



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
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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.

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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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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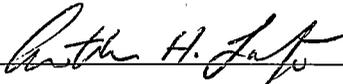
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TABLE OF CONTENTS

I	INTRODUCTION	1
	Project Objective	2
	Thesis Outline	3
II	BACKGROUND	6
	Iron and Manganese	6
	Occurrence in Natural Waters	6
	Iron and Manganese Chemistry	7
	Problems Associated With Iron and Manganese	9
	Acceptable Levels	10
	Treatment Considerations	10
	Available Treatment Technologies	11
	Oxidation	13
	Aeration	13
	Free Chlorine	13
	Potassium Permanganate	15
	Chlorine Dioxide	15
	Ozone	16
	Coagulation / Sedimentation / Filtration	16
	Direct Filtration and Oxide-Coated Media Filtration	17
	Sequestration	20
	Ion Exchange	21
	Membrane Filtration	22
	In Situ Treatment	23
	Biological Filtration	24
	Biological vs. Physical-Chemical Oxidation	25
	Iron and Manganese Oxidizing Bacteria	28

Emergence of "Iron Bacteria".	28
Do Organisms Benefit From Fe and Mn Oxidation?	29
Oxide Characterization	30
Existing Biological Removal Plants	31
Small System Limitations	32
Field Site - Moore, Montana	33
III EXPERIMENTAL PROCEDURES	38
Experimental Approach	38
Chemical Oxidation Approach	38
Biological Oxidation Approach	39
Analyses	40
Chemical	40
Iron Oxide Structure	42
Biological	43
Microscopy	43
Biological Removal Mechanism Investigation	43
Chemical Oxidation Experiments	44
MIOX - Mixed Oxidant Generation Unit	44
Laboratory Procedures	46
Batch	46
Settling - Jar Tests	48
Settling - Column Tests	49
Filtration	50
Fe and Mn Removal vs. Empty Bed	
Contact Time (EBCT).	51
Filtration System	52
Field Procedures - Moore, Montana	52
Batch	52

	Filtration	53
	Biological Oxidation Experiments	57
	Field Procedures - Moore, Montana	57
	Filtration	57
	Chlorine Demand	58
IV	RESULTS AND DISCUSSION - CHEMICAL OXIDATION	60
	Laboratory	60
	Iron Stoichiometry	60
	Manganese Stoichiometry	62
	Settling	66
	Fe and Mn Removal vs. Empty Bed	
	Contact Time (EBCT).	68
	Filter Bed Washing	69
	Filtration System	71
	Field Site - Moore, Montana	78
	Iron Stoichiometry	78
	Filtration	78
	Summary - Chemical Oxidation	82
V	RESULTS AND DISCUSSION - BIOLOGICAL OXIDATION	84
	Laboratory and Field	84
	Redox Potential	84
	Dissolved Organic Carbon	85
	Aeration	86
	Chlorine Demand	87
	Filtration System	90
	Microscopic Identification	93
	Oxide Characterization	96

	Biological Oxidation Mechanism	97
	Summary - Biological Oxidation	99
VI	COST ANALYSIS	102
	System Implementation and Cost Analysis	102
VII	SUMMARY	107
	Removal Mechanisms.	107
	Cost Analysis	109
	Treatment Implementation	110
	LITERATURE CITED	112
	APPENDICES	117
APPENDIX A	RELEVANT TERMS AND CALCULATIONS	118
APPENDIX B	X-ray PHOTOELECTRON SPECTROSCOPY (XPS) DATA	124
APPENDIX C	COST ANALYSIS / TREATMENT TRAINS	134

LIST OF TABLES

Table 1	Available Treatment Technologies	12
Table 2	Oxidation Techniques for Iron and Manganese	14
Table 3	Water Quality - Moore, Montana	34
Table 4	Dissolved Organic Carbon - Moore Filtration System	86
Table 5	Sources of the Chlorine Demand of Moore, Montana Groundwater	88
Table 6	Treatment Implementation Costs	104

