2010

Evaluation Of Oxidized Media Filtration Processes For The Treatment Of Hydrogen Sulfide In Groundwater

Vito Trupiano

University of Central Florida

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations, 2004-2019 by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

STARS Citation
https://stars.library.ucf.edu/etd/4417
EVALUATION OF OXIDIZED MEDIA FILTRATION PROCESSES FOR THE TREATMENT OF HYDROGEN SULFIDE IN GROUNDWATER

by

VITO M. TRUPIANO, E.I.
B.S.C.E., B.S.Env.E., UNIVERSITY OF CENTRAL FLORIDA, 2008

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Civil, Environmental, and Construction Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Summer Term 2010

Major Professor: Steven Duranceau, Ph.D., P.E.
ABSTRACT

This study evaluated alternative sulfide treatment processes for potable water systems that rely on groundwater supplies. The research conducted in this report was conducted at the interconnected Imperial Lakes (IL) and Turner Road (TR) water treatment plants (WTPs) in Polk County, Florida. These WTPs are in the process of refurbishment and expansion, and the system will require the installation of a new groundwater well. The IL and TR WTPs both rely upon groundwater sources that contain total sulfide at concentrations ranging from 1.4 to 2.6 mg/L. Sulfide is a concern because if left untreated it can impact finished water quality, corrosivity, create undesirable taste and odor, and oxidize to form visible turbidity. For this reason, the raw water will require additional treatment per Florida Department of Environmental Protection (FDEP) “Sulfide Rule” 62-555.315(5)(a). This rule does not allow the use of conventional tray aeration (currently in use at the IL and TR WTPs) for wells that have significant total sulfide content (0.6 to 3.0 mg/L) (FDEP, 2003).

This research was commissioned because the potential water treatment method identified in the Sulfide Rule (i.e. forced-draft aeration) would not adequately fit within the confines of the existing sites and would pose undue burden to neighboring residents. In addition, an effective sulfide treatment process was desired that offered a low profile, would not necessitate the need for additional complex chemical feed systems, minimized the extent of electrical infrastructure upgrades, and would be inexpensive to construct and operate.

To meet these goals, several alternative technologies were evaluated at the desktop and bench-scale; these included anion exchange, various oxidation methods, and alternative media filtration processes. From that effort, several processes were selected for evaluation at the pilot
scale: bleach (NaOCl) oxidation preceding electromedia filtration; manganese (IV) oxide (MnO₂) filtration continuously regenerated with bleach; and ferrate (Fe(VI)) oxidation.

Electromedia and MnO₂ filtration were shown to be effective for total sulfide treatment. Both processes reduced total sulfide content to below detection levels (< 0.1 mg/L) for the IL and TR groundwater supplies containing between 1.4 and 2.6 mg/L of total sulfide. The use of bleach oxidation ahead of media filtration also produced finished water with low turbidity (< 1.0 NTU) as compared to conventional tray aeration and chlorination processes (6-16 NTU, as observed in this study). It was determined that the media filtration approach (electromedia and MnO₂) was effective for sulfide treatment and met the County’s site objectives established at the outset of the project. Ferrate was also shown to reduce total sulfide content to below detection levels (< 0.1 mg/L) for groundwater supplies containing between 1.4 and 2.6 mg/L of total sulfide.

An opinion of probable capital costs for installing a sulfide oxidation/filtration process at either the Imperial Lakes or Turner Road WTP was estimated to range from roughly $830,000 to $1,100,000, or between $0.10 to $0.32 $/kgal installed (at 8% for 20 years). An opinion of probable annual bleach chemical costs was estimated to range from $3,500 to $9,800 for the IL WTP and $3,500 to $5,800 for the TR WTP.
To Mandi, Mom and Dad
ACKNOWLEDGMENTS

This work could not have been completed without the support provided by the many individuals who assisted in this project. Special thanks to Dr. Steven J. Duranceau for serving as my thesis committee chair and giving me the opportunity to undertake this research study. Dr. Duranceau constantly and consistently provided mentorship, assistance, guidance, and feedback; I am very much indebted to him for all that I have gained over the last two years. Thank you to Dr. Andrew A. Randall and Dr. Christian A. Clausen for donating their time and effort to review my work, provide feedback and serve as committee members. Additional thanks are offered to UCF research students William Johnson, Jaya Tharmapalan, Christopher Boyd, Amalia Abdelwahab and Yuming Fang who assisted in laboratory and field tasks and dedicated many hours and much hard work to ensure the success of this project.

I would like to also thank the municipality, companies and individuals whom were involved in and assisted the UCF research team in this effort. This work would not have been possible without Polk County Utilities, especially Gary Fries, Mark Lowensine, Jason Hopp, Steve Whidden, Shannon Roberts and Jake Rohrich. The assistance of Robert Beltran is also appreciated. The support offered by Mike Strully and Chris Baggett of Jones Edmunds and Associates, Inc. is noted and recognized. The services provided by participating vendors were instrumental in completing this research: Filtronics, Inc. (Electromedia®), Hungerford & Terry, Inc. (GreensandPlus™), Ferrate Treatment Technologies, LLC, and MIOX, Inc.; their support is noted and appreciated. This project was funded by Polk County Utilities through an inter-government agreement with the University of Central Florida.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................................ x
LIST OF TABLES .......................................................................................................................... xi
LIST OF EQUATIONS ................................................................................................................ xiii
LIST OF ABBREVIATIONS ....................................................................................................... xv

1.0 INTRODUCTION .............................................................................................................. 1
   Project Description ...................................................................................................................... 1
   Objectives .................................................................................................................................... 2

2.0 REVIEW OF EXISTING FACILITIES ............................................................................. 4
   Overview ..................................................................................................................................... 4
   Description of Sites ..................................................................................................................... 4
   Existing Water Quality Conditions .......................................................................................... 5
   Existing Treatment Processes .................................................................................................. 6
   Water Quality .............................................................................................................................. 7
      Hydrogen Sulfide ..................................................................................................................... 7
      Turbidity ................................................................................................................................... 8
      Disinfection By-Products ....................................................................................................... 10

3.0 LITERATURE REVIEW AND TREATMENT ALTERNATIVES DESK-TOP EVALUATION .......................................................................................................................... 14
   Description ................................................................................................................................ 14
   Chemistry of Hydrogen Sulfide ................................................................................................. 14
      Speciation of Hydrogen Sulfide in Water .................................................................................. 16
   Regulation of Hydrogen Sulfide ............................................................................................... 18
      Hydrogen Sulfide Off-Gas Standards ..................................................................................... 21
   Hypochlorite Chemistry ............................................................................................................ 21
   Identification of Treatment Alternatives ................................................................................... 23
      Aeration .................................................................................................................................. 25
      Oxidation ................................................................................................................................ 26
      Hypochlorite Oxidation .......................................................................................................... 29
      Ferrate Oxidation ................................................................................................................... 32
Microbial Filtration ................................................................. 34
Membrane Filtration ............................................................... 35
Media Filtration ................................................................. 35
  Manganese (IV) Oxide Greensand Filtration .................. 37
  Electromedia® Filtration ..................................................... 41
Anion Exchange ................................................................. 45
Discussion of Treatment Alternatives Removed From Consideration ................................. 46
Short-Listing of Treatment Alternatives to be Further Evaluated ......................................... 48

4.0 EXPERIMENTAL PLAN, MATERIALS AND METHODS ............. 50
Introduction ............................................................................. 50
Experimental Plan ............................................................... 50
  Screening Criteria and Water Quality Goals ..................... 51
Pilot-Scale Equipment .......................................................... 52
  Ferrate .............................................................................. 52
  Bleach ............................................................................. 54
  Electromedia® Filter .......................................................... 54
  Manganese (IV) Oxide Filter ............................................... 56
Methods and Materials .......................................................... 57
  H₂S Assessment (Total Sulfides) ........................................... 58
  Post-Treatment Turbidity Formation Evaluation ............... 60
Laboratory Quality Control ................................................ 62
  Precision and Accuracy ....................................................... 62

5.0 RESULTS AND DISCUSSION .............................................. 68
Overview ............................................................................. 68
  Ferrate Holds Promise as a Treatment Alternative .......... 68
  Electromedia® Filter Effective at Sulfide Control ............ 70
  Manganese (IV) Oxide Filtration Reduces Sulfide Effectively 74
  Media Filtration Reduces Post-Filtration Turbidity Formation 78
Additional Observations ....................................................... 81

6.0 CONCEPTUAL COST CONSIDERATIONS ......................... 83
LIST OF FIGURES

Figure 2.1. Schematic of a Conventional Groundwater Treatment System ........................................... 6
Figure 2.2: Existing System Average Turbidity Values (NTU)- Imperial Lakes Well #1 .................... 9
Figure 2.3: Existing System Average Turbidity Values (NTU)- Imperial Lakes Well #2 ................. 9
Figure 2.4: Existing System Average Turbidity Values (NTU)- Turner Road WTP ....................... 10
Figure 3.1: Sulfide Species Distribution Diagram .............................................................................. 18
Figure 3.2: GreensandPlus™ Filter Media (Courtesy of Hungerford and Terry, Inc.) ..................... 40
Figure 3.3: Anthracite Filter Media (Courtesy of Hungerford and Terry, Inc.) ............................... 40
Figure 3.4: Anthracite Filter Media (Courtesy of Filtronics, Inc., Anaheim, Ca.) ........................... 42
Figure 3.5: Filtronics, Inc. Electromedia® I (Courtesy of Filtronics, Inc., Anaheim, Ca.) ............... 43
Figure 3.6: Support Media (Courtesy of Filtronics, Inc., Anaheim, Ca.) ........................................ 44
Figure 3.7: Support Media (Courtesy of Filtronics, Inc., Anaheim, Ca.) ........................................ 45
Figure 4.1: Ferrate Treatment Technologies, Inc. Ferrate Synthesizer ............................................. 53
Figure 4.2: Ferrate Treatment Technologies, Inc. Pilot-Scale Ferrate Treatment Skid .................... 54
Figure 4.3: Electromedia® Pilot-Filter Unit ....................................................................................... 55
Figure 4.4: GreensandPlus™ Pilot-Filter Unit .................................................................................. 56
Figure 4.5: LaMotte (Methylene Blue) Test Kit and Iodometric Titration Setup ............................. 58
Figure 4.6: Pictures from the Turbidity Formation Study ............................................................... 61
Figure 5.1: Post-Treated Sulfide and FAC Residual as a Function of Cl2/S²⁻ Molar Ratio for Electromedia® - IL WTP ......................................................................................... 72
Figure 5.2: Schematic of Electromedia® Filtration Process ............................................................. 74
Figure 5.3: Pressure Drop Across MnO₂ Pilot Filter Bed as a Function of Hydraulic Loading Rate ................................................................................................................................. 75
Figure 5.4: Schematic of Manganese (IV) Oxide Filter Process ...................................................... 78
Figure 5.5: Imperial Lakes Turbidity Study Data – Well #1 ............................................................. 80
Figure 5.6: Turner Road Turbidity Study Data .................................................................................. 81
Figure 5.7: Average Daily Turbidity at the Imperial Lakes WTP .................................................... 82
LIST OF TABLES

Table 2.1: Raw Water Quality Data ................................................................................................ 5
Table 2.2: Existing DBP Concentrations for P.O.E. at the IL WTP (Boyle, 2001) ....................... 11
Table 2.3: Annual Avg. DBP Concentrations for the SW Water District (Provided by Polk County) ......................................................................................................................................... 12
Table 3.1: Common Oxidative States for Sulfur Compounds (Mardigan & Martinko, 2006) ..... 16
Table 3.2: FDEP Chapter 62-555.315(5)(a.) Total Sulfide Treatment Recommendations ....... 20
Table 3.3: Sulfides Treatment Advantage-Disadvantage Comparison ........................................ 24
Table 3.4: Oxidant Redox Potential (Adapted from Jiang & Lloyd, 2002; Lee et al, 2004) ...... 28
Table 4.1: Table of Methods and Equipment ............................................................................. 57
Table 4.2: Precision Analysis of TOC Duplicates ........................................................................ 64
Table 4.3: Accuracy of TOC Analyses as Measured by Percent Recovery .............................. 65
Table 4.4: Precision Analysis of Sulfate Duplicates ................................................................... 66
Table 4.5: Accuracy of Sulfate Analyses as Measured by Percent Recovery ............................ 67
Table 5.1: Ferrate Treatment Data from the Imperial Lakes WTP ........................................... 70
Table 5.2: Electromedia® filter performance at the Imperial Lakes WTP ................................ 71
Table 5.3: Manganese (IV) Oxide Filter Performance Data- Imperial Lakes WTP ................. 77
Table 5.4: Manganese (IV) Oxide Filter Performance Data- Turner Road WTP ....................... 77
Table 6.1: Imperial Lakes WTP Projected Flow Rates (based on demand) ............................. 84
Table 6.2: IL WTP Well Flows .................................................................................................. 84
Table 6.3: Turner Road WTP Projected Flow Rates (based on demand) .................................. 85
Table 6.4: Preliminary Design for Manganese (IV) Oxide Filtration System ......................... 86
Table 6.5: Electromedia® Filter Design for the Imperial Lakes WTP ........................................ 86
Table 6.6: Opinion of Probable Capital Cost for Sulfide Filtration Systems ............................ 87
Table 6.7: Opinion of Probable Chemical Costs for the IL and TR WTPs ............................... 87
Table 9.1: Filtronics Electromedia® Pilot Filter Run Data ......................................................... 94
Table 9.2: Electromedia® Pilot Filter Run Data for Breakpoint Determination ....................... 95
Table 9.3: H&T, Inc. Manganese (IV) Oxide Pilot Filter Run Data ........................................... 96
Table 9.4: Existing System Turbidity Data- IL WTP Well #1 .................................................. 97
Table 9.5: Turbidity Summary Statistics- IL WTP Well #1 ................................................................. 98
Table 9.6: Existing System Turbidity Data- IL WTP Well #2 .............................................................. 99
Table 9.7: Turbidity Summary Statistics- IL WTP Well #2 ................................................................. 100
Table 9.8: Existing System Turbidity- TR WTP ............................................................................... 101
Table 9.9: Turbidity Summary Statistics- TR WTP ........................................................................... 102
Table 9.10: MnO₂ Filter- 24 Hr Simulated Distribution System THM Formation .......................... 103
Table 9.11: MnO₂ Filter- 24 Hr Simulated Distribution System HAA5 Formation..................... 104
LIST OF EQUATIONS

(3-1)............................................................................................................................................... 15
(3-2)............................................................................................................................................... 17
(3-3)............................................................................................................................................... 17
(3-4)............................................................................................................................................... 22
(3-5)............................................................................................................................................... 22
(3-6)............................................................................................................................................... 22
(3-7)............................................................................................................................................... 22
(3-8)............................................................................................................................................... 22
(3-9)............................................................................................................................................... 29
(3-10)............................................................................................................................................. 30
(3-11)............................................................................................................................................. 30
(3-12)............................................................................................................................................. 30
(3-13)............................................................................................................................................. 30
(3-14)............................................................................................................................................. 30
(3-15)............................................................................................................................................. 31
(3-16)............................................................................................................................................. 31
(3-17)............................................................................................................................................. 31
(3-18)............................................................................................................................................. 31
(3-19)............................................................................................................................................. 31
(3-20)............................................................................................................................................. 31
(3-21)............................................................................................................................................. 33
(3-22)............................................................................................................................................. 33
(3-23)............................................................................................................................................. 34
(3-24)............................................................................................................................................. 34
(3-25)............................................................................................................................................. 34
(3-26)............................................................................................................................................. 34
(3-27)............................................................................................................................................. 41
(3-28)............................................................................................................................................. 41
LIST OF ABBREVIATIONS

