Chemical and biological removal of iron and manganese from drinking water

by Arthur Hall Lundquist

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering
Montana State University

Abstract:
In over 40 percent of the groundwater drinking water sources in the United States, iron (Fe) and manganese (Mn) concentrations exceed the recommended levels set by the Environmental Protection Agency (EPA). Iron and manganese are not considered health hazards, although micro-environments may be supported in wells and distribution systems which harbor microorganisms. The main concern with these metals is the color imparted by the oxidized forms that rarely go unnoticed by the consumer. In addition, clothes and plumbing fixtures are easily stained.

This project investigated chemical and biological aspects of removing iron and manganese from groundwater, with treatment design based on implementable practices for small systems. Small water systems are finding it increasingly difficult to meet water regulations, and due to lack of resources, treatments used by larger systems are often not applicable.

The project was broken down into two phases. Phase one investigated chemical oxidation of iron and manganese using a proprietary mixed oxidant solution produced by a device from MIOX Co. The oxidants are formed by passing brine (salt water) through an electrolytic cell, avoiding the handling of volatile substances such as chlorine gas and ozone. Laboratory experiments investigated the effectiveness of this solution on the oxidation of Fe and Mn. The mechanism of soluble manganese removal through oxide coated media was demonstrated, and the sorption capacity of manganese greensand was determined. A side-stream filtration system set up at a local community demonstrated the usefulness of the mixed oxidants under field conditions. Overall, the effectiveness of the mixed oxidant solution was similar to that of sodium hypochlorite.

The second phase of this project investigated the use of biological filtration for iron and manganese removal. A similar side-stream filtration system was set up to demonstrate the use of microorganisms to oxidize and remove ferrous iron without chemical addition. Two forms of aeration were tested that impart dissolved oxygen to the nearly anoxic water to promote biological growth. Laboratory experiments investigated the mechanisms of oxidation by these microorganisms. Oxide structure, microscopic observations, and chemical analyses were used in collecting evidence on removal mechanisms. Several mechanisms are proposed that may explain the oxidation processes occurring in this system.

A cost analysis was conducted to compare the proposed treatments implementable for small systems, while distinguishing the pros and cons of each.

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APPROVAL

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Arthur Hall Lundquist

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

In over 40 percent of the groundwater drinking water sources in the United States, iron (Fe) and manganese (Mn) concentrations exceed the recommended levels set by the Environmental Protection Agency (EPA). Iron and manganese are not considered health hazards, although micro-environments may be supported in wells and distribution systems which harbor microorganisms. The main concern with these metals is the color imparted by the oxidized forms that rarely go unnoticed by the consumer. In addition, clothes and plumbing fixtures are easily stained.

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I

INTRODUCTION

In over 40 percent of the groundwater drinking water sources in the United States iron (Fe) and manganese (Mn) concentrations exceed the recommended levels set by the Environmental Protection Agency (EPA). Oxidized forms of iron and manganese stain clothes and plumbing fixtures, and impart an unhealthy looking tint to the water. Although there are no medical concerns associated with these metals, they do promote viable populations of microorganisms in wells and throughout distribution systems. Many of the utilities associated with elevated iron and manganese concentrations are small (< 1 MGD), and lack the resources to implement intricate treatment systems.

Since iron and manganese are not health hazards, they are often secondary to other contaminants when a treatment system is designed. However, many customer complaints arise from contaminants such as iron and manganese because of the color they impart to the water, and to anything they contact. Small systems have few options to remedy iron and manganese problems. Historically, sequestering the metals with polyphosphates was used by small systems. Sequestering does not remove the metals but prevents them from imparting a color to the water. Due to the low capital costs of sequestration compared to other available treatments, the strict water quality parameters necessary for this treatment are often stretched beyond what is applicable to the treatment. When sequestration is attempted outside of the recommended water quality, often the result is cloudy water and frequent process optimization problems.

Project Objective

The problem this project addresses is the need for a cost effective, successful treatment for small systems with elevated iron and manganese concentrations in their drinking water source. Since this study was aimed at finding technologies that are implementable for small systems, practical use was deemed as the driving factor in determining the direction taken in laboratory experiments as well as system design. It was never a question of whether the iron and manganese could be treated successfully, but rather if a practical, cost effective treatment train could be designed for use by small systems.

This project was broken down into two, one year studies. Initially, chemical oxidation was investigated using mixed oxidants produced from a proprietary device supplied by MIOX Corporation. This unit has inherent advantages that are desirable to small treatment systems, the most important of which is improved safety, since volatile oxidants are not produced. After initial testing of the mixed oxidants for their effectiveness at oxidizing iron and manganese, different scenarios for removing these metals from a local community water system were investigated.

The second phase of this project looked at the biological aspects of removing iron and manganese from water. Biological removal was demonstrated using a direct filtration system and oxidation mechanisms were investigated. Again the focus was on small systems so as to compare biological to chemical treatment.

Thesis Outline

This report begins with a background of iron and manganese, acceptable levels for drinking waters, and treatment considerations. Next, current treatments used to oxidize and remove these metals are presented. Aspects of physical-chemical and biological treatments are compared, followed by an introduction to the needs of small systems and the field site used throughout this project.

The following chapter explains the experimental procedures used for both phases of the project in the order presented in the project schematics (Figures 1 and 2). The results and discussions follow, presented first only for the chemical oxidation phase, followed by those for biological oxidation. A summary of the results of each phase are at the end of each respective chapter.

The concluding two chapters consist of a summary of the cost analyses, comparing several treatments and the relative costs to implement each, followed by a summary chapter that brings together the results of the project. It is hoped that the organization of this report will enable the reader to coherently understand the overall results, while understanding that the conclusions made, especially regarding the costs, are in the context of small, limited resource, treatment systems.

