

CASE STUDIES: AEROBIC VS ANAEROBIC PRETREATMENT OF GROUNDWATER

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Introduction

Groundwater sources usually contain a low level of dissolved oxygen versus surface waters. A dissolved oxygen (DO) level less than 1.0 mg/l is considered anaerobic. It has often been debated throughout the membrane treatment industry if the presence of certain elements in a groundwater source will mandate pre-treatment prior to treatment by a membrane system. There are several considerations that should be evaluated to develop site specific recommendations regarding pre-treatment requirements. The primary considerations are listed below:

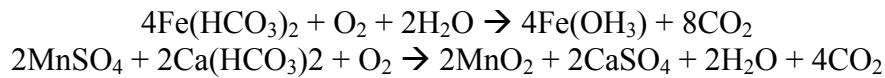
- Age, condition, and materials of construction of raw water feed facilities, i.e., wells and transmission mains
- Level of metal ions in the raw water, specifically iron and manganese
- Amount of hydrogen sulfide in the raw water
- Amount of anaerobic and/or aerobic bacteria and organics in the raw water
- Presence of any other ions that may experience improved removal by the membranes if pre-aerated such as arsenic or boron
- Distance of wells from treatment facility and ability to maintain a relatively air-tight, sealed raw water transmission system

Aerobic Pretreatment

In an anaerobic groundwater common metals such as iron and manganese primarily exist in their soluble forms, Fe^{2+} and Mn^{2+} . In an oxidizing environment, iron and manganese will precipitate. In their precipitated, particulate form they are a foulant to a spiral wound nanofiltration or reverse osmosis membrane. Fouling may be avoided by preventing oxidation of the metals or removing the precipitated iron or manganese after oxidation. Parameters that affect iron oxidation and the rate at which it occurs include water temperature, pH and constituents in the water such as DO, bicarbonate, NOM, sulfate, dissolved silica, bacteria and suspended solids.

Historically it was believed that any iron or manganese in a raw water supply could not be tolerated by a membrane treatment system and would have to be removed through pre-treatment. Typical pretreatment used to remove iron included oxidation with oxygen, chlorine or potassium permanganate followed by adequate mixing and hydraulic detention time and granular media filtration. Sometimes greensand filtration is used, in which oxidation and filtration take place simultaneously. Oxidation with chlorine would not be recommend for membrane system pre-treatment as chlorine will damage the membranes and must be neutralized with sodium bisulfite.

Aeration is a method of oxidizing iron and manganese by mixing air and water together. The oxygen present in air reacts with the iron and manganese, donating an additional electron to elevate the ion to a higher state. Aeration can be used to provide DO to the feed water to convert Fe^{2+} and Mn^{2+} to $\text{Fe}(\text{OH})_3$ and MnO_2 , respectively. Oxidizing reactions for iron and manganese in the presence of DO are shown below.

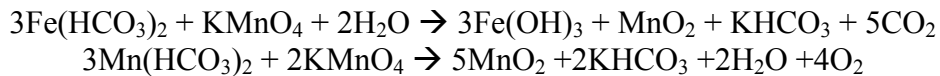


Theoretically, 1 mg of oxygen can oxidize up to 7 mg of soluble Fe^{2+} and 3.4 mg soluble Mn^{2+} . However the rate of oxidation is slow and not practical for manganese at pH levels commonly found in feed water sources. At a pH of 9.5, it takes approximately 1 hour of detention time for manganese to oxidize. In comparison, iron can be completely oxidized in about 15 minutes if the pH level of the water is between 7.5 and 8.0 and the iron is not complexed with naturally occurring organic material (NOM).

Large aerators that use air spargers, retention wells and sedimentation basins are commonly used in this type of process. In order for all the iron to be oxidized, it may be necessary to raise the pH by injecting an alkali. Once iron is in its ferric state, it will tend to precipitate. The iron oxide particulates can then be filtered using a multimedia filter or any other variety of filtration mechanisms. This is usually the most economical method of iron removal in terms of operating costs because air is available for free. However, because large retention tanks may be required, this type of treatment may have higher capital costs.