LIST OF FIGURES

Figure 1	Chemical Oxidation Project Schematic	4
Figure 2	Biological Oxidation Project Schematic	5
Figure 3	Field of Activity of Iron Bacteria	27
Figure 4	Location - Moore, Montana	35
Figure 5	Solubility of Iron in Relation to pH and pe	37
Figure 6	The MIOX Process	45
Figure 7	"Gator" Jar	47
Figure 8	Glass Filter Column	51
Figure 9	Chemical Filtration System - Moore, Montana (Normal Operation)	55
Figure 10	Chemical Filtration System - Moore, Montana (Backwash Operation)	56
Figure 11	Biological Filtration System Schematic - Moore, Montana	59
Figure 12	Soluble Manganese Oxidation Based on Theoretical Stoichiometry - Mixed Oxidants	63
Figure 13	Soluble Manganese Oxidation Based on Theoretical Stoichiometry - Moore, MT Water - Iron Removed - Mixed Oxidants	64
Figure 14	Soluble Manganese Oxidation Based on Theoretical Stoichiometry - Sodium Hypochlorite	65
Figure 15	Iron Removal During Settling	67
Figure 16	Effect of Manganese Concentration on Removal By Filtration - No Oxidant	70
Figure 17	Oxide Coated Pea Gravel Washing	70

Figure 18	Soluble Manganese Removal Through Oxide Coated Pea Gravel - No Oxidant	73
Figure 19	Manganese Release With and Without the Presence of Mixed Oxidants During Filtration	73
Figure 20	Soluble Manganese Removal Through Oxide Coated Pea Gravel - Mixed Oxidants	74
Figure 21	Soluble Manganese Removal for Greensand vs. Oxide Coated Pea Gravel (No Oxidant)	74
Figure 22	Iron Oxide Coating of Silica Sand	76
Figure 23	Soluble Manganese Removal Using Greensand - Mixed Oxidants vs. Sodium Hypochlorite	77
Figure 24	Iron Oxidation Based On Theoretical Requirements - Moore, Montana - Mixed Oxidants	79
Figure 25	Greensand Filtration System - Moore, Montana	81
Figure 26	Greensand vs. Silica Sand - Moore, Montana	81
Figure 27	Columns #1, #2, and #3 from the Moore, Montana Biological Filtration System	91
Figure 28	Filter #1 - Ferrous and Total Iron Removals - Moore, Montana	92
Figure 29	Filter #2 - Ferrous and Total Iron Removals - Moore, Montana	92
Figure 30	Light Microscopy Images of Iron Oxidizing Bacteria	94

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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II

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.