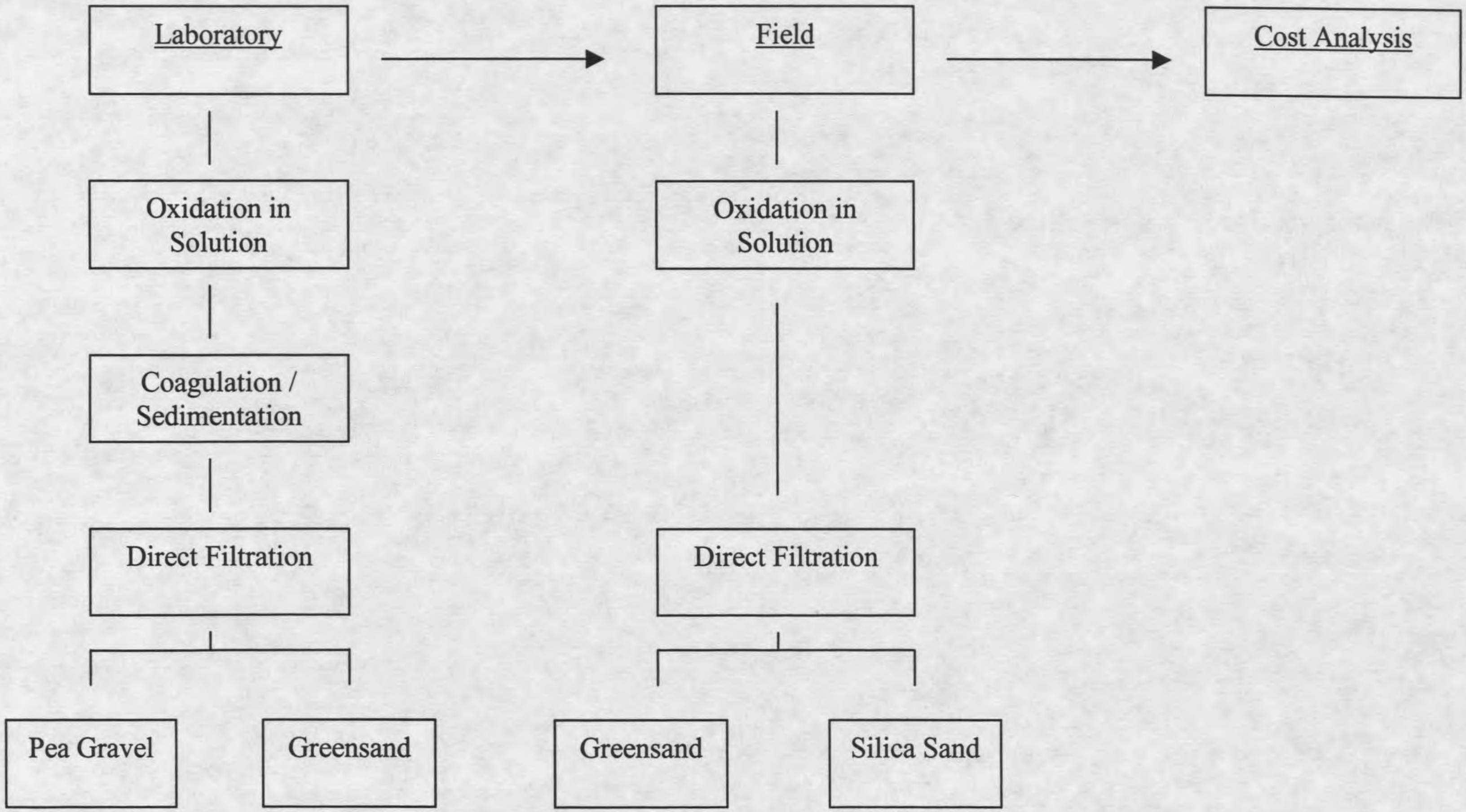

Figure 1 Chemical Oxidation Project Schematic

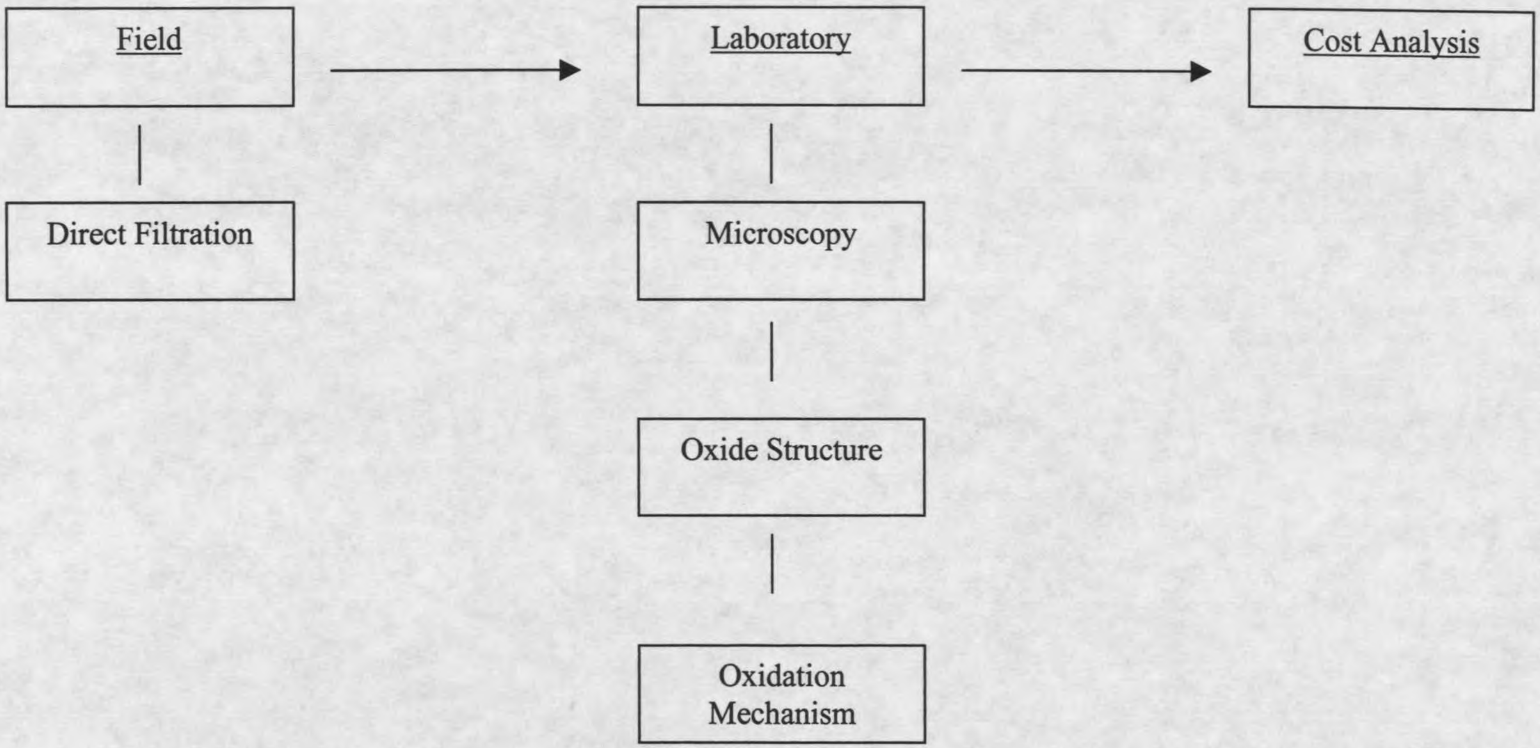

Figure 2 Biological Oxidation Project Schematic

II

BACKGROUND

Iron and Manganese

Iron (Fe) and manganese (Mn) are both inorganic metals found commonly in the earth's crust. They are often found together, with iron making up approximately 5 percent of the crust and manganese making up about 0.1 percent. Iron is the fourth most abundant element by weight. As a rule of thumb, manganese concentrations are 1/10 that of iron concentrations from the same source. Iron is found mostly in igneous rocks and manganese predominantly in metamorphic and sedimentary rocks, although both originate from many sources.

Occurrence in Natural Waters

Iron and manganese are historically a groundwater issue. It is estimated that 40 percent of the wells in the United States have iron concentrations over the 0.30 mg/L recommended limit (Billings 1992; Sung and Forbes 1984). For groundwater high in iron and manganese the occurrence is unchanged by seasons. Iron and manganese are solubilized in the subsurface, anoxic environment, as the water passes through iron and manganese mineral bearing rocks. The presence of CO_2 in the water will further facilitate this solubilization as it is supported by low pH. Since subsurface environments are slow to change, there is virtually nothing that can be done to the water to change the iron and manganese content. If the source is used for drinking water, most often some form of treatment will be necessary to discourage precipitation of the metals upon aeration of the water, or to remove the oxidized particles.

Surface water problems arise when anoxic environments occur at the bottom of lakes, allowing iron and manganese to transform to soluble species. When turnover occurs these soluble metals are brought to the surface where the presence of oxygen causes oxidation and coloring of the water. If this is a source of drinking water then the presence of iron and manganese will demand treatment to remove the color, prior to distribution.

Iron and Manganese Chemistry

Soluble iron and manganese are both divalent cations. For iron this is a semi-stable state below a pH of about 5, whereas for manganese it is semi-stable up to a pH of about 8. Along with pH, the oxidation intensity (Eh), or availability of electrons, must also be examined to determine the stability of these metals. For iron, the reduced state has a +2 charge (Fe^{+2}) and the +3 charge (Fe^{+3}) is the oxidized form. Manganese, like iron, has a +2 charge in the reduced state but may have several different oxidized forms. Oxidation states of +3, 4, and 7 are all possible oxidized forms of manganese, with +4 being the common form found in natural waters. Mn^{+3} is usually only a transition state and is easily changed, and Mn^{+7} is found in permanganate but is uncommon in natural waters. Depending on the environment, iron and manganese will change their forms to the lowest energy state. This transition is what drives the chemical transformations that cause drinking water problems, and it is upon this assumption that treatment techniques are based.

Iron Oxidation:

oxygen	$2\ Fe^{+2} + 1/2\ O_2 + 5\ H_2O$	$\longrightarrow$	$2\ Fe(OH)_{3(s)} + 4\ H^+$		(1)
chlorine	$2\ Fe^{+2} + HOCl + 5\ H_2O$	$\longrightarrow$	$2\ Fe(OH)_{3(s)} + Cl^- + 5\ H^+$		(2)

Manganese Oxidation:

oxygen	$Mn^{+2} + 1/2\ O_2 + 3\ H_2O$	$\longrightarrow$	$Mn(OH)_{4(s)} + 2\ H^+$		(3)
chlorine	$Mn^{+2} + HOCl + H_2O$	$\longrightarrow$	$Mn(OH)_{4(s)} + Cl^- + 3\ H^+$		(4)

Autocatalytic Mechanism:

oxygen	$Mn^{+2} + 1/2\ O_{2(aq)} + H_2O$	$\longrightarrow$	$MnO_{2(s)} + 2\ H^+$	slow	(5)
	$Mn^{+2} + MnO_{2(s)}$	$\longrightarrow$	$Mn^{+2} * MnO_{2(s)}$	fast	(6)
	$Mn^{+2} * MnO_{2(s)} + 1/2\ O_{2(aq)}$	$\longrightarrow$	$2\ MnO_{2(s)} + 2\ H^+$	slow	(7)
chlorine	$HOCl + Mn^{+2} + H_2O$	$\longrightarrow$	$MnO_{2(s)} + Cl^- + 3\ H^+$	slow	(8)
	$MnO_2 + Mn^{+2}$	$\longrightarrow$	$Mn * MnO_{2(s)}$	fast	(9)
	$Mn * MnO_{2(s)} + HOCl + H_2O$	$\longrightarrow$	$2\ MnO_{2(s)} + Cl^- + 3\ H^+$	moderate	(10)

The oxidation of manganese by oxygen and by chlorine involves an autocatalytic mechanism, which uses oxidized manganese particles to catalyze the subsequent oxidation of soluble manganese. Once there are sufficient oxidized particles, the adsorption of the soluble manganese onto the particles increases, and sustains manganese oxidation.

Problems Associated with Iron and Manganese

The presence of iron and manganese in drinking water sources is often understated due to the lack of immediate health risks. Customer complaints often arise primarily from visible signs of contaminants in their tap water. It is safe to say that water colored golden brown, black, or red will seldom go unnoticed by the consumer. Once anoxic source waters are aerated and the soluble iron and manganese are oxidized, the colloidal particles impart a color to the water. Iron particles tend to create a brown color and oxidized manganese imparts a darker, black tint. Plumbing fixtures and laundry can become stained, and iron and manganese can become deposited on well heads and pipe interiors. Home water softeners can become clogged, reducing efficiency (Kothari 1988). In addition to clothes, hair has been known to acquire a reversible reddish tint due to the presence of iron. A bitter, stringent taste is imparted to the water that can be detected even at very low metal concentrations (< 0.3 mg/L, iron and < 0.05 mg/L, manganese). The presence of iron and manganese in the water supports bacteria that can assimilate these metals. These microorganisms can clog well screens and decrease distribution pipe capacity, causing water shortages and increased costs associated with pumping (Wallace and Campbell 1991; Smith 1985).