“Greensand Filtration”

Potassium permanganate (KMnO_4) is a very strong oxidant that can easily oxidize soluble Fe^{2+} and Mn^{2+} over a wide pH range (>5.5). The process is more efficient at pH values above 7.5. The contact time after the oxidant addition is typically 5 minutes at 20 deg C or 10 min at 1 deg C, which is more than enough time for Fe^{2+} and Mn^{2+} oxidation. Reactions for oxidation of iron and manganese with potassium permanganate are listed below.



The typical process for the removal of soluble iron and manganese with potassium permanganate involves injecting KMnO_4 ahead of a pressure filter in order to convert the iron and manganese to their insoluble forms so they can be filtered out. After injecting potassium permanganate, the raw water is sent to greensand pressure filters. These filters are typically constructed as horizontal cylinders with layers of filtering material. The top layer of filtering material is anthracite. The anthracite filters out the precipitated insoluble iron produced by the injection of the potassium permanganate. The middle layer is manganese greensand. The purpose of this layer is to absorb any residual potassium permanganate left over in the water. This layer also oxidizes and remaining iron still left in the water and filters it out. The final layer consists of multi-sized gravel particles whose purpose is to support the upper layers and provide filtering for most of the particles which may have passed through the upper layers.

The key to the success of any aerobic treatment for metal removal is the efficiency of the particle filtration of the oxidized metals. Unfortunately, no particle filtration system is 100% efficient. The problems arise when an unacceptable level of particles pass through the filtration system and then rapidly foul the reverse osmosis system.

Evaluating Pretreatment Requirements

From years of experimentation, pilot studies and studying full-scale plant operational data, it has been postulated that aerobic pre-treatment of groundwaters containing metals is not always required. The factors listed above need to be considered for each site-specific application. The key in evaluating pre-treatment needs is in determining if it is possible to maintain the anaerobic raw water supply in an anaerobic state. Testing has demonstrated that the dissolved metal ions are well rejected by reverse

osmosis membranes. And the membranes do not experience unacceptable levels of fouling from the dissolved ions. Thus is important to determine if the raw water supply has the potential to become aerated from leaks that allow air into the transmission mains, or vertical turbine well pumps that aerate the water through stuffing boxes, or raw water piping that is a long distance from the water plant with many elevation changes requiring extensive use of automatic air release/air vacuum valves. Also, an older raw water supply system that may incorporate many ferrous metals – perhaps steel cased wells, or unlined ductile iron transmission pipes – can contribute to additional metal oxide fouling problems in the reverse osmosis system.

The ideal raw water supply design for a groundwater that contains metals or hydrogen sulfide would include: submersible well pumps with foot valves, all non-metallic materials of construction for wells, pumps and piping, manual air relief valves only and ideally, a fairly compact wellfield layout near the water plant site.

The hydrogen sulfide in the raw water will convert to elemental sulfur which is a particularly bad foulant for a membrane treatment system as it very difficult if not impossible to remove. Metal oxide fouling can generally be cleaned from a membrane system by hydrochloric acid or citric acid cleanings. Biological fouling of an R/O system is often worsened by aerobic pre-treatment of the raw water. Below are descriptions of three case studies that present data on aerobic versus anaerobic pre-treatment of feedwater to membrane treatment systems. The first case, Aledo, Illinois, utilizes an oxidizing iron removal pre-treatment. The other two cases treat fairly high iron groundwaters very successfully with direct membrane treatment.