AADD- Annual Average Daily Demand
AADF- Annual Average Daily Flow
DBP- Disinfection By-Products
EPA- Environmental Protection Agency
FAC- Free Available Chlorine residual
FDEP- Florida Department of Environmental Protection
FTT- Ferrate Treatment Technologies, LLC
gpm- gallons per minute
GST- Ground Storage Tank, for this study it is synonymous with ground storage reservoir
HAA- Haloacetic Acid
H&T- Hungerford and Terry, Inc.
IL- Imperial Lakes
MCL- Maximum Contaminant Level
MCLG- Maximum Contaminant Level Goal
MDD- Maximum Day Demand
MGD- Million Gallons per Day
MSDS- Material Safety Data Sheet
NTU- Nephelometric Turbidity Unit
OSHA- Occupational Safety and Health Association
POE- Point Of Entry
POTWs- Publicly Owned Treatment Works
PRV- Pressure Reducing Valve
SDWA- Safe Drinking Water Act

SM- Standard Methods for Water and Wastewater Examination

TC- Total Chlorine Residual

TOC- Total Organic Carbon

TR- Turner Road

TTHM- Total Trihalomethane

UCF- University of Central Florida

WTP- Water Treatment Plant, synonymous with water treatment facility
1.0 INTRODUCTION

Project Description

Reduced sulfide is a concern for many potable water purveyors relying on groundwater supplies. If sulfide is left untreated it can impact finished water quality, corrosivity, create undesirable taste and odor, and when oxidized will form visible turbidity. This thesis presents the results of research funded by Polk County Utilities (County) that evaluated alternative sulfide treatment processes. The University of Central Florida (UCF) Department of Civil, Environmental, and Construction Engineering (CECS) was contracted by the County to evaluate alternative sulfide treatment processes for the Imperial Lakes (IL) and Turner Road (TR) water supplies located in central Florida. The County is in the process of expanding the drinking water capacity of the IL and TR water treatment facilities that serve a portion of the County’s Southwest Regional Service Area. The County’s expansion project will require the installation of at least one new groundwater well and includes process modifications and refurbishment of existing facilities. The IL and TR water treatment plants (WTPs) currently rely upon groundwater sources that contain total sulfide content ranging from 1.4 to 2.6 mg/L.

The County’s IL and TR water treatment systems currently comply with the provisions of the EPA’s Safe Drinking Water Act (SDWA). Historically, the County has employed a bleach disinfection and tray aeration process for groundwater treatment. The expansion and refurbishment of the IL and TR treatment plants will necessitate compliance with existing regulatory requirements, in particular, those outlined by the Florida Department of Environmental Protection (FDEP) “Sulfide Rule” 62-555.315(5)(a). This rule disallows the use of the County’s existing sulfide treatment process (tray aeration) at the current sulfide levels and
instead, recommends the use of forced-draft aeration (FDEP, 2003). In its’ discovery and planning process, the County turned to UCF to research and provide recommendations regarding possible treatment alternatives due to concerns that the treatment methods identified in the Sulfide Rule (i.e. forced-draft aeration) would not adequately fit within the confines of the existing sites and would pose undue burden to neighboring residents.

Objectives

The necessity to remove H$_2$S from groundwater sources in the state of Florida is a prevalent issue for water purveyors. Traditionally, water purveyors in central Florida that use groundwater have utilized tray or cascade aeration followed by chlorine gas or bleach disinfection. Polk County Utilities, in central Florida, must replace one of these traditional treatment systems in order to maintain compliance with the FDEP Sulfide Rule. The County expressed a desire for UCF to help identify an alternative to the FDEP recommended forced-draft aeration treatment process. In response, a study was conducted to address this issue. The objectives of this research include:

1. Identify treatment alternatives that will meet federal and state regulatory potable water quality requirements, while satisfying the County’s aesthetic and site constraints, which include:
   a. Avoid the need for extensive electrical and treatment infrastructure improvements;
   b. Avoid the need for new, labor and operations intensive processes;
   c. Avoid the need for complex chemical feed systems;
d. Avoid an increase in the number of new chemicals and associated supply deliveries;

e. Identify an acceptable alternative that fits within existing site boundaries;

f. Identify an acceptable alternative with a low vertical profile (≤ 16 ft)

2. Determine if bleach oxidation followed by an Electromedia® filtration process will treat total sulfide from the IL and TR groundwater supplies;

3. Determine if manganese (IV) oxide filtration, continuously regenerated with sodium hypochlorite, will treat total sulfide from the IL and TR groundwater supplies;

4. Perform a preliminary assessment for the use of ferrate (IV) chemical for sulfide oxidation and evaluate its complexity for use at these sites;

5. Perform a preliminary assessment of disinfection by-product (DBP) formation for the identified alternative processes;

6. Assess the impact that the proposed alternatives will have on treated water turbidity;

7. Compare the bleach demand of the existing system to that required by the proposed processes;

8. Identify a cost-effective process solution that can meet the County’s desired study objectives.
2.0 REVIEW OF EXISTING FACILITIES

Overview

The following chapter provides a review of the existing water treatment site facilities where this study was conducted. These sites are located in Polk County and are considered small (less than 2 MGD) water treatment plants (WTPs). This chapter is subdivided into several sections and is presented in the following order: Description of Sites, Existing Water Quality Conditions, Existing Treatment Processes, and Water Quality.

Description of Sites

Research was conducted at two sites in southern Polk County: the Imperial Lakes and Turner Road Water Treatment Plants. The IL WTP has an annual average daily demand (AADD) of approximately 1.7 million gallons per day (MGD), with planned expansion to provide 2.3 MGD by 2028. Demand is lower at the TR WTP, which has an AADD of approximately 1.05 MGD, with plans to reduce demand to 0.95 MGD by 2028 (Jones Edmunds, 2009). The reduction of demand at the TR WTP is part of a regional capacity shift to the IL WTP.

The IL site is accessible through a shared access drive, which runs along a CSX railroad. The site is surrounded on three sides by private property and is visible from the main entrance of a neighboring residential community. The TR WTP is located in manufactured housing residential community. However, its’ access drive is connected directly to a residential roadway and utility traffic (maintenance, chemical deliveries, etc.) must travel through the community in order to gain access. This site is neighbored by homes on both sides, and undeveloped land to its rear.
Existing Water Quality Conditions

The raw water source for the IL and TR WTPs’ is the upper Floridan aquifer, and water quality data indicates that the source water is slightly alkaline with moderate hardness typical of groundwater in central Florida. A summary of the raw water quality is presented in Table 2.1. The total hardness of the well water ranges between 160 and 170 mg/L (as CaCO₃) with an alkalinity between 154 and 166 mg/L (as CaCO₃). At an average pH of 7.2 to 7.6, the alkalinity is primarily in the form of bicarbonate. TDS ranges from 150 to 300 mg/L and contains less than 0.004 mg/L and 0.08 mg/L of lead and copper, respectively. Hydrogen sulfide in the raw water ranges from 1.4 to 2.6 mg/L (as S²⁻) with pH between 7.4 to 7.8 pH units.

Table 2.1: Raw Water Quality Data

<table>
<thead>
<tr>
<th>Raw Water Quality</th>
<th>Imperial Lakes</th>
<th>Turner Road</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Sulfide (mg/L)</td>
<td>1.4 – 2.0</td>
<td>2.5 - 2.6</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>5.2 - 7.7</td>
<td>7.7 - 8.3</td>
</tr>
<tr>
<td>pH</td>
<td>7.4- 7.6</td>
<td>7.4- 7.6</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.12 - 0.32</td>
<td>0.10 - 0.13</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>0.86 - 1.36</td>
<td>1.16 - 1.21</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>0.011 - 0.049</td>
<td>0.011 - 0.012</td>
</tr>
<tr>
<td>Manganese (mg/L)</td>
<td>0.003 - 0.005</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Total Hardness (mg/L as CaCO₃)</td>
<td>164 - 168</td>
<td>169</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>154 - 166</td>
<td>160 - 166</td>
</tr>
</tbody>
</table>
**Existing Treatment Processes**

The IL and TR water treatment plants both utilize a similar treatment process. Raw groundwater is pumped to the top of a ground storage tank (GST) where it is chlorinated and then fed to a tray aerator before falling into a GST for storage. Each site has a series of high service pumps which cycle on and off to meet demand. When the high service pumps are operating, treated water is withdrawn from the GST and is routed through a parallel set of hydropneumatic tanks before leaving the WTP and entering the distribution system. Chlorine is stored in bulk locally at both sites in the form of liquid bleach. Both sites also feed a small dose of caustic to the treated water for pH adjustment prior to entering the distribution system as a means of corrosion control. Figure 2.1 features a schematic of a typical conventional groundwater treatment system. This schematic is representative of both the IL and TR WTPs; also, both of these sites feed their bleach at the top of the aeration trays and do not employ a post chlorine feed. The TR site is located at a lower elevation than the IL site. A pressure reducing valve (PRV) is used to maintain proper system pressure at the two sites.

![Figure 2.1. Schematic of a Conventional Groundwater Treatment System](image-url)
Water Quality

The primary water quality challenge for both of these WTPs is the relatively high concentration of hydrogen sulfide (1.4 to 2.6 mg/L). The IL and TR WTPs both employ tray aeration as a primary method of hydrogen sulfide control. However, tray aeration is only partially efficient for H₂S removal and is inefficient for total sulfides removal. Water treatment systems that utilize this process only realize partial sulfide removal from the use of tray aeration alone. For that reason, bleach, which is added for disinfection, must be applied in significant quantities to allow for sulfide oxidation. The oxidation of hydrogen sulfide with bleach has been shown to produce increased turbidity levels (Lyn, 1992). Also, the use of bleach oxidation in the presence of natural organic material will lead to formation of disinfection by-products (DBPs).

Hydrogen Sulfide

Sulfides are commonly found in groundwater and impoundments where anaerobic conditions prevail. As little as 0.5 mg/L of hydrogen sulfide in potable water is noticeable and the odor imparted by 1.0 mg/L of hydrogen sulfide can be considered offensive (White, 1999). Sulfides can affect the taste of the water as well. The minimum detectable taste of sulfide in water is approximately 0.05 mg/L.

In addition to odor and taste, the presence of hydrogen sulfide in drinking water can impact corrosion rates, and cause maintenance issues in water treatment plants (WTPs) and distribution systems. One primary concern with hydrogen sulfide is that it can accelerate corrosion by reacting with metal ions to form non-protective insoluble sulfides. Sulfide can
attack steel, iron, galvanized and copper piping to form “black water” even when oxygen is not present.

Hydrogen sulfide and colloidal sulfur has also been suspected to promote pitting in copper piping; however, there are many causal factors that impact corrosion. The presence of sulfide of and by itself does not necessarily mean that sulfide causes pitting of copper tube. It has also been shown to damage asbestos-cement piping in some waters through microbial reactions (AWWA, 1999).

Turbidity

One of the end products of bleach oxidation of hydrogen sulfide is colloidal sulfur that is measurable as turbidity (Lyn, 1991). The formation of turbidity following hydrogen sulfide chlorination is well documented in Troy Lyn’s 1991 thesis. His work showed that, not only does turbidity form quickly (within minutes) after chlorination, but it continues to increase with time over a period of many hours. His findings were supported by the water quality observations both the IL and TR WTPs. Compared to the raw water, these facilities both had elevated turbidity levels exiting the aeration trays. Treated water from the aeration trays cascades into a GST where it is stored, and turbidity continues to increase over time. Samples taken from the GSTs indicated that turbidity levels continue to increase after initial bleach dosing. The compiled average turbidity data for the two sites has been included in Figures 2.2, 2.3 and 2.4 for illustration of this understanding.
Figure 2.2: Existing System Average Turbidity Values (NTU) - Imperial Lakes Well #1

Figure 2.3: Existing System Average Turbidity Values (NTU) - Imperial Lakes Well #2
Disinfection By-Products

Although pathogenic organisms provide the primary human health risk from drinking water, chemical disinfection by-products (DBPs) are another, albeit unintentional, health risk. The first published reports for the occurrence of trihalomethanes (THMs) in finished drinking water appeared in 1974 (Rook, 1974). Disinfection by-product precursors include natural organic matter such as humic and fulvic acids, algae and bromide. DBP formation is dependent upon the disinfectant contact time, both initial (primary disinfection) and within the distribution system (secondary disinfection), the water pH and temperature, the quantity of the disinfectant added to the water (relative to the water’s demand), as well as, the type and quantity of precursor material to include bromide and natural organic matter.
Regulations regarding DBPs are complex, as demonstrated by the promulgation of the microbial/disinfection by-product cluster of EPA rules (Federal Register, 1998). The EPA requires water systems to use treatment methods to reduce the formation of DBPs and to meet the following standards: THMs (measured as the sum concentration of chloroform, bromoform, bromodichloromethane, and dibromochloromethane) at 80 parts per billion (ppb); haloacetic acids or HAAs (measured as the sum concentration of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid) at 60 ppb; bromate at 10 ppb; and chlorite at 1.0 part per million (ppm) (EPA, 2001).

Some of the existing DBP data that pertains to this study is provided in Tables 4 and 5. The disinfection by-product data presented in Table 2.2 is from a 2001 Southwest Regional Service Area Water Quality Master Plan (Water Quality Master Plan). These concentrations are for the point of entry at the IL WTP. HAA5 data was not available as it was not regulated at the time the Water Quality Master Plan was produced. Also, DBP data for Turner Road point of entry (POE) could not be found in the Water Quality Master Plan (Boyle, 2001).

<table>
<thead>
<tr>
<th>Disinfection By-Products</th>
<th>Average</th>
<th>Max</th>
<th>Min</th>
<th>St. Dev.</th>
<th>MCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromodichloromethane (μg/L)</td>
<td>3.98</td>
<td>4.00</td>
<td>3.95</td>
<td>0.04</td>
<td>NR</td>
</tr>
<tr>
<td>Dibromochloromethane (μg/L)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>---</td>
<td>NR</td>
</tr>
<tr>
<td>Bromoform (μg/L)</td>
<td>&lt;0.5</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>NR</td>
</tr>
<tr>
<td>Chloroform (μg/L)</td>
<td>10.2</td>
<td>11.0</td>
<td>9.4</td>
<td>1.1</td>
<td>NR</td>
</tr>
<tr>
<td>TTHM (μg/L)</td>
<td>31.5</td>
<td>62.8</td>
<td>14.6</td>
<td>27.2</td>
<td>80 μg/L</td>
</tr>
<tr>
<td>HAA5 [Haloacetic Acids] (mg/L)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>60 μg/L</td>
</tr>
</tbody>
</table>

Note: “---” Signifies that the data is either not available or is non-applicable
Table 2.3 contains recent distribution system data for the Polk County Southwest Regional Water District, wherein the IL and TR WTPs operate. This data is the average of four quarterly readings between October, 2008 and October, 2009. The highest average TTHM and HAA5 readings over this period were 48.08 and 32.70 μg/L, respectively. These concentrations are below the respective MCL’s of 80 and 60 μg/L for TTHM and HAA5.

