{ mg/l}$. A speciation test indicates how a tested substance exists in its different forms in a single sample. With iron, it will show how much is ferrous and how much is ferric. *Manganese resists oxidation in $\text{pH} < 8.4$ (Hem, 1963). Therefore, in most waters it exists as Mn^{2+} .*

Use a resin cleaner to help control ferric iron build-up and help prevent fouling of the resin beads. *Sulfite-based resin cleaners work in preventing ferrous iron from converting to ferric in the brine tank and system, while phosphate sequesters ferric iron and keeps it soluble. These resin cleaners are typically used in small doses and only partly compensate. They are seldom used at high enough doses to remove foulants already formed (Meyers, 2020).*

Any standard softening resin will exchange Fe^{2+} and Mn^{2+} for sodium as it does hardness. Standard resin beads range in size from 16 to 50 mesh. The largest 16 mesh beads are over twice the size of the smallest 50 mesh bead. The larger the bead, the longer the flow (kinetic) path through the bead matrix. (Image 1.)



Media	Nominal Straining
Clinoptilolite Zeolite	5 μm
Multimedia 3-Plus Layers	12 μm
Sand & Anthracite	15 μm
Sand - Eff. Size 0.25 - 2.5 mm	20 μm
Conventional Manufactured	$> 20 \mu\text{m}$

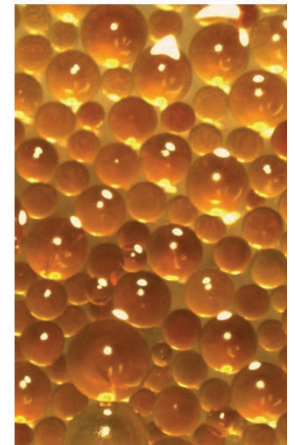
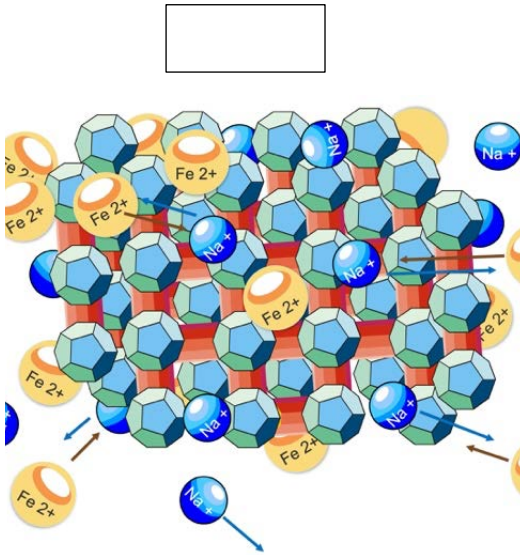
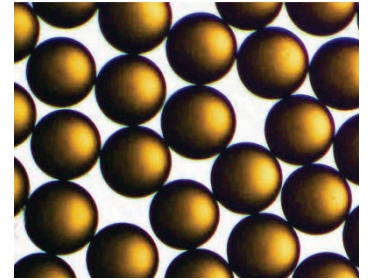


Image 1.



An ion exchange resin bead is a porous structure with 99% of its exchange sites on the inside of the bead. (Image 2.) The longer the Fe²⁺ is inside the bead, the more likely it will oxidize into Fe⁺³ and get trapped inside the resin bead structure. Once the bead is plugged, it is no longer fully functional. A smaller bead has a shorter kinetic path through its matrix and iron is less likely to oxidize inside and create fouling. This makes smaller uniform particle size (UPS) resin beads a better choice in iron water because of its uniform particle size. (Image 3.)

This resin offers a number of economic advantages over conventional 16 x 50 mesh resins. The small uniform bead size results in rapid ion exchange kinetics during operation, more complete regeneration of the resin, and faster, more thorough rinse following regeneration. In addition, this predictability of outcome allows for greater accuracy in sizing, efficiency and throughput – if everything acts the same, outcomes are equivalent.



Captured Air vs. Catalytic Collection

Captured air systems are very popular today. They work by introducing O₂ from an ambient air source – ambient air is 21% oxygen (varies somewhat with elevation.) The air is compressed inside the filter vessel and the O₂ is consumed by the different constituents in the water that accept oxidation; i.e., H₂S, Fe, Mn, etc. In chemistry, stoichiometric ratio equations calculate how much O₂ is needed to oxidize the target elements in water.