City of Aledo, IL

The city of Aledo utilizes anthracite “greensand filters” as a pretreatment method for removing iron and manganese prior to membrane treatment. The Reverse Osmosis membrane system at the City of Aledo was commissioned in 2002. Since being put into operation the R/O system has required frequent cleanings, 2-3 times a year, due to high differential pressure across the first stage of the membrane system. At start-up, the first stage differential pressure was 20 psi. As figure 1 shows, cleanings are typically performed once the differential pressure in the first stage increase to approximately 60 psi. Typical cleanings performed by City personnel have provided a minimal decrease in differential pressure, approximately 20 psi. The differential pressure stays constant for a short period of time before beginning to increase again.

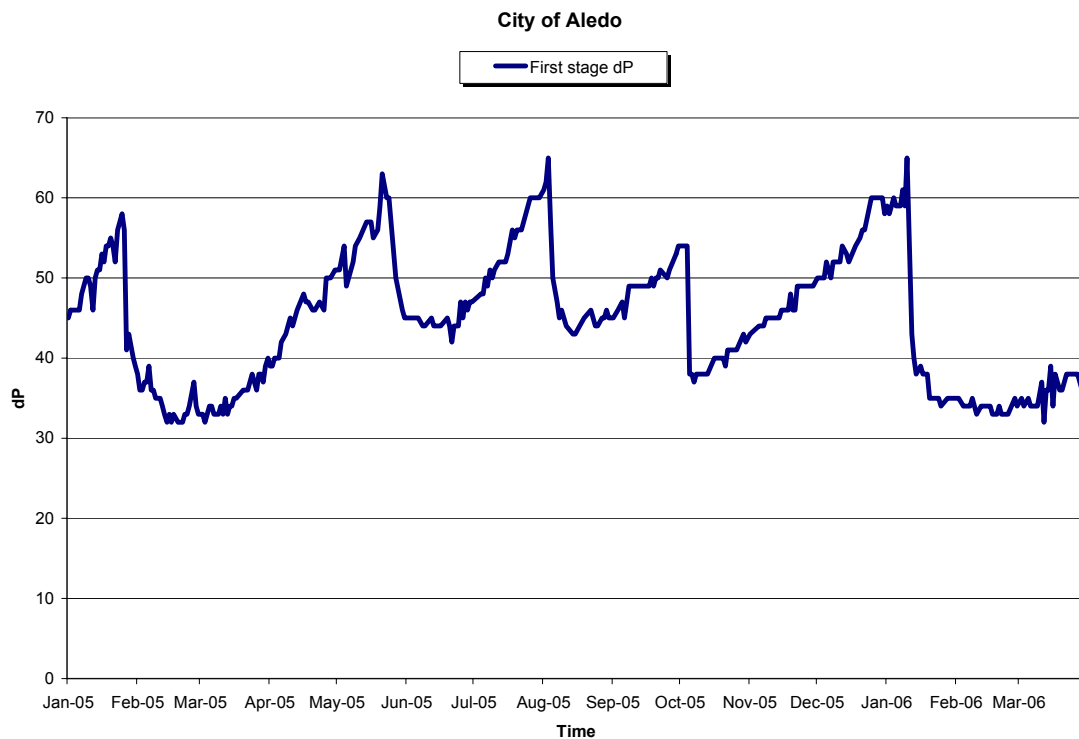


Figure 1 – First Stage Differential Pressure For the City of Aledo, IL. Operational Data Recorded from January 2005 to March 2006.

Figure 1 illustrates the change in first stage differential pressure from the beginning of January 2005 until the end of March 2006. The data shows that four cleanings have been performed since the beginning of 2005. The improvement in differential pressure in October was due to removing one membrane for autopsy and shifting the other lead end elements of the first stage. The membrane autopsy was performed to determine the nature of the foulant causing this increase in first stage differential pressure. Results of the autopsy showed that the cause of the fouling was an organic foulant composed of bacteria, proteins and carbohydrates.

The large increases in differential pressure were being caused by the “bio-slime” building up on the membrane surface and plugging the vexaspacer over time. Changes in cleaning procedures have allowed for better cleaning results with less frequency between cleanings. Biofouling is a common occurrence with membrane systems that have aeration as a pretreatment method. Aerating the feed water allows it to become a medium for the growth of aerobic bacteria.