Table 2.3: Annual Avg. DBP Concentrations for the SW Water District (Provided by Polk County)

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>TTHM (μg/L)</th>
<th>HAA5 (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5763 Cherry Tree Drive</td>
<td>47.86</td>
<td>27.41</td>
</tr>
<tr>
<td>Janeen Circle &amp; Kelley Ct</td>
<td>48.08</td>
<td>32.70</td>
</tr>
<tr>
<td>640 Whisperwoods</td>
<td>39.71</td>
<td>12.38</td>
</tr>
<tr>
<td>Christina Dr &amp; Oak Trail</td>
<td>34.43</td>
<td>10.91</td>
</tr>
<tr>
<td>6529 Foxcrest Lane</td>
<td>18.85</td>
<td>7.91</td>
</tr>
<tr>
<td>5205 Waterwood Dr</td>
<td>24.82</td>
<td>8.36</td>
</tr>
</tbody>
</table>

In the 2001 Water Quality Master Plan, Boyle Engineering Corporation (Boyle) found that the TTHM formation potential (4 days, pH 7.9, Temperature 30° C) at the IL and TR WTPs were 50.4 and 55.7 μg/L, respectively. The HAA5 formation potential (4 days, pH 7.9, Temperature 30° C) for the IL and TR WTPs were 30.5 and 20.5 μg/L, respectively (Boyle, 2001). Note that THM formation is favored at higher pH and temperature conditions. The formation potential is most likely conservative as the IL and TR WTPs currently have raw water pHs between 7.4 and 7.6 and temperatures between 25 and 29°C. However, at these lower pH levels, copper corrosion is of concern. Hence, pH adjustment or use of corrosion control inhibitor may be needed in the future should the County determine there is an impact. Although the County currently complies with the provisions of the DBP rule, it has also been shown that at elevated pH levels (4 days, pH 8.3, Temperature 30° C) the TTHM formation potential at the IL and TR WTPs is approximately 115 and 85 μg/L, respectively. Under the same conditions, the
HAA5 formation potential at the IL and TR WTPs is approximately 31 and 30 μg/L, respectively (Boyle, 2001). Consequently, the County should master plan for future possible DBP rule issues by allocating space in expansion engineering designs that allows for the placement of additional treatment processes if needed in the future.
3.0 LITERATURE REVIEW AND TREATMENT ALTERNATIVES

DESKTOP EVALUATION

Description

This chapter presents a review of existing literature regarding hydrogen sulfide chemistry and treatment. The chemistry concepts covered herein will establish a working knowledge for review of the treatment processes evaluated in later chapters. In this chapter, several alternative hydrogen sulfide removal processes are discussed. Some of the alternative processes that are presented are not covered in-depth, but instead are intended to provide a broad overview of the currently available alternatives. Several other processes that are evaluated in this study are covered in greater detail in the sections that follow.

This chapter is divided into several sections and is presented in the following order: Hydrogen Sulfide Chemistry, Regulation of Hydrogen Sulfide, Hypochlorite Chemistry, Identification of Treatment Alternatives, and Chemistry of Evaluated Alternatives.

Chemistry of Hydrogen Sulfide

Hydrogen sulfide (H₂S) gas is commonly found dissolved in groundwaters and domestic wastewater. Many people (particularly in Florida) may have encountered H₂S gas in shallow irrigation wells, which gives off an obnoxious odor often compared to that of rotten eggs (White, 1999). The rotten egg odor of hydrogen sulfide can occur as a result of anaerobic bacterial action on sulfates (AWWA, 1999). Bacteria reduce the sulfate ion (SO₄²⁻) in a reaction with organic matter (CH₂O-R) that produces bicarbonate (HCO₃⁻), hydrogen sulfide (H₂S), and undefined
radical (represented with R) end products (as shown in equation 3-1). This reaction presented stoichiometrically is as follows:

\[
2(\text{CH}_2\text{O-}R) + \text{SO}_4^{2-} + \text{Bacteria} \rightarrow 2(\text{HCO}_3^-) + \text{H}_2\text{S} + 2R
\] (3-1)

Theoretically (as shown in thermodynamic calculations), sulfate could be reduced to hydrogen sulfide inorganically. However, laboratory studies have shown that the inorganic reaction is only favorable at temperatures in excess of 250°C. These conditions are unlikely to be seen in a natural aquifer system, and thus the reduction of sulfate typically occurs through bacterial mediation of the reaction. Sulfate reducing bacteria assimilate sulfur under conditions common of aquifer systems, which are anaerobic in nature and often have a source of organic carbon available (as low as 0.1 mg/L) (Dohnalek & FitzPatrick, 1983).

The genera most often responsible for sulfide production are Desulfovibrio desulfuricans and Desulfotomaculum. These bacterial genera are known to accelerate the reduction of sulfate and can be a major source of sulfide production in anaerobic environments (Lim, 1979). Other bacterially produced sulfur compounds creating swampy and fishy tastes and odors in distribution systems include Dimethylpolysulfides and Methylmercaptan. Several types of Pseudomonas bacteria can also produce undesirable sulfur compounds (AWWA, 1999).

There are several oxidative states (Table 3.1) of the sulfur atom. These compounds range from sulfur’s most reduced form, organic S or hydrogen sulfide, with a minus two oxidation state, to sulfur’s most oxidized form, sulfate, with a plus six oxidation state. The reduction of $\text{SO}_4^{2-}$ to $\text{H}_2\text{S}$ is an eight electron reduction (Mardigan & Martinko, 2006).
### Table 3.1: Common Oxidative States for Sulfur Compounds (Mardigan & Martinko, 2006)

<table>
<thead>
<tr>
<th>Sulfur Compound</th>
<th>Oxidation State of Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic S (R-SH)</td>
<td>-2</td>
</tr>
<tr>
<td>Sulfide (H₂S)</td>
<td>-2</td>
</tr>
<tr>
<td>Elemental Sulfur (S⁰)</td>
<td>0</td>
</tr>
<tr>
<td>Thiosulfate (S₂O₃²⁻)</td>
<td>+2</td>
</tr>
<tr>
<td>Sulfur Dioxide (SO₂)</td>
<td>+4</td>
</tr>
<tr>
<td>Sulfite (SO₃²⁻)</td>
<td>+4</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>+6</td>
</tr>
</tbody>
</table>

### Speciation of Hydrogen Sulfide in Water

Sulfide exists in three forms in the aqueous hydrogen sulfide system; hydrogen sulfide (H₂S), bisulfide ion (HS⁻), and sulfide ion (S²⁻). The sum of these three compounds is commonly referred to as total sulfides, with the concentration of total sulfides reported in equivalent units as mg/L S²⁻. In this document, total sulfides are often simply referred to as “sulfides”.

As shown in Figure 3.1, in the pH range of 6.0 to 8.0, the predominant reduced sulfur forms are HS⁻ and H₂S. The sulfide (S²⁻) form is negligible at ambient pH levels in groundwater. Thermodynamically stable states, both final and quasi, include sulfate (S⁶⁺) and colloidal sulfur (S⁰) under oxidized water conditions. Consequently, of the thirty or more ionic and molecular sulfur species that exist, only five are thermodynamically stable under conditions found in drinking water, and include: hydrogen sulfide [H₂S], bisulfide [HS⁻], elemental sulfur [S⁰], bisulfate [HSO₄⁻], and sulfate [SO₄²⁻]. Other sulfur states that are found in nature, but are
considered to be thermodynamically unstable include: polysulfides, polythionates, and thiosulfate (Garrels & Naeser, 1958).

In aqueous solutions, hydrogen sulfide dissociates in water and can be described by the following equilibrium equations:

\[ \text{H}_2\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HS}^- \quad \text{pKa}_1 = 7.0 \]  

(3-2)

\[ \text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{S}^{2-} \quad \text{pKa}_2 = \sim 13.8 \]  

(3-3)

Equation 3-2 illustrates that at a pH of 7.0, half of the dissolved sulfide species for any given concentration is bisulfide [HS\(^-\)] and half remains as hydrogen sulfide (gas), as shown in Figure 3.1. Since most ground waters occur near a neutral pH of 7.0, only a portion of the total sulfide can be removed as gas unless a change in pH is induced to artificially shift the equilibrium of the system. At pH values above 13, sulfur chemistry becomes very complex. Chlorination or oxygenation of ground water containing hydrogen sulfide can result in the formation of elemental sulfur and colloidal polysulfides (which can impart a milky-white turbidity to the water). The removal of elemental sulfur and colloidal polysulfides can reduce copper corrosion rates in metallic distribution systems (Rubin, 1974; Hausler, 1979; Duranceau, 1993).
Figure 3.1: Sulfide Species Distribution Diagram

Regulation of Hydrogen Sulfide

Water purveyors across the country often deal with a wide variety of non-regulated inorganic chemicals within their water system, which receive varying degrees of public attention. Arsenic, radionuclides, total dissolved solids (TDS), lead, copper and nitrates (nitrite) are inorganic contaminants viewed as important because of their associated water quality issues. However, “other” important inorganic constituents include calcium, magnesium, iron and manganese. In a qualitative survey of 67 public water systems, the most commonly identified inorganic constituents of concern were iron, manganese, pH adjustment, hardness and the various anions chloride, sulfate, and bromide (AWWA, 2009). Hydrogen sulfide was not recognized as an important inorganic water quality constituent. Consequently, it is not surprising that the unregulated inorganic contaminant hydrogen sulfide has not received significant
attention over the years except in Florida, because the state relies heavily on groundwater as its primary water supply. Hence in recent years Florida has taken the lead with regards to regulating this inorganic water quality constituent.

Recent revisions to FDEP Chapter 62-555 regarding H₂S removal are now in effect for new wells and for modifications to treatment systems at existing well sites. Table 3.2 presents H₂S removal requirements based on revisions to FDEP Chapter 62-555.315(5)(a). The new provisions pertain to public water system wells with respect to various construction operation and maintenance items related to water quality. In an effort to control copper pipe corrosion and black water complaints, new permit provisions were developed under FDEP Chapter 62-555.315(5). Permit applications to connect a new or altered well to a community system after August 28, 2003 must adhere to the following provisions:

1. Include in the preliminary design report results for alkalinity, dissolved iron, dissolved oxygen, pH, total sulfide and turbidity.

2. If total sulfide equals or exceeds 0.3 mg/L the applicant must perform the following:
   i) Provide aeration to remove total sulfide. Recommended types of aeration treatment are provided in Table 3.2. The techniques listed next to each water quality level are recommendations only and not requirements; other treatment techniques used must achieve the same or better removal.
   ii) Provide preliminary design report demonstrating secondary maximum contaminant levels (MCLs) for color and odor will not be exceeded in the water supplier’s drinking water distribution system or in water customers’ potable water systems.
   iii) Odor compliance shall continue to comply with FDEP Chapter 62-296.320(2).
# Table 3.2: FDEP Chapter 62-555.315(5)(A.) Total Sulfide Treatment Recommendations

<table>
<thead>
<tr>
<th>Potential for Impacts without Total Sulfide Removal</th>
<th>Source Water Sulfide Level</th>
<th>Potential Water Treatment Technique*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Total Sulfide (TS) &lt; 0.3 mg/L; or Dissolved Iron (DI) &lt; 0.1 mg/L</td>
<td>Direct chlorination (^2)</td>
</tr>
<tr>
<td>Moderate</td>
<td>0.3 mg/L ≤ TS ≤ 0.6 mg/L @ pH ≤ 7.2</td>
<td>Conventional aeration (^3) (maximum removal efficiency ≈ 40% to 50%)</td>
</tr>
<tr>
<td></td>
<td>0.3 mg/L ≤ TS ≤ 0.6 mg/L @ pH &gt; 7.2</td>
<td>Conventional aeration with pH adjustment (maximum removal efficiency ≈ 40% to 50%)</td>
</tr>
<tr>
<td>Significant</td>
<td>0.6 mg/L ≤ TS ≤ 3.0 mg/L @ pH ≤ 7.2</td>
<td>Forced Draft Aeration (^3) (maximum removal efficiency ≈ 90%)</td>
</tr>
<tr>
<td></td>
<td>0.6 mg/L ≤ TS ≤ 3.0 mg/L @ pH &gt; 7.2</td>
<td>Forced Draft Aeration with pH adjustment (^4, 5) (maximum removal efficiency ≈ 90%)</td>
</tr>
<tr>
<td>Very Significant</td>
<td>TS &gt; 3.0 mg/L</td>
<td>Packed Tower Aeration with pH adjustment (^5, 5) (maximum removal efficiency ≈ 90%)</td>
</tr>
</tbody>
</table>

1.0 High iron content raises concern if chlorination alone is used and significant dissolved oxygen exists in the source water. Filtration may be required to remove particulate iron prior to water distribution.

2.0 Direct chlorination of sulfide in water in the pH range normally found in potable sources produces S\(_2^0\) and increased turbidity. Finished-water turbidity should not be more than two nephelometric turbidity units (NTU) greater than raw-water turbidity.

3.0 Increased dissolved oxygen entrained during aeration may increase corrosivity.

4.0 Reduction of alkalinity during pH adjustment and high dissolved oxygen entrained during aeration may increase corrosivity. Corrosion control treatment such as pH adjustment, alkalinity recovery, or use of inhibitors may be required.

5.0 High alkalinity will make pH adjustment more costly, and use of other treatment may be in order. Treatment that preserves the natural alkalinity of the source water may enhance the stability of finished water.

* Note – These recommendations are listed as “Potential” water treatment techniques; they are to be used as guidance and not as a requirement. Other appropriate treatments may be used in lieu of these recommended processes. Pilot testing can be used to verify the appropriateness of a suggested alternative.
Hydrogen Sulfide Off-Gas Standards

Off-gas standards have not been established for H$_2$S by the FDEP; however, FDEP Chapter 62-555 references FDEP Chapter 62-296 and FDEP Chapter 62-210 for objectionable odor guidelines. FDEP Chapter 62-210 defines objectionable odor as: “any odor present in the outdoor atmosphere which by itself or in combination with other odors, is or may be harmful or injurious to human health or welfare, which unreasonably interferes with the comfortable use and enjoyment of life or property, or which creates a nuisance.” The Occupational Safety and Health Administration (OSHA) recommends 20 parts per million by volume (ppmv) threshold for H$_2$S off-gas concentrations on-site for operators. While other sources cite 7.3 ppmv at the property boundary to avoid odor complaints, H$_2$S can be discharged into the air untreated or the air can be discharged following sulfide removal on-site.

Hypochlorite Chemistry

Sodium hypochlorite (NaOCl) is an oxidant that is widely used for disinfection of potable water and wastewater. This chemical is more commonly known as liquid bleach, although it is also referred to as soda bleach liquor. Liquid hypochlorite is also available as high-test calcium hypochlorite. The higher strength of calcium hypochlorite translates into reduced storage and transportation costs. However, calcium hypochlorite can be more difficult to handle and can lead to greater maintenance problems with pumping and metering equipment (White, 1999).

In Florida, for drinking water disinfection, it is common for water purveyors to use either liquid bleach or chlorine gas (Cl$_2$). In this current work, the system being evaluated uses liquid
bleach. Bleach (NaOCl) is produced in bulk by mixing caustic soda and chlorine, as shown in equation 3-4.

\[
2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O} + \text{Heat}
\] (3-4)

Based on the stoichiometry shown in equation 3-4, 1 lb of chlorine mixed with 1.128 lbs of caustic soda (NaOH) yields 1.05 lbs of sodium hypochlorite and 0.83 lbs of sodium chloride. In actual production, excess caustic soda is added to serve as a stabilizer (White, 1999).