In this O₂ Required calculator, the existing values for the target nuisance metals and gas of Fe²⁺, Mn²⁺ and H₂S are loaded into the equation and the resulting Theoretical O₂ Demand show



O₂ Required = Xf + Xm + Xhs				
Where	Reaction Factor	Fe (iron) mg/l (ppm)	Mn (manganese) mg/l (ppm)	H ₂ S (sulfide gas) mg/l (ppm)
Xf = Fe Reaction Factor	0.14	2		
Xm = Mn Reaction Factor	0.29		0.6	
Xhs = H ₂ S Reaction Factor	0.49			1
			Theoretical O₂ Demand	0.944
System	Size Dia Tank	Cu.Ft. Compressed Air	mg/l O ₂ in Cubic Foot	Gallons per Recharge
Dual Tank OIF	10	3.03	271.4	870
Single OIF	10	1.01	271.4	290

this water needing 0.94 mg/l of O₂ to oxidize the Fe, Mn and H₂S to ferric, manganic and sulfur or sulfate.

In these forms they will mechanically strain using a filter media. The calculator goes on to show the available O₂ in either a two-tank or single tank configuration for a particular tank size. The calculator (Example A) looks at a standard 10" x 54" filter, after air loading and compression, has enough air to process 870 gallons of this challenge water in a two-tank system and 290 gallons in a single tank system.

The cautions with this technique are as follows:

1. The time required for oxidation is pH and temperature driven. Water with a pH less than neutral slows reactions times. Conversion of the targeted constituents may be incomplete, allowing them to pass through filtration.
2. The required O₂ demand becomes problematic if the demand is greater than reasonable satisfied by the system – throughputs are determined by available O₂ in the vessel(s).
3. Oxidized metals begin to form solids when exposed to air and will collect in the upper diffuser and inside the control valve.
 - a. These filters require preventive maintenance annually or sooner.

The water treatment industry has numerous choices for media that incorporates the use of a catalyst. A catalyst is a substance that accelerates, or changes, the rate of a chemical reaction without being consumed or chemically changed by that chemical reaction. Pyrolusite and manganese greensand are two natural mediums that support a catalytic action. In addition, several manufacturers commercially produce specialized media designed to work in conjunction with a catalyst. Some of these media choices require regeneration and others work with naturally and/or introduced O₂ in combination with the catalyst. One thing common to most filtration media is the requirement for high backwash flow rates – from 8 to 25 gallons per minute per square foot. Systems using these media choices require considerable water – in the hundreds of gallons – to backwash, cycle, and rinse.

In an application where only ferrous iron is present in the source water – where the Mn 2+ is ≤ 0.05 mg/l and H₂S is non-detect – consider using catalytic collection without the use of aeration. These systems function without captured air. It leaves the Fe²⁺ in solution. As Fe²⁺ passes through the filter, it encounters the catalyst on the media. Oxygen released by this hybrid exchanger reacts with Fe²⁺ to form insoluble red ferric oxide (Fe₂O₃). Ferric oxide precipitates on the surface of the substrate and is thus trapped in the media bed.

During use, oxygen atoms are gradually depleted from the catalyst and a ferric oxide crust forms on the surface of the media. Before all the oxygen is depleted, a cleaning cycle is initiated to remove the accumulated Fe³⁺ and to replenish the media with fresh O₂. The cleaning cycle begins with an air scour which breaks the iron oxide crust away from the surface of the media substrate and provides the oxygen (from the air) needed to replenish the catalyst. Air scour is followed by a backwash to remove the ferric oxide crust, then by a brief rinse. Following the cleaning cycle, the system is ready for its next service run.

The media substrate that supports the catalyst is a thermoplastic and very light weight. The advantage to this is low backwash flow rates. This media backwashes at 3 gpm/ft² – making it an excellent choice for low producing wells and water conservation. *This media does require air scour to insure proper cleaning and recharge.* In addition to using less water to cycle, this system eliminates the issues of iron oxide formation in the controls and diffuser related to captured air.