Grand Forks WTP

Grand Forks Trail Water Users Utility had an existing raw water supply that was treated with greensand filtration for iron and manganese removal. The raw water entering the plant has an iron level of .567 mg/L and a manganese level of .515 mg/L. The groundwater was also high in hardness and alkalinity, therefore, the utility decided to construct a membrane softening plant in addition to the existing greensand filtration plant. The hardness and alkalinity of the raw water are approximately 320 mg/L as CaCO₃ and 250 mg/L as CaCO₃, respectively. The NF plant was completed in September of 1997 and houses two equally sized NF trains, each designed to produce 600 gpm of permeate.

At times the greensand filters at the water plant have not provided adequate manganese removal. The reason for this fluctuation is not known; however, it may be due to fluctuations in the iron and

manganese concentrations which leads to an inadequate dosing of potassium permanganate. Periodically, the concentration of manganese in the concentrate leaving the membrane system approaches 1.0 mg/L. Normal operation typically shows trace levels of manganese in the membrane concentrate. These are the levels expected since the purpose of the pretreatment system is to remove the manganese present in the raw water.

The membrane system operates at 80% recovery which corresponds to a 5 times concentration factor. Based on this operational data the concentration of manganese in the membrane feed water is approximately 0.2 mg/L. Therefore the efficiency of the greensand filter for manganese removal can be as low as 60%. Samples taken from the membrane system show that the manganese concentration in the permeate is less than 0.01 mg/L whether or not the greensand filter is adequately removing the manganese present in the raw water.

Pinewoods Water Treatment Plant

The Pinewoods Water Treatment Plant in Lee County, FL was upgraded in 2005 to increase the total permeate capacity of the three membrane trains from 2.1 mgd to 2.3 mgd. These three trains use nanofiltration membrane elements. It has been shown that nanofiltration membranes are very effective for the removal of soluble Fe^{2+} and Mn^{2+} . The feed water for the Pinewoods WTP has a dissolved iron concentration of 2.95 mg/L.

Results of water analysis tests for permeate samples show that the nanofiltration membranes are effective in removing the dissolved iron and manganese from the raw water. The concentrations of iron and manganese in the permeate is less than .01 mg/L.

The natural pH of the raw feed water entering the plant is 7.2. At pH values greater than 5.5, the rate of oxygenation of Fe^{2+} increases by 100 times per pH unit. Even a small amount of oxidized iron will foul membranes and cause a decrease in their effectiveness. Therefore, to minimize the chance of iron oxidation, sulfuric acid is added upstream of the membrane system to lower the feed water pH from 7.2 to 5.5 pH units.

Clay Rural Water

Clay Rural Water Systems performed a pilot study to test the effectiveness of membrane technology to treat their groundwater. Their groundwater source has a high concentration of dissolved iron and manganese, 1.7 mg/L and 0.16 mg/L respectively. The pilot test was designed to keep the feed water anaerobic in order to see if additional pretreatment would be necessary for the future full-scale plant. During operation of the pilot unit, permeate samples were periodically analyzed for iron and manganese concentration in order to verify the removal efficiency of the nanofiltration elements. Results from these tests show the iron and manganese levels to be less than 0.1 mg/L in the permeate.

Operational data was also reviewed to determine if the any fouling of the membranes had occurred throughout the duration of the pilot test. Figure 2 displays the differential pressure for the first and second stages of the membrane system. The pilot was operational for two months, and the differential pressures stayed relatively constant throughout the duration of the pilot study.

After the pilot study was completed, a lead-end first stage element and a tail-end second stage element were autopsied in order to determine if any fouling or scaling of the membranes had occurred. Autopsy results determined both elements were within manufacturer's specifications for differential pressure.