When liquid bleach is used for disinfection in municipal water treatment, it is usually purchased in bulk or produced on site. Sodium hypochlorite is only available in liquid form and is most commonly offered in strengths of 12 to 15 percent available chlorine (Tchobanoglous et al, 2003). Bleach strength is often expressed in terms of available chlorine content as a “trade” percentage (i.e. percent by volume). In his book, White points out that a more accurate expression of strength would be the actual weight percentage of the available chlorine or sodium hypochlorite (White, 1999). The relationship between these values is shown in equations 3-5 thru 3-8.

\[
\text{Trade percent (percent by volume)} = \frac{g/L \text{ available Cl}_2}{10}
\] (3-5)

\[
\text{Weight percent available Cl}_2 = \frac{\text{trade percent}}{\text{specific gravity of solution}}
\] (3-6)

\[
\text{Weight percent sodium hypochlorite} = \frac{g/L \text{ available hypochlorite}}{\text{specific gravity of solution} \times 10}
\] (3-7)

\[
\text{Weight percent sodium hypochlorite} = \frac{g/L \text{ available Cl}_2 \times 1.05}{\text{specific gravity of solution}}
\] (3-8)
When using liquid bleach, considerations must be made for the degradation of bleach strength. Bleach has been shown to degrade quickly due to exposure to light and heat. For instance, a 16.7 percent solution stored at 80°C (26.7°C) will lose approximately 10 percent of its strength in 10 days, 20 percent in 25 days, and 30 percent in 43 days (Tchobanoglous et al, 2003). For this reason, it is recommended that bleach solutions be stored in a cool location, out of the sun and in a corrosion-resistant tank. In practice, it is not uncommon for liquid bleach to be stored outdoors (without temperature regulation) and in the presence of sunlight. These conditions can lead to greater degradation rates.

Identification of Treatment Alternatives

There are a number of methods available to treat sulfide for drinking water supplies. A desktop evaluation was conducted to evaluate alternatives that would achieve County goals at the IL and TR water treatment sites. The methods evaluated included:

- Aeration (cascade tray aeration; forced-draft aeration; fine bubble aeration; volatilization)
- Oxidation (oxygen, chlorine, ozone, potassium permanganate, hydrogen peroxide, ferrate)
- Microbiological filtration
- Oxidation followed by membrane filtration
- Oxidation followed by media filtration (Filtration with continuous regeneration)
- Anion exchange (adsorption to media)

Table 3.3 presents a summary of the advantages and disadvantages of some of the currently available water treatment process alternatives for sulfide removal. Specific discussion regarding each water treatment process evaluated is provided in the following sections.
<table>
<thead>
<tr>
<th>Treatment Method</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Aeration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-Cascade or Tray</td>
<td>Inexpensive</td>
<td>Insufficient removals; not effective; turbidity formation.</td>
</tr>
<tr>
<td>-Volatilization</td>
<td>Inexpensive</td>
<td>Control is difficult; not effective; sulfide bacteria regrowth.</td>
</tr>
<tr>
<td>-Forced-Draft</td>
<td>Effective treatment method and simple operation is attractive; documented experience</td>
<td>Increased capital costs; acid pretreatments must be employed; odor generator requires use of expensive scrubber systems; scrubbate impacts POTW operations; aerated water can contain undesired microbiological constituents (thiothrix, pseudomonas aeruginosa).</td>
</tr>
<tr>
<td>-Fine Bubble</td>
<td>Moderate costs and amenable to GST retrofits</td>
<td>Insufficient removals at neutral pH levels; odor generator not easily treated; not typical in drinking water treatment</td>
</tr>
<tr>
<td>2. Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-Oxygen</td>
<td>Minimal capital costs; simple process</td>
<td>Incomplete oxidation can create colloidal sulfur and polysulfides; design and control difficult; turbidity</td>
</tr>
<tr>
<td>-Chlorine</td>
<td>Minimal capital costs; controllable process</td>
<td>Incomplete oxidation; may increase DBPs; high dosages required, safety concerns, turbidity formation.</td>
</tr>
<tr>
<td>-Ozone</td>
<td>Controllable process; produces high quality finished water</td>
<td>Reaction chambers required; high operating and capital costs; may not be cost effective for systems having greater than 1.5 mg/L total sulfide in raw water; turbidity formation.</td>
</tr>
<tr>
<td>-Potassium Permanganate</td>
<td>Controllable process; inexpensive capital cost</td>
<td>Requires filters for residual MnO₂; requires large chemical dose; expensive chemical; pink water concerns</td>
</tr>
<tr>
<td>-Hydrogen Peroxide</td>
<td>Controllable process; inexpensive capital cost</td>
<td>Requires optimum mixing and long detection/contact times; incomplete oxidation; large dosages needed; turbidity</td>
</tr>
<tr>
<td>-Ferrate</td>
<td>Powerful oxidant; inexpensive capital cost</td>
<td>Process has not been demonstrated at a large scale for drinking water treatment</td>
</tr>
<tr>
<td>3. Oxidation Filtration</td>
<td>Controllable process; effective; affordable</td>
<td>Typically used for iron and manganese control; sulfide removal is secondary benefit; discharge of waste streams; discoloration of basin equipment; breakthrough of permanganate if used can cause discoloration (pink)</td>
</tr>
<tr>
<td>4. Membrane Filtration</td>
<td>Controllable process; effective if controlled at optimum conditions</td>
<td>Expensive; requires colloidal sulfur formation to be complete prior to filtration step; irreversible fouling of membranes may occur</td>
</tr>
<tr>
<td>5. Microbiological Filtration</td>
<td>Natural process; chemical-free method; safe to operate</td>
<td>Detachment and clogging are issues; design and control difficult; not proven process for drinking water</td>
</tr>
<tr>
<td>6. Anion Exchange</td>
<td>Controllable; moderate cost compared to others</td>
<td>Biological fouling can foul resin; salt regeneration impacts discharge permits.</td>
</tr>
</tbody>
</table>
Aeration

Aeration has historically been used as a common method of treatment for sulfide (Roe, 1935; Flentje, 1937; Powell & Von Lossberg, 1948). Since the total sulfide species in water is dependent upon the pH, only the portion of the total sulfide that is present as hydrogen sulfide gas can be removed from water by aeration (tray, packed-tower, diffused air, or spray-nozzle methods). Beneficial outcomes of hydrogen sulfide treatment using aeration include:

1. The reduction of taste and odors;
2. A decrease in the corrosive effects of hydrogen sulfide on metals and concrete; and
3. A reduction in the demand of chlorination for disinfection.

For ground water facilities not utilizing softening and filtration, sulfide removal is typically accomplished by cascade or tray aeration and volatilization in ground storage facilities. However, cascade tray aeration and volatilization are only partially effective in removal of sulfide (approximately 15 to 25 percent total sulfide removal) and are dependent on pH and atmospheric condition (more sulfide is removed on windy, warm days). Under high flow conditions, tray aerators do not provide adequate sulfide removals for most groundwaters.

Packed towers utilize tower arrangements with plastic packing materials to increase the water/air effectiveness for stripping gaseous sulfide from the water. Packed towers rely on either structured or random-loosely packed materials and are counter-current water-air processes. In this process, hydrogen sulfide laden water is introduced at the top of the tower and clean air is introduced at the bottom of tower. Clean water then exits at the bottom of tower and hydrogen sulfide laden air leaves at the top of tower. Packed towers have higher stripping efficiencies than
tray aerators and are an effective method for sulfide removal. However, the use of packed towers has been shown to negatively impact finished water due to microbiological growth in the packing and release of the growth into the distribution system (Duranceau et al, 2003).

Carbon dioxide is a smaller molecule than hydrogen sulfide and will be released at a faster rate than hydrogen sulfide (Garrels & Naeser, 1958). Thus as the dissolved carbon dioxide and hydrogen sulfide gases are removed, the pH of the water flowing down over the packing increases. The pH rise causes the ionization of hydrogen sulfide and carbonic acid, thereby decreasing the removal efficiency of the tower. However, if carbon dioxide is present in concentrations of about 10 percent (whether present initially or added as a packed tower pretreatment method), the hydrogen ion concentration is raised to favor the release of hydrogen sulfide gas (Roe, 1935). The use of carbonic acid for pH adjustment prior to packed tower aeration processes has been demonstrated to be an effective pretreatment method that assists in corrosion control treatment (Duranceau et al, 1999).

Fine bubble aeration is a limited process for sulfide removal and has not been utilized effectively for this specific contaminant primarily because of design limitations and cost. Volatilization would be relied on in place of fine bubble aeration; however, volatilization is an unpredictable process and is limited by tank geometries and atmospheric conditions.

**Oxidation**

Oxidation of sulfide can be accomplished with oxygen, chlorine, ozone, potassium permanganate, hydrogen peroxide, and ferrate (VI) ion, among others. In Table 3.4, the standard electrode potential (E°) for several oxidation-reduction (redox) half-reactions is shown. These values, often called “redox potential”, are a measure of the “driving force” for a reaction to occur
as written. The reactions presented in Table 3.4 are written as oxidation reactions (when proceeding from left to right); therefore, the greater the (positive) redox potential is for one of these reactions, the more likely it is to proceed as written. A negative redox potential, in this instance, would indicate the compound is actually a reducing agent under standard conditions (Brown et al, 2006).

These redox potentials can also be used to illustrate the relative strength of a given set of oxidants, assuming that the potentials are derived under the same conditions for all compounds. However, while these redox potentials may indicate if a reaction is likely to proceed as written, they do not indicate the rate at which the reaction will proceed (Tchobanoglous et al, 2003). For instance, according to this data, hydrogen peroxide is a relatively strong oxidant (high $E^\circ$). However, it may not be practical for use in some treatment scenarios as it has relatively slow kinetics and would require prohibitive contact time, or a catalyst, to be an effective oxidant/disinfectant option. These factors should be considered when selecting an appropriate oxidant.

One of the most commonly used oxidants, particularly for disinfection, is chlorine gas (or liquid bleach). Historically, chlorine (Cl$_2$) gas or liquid bleach has been used to remove residual sulfides after tray aeration and/or volatilization. The decision to use chlorine (or bleach) for residual total sulfide removal has typically been one of convenience, as the chemical is often already in use, post-tray aeration, for disinfection. One of the concerns with chlorine (or bleach) oxidation of sulfides is that it results in the formation of colloidal elemental sulfur turbidity (Lyn, 1991).
Table 3.4: Oxidant Redox Potential (Adapted from Jiang & Lloyd, 2002; Lee et al, 2004)

<table>
<thead>
<tr>
<th>Disinfectant/Oxidant</th>
<th>pH</th>
<th>Reaction</th>
<th>$E^\circ$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Oxygen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>acidic</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>basic</td>
<td>$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^-$</td>
<td>0.40</td>
</tr>
<tr>
<td>Chlorine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>$\text{Cl}_2(\text{g}) + 2\text{e}^- \leftrightarrow 2\text{Cl}^-$</td>
<td>1.36</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>acidic</td>
<td>$\text{HClO} + \text{H}^+ + 2\text{e}^- \leftrightarrow \text{Cl}^- + \text{H}_2\text{O}$</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>basic</td>
<td>$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{Cl}^- + 2\text{OH}^-$</td>
<td>0.84</td>
</tr>
<tr>
<td>Ozone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>acidic</td>
<td>$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{O}_2 + \text{H}_2\text{O}$</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>basic</td>
<td>$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{O}_2 + 2\text{OH}^-$</td>
<td>1.24</td>
</tr>
<tr>
<td>Permanganate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>acidic</td>
<td>$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \leftrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>acidic</td>
<td>$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>basic</td>
<td>$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \leftrightarrow \text{MnO}_2 + 4\text{OH}^-$</td>
<td>0.59</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>acidic</td>
<td>$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>basic</td>
<td>$\text{H}_2\text{O}_2 + 2\text{e}^- \leftrightarrow 2\text{OH}^-$</td>
<td>0.88</td>
</tr>
<tr>
<td>Ferrate(VI)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>acidic</td>
<td>$\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \leftrightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>basic</td>
<td>$\text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \leftrightarrow \text{Fe(OH)}_3 + 5\text{OH}^-$</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Ozone oxidation is a beneficial process and has been demonstrated to be an effective and practical method for sulfides treatment of groundwater having nominal total sulfide content. An ozone to hydrogen sulfide weight ratio of 5.65 mg/L to 1 mg/L is required for conversion from hydrogen sulfide to sulfate. Ozone oxidation for hydrogen sulfide is not cost-effective for ground waters having total sulfide concentrations of 2.0 mg/L or greater. Although this method has been successfully implemented by the Orlando Utilities Commission, the County was concerned regarding small system applications, electrical costs and sulfide loadings.

For conversion of hydrogen sulfide to sulfate using hydrogen peroxide oxidation, a stoichiometric ratio of 4.0 to 1.0 is required for water having a pH greater than 8.0 units. However, the treatment method has not been effectively demonstrated for treatment of groundwater for hydrogen sulfide. Approximately 12.4 mg/L of potassium permanganate is
required to oxidize 1.0 mg/L of hydrogen sulfide. Both peroxide and permanganate have been shown to provide complete removal of sulfide, but both yield sulfate and colloidal sulfur as reaction products (Dohnalek & FitzPatrick, 1983).

Ferrate ($\text{FeO}_4^{2-}$) is a relatively strong oxidant, as shown in Table 3.4. While ferrate has been known to science for over one hundred years, it has only been studied more rigorously in recent years for use in water and wastewater treatment. Ferrate has been proposed for use as a green oxidant, coagulant, disinfectant (oxidant) and antifoulant in a variety of waste/wastewater applications (Lee, et. al., 2004). One of the issues with the oxidation of hydrogen sulfide, particularly with bleach or chlorine, is the formation of turbidity in the form of colloidal sulfur. The coagulant properties of ferrate may be useful for the management of this colloidal turbidity. However, little research regarding ferrate and $\text{H}_2\text{S}$ at the pilot-scale has been conducted (a notable exception is the study by Sharma, et. al. at Texas A&M University) and there are currently no full scale implementations of the process solely for drinking water $\text{H}_2\text{S}$ removal.