The *Trace Inorganic Substances Committee* concluded in 1987 that much still needs to be learned about the "chemistry, treatment, and control of iron and manganese and that there is still room to improve treatment effectiveness while reducing treatment costs. Such goals are especially relevant to small water systems, which are frequently afflicted with iron and manganese problems." Conclusions from the Committee Report call for research on oxidation kinetics and mechanisms, and in determining the role microorganisms play in metal transformation to aid in controlling growth that is beneficial and detrimental to treatment.

Acceptable Levels

Currently there are no enforceable standards for iron and manganese concentrations in drinking water. Secondary Maximum Contaminant Levels (SMCLs) are set as guidelines for contaminants that are deemed non-critical, as opposed to Primary MCLs set for critical contaminants. SMCLs for iron and manganese are 0.30 and 0.05 mg/L, respectively. These recommended levels are not below the threshold of taste for all people, and many industrial processes require lower levels. The American Water Works Association (AWWA) sets goals for many contaminants for drinking water and industrial use. These goals for iron and manganese, set well below those by the EPA, are 0.05 mg/L for iron and 0.01 mg/L for manganese.

Treatment Considerations

Important raw water quality parameters must be determined before a treatment train can be developed. For iron and manganese, pH is the primary factor. Oxidation by aeration can occur in a matter of seconds at high pH and at an impracticably slow rate at low pH. For most natural waters, with near neutral pH, iron oxidation is fairly rapid (seconds to minutes), whereas manganese does not, for any practical purpose, oxidize without the addition of chemicals. Natural organic matter present in the water may combine with the iron and manganese creating a complex that increases the resistance to oxidation (Knocke et al. 1994; Knocke et al. 1990). The alkalinity of the water should be noted to determine the likelihood of a drop in pH as oxidation occurs. A drop in pH due to the release of protons during oxidation will in turn slow further oxidation. Sufficient alkalinity should be maintained to avoid this situation. Lower limits for alkalinity have been suggested at 50 to 120 mg/L as $CaCO_3$. Oxidation potential (Eh) of the water describes how reduced or oxidized the environment is, and along with pH, affects the rate and extent of oxidation that is possible in the water.

Available Treatment Technologies

Currently there are several methods for treating iron and manganese in drinking water. Not all are appropriate for small systems, and conversely some that are used by small systems are uncommon for larger systems. Available methods of treatment are summarized in Table 1 and include:

- Oxidation, followed by Coagulation / Sedimentation / Filtration
- Direct Filtration and Oxide-Coated Media Filtration
- Sequestration
- Ion Exchange
- Membrane Filtration
- In Situ Treatment
- Biological Filtration

treatment	effectiveness	advantage	disadvantage	relative cost
oxidation - coag/floc/sed	very	high removals	size, requires constant monitoring, capital costs	moderate - high
direct filtration and oxide coated media filtration	moderate - very	simple, low maintenance	requires certain water characteristics	low - moderate
sequestration	low	very low tech, corrosion control	does not remove contaminants, concentration sensitive	low
ion exchange	very	complete removals can be obtained	fouling, high maintenance, only for low concentrations	moderate - high
membrane filtration	very	high quality effluent	fouling, high maintenance, only for low concentrations	high
in situ	low – very	stop problem at source, usually no chemicals needed	unproven, non - conventional	low - high
biological filtration	very	no chemical addition, high removals, shock resistant	still in early stages of development, requires soluble forms	low

Table 1 Available Treatment Technologies

Oxidation

Removal through coagulation / sedimentation / filtration requires that the soluble iron and manganese be oxidized prior to the addition of chemicals designed to aid in settling. Oxidation may be accomplished a number of ways (Table 2).

Aeration Aeration consists of either bubbling air through the water or cascading the water, to induce oxygen transfer into the liquid. At the pH of natural waters, aeration can effectively oxidize iron from the ferrous to ferric state. Aeration is generally recommended for high levels of iron (> 5.0 mg/L) to reduce chemical costs. The catalytic properties of iron oxidation are not as well documented as with manganese, but the presence of ferric iron has been shown to increase the oxidation of the ferrous species (Sarikaya 1990). Coagulation / sedimentation / filtration, or some other removal method is required downstream. Manganese is not readily oxidized by oxygen throughout the pH range of natural waters.

Free Chlorine For iron alone, the most common method of oxidation is by the addition of free chlorine (HOCl). As long as the iron is not complexed by organics, oxidation is very rapid, with the exact times depending on temperature and pH. Free chlorine is not effective at oxidizing complexed iron (Knocke et al. 1990). Oxidation of manganese by free chlorine is significantly slower than for that of iron (Knocke et al. 1990; Knocke et al. 1992; Wallace and Campbell 1991; Hao et al. 1991). Manganese oxidation is highly pH dependent and may be impracticably slow below a pH of 8.5. Reaction times of several hours are required at near neutral pH, even with chlorine doses

method	Fe	Mn	advantage	disadvantage	relative cost	comment
aeration	e	n	no chemicals	not applicable to manganese	low	used for high concentrations
free chlorine	e , f	n , s	common	disinfection by-product formation	mod	pH dependent, public concern
permanganate	e , f	e , f	no by - products	dose sensitive - colored water	mod	reqs. skilled operators
chlorine dioxide	e , f	e , f	generated onsite	by - products	high	reqs. skilled operators
ozone	e , f	e , f	generated onsite	no residual	high	reqs. skilled operators

e = effective   f = fast
n = not effective   s = slow

Table 2 Oxidation Techniques for Iron and Manganese on the order of 1000 percent or more of the stoichiometric requirement (Knocke et al. 1990). Increased doses of free chlorine increase the reaction rates, while lower solution temperatures significantly reduce the rate of oxidation. Complexation of manganese with organics slows the oxidation rate.

Potassium Permanganate In contrast to free chlorine, potassium permanganate ($KMnO_4$) oxidizes manganese rapidly. Solution temperature plays the greatest role in oxidation rate, but oxidation still proceeds within several minutes. Iron and manganese oxidation by potassium permanganate is very rapid for all natural pH ranges (Knocke et al. 1990; Knocke et al. 1991b). For complexed iron, oxidation does occur, but higher permanganate doses and longer times than those usually found for water treatment are necessary.

Chlorine Dioxide An alternative oxidant used for iron and manganese treatment is chlorine dioxide (ClO_2). Generated onsite, chlorine dioxide requires specialized training and handling, and therefore, may be unsuitable for small systems. Chlorine dioxide is as effective as potassium permanganate for the oxidation of both iron and manganese. For manganese alone, the oxidation rate increases with increasing temperature and pH (Knocke et al. 1991b; Van Benschoten et al. 1992). When chlorine dioxide oxidizes manganese, ClO_2 reduces to ClO_2^- (chlorite), contributing only one electron. This dictates a high stoichiometric requirement, since not all of the oxidizing power of chlorine dioxide is used. Chlorite has been shown to be ineffective at oxidizing manganese at near neutral pH (Knocke et al. 1990), and is a by-product that is of health concern. Due to the health concerns associated with chlorite, chlorine dioxide may prove to be limited in its usefulness at oxidizing manganese. Oxidation of ferrous iron by chlorine dioxide is very rapid, generally within seconds. However, it has been shown to be ineffective at oxidizing complexed soluble iron (Knocke et al. 1992; Knocke et al. 1994).

<u>Ozone</u> As with chlorine dioxide, ozone (O_3) must also be generated onsite. Ozone is highly reactive, requiring skilled operators trained in handling and safety. For oxidation of manganese, ozone reacts within seconds, with reaction times decreasing as pH increases. With a pH increase, the decomposition of ozone increases, and doses in excess of the stoichiometric requirements may be needed. Iron oxidation by ozone is also very rapid, on the order of a few seconds (Knocke et al. 1990).

<u>Coagulation / Sedimentation / Filtration</u>

Once soluble iron and manganese are oxidized into a particulate form, they may be settled from solution. However, due to their size and density, and the forces acting upon them in solution, these settling velocities may be very slow. To increase the settling velocities of these particles, coagulants are added to conglomerate the particles into larger flocs that settle out more quickly. The coagulant, commonly either an inorganic salt or a synthetic polymer, is added during a rapid mix stage. This stage consists of a short (1-2 minute) turbulent mixing phase when the coagulant is added, followed by a longer, less turbulent, flocculation phase, that may last for 30 minutes or more. During flocculation the particles are given time to adhere to one another, growing into larger flocs with higher settling velocities. Sedimentation follows, as a laminar stage where no mixing occurs, allowing the flocs to settle out. This stage is variable in residence time depending on the time needed to remove the large particles to an acceptable level. In order to remove the remaining smaller particles that were not removed during settling, some type of filtration is often required. If sedimentation is successful, large filter clogging particles are removed, and filtration can proceed at a reasonable filter run time. This eliminates excessive pressure drop across the filter, and less frequent backwashing is required.

Direct Filtration and Oxide-Coated Media Filtration

If metal concentrations are fairly low or if space or capital costs are a problem, then the sedimentation phase may be eliminated, and filtration may follow coagulation. This process is called direct filtration. In this system the metals are oxidized and, if needed, a coagulant (filter aid) is added to increase the size of the particulates. The goal is to produce small, pin flocs that will be trapped in the filter, rather than ones large enough to quickly clog the filter and create high pressure drops. Backwashing will usually be required more frequently as compared to filtration after sedimentation. The effectiveness of direct filtration is unique for each system.