Because the system uses collection, it has a finite throughput. This is not a filter. Once the media is loaded with iron oxide, it must be scoured and backwashed. This throughput is governed by the water severity. It is therefore necessary to speciate the iron and know the ratio of Fe²⁺ to Fe³⁺. The ferric iron needs to be at, or below, the Secondary Standard for Fe of 0.3 mg/l – with the balance of the iron being ferrous to avoid staining issues downstream.

Cautions:

1. This technology is for ferrous iron only. While it can attract manganese, there are no claims to this effect. It is a “Clear Water Iron Solution.”
2. If the Fe³⁺ is greater the 0.3 mg/l, the system may require process filtration downstream.
3. Once the media is loaded, it is no longer effective. The system requires meter-initiated operation and a liberal reserve.
4. This media is NOT compatible with ozone or chlorine.

Mechanical Straining and Ozone

Ozone (O₃) technology is nothing new. On large scale projects it is quite complex. Used in conjunction with low voltage 12 and 24 VDC Corona discharge generators, it is a useful tool for captured air filtration systems. The biocidal effects of O₃ helps in controlling biofilm buildup inside captured air filters. Biofilm collects iron oxides and creates plugging issues on these types of filters. In addition, bring in untreated ambient air can introduce outside contaminants into the customer’s potable water. Ozone destroys air borne contaminants before they enter water systems while the O₃ charged air column inside the tank works to control biofilm and organic fouling.

Cautions:

1. Always ensure that the materials contacted by ozone are ozone compatible. O₃ is a powerful oxidizer and will degrade some materials.
2. Be aware of the O₃ levels introduced into the water. The small generator will produce a few tenths of a grams per hour. Their intent is not to treat continuous flow applications. That takes considerably more O₃ and considerably more system components – see X for an example of O₃ demand for a typical 5 gpm flow rate. The Captured air system batch treat with ozone during regeneration. Continuous O₃ treatment requires continuous

introduction of ozone – in this example the water requires 4.48 grams/hour. (Example B.)

- Ozone, while a powerful biocide, is not intended as a solution for microbiologically unsafe water when introduced in a batch application in captured air filters. In addition, while it can assist in the control of sulfur reducing bacteria and iron bacteria in a batch application within the filter, its effectiveness downstream is marginal or absent.

Example B.

Contaminants	Ozone Dosage Required per MG/L of Contaminant	MG/L Contaminant Level (From Water Analysis)			Ozone Dosage Required
Iron (Fe ²⁺)	0.43 mg/l	X	3	mg/l =	1.29 mg/l
Manganese (Mn ²⁺)	0.88 mg/l	X	0.5	mg/l =	0.44 mg/l
Sulfide (S ²⁻)	2.20 mg/l	X	1	mg/l =	2.2 mg/l
Total Ozone Dosage Required =					3.93 mg/l
Assigned Max Flow Rate =		5 GPM			
Total Ozone Required Based on Flow Rate =		4.480 Grams/Hour = Dosage Required X Flow Rate (GPM)			

Hydrogen Sulfide as H₂S

For this discussion, the presence of H₂S in source water plays a role in consumption of available O₂ for oxidation. Again, looking at Example A and B see that hydrogen sulfide requires several times more oxygen to convert H₂S to elemental sulfur and H₂O. This reaction limits the available O₂ needed for conversion of ferrous iron to ferric. Therefore, when sizing aeration/oxidation solutions, consider the effect H₂S plays in the equation. *H₂S and SRB (sulfur reducing bacteria) are detailed topics and best discussed in a dedicated article.*

For information on H₂S, check out Bryan Swistock (Senior Extension Associate; Water Resources Coordinator) at Penn State. His article explains sources of hydrogen sulfide and solutions. <https://extension.psu.edu/hydrogen-sulfide-rotten-egg-odor-in-water-wells>.

Conclusion

The Laws of Chemistry, hydraulics and physics are static. Try as we might, one cannot fool science.... There are solutions, but there is not “One” solution to controlling nuisance problem water issues. Do the testing, consult with the operating specifications, and do the math. Miss one key piece of data and a solution quickly becomes a problem. Investigate and be skeptical of claims that sound too good to be true – to this author’s knowledge a single-source answer does not exist to the many levels of water severity across the country. Do not be afraid to consult with people-of-knowledge in the effort to satisfy the needs of the end-users who rely on experts for answers.