**Hypochlorite Oxidation**

As previously stated, chlorination is usually performed using either chlorine gas or liquid bleach (sodium hypochlorite; NaOCl). In this study, chlorination of sulfides was performed solely through the use of liquid bleach. When sodium hypochlorite is added to water, the chemical disassociates into sodium and hypochlorite, as shown in equation 3-9.

$$\text{NaOCl} \rightarrow \text{Na}^+ + \text{OCl}^- \quad (3-9)$$

The conjugate acid of the hypochlorite ($\text{OCl}^-$) ion is hypochlorous acid (HOCl) which is a monoprotic acid. The pKa of HOCl is 7.5; therefore, in most drinking waters (which tend to be
near neutral pH) both hypochlorite and hypochlorous acid will be present in significant concentrations. Once the pH of a solution reaches 11 or 12, HOCl is said to be completely dissociated to $H^+$ and $OCl^-$, as shown in equation 3-10 (White, 1999).

$$\text{HOCl} \leftrightarrow H^+ + OCl^- \quad (3-10)$$

HOCl and $OCl^-$ both contribute to the oxidation of $H_2S$. In equations 3-11 through 3-18, the stoichiometry for the bleach oxidation of hydrogen sulfide and bi-sulfide ($HS^-$) are shown (Lyn, 1991). The oxidation of $H_2S$ and $HS^-$ to elemental sulfur is shown in equations 3-11 through 3-14. As with $Cl_2$ oxidation, one mole of HOCl or $OCl^-$ is required to convert one mole of a sulfide species ($H_2S$ or $HS^-$) to elemental sulfur ($S^0$). In order to oxidize 1 mg/L of $H_2S$ to elemental sulfur, it requires 1.54 and 1.51 mg/L of HOCl and $OCl^-$, respectively. These values are similar to the 2.08 mg/L of $Cl_2$ required to oxidize 1 mg/L of $H_2S$ to $S^0$.

$$\text{HOCl} + H_2S \rightarrow S^0 + H^+ + Cl^- + H_2O \quad (3-11)$$

$$\text{HOCl} + HS^- \rightarrow S^0 + Cl^- + H_2O \quad (3-12)$$

$$\text{OCl}^- + H_2S \rightarrow S^0 + Cl^- + H_2O \quad (3-13)$$

$$\text{OCl}^- + HS^- \rightarrow S^0 + Cl^- + OH^- \quad (3-14)$$

Oxidation of $H_2S$ and $HS^-$ to sulfate is shown stoichiometrically in equations 3-15 through 3-18 (Lyn, 1991). Reviewing Table 3.1, sulfate is the most oxidized form of sulfur; therefore, the conversion of hydrogen sulfide to sulfate is said to be the complete oxidation of $H_2S$. Four moles of HOCl or $OCl^-$ are required to oxidize 1 mol of $H_2S$ to $SO_4^{2-}$. This equates to a stoichiometric requirement of 6.17 and 6.05 mg/L of HOCl and $OCl^-$, respectively, to
completely oxidize 1 mg/L of H₂S. The advantage of complete oxidation is the avoidance of elemental sulfur turbidity; however, complete oxidation is typically not observed in practice (Lyn, 1991).

\[
4\text{HOCl} + \text{H}_2\text{S} \rightarrow \text{SO}_4^{2-} + 6\text{H}^+ + 4\text{Cl}^- \quad (3-15)
\]

\[
4\text{HOCl} + \text{HS}^- \rightarrow \text{SO}_4^{2-} + 5\text{H}^+ + 4\text{Cl}^- \quad (3-16)
\]

\[
4\text{OCl}^- + \text{H}_2\text{S} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 4\text{Cl}^- \quad (3-17)
\]

\[
4\text{OCl}^- + \text{HS}^- \rightarrow \text{SO}_4^{2-} + \text{H}^+ + 4\text{Cl}^- \quad (3-18)
\]

Stoichiometrically, 8.34 mg/L and 2.08 mg/L of chlorine (Cl₂) are required to oxidize 1 mg/L of hydrogen sulfide to sulfate (completely oxidized) and elemental sulfur, respectively (Cadena & Peters, 1988). Incomplete oxidation typically occurs under actual operating conditions; however, in a 1993 patent by Kerollis and Mowery a chemical process involving pH adjustment is outlined that results in the oxidation of H₂S without producing a substantial amount of elemental sulfur end-product. They assert that the pH of the untreated water must be reduced to below 6.0 and preferably to within the range of 4.2 to 5.5. This is important, because below a pH of 6.0 bicarbonate ions (HCO₃⁻) are converted to carbon dioxide (CO₂). The pH may be adjusted using a strong mineral acid such as hydrochloric (HCl) or sulfuric (H₂SO₄) acid, as illustrated in equations 3-19 and 3-20 (Kerollis & Mowrey, 1993).

\[
\text{HCO}_3^- + \text{H}^+ + \text{Cl}^- \leftrightarrow \text{CO}_2 + \text{Cl}^- + \text{H}_2\text{O} \quad (3-19)
\]

\[
2\text{HCO}_3^- + 2\text{H}^{30} + \text{SO}_4^{2-} \leftrightarrow 2\text{CO}_2 + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad (3-20)
\]
Once the pH of the water is adjusted, it can be treated with a suitable oxidant such as liquid bleach or chlorine gas, which reacts with the H₂S to form H₂SO₄ and HCl. Kerollis and Mowrey recommend that at least a stoichiometric amount of the oxidizing agent be added to allow for the H₂S to fully react with the oxidant. Since an end product of the oxidation process is an acid, the addition of an oxidizing agent further reduces the pH to 3.5 or below. Under these conditions, treated water is produced that is substantially free of both H₂S and elemental sulfur content. The pH of the water can then be adjusted upwards, with a base or basic salt, to an appropriate level for distribution or further treatment (Kerollis & Mowrey, 1993).

Ferrate Oxidation

Ferrate (VI) salts are said to have first been observed by Stahl in 1702, and the solution was noted as an unstable, red-purple colored product. Stahl created the product while conducting an experiment where he dissolved the molten residue of a detonated mixture of saltpeter and iron filings in water. In 1834, Eckenberg and Becquerel found that the same color was produced from mixtures of potash (potassium hydroxide) and iron ores. Fremy, in 1840, hypothesized that the solution’s color was from an iron species of high valence. The systematic study of Ferrate (VI) synthesis began around the turn of the twentieth century (Jiang & Lloyd, 2002).

There are several ways to produce ferrate (VI). They include: wet oxidation, oxidizing a Fe (III) salt at high pH conditions and using hypochlorite or chlorine as the oxidant; dry oxidation, heating/melting various iron-oxide-containing minerals at high pH and oxygen rich conditions; and an electro-chemical method, achieved by anodic oxidation with an iron or alloy anode and KOH or NaOH electrolyte (Jiang & Lloyd, 2002). Typically, ferrate (VI) salts are produced in the form of potassium ferrate (K₂FeO₄) or sodium ferrate (Na₂FeO₄).
The ferrate (VI) ion is a powerful oxidant with a plus six valance. It has the molecular formula FeO$_4^{2-}$ and its’ redox potential varies from 0.7 V to 2.2 V under alkaline and acidic conditions, respectively (Dohnalek & FitzPatrick, 1983). In nature, Iron is more commonly found as a metal or in the +2 (Fe(II)) and +3 (Fe(III)) oxidative stages. Other, hyper-valence states of iron (Fe(IV), Fe(V), Fe(VI)) are observed from time to time; however, most tend to be unstable under standard conditions. Ferrate (Fe(VI)) is the only one of these states that has been obtained in the form of a stable salt (Lee, et. al, 2004).

Recent studies have stated that there exist four Fe(VI) species in aqueous solutions: H$_3$FeO$_4^+$, H$_2$FeO$_4$, HFeO$_4^-$, FeO$_4^{2-}$. The respective pK’s for these species are 1.6, 3.5, and 7.8. This would indicate that at the near neutral pH’s typically seen in water/wastewater treatment, the predominant species would be HFeO$_4^-$ and FeO$_4^{2-}$. Ferrate is known to be relatively stable under these alkaline conditions (Lee, et. al. 2004; Sharma, et. al. 1997). Ferrate(VI) is reduced to Fe(III) when oxidizing other compounds, as shown in equations 3-21 and 3-22 (Sharma et. al., 1997).

\[
\begin{align*}
HFeO_4^- + H_2S & \rightarrow \text{Fe(III)} + \text{product(s)} \quad (3-21) \\
FeO_4^{2-} + H_2S & \rightarrow \text{Fe(III)} + \text{product(s)} \quad (3-22)
\end{align*}
\]

A study by Sharma et al, published in 1997, looked at the oxidation of H$_2$S with potassium ferrate (K$_2$FeO$_4$). In the study, they proposed a complex mechanism by which ferrate(VI) oxidizes H$_2$S to sulfate, elemental sulfur and other intermediate products. The summary reactions for these mechanisms are presented in equations 3-23 and 3-24 (for reactions...
occuring at a pH of 7) and equation 3-25 (for reactions occurring under alkaline conditions) (Sharma et al, 2007).

\[
3\text{HFeO}_4^- + 4\text{H}_2\text{S} + 7\text{H}^+ \rightarrow 3\text{Fe}^{2+} + \text{S}_2\text{O}_3^{2-} + 2\text{S}(s) + 9 \text{H}_2\text{O} \tag{3-23}
\]

\[
20\text{HFeO}_4^- + 16\text{H}_2\text{S} + 10\text{H}_2\text{O} \rightarrow 20\text{Fe(OH)}_3 + 2\text{H}_2\text{S}_2 + \text{SO}_3^{2-} + 3\text{S}_2\text{O}_3^{2-} + 3\text{SO}_4^{2-} + 6\text{OH}^- \tag{3-24}
\]

\[
2\text{HFeO}_4^- + 48/11\text{H}_2\text{S} + 4/11\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)} + 1/11\text{SO}_3^{2-} + 1/11\text{S}_2\text{O}_3^{2-} + 1/11\text{SO}_4^{2-} + 2\text{H}_2\text{S}_2 + 16/11\text{OH}^- \tag{3-25}
\]

In Sharma’s study, the complete oxidation of \( \text{H}_2\text{S} \) is said to have the following stoichiometry:

\[
8\text{HFeO}_4^- + 3\text{H}_2\text{S} + 6\text{H}_2\text{O} \rightarrow 8\text{Fe(OH)}_3 + 3\text{SO}_4^{2-} + 2\text{OH}^- \tag{3-26}
\]

The stoichiometry of this model (equation 3-26) matches closely to the experimental \([\text{Fe(VI)}]/[\text{H}_2\text{S}]_T \) demand of approximately 2.5. It is hypothesized that complete oxidation is possible with the ferrate oxidant because the half-lives for the oxidation reactions of Fe(VI) with \( \text{S}_2\text{O}_3^{2-} \) and \( \text{SO}_3^{2-} \) are shorter than that of the Fe(VI) reaction with \( \text{H}_2\text{S} \). They also claim that Fe(V) and Fe(VI) react with sulfur intermediates. A result of this study was the claim that sulfate (\( \text{SO}_4^{2-} \)) is formed when \([\text{O}_2]>>[\text{H}_2\text{S}]_T \) and elemental sulfur is formed when \([\text{O}_2]<<[\text{H}_2\text{S}]_T \) during the autooxidation of \( \text{H}_2\text{S} \) (Sharma, et. al., 1997).

**Microbial Filtration**

Aerobic bacteria, such as *Beggiatoa* and *Thiothrix*, will uptake reduced sulfide and convert the mass to sulfate. Although effective for sulfide removals, the organisms can slough
off surfaces and cause turbidity downstream of storage facilities. No known controlled biofiltration process utilizing this method has cost-effectively been demonstrated for the removal of sulfide from a water stream for drinking water, although sulfide-laden air streams have been treated with the use of biofilters.

Membrane Filtration

This method would involve the use of a synthetic membrane process for elemental sulfur removal. This method is considered to be an experimental method and currently represents a high-cost alternative. Also, since an oxidation step is required to form elemental sulfur prior to removal by the membrane, only chlorine-tolerant membranes can be used and membrane fouling is typical (which adds to operating and membrane replacement costs). Control of this process is uncertain and demonstrated use has not been shown; hence, this method is not considered to be favorable for sulfide removal at this time.

Media Filtration

In general, the term “media filter” is applied to filters that use a granular material for filtration. Media filters can be found in single-medium, dual-media, or multimedia arrangements (depending on the number of distinct media layers, one, two, or three+, respectively). Single-medium filters typically use anthracite or sand. While in the case of multimedia filters, three or more layers may be used, a common configuration being: anthracite, sand, and garnet. Most media filters also rely on an additional bottom layer(s) of support media. Gravel is the material typically used in this application. It serves as an intermediate between the filter media and the
effluent underdrain openings. The support layer is intended to prevent the underdrain openings from becoming clogged with filter media (Reynolds, 1996).

Media filtration can be used for a variety of applications. In water treatment it has been used to filter chemically coagulated and settled waters. In wastewater treatment it has been used to filter untreated secondary effluents, chemically treated wastewaters, and chemically treated secondary effluents (Reynolds, 1996). In this study, media filtration processes, traditionally used for iron and manganese removal, have been evaluated solely for the use of H$_2$S treatment. A common type of media used in this application is manganese greensand, which is impregnated with manganese (IV) oxide (MnO$_2$), and must be either continuously or intermittently regenerated. Feeding an oxidant (bleach or potassium permanganate) ahead of the media bed serves as a continuous regenerate for the filter media. These manganese greensand filters can be used in single-medium, or dual media configurations, with anthracite serving as a pre-filtration layer. An alternative to manganese greensand is an “electromedia” filter material that is also commonly used for iron and manganese removal. These dual media filters use anthracite, a pre-filtration layer, and Electromedia®, a proprietary blend of minerals having a garnet like appearance.

One of the advantages of an oxidant/filtration process is that it allows for the use of a low profile, horizontal vessel. This is in comparison to a stripper/scrubber process which requires the use of tall vertical towers. This quality can become important in situations where visual aesthetics are a key priority for neighboring residents.
Manganese (IV) Oxide Greensand Filtration

Manganese greensand is an oxidizing filter media that is conventionally used to remove iron and manganese from municipal wastewaters, industrial well waters and other waters containing these substances (Zabel, 2007). While it is widely known and recognized that manganese greensand can also oxidize and remove hydrogen sulfide, there exist little literature on the use of this media solely for sulfides treatment. Most of the data that does exist is mainly a result of studies on the treatment of iron and manganese in waters which happen to have hydrogen sulfide in them. Other studies that have focused on the use of manganese greensand solely for H₂S treatment, such as the one by Brune and Perez, have used potassium permanganate as the bed regenerate (Brune & Perez, 1985; Brune & Perez, 1990). In the literature search performed for this document, a study could not be identified where manganese greensand was used solely for H₂S treatment while being regenerated with sodium hypochlorite (commonly known as bleach).

Greensand is a common name for glauconite, a natural material that was first used as a water softening zeolite in the early 20th century. Deposits of the naturally occurring greensand could be found in much of the country, especially coastal regions, including the eastern parts of New Jersey, Delaware, Maryland, Virginia, and North Carolina (Hugerford, 1931). Glauconite is present in marine deposits dating as far back as the pre-Cambrian age and is found in many modern marine sediments. Much of the traditional manganese greensand used in the United States has been produced by processing “New Jersey greensand”, a term given to glauconite extracted from the New Jersey coast. A study conducted in 1941, and published in the Journal of the Mineralogical Society of America, found that glauconite is primarily composed of silicone dioxide (≈48%), iron(III) oxide (≈17%), aluminum oxide (≈14.5%) and potassium superoxide
(≈11%). It also contains lesser amounts of iron (II) oxide (≈2.7%), magnesium oxide (≈2.5%), and dihydrogen monoxide (≈4.2%). Typically, glauconite is found as rounded pellets from one to several millimeters in diameter (Hendricks, 1941).

Manganese greensand was first used for the removal of iron, manganese and hydrogen sulfide in the early 1950’s. It is manufactured in a process which uses the ion exchange properties of its stabilized glauconite (greensand) substrate to form an active MnO₂ coating (Zabel, 2007). The MnO₂ effectively fouls the glauconite zeolite and gives it its oxidative qualities. For this reason, the MnO₂ is sometimes called a “useful foulant”. In the manganese greensand production process, naturally occurring grains of glauconite are washed and undergo a sieve graduation (18 x 60 mesh) resulting in an effective grain size of 0.3-0.35 mm and a uniformity coefficient of 1.60 or less. Once washed and sorted, the media is stabilized and then impregnated with manganese (IV) oxide (Inversand, Co., 2010).