When water containing soluble iron and manganese is filtered through the same media for an extended period of time a surface oxide coating will form that in turn promotes iron and manganese adsorption (Knocke et al. 1988; Knocke et al. 1991a). When treating water higher in iron concentration than manganese the iron must be oxidized before entering the filter. Without previous oxidation, the iron will adsorb to the media and block manganese removal, due to the low affinity of manganese for iron oxides. To eliminate the need for formation of natural oxide coatings, commercial pre-coated media is available. A common treatment for manganese is the use of the alumino-silicate mineral glauconite, treated with permanganate, known as manganese greensand. This coating of manganese oxide can be generated naturally over time (natural greensand effect, NGE) or by coating the media with a synthetic oxide (Merkle et al. 1997a). Manganese oxide has a high adsorption attraction for inorganic species, such as Ra^{+2}, Zn^{+2}, Cd^{+2}, Cu^{+2}, Pb^{+2}, and Cr^{+2}, giving it potential for treatment in a variety of applications. The theory behind the removal of manganese with greensand has been studied extensively (Knocke et al. 1991a; Coffey et al. 1993; Merkle et al. 1997b; Knocke et al. 1988). Common agreement is that the oxide coating adsorbs soluble manganese at a finite number of adsorption sites. Without the presence of an oxidant the adsorption sites fill, eventually reducing the removal capacity of the media. When an oxidant is added to the filter, the adsorbed manganese is oxidized at the media surface and becomes a part of the media itself, thereby opening up more sites for further adsorption. The dosing of the filter with an oxidant at set intervals is known as intermittent regeneration, and takes the filter out of service for a brief time. Work has been conducted on continuous regeneration, where low levels of oxidant are mixed into the influent stream (Knocke et al. 1991a). The adsorbed manganese on the media becomes oxidized, continually creating sites for removal without taking the filter out of line. Permanganate has historically been used as the oxidant for intermittent regeneration. Recently work has been conducted that indicates chlorine may be a superior oxidant for continuous regeneration, eliminating the difficulties associated with permanganate (Knocke et al. 1991a; Weng et al. 1986). When oxidants stronger than chlorine (permanganate, chlorine dioxide, ozone) are used for continuous regeneration, the influent manganese is of the colloidal form prior to entering the filter. This treatment has been shown to initially produce lower removals, due to the colloids passing through the filter (Knocke et al. 1988; Weng et al. 1986). As the filter ripens removals increase. Current findings (Merkle et al. 1997b) indicate the following mechanism occurs at the media surface when manganese is in the soluble form entering the filter column:

reversible sorption $$Mn^{+2} + MnO(OH)_{2(s)} \longleftrightarrow MnO_2MnO_{(s)} + 2\ H^+ \quad (11)$$

oxidation $$MnO_2MnO_{(s)} + HOCl \longrightarrow 2\ MnO_2 + H^+ + Cl^- \quad (12)$$

Incorporating both of the above equations, where $MnO_2MnO_{(s)}$ is considered the site available for regeneration:

$$Mn^{+2} + MnO(OH)_{2(s)} + HOCl + H_2O \longrightarrow MnO_2 + MnO(OH)_{2(s)} + 3\ H^+ + Cl^- \quad (13)$$

or

$$Mn^{+2} + SITE + HOCl \longrightarrow MnO_{x(s)} + SITE \quad (14)$$

This mechanism indicates that soluble manganese, in the presence of an oxidant, is adsorbed to the media surface at a specific site, becomes oxidized, and forms an identical adsorption site. It further assumes that the total number of sites is independent of the oxide accumulation, which may not be valid throughout the entire life of the media.

Sequestration

In sequestration, iron and manganese are not removed, but are prevented from imparting color to the water. A sequestering agent such as a phosphate or silicate is added to the water, that reacts with the "soluble" iron and manganese to prevent them from oxidizing and creating discoloration or turbidity, for a period longer than the detention time in the distribution system. For successful sequestration the metals cannot remain in their reduced states, a common misconception in the process of sequestering. Current literature (Robinson et al. 1992; Klueh and Robinson 1992) has concluded that for effective sequestration to occur an oxidizing agent should be added prior to, or within a short time of the addition of the sequestering agent. Tests on the species of the sequestered iron indicated that it was primarily in the ferric state, supporting the belief that metals need to be oxidized for proper sequestration. The sequestering agent does not keep the metals in a reduced state, but maintains the oxidized particles in a colloidal form where they are prevented from growing into flocs. The colloidal particles are microscopic and do not impart any color to the water. Since the metals must be oxidized nearly simultaneously for successful sequestration, current work (Robinson et al. 1992) indicates that the use of chlorine as the oxidant when manganese is to be sequestered fails, due to the slow oxidation of manganese by chlorine. A problem associated with sequestering is the fact that it breaks down with heat; depolymerization has been documented to occur at temperatures as low as 18°C (Klueh and Robinson 1992). One study (Robinson et al. 1992) showed there was precipitation of iron in hot water heaters leaving little at the tap for discoloration.

If silicates are used, dosing at a ratio of 34 - 12 mg SiO_2 / mg Fe is acceptable for iron concentrations between 0.2 and 1.5 mg/L (Robinson et al. 1992). Higher concentrations of silicates are required as iron concentrations increase.

Polyphosphates have the same drawbacks as silicates. In addition to depolymerization due to heat and time, the presence of calcium has been shown to inhibit sequestration success (Klueh and Robinson 1992). Due to this inhibition, greater dosages are needed for sequestration. An upper limit on polyphosphate dose exists, due to unexplained increases in turbidity as doses increase above 7.5 mg/L PO_4 (Klueh and Robinson 1992). Common polyphosphate doses are 2.0 - 2.5 mg/L and are limited to 10 mg/L in most states for potable use. The information on polyphosphates is almost totally anecdotal, therefore, many engineers discount polyphosphate sequestering as a feasible treatment technique under any circumstances (Klueh and Robinson 1992).

Despite the problems associated with sequestration, it is a common treatment for small systems due to economic considerations, and the fact it does prove successful for certain water qualities. For example, total iron and manganese concentrations should not exceed approximately 1.5 mg/L, distribution residence time should be fairly short, and water hardness should be low to limit depolymerization. One advantage of using sequestering agents is the corrosion inhibition gained in the distribution system (Boffardi 1993).

Ion Exchange

The ion exchange process uses a resin through which the untreated water passes. The iron and manganese must be in their reduced state upon entering this system to prevent fouling. The resin, which may consist of small synthetic resin beads on the order of 1 mm in diameter, has sites available for iron and manganese to bind, exchanging with other cations. The process of exchanging the dissolved metal for the resin coating removes the metals from solution and replaces them with less objectionable ions. Usually the resin contains sodium ions that are replaced over time with divalent cations, including iron and manganese ions. As these sites fill the resin must be regenerated by flushing with a strong salt solution. Ion exchange should only be selected for low flow applications, where manganese is the principle metal to be removed, since manganese is more easily exchanged than iron (Davis 1997). In addition to metal removal, softening occurs as the calcium and magnesium ions are removed. Since the regeneration cycle is dependent on the amount of ions exchanged, and because calcium and magnesium compete effectively with iron and manganese, treatment should only be applied to low hardness waters. This process is usually limited to waters containing combined iron and manganese concentrations of 1 mg/L or less (Wallace and Campbell 1991; McFarland 1985). Very high quality water can be obtained using ion exchange. Near 100 percent removals are often accomplished, but due to the costs of maintaining the system, ion exchange is usually reserved for industrial use.

Membrane Filtration

Membrane filtration provides several different options for iron and manganese removal. First, sieving membranes contain tiny pores, which under pressure, do not allow anything smaller than the pore to pass. Ultrafiltration, microfiltration, and nanofiltration are examples of sieving membranes. For removal, metals must be in an oxidized state in order to be maintained on the membrane. Eventually the iron and manganese that build up on the membrane cause it to foul, thereby lessening its capacity to treat water. The membrane must then be chemically cleaned before returning it to operation. The hydraulic capacity of the membrane is reduced each time it fouls until it becomes too inefficient to be put back into use, and is termed irreversibly fouled or poisoned (Odendaal et al. 1996). In general, sieving membranes are not used for iron and manganese control due to their expense and limited life caused by fouling. Another type of membrane filtration is reverse osmosis (RO), where the membrane is dense and nonporous. In contrast to other membranes, the iron and manganese must be in their soluble forms so as not to foul RO membranes. In reverse osmosis treatment, purified water passes through the membrane, with the exact mechanism of contaminant separation still debated. One hypothesis is that through hydrogen bonding the water passes through the membrane leaving any contaminants behind (Odendaal et al. 1996). Since the membrane is nonporous it is especially subject to fouling. For iron and manganese the influent concentrations must remain very low; levels below the drinking water standard are recommended. Due to this constraint, and the fact that membrane filtration is quite expensive, it is usually reserved for treatment systems that require ultrapure water. Immersed membrane filtration has recently emerged as an alternative to conventional membrane filtration (Mourato et al. 1998).