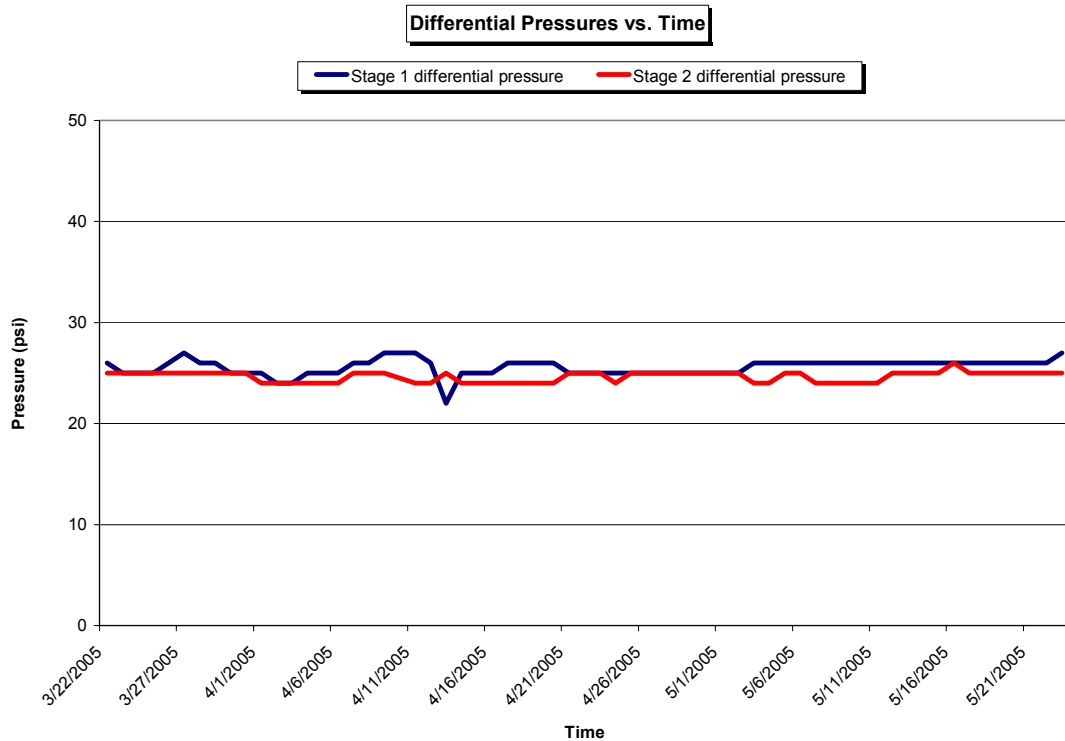


Figure 2 – Differential Pressure Operating Data taken from Wynstone Pilot Unit

Conclusion

As demonstrated from the case studies presented herein, membrane treatment can be used successfully directly on waters containing high levels of metals. If other ions such as boron or arsenic dictate a need for aerobic pretreatment, utmost care must be taken to ensure no oxidized particles carry-over from the filtration step. If there is any concern regarding metal rejection or potential for metal oxide or elemental sulfur fouling, a pilot study is highly recommended. Although it is uncommon to measure groundwaters for dissolved oxygen levels, it is a good idea as sometimes a surprising amount of DO can be present even in groundwater. The well should be thoroughly flushed and the measurement be taken while the well is being pumped at its design flow. Also, there are several scale inhibitor/dispersants that are available that cite an increased ability to minimize metal oxide fouling in the membrane treatment system. If high metal levels are a limiting factor for raw water blending, consider just treating the blend sidestream with a conventional iron removal filtration process and feeding the anaerobic groundwater directly to the R/O unit. In conclusion, a high level of metals in a raw water source should not automatically mean that a water is not suited for membrane treatment or that extensive pre-treatment will be required. Often times the pre-treatment process not only adds capital and operating and maintenance cost, but actually is detrimental to the membrane treatment operation.

References

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