Since the base substrate for manganese greensand is a naturally occurring mineral, it is a finite resource and in recent years demand for the product has put stress on product availability leading to spot shortages and long lead times (Zabel, 2007). This has prompted companies to develop and produce synthetic substitutes for manganese greensand. One such substitute is “GreensandPlus”, which is manufactured in Brazil by Fermavi Electrochemistry Ltd. and distributed in the United States by Inversand, Inc. According to distributor’s literature, the GreensandPlus™ media is said to be a direct replacement for manganese greensand, because it can be used in an existing manganese greensand processes without alterations to services rates, run lengths, backwash, air/water wash times or rates, or chemical feeds. While it can be used in place of traditional manganese greensand, it also has some advantages. It can be used at higher temperatures and with water’s having lower dissolved solids and low-silica. In addition,
GreensandPlus™ is claimed to be capable of safely exceeding the 10 psi differential pressure that is associated with crushing of traditional manganese greensand (Zabel, 2007).

GreensandPlus™ differs structurally from manganese greensand in that it is not produced using a glauconite base. The synthetic GreensandPlus™ media is manufactured by thermally fusing an active manganese (IV) oxide (MnO$_2$) coating onto a special-density silica sand particle (Zabel, 2007). According to the MSDS, GreensandPlus™ is 3.2 to 4.8 % MnO$_2$ by weight and 96 to 98 % Quartz (SiO$_2$) by weight (Inversand, Co., 2005). Physically, GreensandPlus™ (pictured in Figure 3.2) is a black, nodular granule with a screen grading of 18 x 60 mesh and an effective size of 0.3 to 0.35 mm. The media has an apparent density of 88 pounds per cubic foot net (90 lb/cu.ft. gross shipping weight), a porosity of approximately 0.45 and a uniformity coefficient of less than 1.60. Minimum bed depth for GreensandPlus™ is 30 inches when used alone and 15 inches for each media when used in a dual media bed (Inversand, Co., 2010).

Anthracite is typically used in conjunction with the GreensandPlus™ when operated in a dual media configuration. The anthracite (pictured in Figure 3.3) is provided as a pre-filtration layer to remove insoluble compounds, which helps to prevent clogging within the greensand media (Wong, 1984). Anthracite is a crushed coal, medium density filtration media. The anthracite used in this study originates from coal mined in Pennsylvania. The media has a mesh size of 14 x 30, an effective size of 0.6 to 0.8 mm, a uniformity coefficient of <1.7 and a density of 50 pounds per cubic foot. Anthracite has a lower density than greensand and will hydraulically classify, remaining above the greensand after backwash (F. B. Leopold Co, Inc., 2009).
Figure 3.2: GreensandPlus™ Filter Media (Courtesy of Hungerford and Terry, Inc.)

Figure 3.3: Anthracite Filter Media (Courtesy of Hungerford and Terry, Inc.)
According to the GreensandPlus™ Technical Data sheet provided by Hungerford and Terry, Inc., the media should be operated within a pH range of 6.2 to 8.5 and a service flow rate of 2 to 12 gpm/sq. ft. Backwashes should be performed at a minimum rate of 12 gpm/sq. ft. at 55°F. According to H&T’s documentation, the chlorine demand for Continuous Regeneration (CR) operation of the MnO₂ filtration system can be estimated using the following equation:

\[
\text{mg/L Cl}_2 = (1 \times \text{mg/L Fe}) + (3 \times \text{mg/L Mn}) + (6 \times \text{mg/L H}_2\text{S}) + (8 \times \text{mg/L NH}_3)
\]  

(3-27)

For example, consider a source water having the following water quality: 1.7 mg/L of iron, 0.2 mg/L of manganese, 1.9 mg/L of hydrogen sulfide and 0.1 mg/L of ammonia. The bleach demand for this source water would be estimated using equation 3-27 as follows:

\[
\text{Demand} = (1 \times 1.7) + (3 \times 0.2) + (6 \times 1.9) + (8 \times 0.1) = 14.5 \text{ mg/L Cl}_2
\]  

(3-28)

The distributor recommends that the chlorine be fed at least 10-20 seconds ahead of the filter and that a residual be carried through the greensand filter in order to regenerate and protect its manganese (IV) oxide coating (Inversand, Co., 2010).

**Electromedia® Filtration**

Electromedia® I is a NSF 60/61 certified proprietary filter media produced by Filtronics, Inc. and typically used for iron, manganese and arsenic removal. The product is a granulated and naturally occurring, with an appearance similar to that of garnet (Figure 3.5). The media is a proprietary blend of minerals that are mined and processed in the United States. It is not a resin, plastic or silica product (Filtronics, Inc., 2002).
Unlike manganese greensand, Electromedia® does not require chemical regeneration. The manufacture claims that Electromedia® can be operated with a hydraulic loading up to 15 gpsfm, can filter particles as small as 5 to 7 microns and requires 4 minute backwash cycles. They also claim that Electromedia® is design to last 2 to 4 decades before bed replacement (Filtronic, Inc., 2002).

Images of the materials used in the dual-media, Electromedia® I system are provided in Figures 3.4 through 3.7. These media images are presented in the order which they are stratified, from the top-most layer to the bottom support layers in the filter bed. Anthracite, shown in Figure 3.4, is used as a pre-filtration layer (as it is in the manganese greensand filter). The Electromedia®, in Figure 3.6, is finer grained material with a garnet color. The materials shown in Figures 3.6 and 3.7 are gravel media that support the Electromedia® and anthracite and protect the underflow drains from plugging.

Figure 3.4: Anthracite Filter Media (Courtesy of Filtronics, Inc., Anaheim, Ca.)
As stated in the hypochlorite oxidation section, in practice chlorination rarely yields complete conversion of sulfide species to sulfate. The Lyn study showed that the chlorination of $\text{H}_2\text{S}$ in aqueous solution produces elemental sulfur turbidity in addition to sulfate end products. Over time, free sulfur will oxidize to sulfate in the presence of an oxidant such as dissolved oxygen or hypochlorite. However, the residence time in drinking water systems does not allow for complete conversion before the turbidity formed during treatment is sent into the system. At the same time the oxidation of $\text{H}_2\text{S}$ to $\text{S}^0$ is not instantaneous, but as Lyn illustrated, happens over time. While the manganese greensand filter system seeks to limit turbidity formation by catalyzing the oxidation reaction to sulfate and filtering any residual colloidal sulfur formation, the Electromedia® system takes a slightly different approach.
In the Filtronics system, the bleach oxidant is fed to a contact chamber (as opposed to just ahead of the media bed for the GreensandPlus® system) before it enters the media filter vessel. In this system, turbidity is allowed to form ahead of the bed, so that it may be filtered out with the Electromedia®. Filtronics, Inc. also suggests an additional step that requires the use of added chemical but provides for the complete conversion of \( \text{H}_2\text{S} \). In this arrangement, the water would first be oxidized in a primary contact chamber, and then, before entering the filter chamber, sodium bisulfite would be added to convert colloidal sulfur to thiosulfate. The thiosulfate would then be converted to sulfate in a re-chlorination step in the Electromedia® filter bed. Re-chlorination would not be necessary if a free chlorine residual was carried throughout the process.

Figure 3.6: Support Media (Courtesy of Filtronics, Inc., Anaheim, Ca.)
Anion Exchange

Anion exchange is a process in which negatively charged ions are reversibly interchanged with ions of a similar charge from a solid phase (resin) to an aqueous phase. Different resins have varying affinities for different ions based on ion valence and atomic weight. For strong base resins, the selectivity of some common ions would be as follows: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{HAsO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$. The resin will continue to exchange ions, thus removing certain contaminants, until “breakthrough”. Breakthrough occurs when a threshold concentration of the target contaminant is exceeded. In order to restore the resin once breakthrough occurs, the resin must be regenerated. Regeneration involves the following steps: backwashing, brining, and rinse (slow and fast). The average duration of backwash can range from 5 to 15 minutes (Cotrino, 2006).
Some of the advantages of anion exchange include: effective removal of anionic forms of hydrogen sulfide, sulfate removal, reduction of disinfection byproduct precursors and the reduction of chlorine demand in the effluent (Cotrino, 2006). The disadvantages of anion exchange are that high levels of sulfate can interfere with the removal of the target anion and a brine waste stream is generated (Cotrino, 2006; Cotrino et al, 2007).

Discussion of Treatment Alternatives Removed From Consideration

One of the most widely used, FDEP recommended, methods of sulfide treatment is packed tower aeration. Since FDEP Rule 62-555-315 was implemented in 2003, packed tower and forced draft aeration systems have become the predominant choice of utilities looking to remove sulfide. In full-scale use, these systems have been shown to work reliably, although considerations should be made for the maintenance involved in operating them properly. However, the County has expressed concerns with using this system. Firstly, the wastewater generated from the odor scrubber is of concern to the County as it will contribute to elevated conductivity levels in the municipal sewer system. Secondly, due to Polk County’s site constraints and the neighboring communities concerns over the aesthetics of packed tower systems. This option was not evaluated further considering these issues.

Ozone is a powerful oxidant and has been shown to effectively treat and remove sulfide from drinking waters. It is a proven technology and is currently in use at several full-scale water treatment facilities (O.U.C – Orlando) in Florida. Ozone has been shown to be cost effective by OUC in Orlando for groundwater containing less than 1.5 mg/L of dissolved sulfide, but costs can significantly increase at higher sulfide levels (>2 mg/L). Ozone was initially considered because it has been successfully demonstrated in full scale use by OUC, however, it was
ultimately removed from consideration because the County expressed a desire to find a process which would not require extensive investment in electrical infrastructure and would minimize operational costs and labor. Ozone was perceived to be a process that required additional electrical infrastructure and increased operational needs beyond the level of effort that the County currently experiences.

The anion exchange process was reviewed and deemed to be a potential sulfide treatment solution. However, in the anion exchange process salt would be used in the required regeneration step, which would produce a saline discharge. The County has expressed concern about increasing the conductivity of the waste stream received at its publicly owned treatment works (POTW). Hence, this process alternative was not further considered for the pilot-scale evaluation.

Tampa Bay Water, in an effort to explore sulfide treatment alternatives to their existing forced-draft aeration and off-gas odor control scrubbing processes at the Keller water treatment facilities and biological oxidation at their Lithia Springs water treatment facilities, investigated the following: chlorine and coagulation followed by ultrafiltration, ozone oxidation followed by biologically active filtration and biological oxidation followed by ultrafiltration processes (Malcolm Pirnie 2007). These processes were chosen based on an assessment of existing facility conditions, treatment effectiveness and potential cost savings as compared to existing infrastructure. It was determined that these treatment processes were capable of effectively removing hydrogen sulfide, but overall the two membrane configurations produced a higher water quality than the conventional ozonation followed by biologically active filtration. Since the Lithia Springs facility already practiced biological oxidation, it was recommended that ultrafiltration be added to this facility for enhanced hydrogen sulfide control. The available space
at the Imperial Lakes and Turner Road facilities is inadequate for these processes based on Tampa Bay Water’s evaluation of their space requirements. Therefore, these processes were not pursued in UCF’s testing program.

Short-Listing of Treatment Alternatives to be Further Evaluated

Based on the desk-top evaluation, a testing plan and protocol was designed to evaluate the following short-listed technologies: ferrate, proprietary electromedia filtration and manganese (IV) oxide filtration. These processes were selected because they appeared to be potential substitutes for the bleach-tray aeration process currently in use at both the IL and TR WTPs.

The focus of the pilot-scale effort were the electromedia or manganese (IV) oxide filtration processes. The ferrate oxidant was also selected for preliminary bench and pilot-scale testing. The filtration processes were selected for pilot-scale testing for a number of reasons. Most literature pertaining to the use of these filters has traditionally been focused on iron and manganese removal, where the treatment of H₂S is only an ancillary reaction. Other studies that have focused on the use of manganese greensand solely for H₂S treatment, such as the one by Brune and Perez, have used potassium permanganate as the bed regenerate (Brune and Perez, 1985; Brune and Perez, 1990). The application of these processes in this study is unique in that (1) the concentrations of both iron and manganese are relatively low, while the concentration of sulfide is significant and (2) bleach is used as a bed regenerate in lieu of potassium permanganate. In this application, H₂S treatment becomes the primary function of the filter. For this reason, pilot-scale testing was deemed necessary to determine the viability of these filtration processes for this application.
The oxidant/filtration process was also attractive because of the nature of the media bed themselves. One of the County’s considerations was the profile of the treatment process. The oxidant/filtration process allows for the use of a low profile pressure vessel. This is in comparison to a stripper/scrubber process that would require the use of tall vertical towers.

The ferrate oxidant was studied at the pilot-scale due to its potential as a replacement for chlorine. It was also a practical decision as it is difficult to maintain the ferrate solution at the diluted concentrations required for bench-scale and low flow testing. A pilot-scale evaluation of the technology allows for the use of concentrated ferrate, which has a greater stability and was anticipated to produce more reliable results.
4.0 EXPERIMENTAL PLAN, MATERIALS AND METHODS

Introduction

This chapter provides an overview of the experimental plan, materials (pilot-equipment, lab equipment, etc.) and methods used to conduct this study. This chapter provides a description of the experimental plan; a review of the equipment, materials, and setup required for the pilot-scale testing; an overview of the water quality methods (and materials) used for water quality testing; and a review of laboratory quality control.

Experimental Plan

Based on desk-top evaluations, a testing plan and protocol was designed to evaluate the following short-listed technologies: proprietary Electromedia® filtration and manganese (IV) oxide (GreensandPlus™) filtration and ferrate oxidation. These processes were evaluated primarily at the pilot-scale, although some bench-scale screening was performed with ferrate. Field evaluations at both sites (IL and TR WTP) began in February of 2009, and ran through September of that same year.

The focus of the pilot-scale effort was to evaluate the effectiveness of the electromedia and manganese greensand filtration processes for total sulfide treatment. The majority of literature pertaining to the application of these filters has traditionally been focused on iron and manganese removal, where the treatment of total sulfide is only an ancillary reaction. This research was aimed at determining the viability of using these filtration processes in an application where total sulfide treatment was the primary objective and sodium hypochlorite was
used as the oxidant/regenerate. These filtration processes were also pilot-tested to determine their impact on finished water turbidity generated in the treatment of total sulfide.

Ferrate oxidant was selected for some screening and preliminary pilot-scale testing in order to evaluate its effectiveness as an alternative to bleach in total sulfide treatment. In addition to its merit as a treatment alternative, the pilot-scale portion of the ferrate evaluation was implemented as a practical decision as it is difficult to maintain the ferrate solution at the diluted concentrations used in bench-scale testing. A continuous flow pilot-scale evaluation of the technology allowed for the use of more stable, concentrated ferrate solution that was anticipated to produce more reliable results.

Screening Criteria and Water Quality Goals

This work was not intended to be an exhaustive water quality evaluation of the IL and TR WTPs; rather, the scope focused on examining process alternatives. Although a wider array of water quality parameters were measured, the primary parameters evaluated were pH, turbidity, total sulfide and free available chlorine residual concentrations. One primary component considered when evaluating treatment methodologies was post-treated total sulfide concentrations. Turbidity was also an important water quality parameter, as a need for the reduction of existing finished water turbidity levels became a key assessment criteria. Other parameters that were evaluated in this study included: cations [calcium, magnesium, iron, manganese], anions [sulfate], conductivity, total suspended solids (TSS), total dissolved solids (TDS), microorganisms [biologically active reagent tests (BART) and heterotrophic plat counts (HPC)], organics [total organic carbon (TOC), HAA5, DBP] and total chlorine residual.
Pilot-Scale Equipment

There were three processes evaluated at the pilot-scale: ferrate oxidation, bleach oxidation followed by Electromedia® filtration and manganese (IV) oxide filtration continuously regenerated with bleach.