In Situ Treatment

In situ treatment entails treatment in the natural place of occurrence. While few studies have been done on in situ treatment of iron and manganese, there has been documented success (Zienkiewicz 1985). One proprietary method involves oxygenation of the well water and then recharging this water back into the aquifer by way of wells that surround the production well. The oxygen rich water precipitates the iron and manganese in the aquifer, allowing lower metal concentrations to be pumped out of the production well. The goal is to maximize the volume of water that can be pumped from the production well for each volume of water recharged. In one case, recharge occurred every 2 - 3 weeks with the metal concentrations in the production water decreasing with each recharge. After several recharges (6 for iron and 19 for manganese) the levels of iron and manganese were below the SMCLs and the production volume was more than 10 times the recharge volume (Zienkiewicz 1985). The number of recharge iterations needed before production volume is satisfactory depends on the ratio of iron to manganese, as well as the combined amounts. This method is applicable to very high metal concentrations, with the system cited having a manganese concentration of 6 mg/L. Future innovative methods like the one described may make similar in situ treatment processes common techniques in years to come.

Biological Filtration

Biological filtration consists of a filter column with active microorganisms on the media. These filters become seeded with naturally occurring microorganisms after a few weeks of passing water containing iron and manganese through them (Cameron 1996). Once the filters contain significant populations, the iron and manganese fed to the system is transformed possibly via the organism's metabolic activity. Very high removals (95 - 100 percent) can be achieved through biofiltration (Yannoni et al. 1995). Since iron and manganese must be in their reduced states for organisms to benefit, no chemical addition is needed prior to the filters. These filters can handle high influent concentrations, as well as shock loads and infrequent loading. Biological filters are capable of oxidizing iron complexed with organics, where physical-chemical means may not be applicable due to the necessity of long contact times (Mouchet 1992). For biological filtration to efficiently remove iron and manganese it must be optimized for either iron or manganese removal. Simultaneous removals are not likely, as different organisms must thrive for removals of each metal to occur.

In addition to the use of biological filtration for iron and manganese removal, biologically active filters are an effective treatment for reducing the assimilable organic carbon (AOC) content of water. This reduction in carbon has been shown to reduce regrowth of heterotrophic organisms in distribution systems (Lechevallier et al. 1991; Smith and Emelko 1998; Huck et al. 1991; Carlson and Amy 1998). Treatment systems that do not chlorinate upstream of the filters are in fact practicing biofiltration, and all filters have some sort of biological growth in them.

Biological vs. Physical-Chemical Oxidation

Determining the actual mechanism of ferrous iron oxidation in a biological filter is a process of gathering circumstantial evidence. The main problem arises from the quick oxidation of ferrous iron by aeration at neutral pH. It should be noted that, when dealing with iron removal, there will be both physical-chemical and biological mechanisms occurring simultaneously. This is an inevitable by-product of aerating the water prior to treatment.

There are several requirements that should be met to be certain that biological removal is occurring. The first, and most important requirement is the presence of iron oxidizing organisms. Their presence is often indicated by long, sheathed structures that may or may not contain cells. These organisms will be covered with iron oxides and are often difficult to find due to the large amount of oxide versus the relatively low numbers of organisms. If there are a large number of organisms and a relatively small amount of oxides then the source of energy of the organisms is not iron (Starkey 1945). Large amounts of ferrous iron are needed to sustain each organism due to the low amount of energy gained per mole of iron oxidized. The second requirement is to determine if the water characteristics fall into those specified by Figure 3. This figure displays the field of activity of iron bacteria, as well as the characteristics where physical-chemical mechanisms will begin to dominate the oxidation processes. In addition to requiring pH and Eh to fall within the specified values in Figure 3, zinc and hydrogen sulfide concentrations must be very low; inhibition has been noted at concentrations > 0.01 mg H_2S/L (Mouchet 1992).

Several tests can be conducted to see if biological removal is occurring. A seeding time should be apparent when the filters are put in-line, where removal efficiency increases as the organisms populate the filter media. The backwash water can be settled; the particulates should settle quickly due to the dense, slightly hydrated structure associated with biological oxidation. Additionally, shock chlorination of the filters can be conducted, which should result in a rapid decrease in the removal efficiency. If large diameter media (~ 2 mm) is used for biological treatment, as recommended by Mouchet (1992), removals above 50% should be considered to have at least some biological processes occurring. Physical-chemical removal requires much smaller media (~ 0.4 mm) to trap particles oxidized up-stream of the filter.

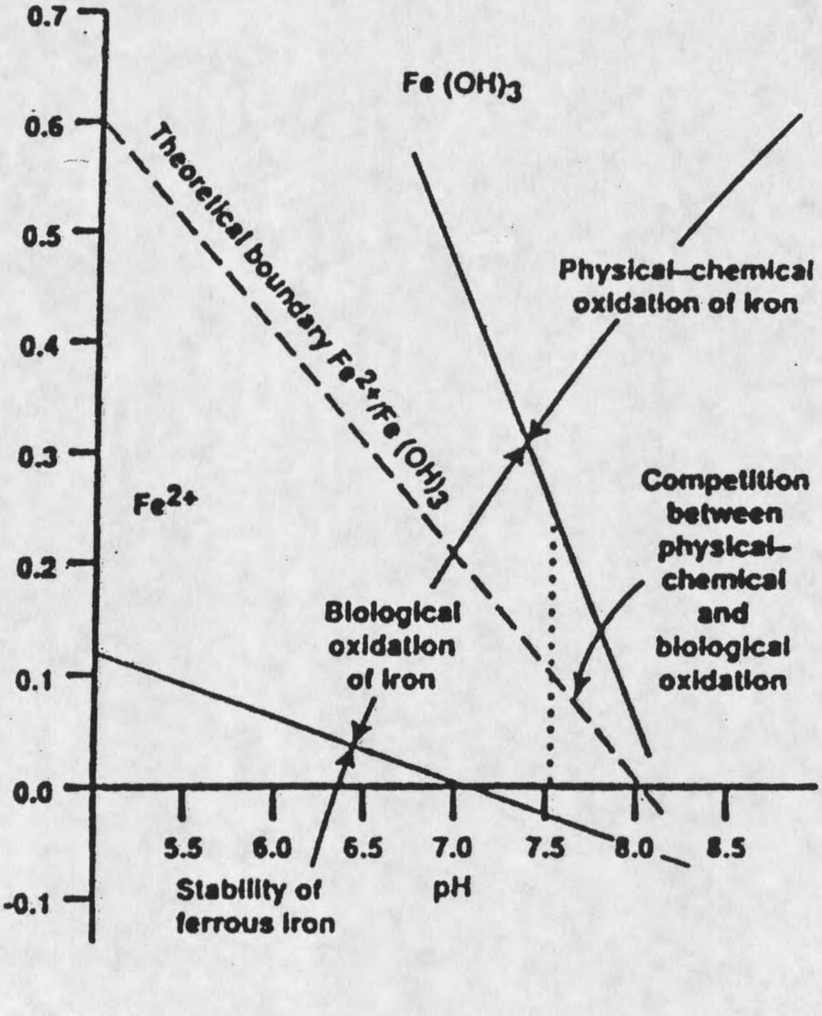

Figure 3 Field of Activity of Iron Bacteria
(from Mouchet 1992)

Iron and Manganese Oxidizing Bacteria

Emergence of "Iron Bacteria"

It has long been recognized that bacteria have the ability to deposit iron and manganese oxides outside their cells. The term "iron bacteria", traditionally *Gallionella*, *Sphaerotilus*, *Leptothrix*, *Crenothrix*, and *Clonothrix*, was first coined by Winogradsky in the nineteenth century. The original definition of "iron bacteria" was meant to only include those bacteria that were able to grow from the energy liberated by the oxidation of ferrous iron to ferric hydrate. Winogradsky studied *Leptothrix ochracea* and postulated, but never proved, that they could grow autotrophically by deriving energy from iron oxidation to fix CO_2 (Ghiorse 1984). Due to unknowns about this group of bacteria problems arose in their cultivation and nomenclature, some of which still cause controversy today. Starkey (1945) stated that the study of these bacteria may be "limited almost entirely to microscopic observations and simple chemical tests."

The crux of the nomenclature problems arose from the observation by Pringsheim in 1949 that these bacteria could change form under different cultural conditions. Although total agreement on nomenclature is not resolved today, the more problematic question facing researchers is why and how these bacteria oxidize soluble iron and manganese.

Iron bacteria can be found in ferromanganese deposits that form in natural waters of lakes, ponds, springs, etc. These bacteria also thrive in well casings and distribution systems where they may clog pipes and cause significant problems. Tubercles formed by these bacteria lead to corrosion problems and may provide shelter for other bacteria.

The most common iron oxidizing bacteria can be recognized by their metal-encrusted structures. Stalked and sheathed bacteria are easily identifiable. They appear as long narrow bands approximately 1-10 microns in width and up to several hundred microns in length, surrounded by dark deposits of iron or manganese oxide.

Possibly the most common iron-ensheathed bacterium is *Leptothrix ochracea.* There is no confirming evidence that this organism oxidizes iron for energy. Difficulties in growing the organism in pure culture complicate advances in this subject (Mulder 1964). *Leptothrix ochracea* has the ability to deposit large amounts of ferric oxides on their sheaths, with the amounts deposited increasing with increasing iron concentrations. When the ambient concentration of iron increases, the iron content of the cells increases only a fraction of this amount. This phenomenon allows them to grow in waters containing very high iron concentrations (Starr 1981).

Do Organisms Benefit From Fe and Mn Oxidation?

Except for *Gallionella ferruginea* and acidophilic iron oxidizer *Thiobacillus ferrooxidans*, the exact reason why microorganisms oxidize iron and manganese is unknown. Historically, geochemists agree that microorganisms may produce micro-environmental conditions (elevated pH and Eh) conducive to metal oxidation (Ghiorse 1984).