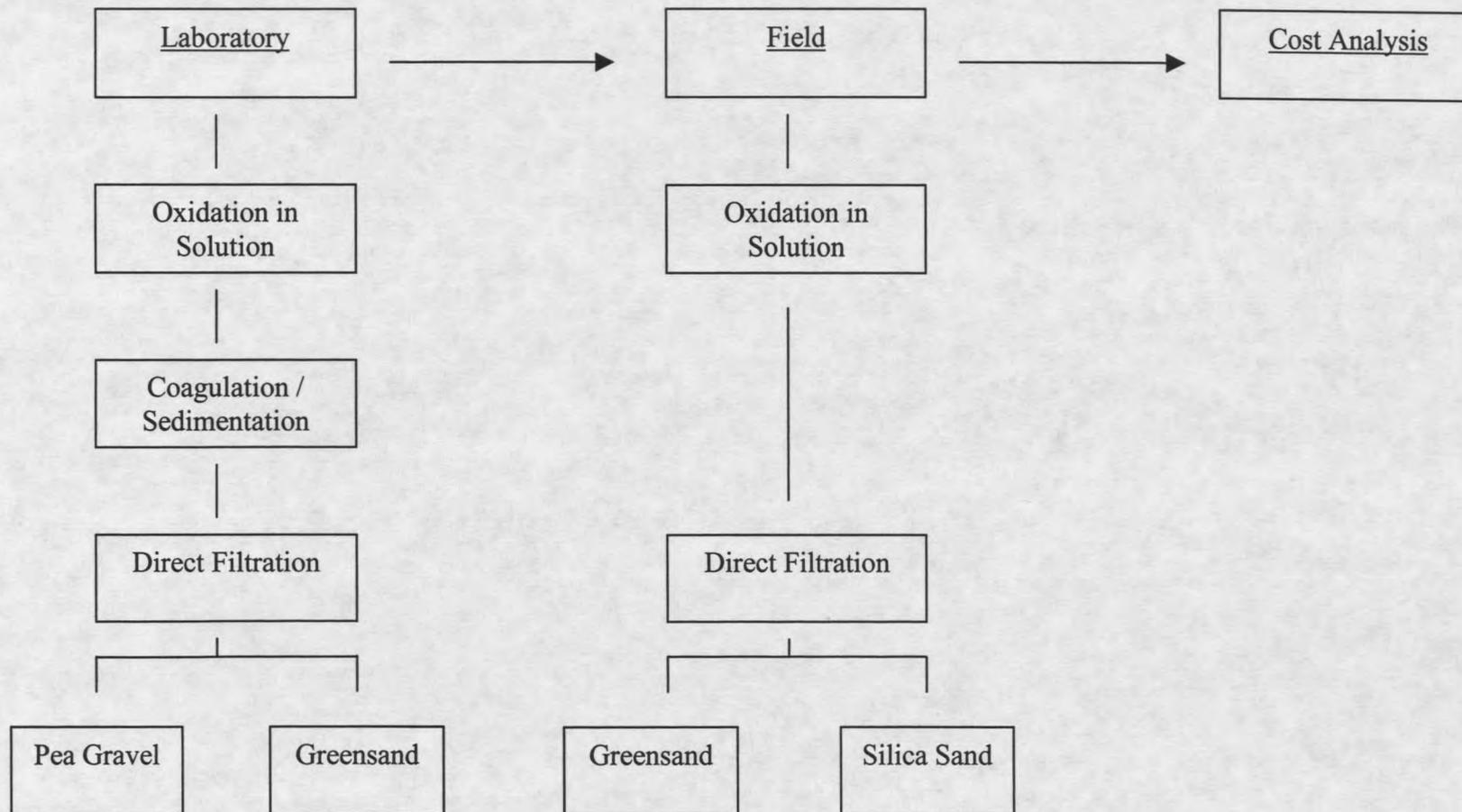
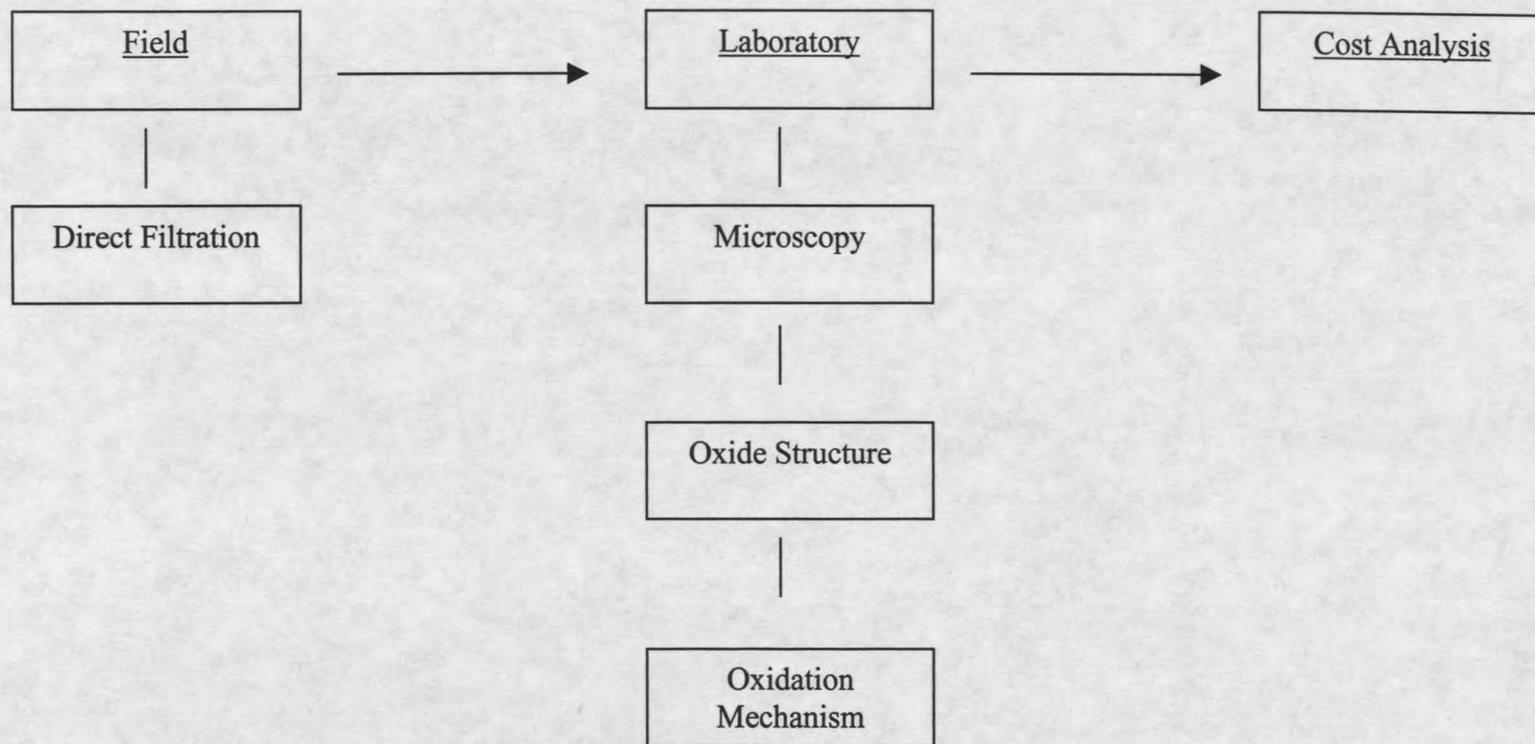