Ferrate

The ferrate studies were performed with the assistance of Ferrate Treatment Technologies (FTT), LLC, (6432 Pinecastle Blvd C, Orlando, Florida). Aqueous ferrate is volatile and should be generated on-site. However, due to the small-scale on which the jar testing was performed, the ferrate used for bench-scale evaluations was produced at the FTT lab (in Orlando) and transported to the site in concentrated form. The solution was kept in a chilled container to minimize degradation. Dilutions were performed by weight, on a sample by sample basis, just before dosing. Raw water samples were taken directly from the well spigot. The jar mixer used was a Peeps and Bird four place jar tester with paddle mixers, and care was taken to minimize losses of H₂S to the atmosphere. However, due to the open nature of jar testing, it was anticipated that there would be error in this type of evaluation. For this reason, the ferrate jar tests were performed in comparison to bleach oxidant for use as a benchmark.

The ferrate pilot-scale studies were also performed with the assistance of FTT. The ferrate synthesis process in a full-scale treatment application is fully automated and self contained. The ferrate is produced on-site and subsequently fed to the process stream in a closed-loop system, minimizing the degradation of the oxidant. FTT does have a self contained ferrate synthesis unit that can be used in pilot studies. Unfortunately the full-scale ferrate pilot unit
could not be used due to the hydraulic constraints at the IL and TR test sites; therefore, a smaller pilot-scale system was fabricated by FTT for this study. When using the smaller sized pilot-scale system, the ferrate had to be synthesized by hand using a bench-scale batch reactor (Figure 4.1). It should be noted that this practice would result in a greater degree of $\text{FeO}_4^{2-}$ degradation (when compared to the full-scale pilot process) and could contribute as a source of error. However, any such error would be conservative according to the manufacture.

![Figure 4.1: Ferrate Treatment Technologies, Inc. Ferrate Synthesizer](image)

Once the ferrate was generated on-site by the vendor, it was fed into the process stream using the device shown in Figure 4.2. The pilot-unit minimizes degradation of the concentrated ferrate solution by storing it in a refrigerated container that allows for the cooled supply line to be run from the feed pump. Immediately following the injection quill, the prepared ferrate stream was passed through a static mixer to achieve proper mixing. Treatment with the ferrate oxidant was evaluated in two ways: treatment with the oxidant alone and treatment with the oxidant followed by manganese (IV) oxide filtration.
Bleach

Two brands of liquid bleach (sodium hypochlorite) were used in this study: store-purchased Clorox® bleach and the County’s on-site bulk bleach stock (Ultra CHLOR™) that is supplied by Odyssey Manufacturing Co (1484 Massaro Blvd., Tampa, Florida). The Clorox® bleach is listed at 6.15% sodium hypochlorite with a specific gravity of 1.1 (The Clorox Company, 2005). The bulk stock bleach is 12.5 trade percent chlorine, and according to the Odyssey Manufacturing Co. website (www.odysseymanufacturing.com), is guaranteed to be at least 10.83 % sodium hypochlorite by weight (10.31% Cl₂ by weight) with a specific gravity between 1.159 and 1.170.

Electromedia® Filter

The Electromedia® filter used in this study was supplied by Filtronics, Inc., Anaheim, CA, and is shown in Figure 4.3. This pilot filter was shipped to Polk County pre-assembled with
the media in place. However, the unit arrived with a crack in the clear plastic pressure vessel that allowed the media to spill out of the shipping container. The vendor, while on-site, provided a replacement vessel. The media was collected and reinserted into the pressure vessel of the pilot unit. Figure 4.3 depicts the unit after it was repaired. The pilot skid was designed with two vertical 3 in. (I.D.) plastic pressure vessels. Figure 4.3 depicts the grey pressure vessel on the left that served as a reaction vessel with baffling at the center for increased mixing. The vessel on the right of Figure 4.3 held the media bed, which was comprised of layers of anthracite and Electromedia®, followed by a layer of granular support media. The manufacturer recommended hydraulic loading was 10 gpm/sf and for backwash cycles a loading rate of 24-25 gpm/sf was recommend. The white platform, shown in Figure 4.3, behind the pilot unit supports the bleach feed pump and a 1000 mL graduated cylinder was used to hold the bleach feed solution.

![Figure 4.3: Electromedia® Pilot-Filter Unit](image-url)
Manganese (IV) Oxide Filter

The pilot unit used for the manganese (IV) oxide filter bed was supplied by Hungerford and Terry, Inc., (226 Atlantic Ave., Clayton, New Jersey) and was slightly larger than that used for the Electromedia® bed. Instead of clear plastic tubing, this unit used a vertical fiberglass pressure vessel. The vessel, pictured in Figure 4.4, is 6 inches in diameter (internal diameter (ID)) and the bleach was fed just prior to entering the top of the filter bed. The bed of the pilot unit was filled with 27 pounds of anthracite and 88 pounds of GreensandPlus™ (manganese (IV) oxide) filter media followed by 15 pounds of gravel support media. The bleach fed to this pilot unit was obtained from the TR and IL WTP’s on-site day storage tanks. This bleach was diluted to a known concentration, stored in a 45 gal temporary “day tank” (shown in Figure 4.4) and fed with a modular peristaltic pump. The bleach concentration was determined by dilutions and the use of the Hach DPD colorimetric method.
Methods and Materials

The methods and equipment used for lab and field analysis is presented in Table 4.1. The primary source for analyte methods was the Standard Methods for the Examination of Water & Wastewater (Eaton et al, 2005).

Table 4.1: Table of Methods and Equipment

<table>
<thead>
<tr>
<th>Test</th>
<th>Location of Test</th>
<th>Method Description</th>
<th>Method Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide</td>
<td>Field</td>
<td>SM 4500-S² F. Iodometric Method; 4500-S² D. Methylene Blue, LaMotte 4630 CC-PS</td>
<td>0.1 mg/L as S</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Field</td>
<td>Hach Turbidimeter 2100N</td>
<td>0.01 NTU</td>
</tr>
<tr>
<td>Total氯ine</td>
<td>Field</td>
<td>Hach Spectrophotometer DR/890</td>
<td>0.01 mg/L</td>
</tr>
<tr>
<td>Free Chlorine</td>
<td>Field</td>
<td>HACH DPD Method 8021, HACH Spectrophotometer DR/890</td>
<td>0.02 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>Field/Lab</td>
<td>Hana pHep; Accumet Research AR 50</td>
<td>0.01 pH Units</td>
</tr>
<tr>
<td>Temperature</td>
<td>Field/Lab</td>
<td>Hana pHep; Accumet Research AR 50</td>
<td>0.01 °C</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Field/Lab</td>
<td>Fisher Scientific Traceable Conductivity, Resistivity, and TDS Meter</td>
<td>0.01 μS/cm</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>Field/Lab</td>
<td>YSI Model 58: Dissolved Oxygen Probe</td>
<td>0.01 mg/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>Field/Lab</td>
<td>SM 2320 B. Titration Method, Accumet Research AR 50</td>
<td>20 mg/L as CaCO₃</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>Lab</td>
<td>Dohrmann Phoenix 8000: The UV-Persulfate TOC Analyzer</td>
<td>0.05 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Lab</td>
<td>SM 4500 SO₄²⁻ E. Turbidimetric Method, HACH Spectrophotometer DR6000; Dionex DX-120 Ion Chromatograph</td>
<td>0.1 mg/L as SO₄²⁻</td>
</tr>
<tr>
<td>Iron</td>
<td>Lab</td>
<td>Perkin Elmer Optima 2100DV ICP-OES</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Manganese</td>
<td>Lab</td>
<td>Perkin Elmer Optima 2100DV ICP-OES</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>Lab</td>
<td>Perkin Elmer Optima 2100DV ICP-OES</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Lab</td>
<td>Perkin Elmer Optima 2100DV ICP-OES</td>
<td>0.1 mg/L</td>
</tr>
</tbody>
</table>
H₂S Assessment (Total Sulfides)

The analytical evaluation of hydrogen sulfide in water supplies is difficult due to the volatility of hydrogen sulfide gas. Hence, two methods were used in the measurement of total sulfides (as S²⁻): the methylene blue method and iodometric method. The methylene blue method is based on the reaction of sulfide, ferric chloride, and dimethyl-p-phenylenediamine to produce methylene blue (Eaton et al, 2005). The methylene blue method was used for primary analysis and total sulfides screening. In some cases (such as post treated water testing) the methylene blue test was used as an absence or presence test prior to the use of a more sensitive test. In situations where total sulfides were shown (through the methylene blue test) to be present, or in situations where total sulfides were known to be present (i.e. raw water), the iodometric method (Figure 4.5) was used to verify and determine a total sulfides concentration. The iodometric method is a back titration involving the oxidation of sulfide using iodine and then back titrating with sodium thiosulfate (Eaton et al, 2005).

Figure 4.5: LaMotte (Methylene Blue) Test Kit and Iodometric Titration Setup
The methylene blue method was performed using two different test kits: a Hach Hydrogen Sulfide Test Kit- Model HS-WR and a LaMotte 4630 H₂S test kit (Figure 4.5). Both kits evaluate total sulfide.

The iodometric method was performed according to Standard Method 4500-S²⁻ F. (Eaton et al, 1995). Specific precautions were taken to avoid the volatilization of H₂S during testing. The following procedure was observed:

1. The raw water was taken from the well with a standard ¾” garden hose. The hose was first flushed, and that water was analyzed to detect possible interferences; none were found. The hose was placed into a 1000 mL erlenmeyer flasks and the water was allowed to gently overflow.

2. A 250 mL erlenmeyer flask was used in the titration procedure. This container was prepared by adding the following solutions:
   a. 2 mL of iodine solution
   b. 10 mL of DI water
   c. 2 mL of 6 M hydrochloric acid

3. Once the 250 mL flask was prepared, the raw water was extracted from the 1000 mL flask with two 100 mL pipets. Using the pipet, the water was extracted at a depth below the sample surface to minimize H₂S volatilization. The filled pipet was then inserted below the surface of the iodine solution in the 250 mL flask, and the water sample was released into the flask. This procedure was conducted in such a manner to minimize the loss of H₂S gas.

4. A magnetic stir bar was placed into the sample flask and then placed onto a stir plate.
5. A 50 mL burette was fitted with a rubber stopper, filled with a sodium thiosulfate solution and then lowered into the flask so that the rubber stopper formed a tight seal between the flask opening and the tip of the burette. Note: The iodine oxidation of the sulfides in the water sample is believed to be a near instantaneous reaction. The use of a rubber stopper is a precautionary measure and may not be necessary, but was included to provide highest quality of care in an effort to minimize H₂S losses.

6. The titration was then carried out in accordance with Standard Method 4500-S²⁻ F (Eaton et al, 2005).

Post-Treatment Turbidity Formation Evaluation

A post-treatment evaluation was also conducted as part of the overall process evaluations in order to confirm relative treatment effectiveness. Turbidity was used as a simple water quality parameter for determining such effectiveness. As has been previously documented, once the water is chlorinated in the existing IL and TR systems, it then passes over a series of aeration trays prior to cascading into a GST where it is stored. An additional study was conducted to evaluate the effect, if any, that tray aeration would have on turbidity formation following media filtration. Although the filtration method being tested would not need aeration for sulfides removal, tray aerators would be needed for CO₂ removal and to increase the dissolved oxygen (DO) concentration for palatability concerns. For this reason, a temporary pilot tray aerator was constructed to mimic a bleach, media and tray aeration process configuration. This also allowed for direct comparisons of the pilot configuration to the the existing IL and TR WTP processes with regards to turbidity formation as a function of time.
The apparatus constructed to simulate tray aeration for the turbidity formation study is shown in Figure 4.6. In Figure 4.6.a., the pilot scale aeration trays are shown. These “trays” are actually gutter downspout splash blocks with ridges on them. A series of three splash blocks were arranged in a 30 gallon Rubbermaid garbage can in a zigzag pattern with water flowing from one tray to another. This effectively acted as a step/tray aeration system. The water exited the apparatus via a short PVC pipe extending downward from a hole cut into the center of the garbage can. This water outlet was made accessible by placing the system on an elevated wooden platform. The image in Figure 4.6.b. shows the aeration trays mounted atop of the GST at the Turner Road WTP. The PVC pipe extruding from the bottom of the trays was the sampling point for the existing system in the turbidity study. The amber bottles in Figure 4.6.c. are just a few of the many samples that were collected for analysis in the turbidity formation experiments. This photo was taken in one of UCF’s wet labs.

The water samples for the turbidity formation study were collected at two locations: from the drain port (Figure 4.6.b.) at the bottom of the aeration trays mounted on top of the GST
(existing systems) and from the drain port of the pilot aeration trays (Figure 4.6.a.) that followed the pilot filtration unit. These samples were collected in 1 L amber bottles. Each bottle was labeled for sampling at a specific time interval. At the specified time, the bottle was shaken and measurements were taken for turbidity, pH, conductivity and DO. Readings were taken at the same time intervals for both the existing and pilot systems.

**Laboratory Quality Control**

Quality assurance and control is a necessary component of laboratory analysis and quantitative measurement. Several actions were employed during the operation of this project to maintain that analytical results were both precise and accurate and included strict adherence to the analytical procedures and methods previously outlined in this chapter. Care was taken to wash glassware thoroughly. Glass sample bottles were acid washed with 1:1 HCl, rinsed, dried and then “ashed” in a kiln at 450°C for 1 hour. Other measures that were taken to assure quality included adherence to proper sample collection, storage and preservation procedures, observance of maximum storage periods as outlined in the Standard Methods and proper maintenance of analytical equipment (Eaton et al, 2005). In order to provide a quality assessment, sample replicates and spikes were analyzed and evaluated. This data was used to establish quality control limits for continuous monitoring of analytical precision and accuracy.

**Precision and Accuracy**

Precision was determined for TOC, sulfate, calcium, magnesium, iron and manganese by performing duplicate analyses on samples during the study period. Duplicate data was evaluated
using the industrial statistic, $I$, shown in equation 4-1, as described in the EPA Handbook for Quality Control in Water and Wastewater Laboratories (USEPA, 1979).

\[ I = \frac{[A \cdot B]}{[A + B]} \]  \hspace{1cm} (4-1)

Where: $I$ = Industrial Statistic; $A$ = Duplicate Value 1; $B$ = Duplicate Value 2

The average (Mean) and standard deviation (St. Dev.) of the $I$ statistic was calculated for each water quality parameter and used to define an acceptable region for duplicate analysis. In addition to the mean and st. dev., upper control level (UCL) and upper warning level (UWL) limits were established. The UCL is defined as the average value of $I$ plus three standard deviations. Samples with $I$ statistics that exceed the UCL are deemed to be “out of control”, in which case analysis should be halted until the cause of the out of control condition can be determined and corrected. All data since the last known “in control” sample should be rejected. If the $I$ statistic falls within the UCL but exceeds the UWL the measurements may be accepted unless the next sample also exceeds the UWL, at which point, all data up to the last known in control sample should be discarded. Control should be reestablished before data is again accepted. Reestablishment of control should be demonstrated by the observance of three consecutive in control measurements (Taylor, 1987).