Chemolithotrophy, the ability of organisms to derive energy through chemical oxidation, use inorganic substances as electron donors, and fix CO_2 as a carbon source, has been shown for *Gallionella ferruginea* (Smith and Smith 1994; Starr 1981). The exothermic reaction by which these autotrophs receive energy :

$$4\ Fe^{+2} + O_2 + 10\ H_2O \longrightarrow 4\ Fe(OH)_3 + 8\ H^+ + Q\ cal. \quad (15)$$

does not release much energy. Approximately 600 moles of iron must be oxidized to absorb one mole of carbon, so large amounts of iron must be oxidized to satisfy the energy requirements of these bacteria (Mouchet 1992). This is one explanation of why biological filters can be operated successfully at high loading rates.

Dubinina (1978) cited evidence for a peroxidase mechanism using an isolated culture of *Leptothrix pseudo-ochracea*. It was established that hydrogen peroxide liberated during the oxidation of organic substances takes part in the oxidation of iron and manganese in a Fenton reaction:

$$2\ Fe^{+2} + H_2O_2 + 2\ H^+ \longrightarrow 2\ Fe^{+3} + 2\ H_2O \quad (16)$$

The benefit organisms gain from this oxidation is unclear. It has been proposed (Mouchet 1992) that the oxidation of these metals may be solely to detoxify the ambient medium. It is unlikely, yet unproven, whether these organisms gain energy from the oxidation of iron and manganese. Previous to the work by Dubinina, Balashova and Zavarzin (1972) investigated *Mycoplasma laidlawii* to determine the mechanism of iron oxidation. They concluded that the H_2O_2 produced by the organism was the source of the oxidation, and that the introduction of catalase inhibited this oxidation. They believed that the oxidation was a secondary result of the organism's vital activities.

Oxide Characterization

The precipitates formed by these organisms are believed to be slightly hydrated iron oxides, often lepidocrocite (γ-FeOOH) and goethite (α-FeOOH), although no data is presented to confirm these beliefs (Mouchet 1992). These are considered crystalline forms that are much more compact than amorphous precipitates formed during physical-chemical treatment (ferrihydrite ($5Fe_2O_3 \cdot 9\ H_2O$) and iron hydroxide ($Fe(OH)_3$). The biological precipitates are said to be denser, less likely to clog filters, and easier to settle than amorphous precipitates.

Existing Biological Removal Plants

The use of biological iron removal for water treatment has not reached acceptance in the United States but has been used in Europe for over 75 years, with several hundred plants in use today. In France alone there are more than 100 biological treatment plants, with Germany, Belgium, Finland, Bulgaria and the Netherlands also incorporating this technology (Mouchet 1992). These plants are designed mostly for groundwater sources and can successfully remove all of the iron at loading rates up to 20 gpm / ft^2 (Mouchet 1992). This is in contrast to conventional plants which load between 2 - 6 gpm / ft^2. In addition to high loading rates, the concentration of iron and manganese that can be fed to the filters is also high. One study (Yannoni et al. 1995) showed 99 percent removals over a run time of 100 hours, with an influent iron concentration of 9 mg/L. To aerate anoxic groundwater, plants often use forced air systems, introducing compressed air into the flow stream. Cascading aeration systems, where water flows in sheets off of step like features, have also been implemented (Mouchet 1992).

Pilot and full scale facilities using biological iron removal have often published the reductions in operating costs, comparing biological removal to conventional physical-chemical removal, as additional advantages to biological treatment. Bourgine et al.

(1994) compared the Saints Hill biological treatment plant to the Grombridge conventional treatment plant (both located in the United Kingdom), and concluded the following reductions in costs associated with the Saints Hill plant:

15% reduction in electricity costs

93% reduction in manpower costs

96% reduction in chemical costs

75% reduction in other costs

Small System Limitations

Small water utilities are often overlooked in the present economies-of-scale water industry. Small systems, serving less than 10,000 people, account for approximately 80 percent of the community water suppliers in the United States (Clark 1987). Of these utilities many are privately owned and must request rate increases from public commissions. This complicates the process of increasing rates for water consumption that would result from system upgrades.

The question for small systems trying to meet the increasingly stringent water regulations is not "can we meet the new regulations?", but "can we economically meet the new regulations?" Available treatment trains exist to remove just about any contaminant from drinking water, but whether there is a choice for economic implementation of that treatment is often the question. Many small systems, as with the one in this study, are in the size range (less than 1 MGD) where unit costs are maximal. Nothing can be done to change the fact that small system treatment processes cost more on a unit basis. When new treatment processes must be added to meet new regulations it is again the small systems that are hit hardest. For example, the unit costs for adding an ion exchange system for nitrate removal more than doubled the unit costs for one small system (Clark 1987). Designing an alternative method solely for a small system who needs to meet newly required MCLs, will mean a substantial rate increase, and with the price inelasticity of water, demands will not decrease as prices increase.

Field Site - Moore, Montana

We initiated our process of choosing a field site by obtaining a list of communities from the Montana Department of Environmental Quality (DEQ) with potentially high iron and manganese concentrations in their water supply. After contact with many communities we chose the town of Moore, Montana as our field location. Iron levels were fairly high and manganese was present, but at low concentrations (see Table 3). The pumphouse was close to the wellhead and a side stream system could be installed. The town currently had a problem with cloudy water and was interested in investigating alternative treatments to their existing system.

Moore, Montana is a small town located approximately fifteen miles west of Lewistown (Figure 4). Moore has a population of 202, with 100 hook-ups that are fed by a central well. The current well was drilled in 1992 to a depth of 1800 feet. The well water is pumped at 100 gallons per minute (gpm) to a 60,000 gal holding tank underneath the pumphouse, then as needed, it is pumped from this reservoir by one or both of two 80

Table 3 Water Quality - Moore, Montana

Temperature	17	°C
pH	7.3	units
Eh	20	mv (hydrogen std.)
Fe^{+2}	1.50	mg/L
Fe total	1.50	mg/L
Mn^{+2}	0.030	mg/L
Mn total	0.030	mg/L
Mg^{+2}	85	mg/L as $CaCO_3$
Ca^{+2}	100	mg/L as $CaCO_3$
Total Hardness	185	mg/L as $CaCO_3$
Total Alkalinity	220	mg/L as $CaCO_3$
Dissolved Oxygen	0.18	mg/L
Ammonia	0.32	mg/L NH_3-N
Hydrogen Sulfide	0.12	mg/L

gpm pumps up to a 50,000 gallon water tower. Daily use varies depending on the time of year, with winter averages in the range of 20,000 gallons per day (gpd) to a maximum summer use of approximately 80,000 gpd. Throughout the year an average of 40,000 gpd are pumped from the well. The water characteristics (Table 3), show an iron concentration of approximately 1.50 mg/L, and a relatively low manganese content of 0.030 mg/L. Although the simultaneous presence of hydrogen sulfide and soluble iron is uncommon, solubility calculations allow the concentrations detected (considering precision of analyses) to be theoretically possible, without precipitation to iron sulfide.

Current treatment consists of sequestration by means of blended polyphosphates dosed at the wellhead, and chlorine gas residual dosing as the water enters the first holding tank. Sequestration seems only adequate for this system, as water is often turbid but potable. Since sequestration is actually most effective on oxidized particles that are