Figure 1 Chemical Oxidation Project Schematic



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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 CO₂ 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

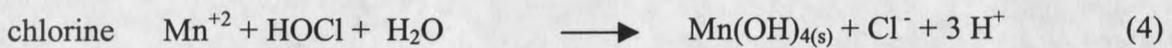
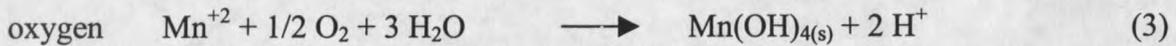
Soluble iron and manganese are both divalent cations. For iron this is a semi-stable state below a pH of about 5, whereas for manganese it is semi-stable up to a pH of about 8. Along with pH, the oxidation intensity (Eh), or availability of electrons, must also be examined to determine the stability 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.

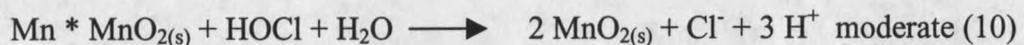
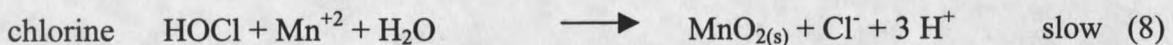
Iron Oxidation:



Manganese Oxidation:



Autocatalytic Mechanism:



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 CaCO₃. 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