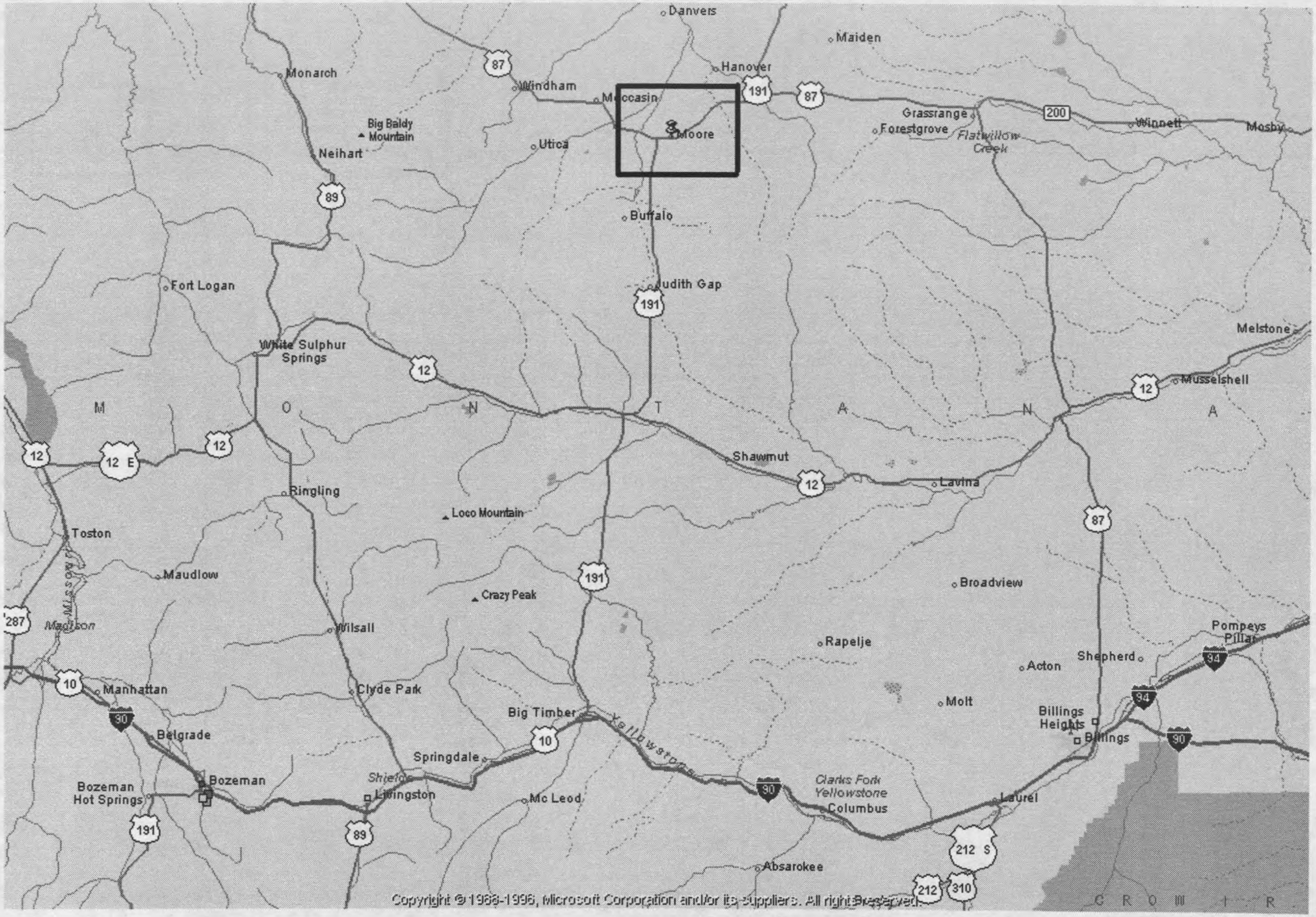

Figure 4 Location - Moore, Montana

maintained in their colloidal state, as the upper limit of colloid stability is approached, water cloudiness may be an inevitable by-product. Customer complaints usually arise from cloudiness, although several customers have intermittent hydrogen sulfide occurrences, generally only in the low use houses. Water cloudiness is intermittent and can sometimes be seen in the first holding tank. Changing the dosing of the polyphosphate clears up the cloudiness temporarily, but long term solutions are yet to be found. It has been noticed that intermittent colored water will show up when faucets are first turned on or when hot water is used. This is expected, as the sequestering agent breaks down over time and under high temperatures. The iron concentration of 1.50 mg/L has placed Moore on the suggested upper limit for successful sequestration. In addition, the high calcium content may decrease the effectiveness of the sequestering agent. Intermittent coloring of tap water indicates some iron deposition in sections of their distribution system, where the sequestering agent may be losing effectiveness.

The water chemistry at Moore, MT may be a mixture of the common water characteristics found in iron bearing groundwater. The presence of hydrogen sulfide is apparent from the strong odor emanating from the water. Iron concentrations are significant, but not as high as those expected to accompany elevated hydrogen sulfide concentrations. Three common subsurface environments for iron bearing waters are illustrated in Figure 5 (Snoeyink and Jenkins 1980), which may or may not depict the subsurface environment at Moore. The subsurface at Moore may be a combination of two of the distinct layers in this figure. The three zones depicted contain different concentrations of dissolved iron. Zone 1 is common for a shallow well drilled into the unsaturated zone. Zone 2 is governed by $FeCO_3$ equilibrium and is indicative of very high concentrations (20 mg/L) of dissolved iron; therefore it should be avoided as a drinking water source. Zone 3 has very low concentrations of iron (1 μg/L) and a high concentration of hydrogen sulfide. One theory may be that the Moore well is drawing water from the boundary between zones 2 and 3. This would produce water with elevated concentrations of iron and hydrogen sulfide, without being extremely high in either one. The redox potential of the Moore water is 20 mV, and the pH is 7.3, placing Moore water just outside of the characteristics found at the interface of zones 2 and 3.

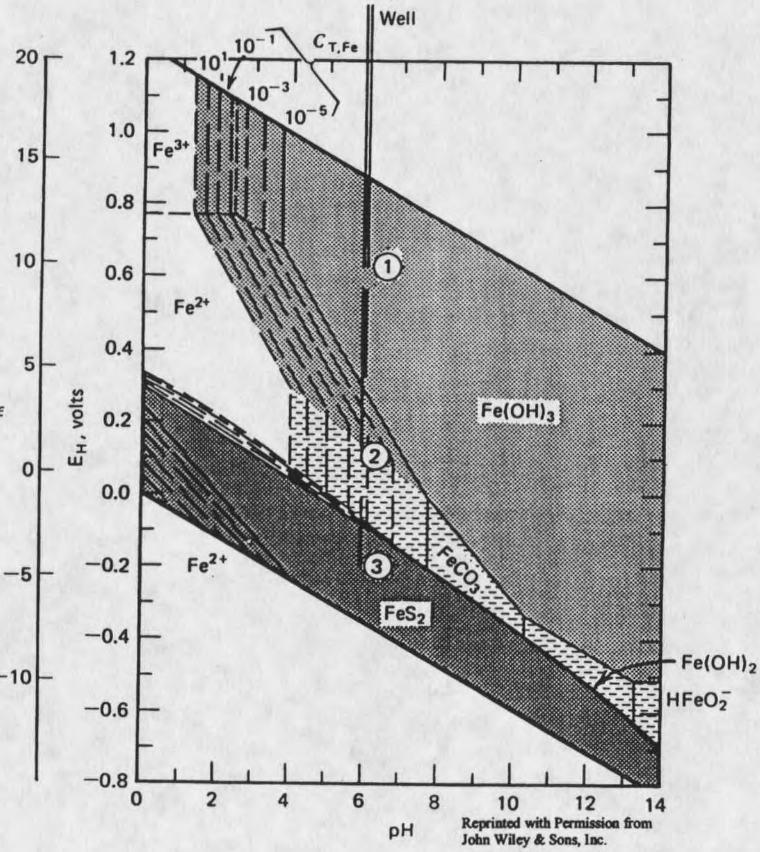

Figure 5 Solubility of Iron in Relation to pH and p∊
(from Snoeyink and Jenkins 1980)

III

EXPERIMENTAL PROCEDURES

Experimental Approach

The experimental approach of this project evolved as experiments were conducted, allowing the direction of the project to be customized towards building on the positive results obtained from previous testing. The project was broken into two phases, investigating **chemical** and **biological** removal of iron (Fe) and manganese (Mn) from drinking water. The ultimate goal of the project was to investigate efficient, low cost chemical and biological treatments that could be tested at a local small water treatment system.

Chemical Oxidation Approach

The first phase investigated the efficiency of a proprietary mixed oxidant solution at oxidizing iron and manganese. Experiments began by looking at the ability of the mixed oxidants to oxidize the metals in solution. The stoichiometry between the mixed oxidants and the metals was investigated using batch experiments, where oxidant was added to soluble iron and manganese, noting the amount of oxidant needed to oxidize a known amount of a reduced metal. Following these batch experiments it was desired to know how the particulates formed during oxidation would settle out of the water. Column tests were conducted to determine the time needed for settling and the amount of residual Fe and Mn concentrations in the water. Specifically it was desired to know if filtration was a necessary downstream process to sedimentation.

Manganese removal is often accomplished using filtration though manganese oxide coated media. Tests were conducted to see if the mixed oxidants used in this project could aid in the removal of manganese during filtration. The removal mechanism of manganese during filtration through oxide coated media was determined, so as to compare the mechanism using mixed oxidants to other oxidants (chlorine, permanganate, etc.).

Once the effectiveness of the mixed oxidants was known, a treatment system was designed and installed at a local community to test the efficacy of this treatment under field conditions.

Biological Oxidation Approach

To accompany the chemical oxidation results of this project, biological aspects of iron and manganese removal were investigated. This phase started by designing a side-stream filtration system that could be installed at a local small community. The filtration system contained three parallel streams to compare the use of packed tower aeration, forced aeration, and no aeration. These three treatments were chosen to (1) see if aeration was necessary to promote biological growth, and (2) compare the effectiveness of these aeration techniques at imparting dissolved oxygen to the water, and reducing chlorine demand.

In addition to demonstrating the use of biological filtration for small systems, the mechanism of oxidation during biological treatment was investigated. Literature gives little insight about how organisms oxidize Fe and Mn, or why. Microscopic observation confirmed the presence of iron oxidizers and surface analysis was conducted on the iron oxides formed in the filters. Lastly, chemical analysis was conducted on the effluent water of the filters to aid in the understanding of the mechanism of biological oxidation of iron.

Analyses

Chemical

- Alkalinity was determined using 2320 B. Titration Method adopted from Standard Methods (19th edition, 1995).
- Non - purgeable organic carbon was determined using a Shimadzu (Columbia, MD) TOC - 5000A analyzer with a high sensitivity catalyst.
- Redox potential was determined using a Cole Parmer (Vernon Hills, IL) redox probe model 27013-21 containing 4 M KCI. Probe accuracy was confirmed using Zobell's standard solution (Standard Methods 1995).
- Dissolved oxygen was determined using a YSI (Yellow Springs, OH) meter model 58 with probe YSI-5905.
- Hydrogen peroxide was determined using a Hach (Loveland, CO) HYP-1 test kit (0 - 10 mg/L) and confirmed using the method of Kolthoff and Sandell (1952) based on the following reaction:

  Hydrogen peroxide reacts with iodide in acid medium in the following way:

$$H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow I_2 + 2\,H_2O \qquad (17)$$

Procedure:

Add to 25 ml of sample: 10 ml 4 N sulfuric acid

1 g potassium iodide

3 drops neutral 3% ammonium molybdate solution

1 ml 2 g/L sterile soluble starch

Titrate until loss of color using standard solution of sodium thiosulfate.

The following analytical procedures were conducted using colorimetric spectrophotometry with a Hach DR2000 spectrophotometer.

- Ferrous iron was determined using Hach Method 8146 (1,10 Phenanthroline Method, using powder pillows) for water, wastewater, and seawater. Precision - ±0.006 mg/L Fe^{+2}.
- Total iron was determined using Hach Method 8147 (FerroZine Method) for water and seawater. Precision - ±0.0027 mg/L Fe.
- Total manganese was determined using Hach Method 8149 (Pan Method, Low Range) for water and wastewater. Precision - ±0.0049 mg/L Mn.
- Soluble manganese was determined using the above total manganese method after the sample had been filtered through a 25 mm Corning (Corning, NY) 0.20 μm cellulose acetate membrane syringe filter.
- Free chlorine was determined using Hach Method 8021 (DPD Method, using Powder Pillows), USEPA accepted for water and wastewater analysis. Precision - ±0.012 mg/L Cl_2.

- Total chlorine was determined using Hach Method 8167 (DPD Method, using Powder Pillows), USEPA accepted for water and wastewater analysis. Precision - ± 0.012 mg/L Cl_2.
- Total, calcium, and magnesium hardness were determined using Hach Method 8030 (Calmagite Colorimetric Method) for water, wastewater, and seawater. Precision - ±0.006 mg/L Mg as $CaCO_3$, ±0.02 mg/L Ca as $CaCO_3$.
- Turbidity was determined using Hach Method 8237 (Absorptometric Method) for water, wastewater, and seawater. Precision - ± 2 FTU.
- Low range dissolved oxygen was determined using Hach Method 8316 (Indigo Carmine Method using Accu Vac Ampuls).
- Ammonia nitrogen was determined using Hach Method 8155 (Salicylate Method).
- Nitrate was determined using Hach Method 8039 (Cadmium Reduction Method) for water, wastewater, and seawater.
- Nitrite was determined using Hach Method 8507 (Diazotization Chromotropic Acid Method) for water, wastewater, and seawater.

Iron Oxide Structure The crystalline structure of the iron oxides was tested by X-ray Diffraction (XRD) using a Scintag (Cupertino, CA) X1 Advanced Diffraction System. Samples were prepared by vortexing filter media to release the oxides then by filtering the liquid through Millipore (Bedford, MA) 0.20 μm polycarbonate filters.

The oxide state was investigated using X-ray Photoelectron Spectroscopy (XPS). A Physical Electronics Laboratories (Eden Prairie, MN) PHI - 5600 ESCA spectrometer was used for analysis. Samples were analyzed according to the specifications shown on the data collection sheets (Appendix B). Samples were analyzed for $2P_{3/2}$ shell electrons, the customary shell for iron oxide identification. This allowed for comparison to literature values. Samples were prepared identically to those for XRD. The residue on the polycarbonate filter was then transferred to silicone wafers for analysis. (Oxide structure was investigated at the Image and Chemical Analysis Laboratory (ICAL) at Montana State University).

Biological

Microscopy Light microscopy work in identifying organisms was conducted using an Olympus (BH2-RFCA) microscope. Samples were prepared according to Ahmed and Smith (1988), or by vortexing filter media then filtering the liquid through Millipore (Bedford, MA) 0.20 μm polycarbonate filters. Filters were then viewed dry using ultra long working distance lenses or using oil immersion procedures at magnifications ranging from 200x to 1500x.

Biological Removal Mechanism Investigation Filter media from the field-site filtration system was placed into three 250 ml Erlenmeyer filter flasks and supplemented with an altered form of the medium of Rouf and Stokes (1964), as described in Starr (1981). It was composed of the following in grams per liter: dextrose, 0.5; peptone, 0.05; ferric ammonium citrate, 0.15; $MgSO_4 \cdot 7H_2O$, 0.2; $CaCl_2$, 0.05; $MnSO_4 \cdot H_2O$, 0.05; and $FeCl_3 \cdot 6H_2O$, 0.01. The pH was adjusted with sodium hydroxide and sulfuric acid. The organisms were continuously supplied with the medium for acclimatization then flow was stopped, allowing time for reactions to occur. Dissolved oxygen was maintained by way of aquarium air pumps. When ferrous iron was desired it was supplied by ferrous ammonium sulfate. One of the three flasks was an autoclaved sterile control. Samples were taken periodically and tested for pH, dissolved oxygen, iron oxidation, nitrite, nitrate, and hydrogen peroxide evolution.

The above procedure was repeated in the laboratory using groundwater from Moore, MT. Ferrous iron was supplied using ferrous ammonium sulfate or ferrous sulfate and when desired the carbon content was increased using dextrose.

Chemical Oxidation Experiments

MIOX - Mixed Oxidant Generation Unit

MIOX Corporation (Albuquerque, NM) supplied a mixed oxidant generation unit (SAL-20) for use in the chemical oxidation study. The unit contains a proprietary membraneless electrolytic cell that produces mixed oxidants by means of electrolyzing salt water (brine). The brine is made by dissolving water softener salt in the brine reservoir. The brine solution is mixed with source water to create a sodium chloride concentration of approximately 10 g/L, that enters into the cell where the oxidants are generated (Figure 6). Two streams exit the electrolytic cell of the MIOX unit. The anode, containing the mixed oxidants, is separated from the cathode, containing mostly hydrogen gas and sodium hydroxide. This separation maintains several species of oxidants in the mixed oxidant solution. Although the exact constituents making up this solution are unknown, it is believed to contain hypochlorous acid, chlorine dioxide, and ozone, among others. Power for this system is standard 120 VAC or 12 VDC. The oxidant solution is injected into the source water stream where disinfection / oxidation may occur. The cathode may be discarded down the drain or combined with the anode for injection. If the two streams are combined only hypochlorous acid remains in the oxidant solution. A water softener attachment is available for hard waters, as the cell will foul with a calcium hardness greater than 17 mg/L as Ca^{+2}. The softener uses the same brine reservoir as the electrolytic cell. Several different MIOX units are available from MIOX Corporation depending on the oxidant demands of the system (Appendix C).

The raw oxidants ranged from 150 to 200 mg/L as free available chlorine. Exact concentrations were determined prior to each experiment and the concentrated solutions were diluted with chlorine free distilled or reverse osmosis (RO) treated water to desired concentrations. During oxidant generation the anode and cathode effluent streams were not combined.

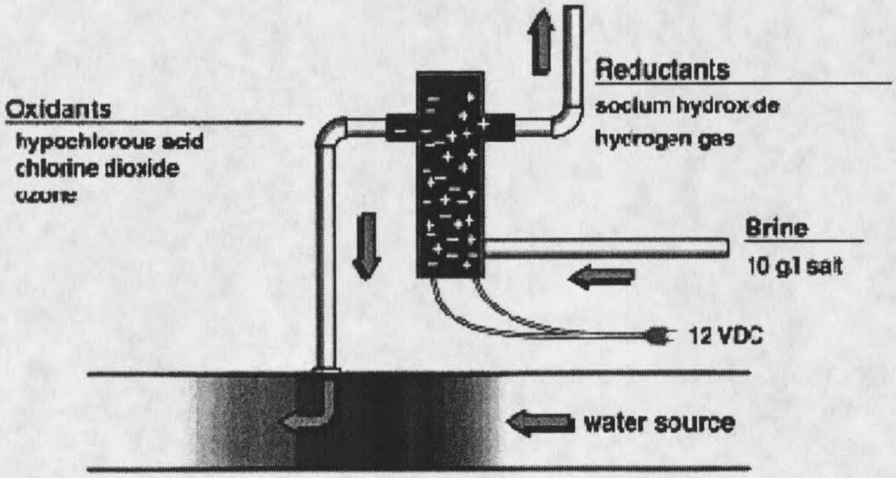

Figure 6 The MIOX Process

Laboratory Procedures

Batch All batch tests were conducted using square PVC "gator" jars unless otherwise noted. Interior jar dimensions were 11.5 cm square by 21 cm high (Figure 7). A 1/4 in. sampling port was installed 10 cm below the water surface. All tests using these jars were conducted with 2 liters of water unless otherwise noted.

A six jar mechanical mixer (Phipps and Bird, Inc. Richmond, Virginia) was equipped with flat, two blade, impellers of diameter 7.6 cm. The blades were immersed to a level 2/3 the depth of the water.

Field well water simulation was accomplished by the addition of hardness, alkalinity, and iron and/or manganese to reverse osmosis treated water. Hardness and alkalinity for most tests were maintained in the range of 180 to 220 mg/L and 200 to 250 mg/L respectively as $CaCO_3$, by the addition of sodium bicarbonate ($NaHCO_3$), calcium chloride ($CaCl_2$) and magnesium carbonate hydroxide pentahydrate ($(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$). Magnesium hardness and calcium hardness were in the range of 90 and 100 mg/L, respectively as $CaCO_3$. Iron was added in the form of ferrous ammonium sulfate ($Fe(NH_4)_2 \cdot (SO_4) \cdot 6(H_2O)$) and manganese was added in the form of manganese sulfate ($MnSO_4 \cdot H_2O$). These, as well as all of the chemicals used in this project, were reagent grade Fisher (Pittsburgh, PA) chemicals. Water temperature was maintained within the range of 18 to 22°C.