In addition to duplicates, spikes were performed on the water samples in order to allow for accuracy monitoring. In some analyses, an analyte standard(s) was measured at the end of a given testing cycle as an additional gauge of accuracy and to verify that the testing equipment remained properly calibrated. The results from the sample spikes were used to determine percent
recovery (%R). The %R statistic is calculated with either equation 4-2 or 4-3 for standards and sample spikes, respectively.

\[
\%R = 100 \times \frac{\text{Determined Value}}{\text{Standard Concentration}} \tag{4-2}
\]

\[
\%R = 100 \times \frac{\text{Determined Value} - \text{Sample Concentration}}{\text{Spike Concentration}} \tag{4-3}
\]

In laboratory analyses, duplicates and spikes were required for at least every fifth sample. Results of the TOC sample duplicate analysis are provided in Table 4.2. The average value for I was determined to be 0.0153, indicating that the average variability of the TOC analysis was 1.5 percent based on the mean of the I statistic. Also, the data shows that the TOC analyses yielded satisfactory reproducibility as not one of the 10 sample duplicates analyzed exceeded either the UWL or the UCL.

<table>
<thead>
<tr>
<th>Table 4.2: Precision Analysis of TOC Duplicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duplicate A (mg/L)</td>
</tr>
<tr>
<td>0.80</td>
</tr>
<tr>
<td>0.79</td>
</tr>
<tr>
<td>1.16</td>
</tr>
<tr>
<td>0.73</td>
</tr>
<tr>
<td>1.21</td>
</tr>
<tr>
<td>0.89</td>
</tr>
<tr>
<td>0.83</td>
</tr>
<tr>
<td>0.75</td>
</tr>
<tr>
<td>1.21</td>
</tr>
<tr>
<td>1.01</td>
</tr>
</tbody>
</table>

Mean I = 0.0153
St. Dev. = 0.0091
UWL = 0.0334
UCL = 0.0425
Both sample spikes and standards were measured in TOC analyses. The results of these tests are shown in Table 4.3. Percent recovery numbers are said to be acceptable when they fall within the range of 80-100%. The 16 spikes and standards measured in TOC analyses fell within the range of acceptability. The average percent recovery for the TOC analyses was 102.3% with a standard deviation of 7.1%.

\[\text{Avg} = 102.3\]
\[\text{St. Dev.} = 7.1\]

Results of the sulfate sample duplicate analysis are provided in Table 4.4. The average value for I was determined to be 0.0183, indicating that the average variability of the TOC analysis was 1.8 percent based on the mean of the I statistic. Also, the data shows that the TOC

65
analyses yielded satisfactory reproducibility as not one of the 8 sample duplicates analyzed exceeded either the UWL or the UCL.

The results of the spiked sulfate samples are shown in Table 4.5. Percent recovery numbers are said to be acceptable when they fall within the range of 80-100%. The 9 spikes measured in sulfate analyses fell within the range of acceptability. The average percent recovery for the sulfate analyses was 98.7% with a standard deviation of 11.5%.

Table 4.4: Precision Analysis of Sulfate Duplicates

<table>
<thead>
<tr>
<th>Duplicate A (mg/L)</th>
<th>Duplicate B (mg/L)</th>
<th>Industrial Statistic (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>3.7</td>
<td>0.0478</td>
</tr>
<tr>
<td>1.3</td>
<td>1.3</td>
<td>0.0000</td>
</tr>
<tr>
<td>3.9</td>
<td>3.9</td>
<td>0.0000</td>
</tr>
<tr>
<td>4.1</td>
<td>4.1</td>
<td>0.0000</td>
</tr>
<tr>
<td>4.4</td>
<td>4.2</td>
<td>0.0302</td>
</tr>
<tr>
<td>3.6</td>
<td>3.6</td>
<td>0.0000</td>
</tr>
<tr>
<td>3.9</td>
<td>3.8</td>
<td>0.0132</td>
</tr>
<tr>
<td>7.3</td>
<td>8.2</td>
<td>0.0556</td>
</tr>
</tbody>
</table>

Mean I = 0.0183  
St. Dev. = 0.0232  
UWL = 0.0647  
UCL = 0.0879
Table 4.5: Accuracy of Sulfate Analyses as Measured by Percent Recovery

<table>
<thead>
<tr>
<th>Sample (mg/L)</th>
<th>Spike (mg/L)</th>
<th>Determined Value (mg/L)</th>
<th>Percent Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.22</td>
<td>2.0</td>
<td>5.08</td>
<td>93.0</td>
</tr>
<tr>
<td>3.73</td>
<td>2.0</td>
<td>5.85</td>
<td>106.0</td>
</tr>
<tr>
<td>1.26</td>
<td>2.0</td>
<td>3.04</td>
<td>89.0</td>
</tr>
<tr>
<td>3.88</td>
<td>2.0</td>
<td>5.78</td>
<td>95.0</td>
</tr>
<tr>
<td>2.93</td>
<td>2.0</td>
<td>4.74</td>
<td>90.5</td>
</tr>
<tr>
<td>4.43</td>
<td>2.0</td>
<td>6.78</td>
<td>117.5</td>
</tr>
<tr>
<td>3.60</td>
<td>2.0</td>
<td>5.50</td>
<td>95.0</td>
</tr>
<tr>
<td>3.85</td>
<td>2.0</td>
<td>5.58</td>
<td>86.5</td>
</tr>
<tr>
<td>7.31</td>
<td>2.0</td>
<td>9.62</td>
<td>115.5</td>
</tr>
</tbody>
</table>

Avg = 98.7
St. Dev. = 11.5
5.0 RESULTS AND DISCUSSION

Overview

Pilot-scale configurations used for water treatment evaluations inherently provide more representative data than a bench-scale configuration. This is typically the case when investigating highly volatile water quality parameters. The “closed system” nature of a pilot-scale system minimizes the errors associated with fugitive emissions of H₂S gas. The treatment stream in these pilot evaluations would not be exposed to the atmosphere until after the water stream had undergone some form of treatment. The pilot-scale effort was comprised of three components: ferrate oxidation with and without filtration, bleach oxidation preceding Electromedia® filtration and manganese (IV) oxide filtration with continuous bleach regeneration.

Ferrate Holds Promise as a Treatment Alternative

Ferrate was first evaluated at the bench-scale. The results of those initial evaluations were inconsistent because of the difficulty in maintaining a stable ferrate solution (an issue which arises from the excessive dilutions required for bench-scale testing) that introduced significant error into the bench-scale data. While the data did show that the ferrate would remove sulfide, the concentration at which successful oxidation occurred was uncertain and could not be quantified due to the conditions of the test. Based on the results of this early bench-scale testing, it was decided that a larger pilot-scale test would be required in order to produce more reliable data. Consequently, ferrate was re-evaluated at the pilot-scale.
While the application of the ferrate technology at the pilot-scale was not subject to many of the pitfalls associated with a bench-scale study, there were a few challenges that arose with respect to the design of the chemical feed system on the ferrate feed skid. The feed pump would pulse ferrate into the flow line at intermittent intervals, and although the skid had a static mixer, the lack of a contact chamber or basin resulted in variable flow regimes. Hence the system behaved in a plug flow fashion which did not promote mixing. This issue was alleviated by using a 45 gallon day tank as a post-mixing basin. When fed directly from the ferrate feed skid to the media bed, the bed itself allowed for mixing of the ferrate into the feed water stream, overcoming this challenge.

The data in Table 5.1 are results from a pilot run where ferrate oxidant was fed ahead of the manganese (IV) oxide filter bed. The feed concentration of ferrate presented in Table 5.1 is the concentration that was calculated when the ferrate solution was synthesized. Due to dilution effects and degradation, it is most likely that these results are greater than the actual active ferrate content at the time of pilot testing. It was acknowledged by the vendor that in future studies an online monitor would be used to generate real time ferrate strength readings; however, this additional equipment was not available for use in the experiments conducted in this work. That issue aside, the ferrate was effective in oxidizing the sulfide in the groundwater to below detection limit (<0.1 mg/L) before filtration. Ferrate oxidation created a flocculant that manifested itself as turbidity. This turbidity was different than the turbidity associated with colloidal sulfur and appeared in the form of a settleable particle. This was not unexpected as ferrate has been used as a coagulant in other studies (Ma & Liu, 2002; Jiang & Llyod, 2002; Jiang et al, 2006), because it generates a ferric coagulating species during use. Additional experiments would be required to evaluate either sedimentation, traditional filtration or a
combination thereof to remove the floc formed in the ferrate oxidation process. As shown in Table 5.1, the free chlorine residual prior to filtration was 0.62 mg/L and reduced to essentially zero after filtration. In order to provide a proper disinfectant residual in the system, a post-chlorine feed system would be required for this type of process application.

**Table 5.1: Ferrate Treatment Data from the Imperial Lakes WTP**

<table>
<thead>
<tr>
<th>Ferrate Feed Concentration (mg/L)</th>
<th>Post Treated Total Sulfide (mg/L)</th>
<th>Average FAC Residual (mg/L) Pre-Filtration</th>
<th>Average FAC Residual (mg/L) Post-Filtration</th>
<th>Average Turbidity (NTU) Pre-Filtration</th>
<th>Average Turbidity (NTU) Post-Filtration</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.25</td>
<td>&lt;0.1</td>
<td>0.62</td>
<td>0.01</td>
<td>27.37</td>
<td>0.43</td>
</tr>
</tbody>
</table>

**Electromedia® Filter Effective at Sulfide Control**

Results of the Electromedia® filter test runs at the Imperial Lakes WTP are provided in Table 5.2. This pilot-filter was operated at several different bleach dose rates, and evaluations were made at a hydraulic loading rate of 10 gpm/sf. The target free chlorine residual was 1.0 mg/L for most of the testing. As shown in Table 5.2, the target residual was obtained at the IL site with a bleach feed concentration of approximately 11.1 mg/L. A more comparative operating point residual of 2.33 mg/L (the County prefers a residual of 2.5 to 3.0 mg/L at POE) was reached with a slightly higher bleach feed concentration of 13.8 mg/L. In that same residual range, the County currently applies approximately 14 to 15 mg/L of bulk bleach at the IL WTP. Turbidity remained below 1.0 NTU during testing except for those times during filter bed startup. During start-up, the turbidity could be upwards of 5 NTUs but reached a steady operating state of below 1 NTU within minutes of initiating flow. This understanding would
have to be taken into account during full-scale operation, most likely by implementing a blow-down start up operation sequence for this technology.

![Table 5.2: Electromedia® Filter Performance at the Imperial Lakes WTP](image)

<table>
<thead>
<tr>
<th>Cl₂ Feed Concentration (mg/L)</th>
<th>Post Treated Total Sulfide (mg/L)</th>
<th>Cl₂ (FAC) Residual (mg/L)</th>
<th>Average Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Average</td>
<td>Pre-Filtration</td>
</tr>
<tr>
<td>11.0</td>
<td>&lt;0.1</td>
<td>0.28 – 2.18</td>
<td>0.85</td>
</tr>
<tr>
<td>11.1</td>
<td>&lt;0.1</td>
<td>0.35 - 1.35</td>
<td>0.94</td>
</tr>
<tr>
<td>12.4</td>
<td>&lt;0.1</td>
<td>1.24 - 2.16</td>
<td>1.78</td>
</tr>
<tr>
<td>13.8</td>
<td>&lt;0.1</td>
<td>1.16 - 3.08</td>
<td>2.33</td>
</tr>
</tbody>
</table>

The information illustrated in Figure 5.2 was generated using data obtained from operation of the Electromedia® pilot-filter at the IL WTP well #2. This figure shows the breakpoint for raw water total sulfide removal as a function of the Cl₂ to sulfide molar ratio. This same figure also provides information regarding free chlorine residual formation as a function of the Cl₂ to sulfide molar ratio. Figure 5.2 illustrates total sulfide removal with respect to two distinct operating zones: a “Demand Zone” where sulfides are exerting a demand on the bleach oxidant and a “Free Residual Zone” where sulfides are no longer present (for this work the method detection limit was 1.0 mg/L) and are in the presence of a free chlorine residual. These “zones” are operating regimes for the Electromedia® process. Total sulfide Cl₂ demand decreases from left to right in the demand zone (DZ) and free Cl₂ residual increases from left to right in the free residual zone (FRZ). In the DZ, 74% of the variation in the data could be explained by linear regression. At breakpoint there is a transition to the FRZ, whereupon 89% of the variation in the data could be explained by linear relationship. At the IL WTP, the County maintains a positive chlorine residual between 2.5 and 3 ppm, depending on the temperature. For
example, the summer requires a higher residual. According to the linear model, to achieve a 3 ppm free chlorine residual (using the Electromedia® process) a Cl₂ to sulfide molar ratio of 4.1 would be required. In practice, this system would be operated in the FRZ (i.e. the post-filtered water would carry a residual as required by law).

Figure 5.1: Post-Treated Sulfide and FAC Residual as a Function of Cl₂/S²⁻ Molar Ratio for Electromedia® - IL WTP

Clorox® bleach was used as the chlorine oxidant in the pilot test runs at the IL WTP. The calculations upon which the listed feed concentrations were determined relied upon the manufacture specified bleach strength. The Clorox® was stored on-site, replaced regularly, and was protected from the elements; however it was stored in non air-conditioned buildings which may have increased its degradation. This most likely means that these numbers are fairly
conservative. Once testing began at the Turner Road WTP, the research team switched to the use of the county’s on-site bleach stock. In these calculations, the actual bleach stock concentration was calculated and used to determine a more accurate chlorine dose concentration. Subsequent testing suggested that the data obtained from the former method may be conservative by as much as 10-60%. For the Turner Road WTP, data indicated that total sulfide removal (<0.10 mg/L) with sufficient free chlorine residual (0.97 mg/L FAC) was obtained with a feed concentration of 12.9 mg/L. However, if that dose concentration were to be calculated using the initial method, it would have given a dose concentration of 20.3 mg/L (an over-estimate of approximately 57%). This may be a worst case scenario, but it helps to explain why a similar dose concentration to that used at the IL WTP was effective at the Turner Road WTP even though there is greater total sulfide content in the TR well water. It should also be noted that the Electromedia® pilot produced slightly higher turbidity at the TR WTP with an average post-filtration value of 0.8 NTU compared to ~0.2 NTU at the IL WTP. Switching from the Clorox® to the county’s bleach stock also appears to have increased the turbidity of the finished water. Evaluation of the Electromedia® process at the Turner Road WTP was not as complete as that performed at the Imperial Lakes WTP because hydraulic limitations at the TR site limited run times.

The schematic presented in Figure 5.2 is representative of a full scale electromedia process. Additional pumping would be required to carry the treated water from the filter vessels to the GST, and a backwash disposal and conveyance system would also be required, but is not shown in the schematic.
Manganese (IV) Oxide Filtration Reduces Sulfide Effectively

One of the objectives when evaluating the manganese (IV) oxide filter (MnO₂) process was to evaluate sulfur removal using this bed without the use of potassium permanganate regenerate. UCF developed a concept for the use of on-site chemicals to minimize the need for new chemical feed systems, because this would be an aid to meeting one of the criteria established for the study. Hence, bleach was used to regenerate the bed instead of potassium permanganate. Therefore, determination of the required Cl₂ feed concentration and pressure drop across the bed at varying hydraulic loading rates would be important to this component of the work. The evaluations of the manganese (IV) oxide filter were performed using on-site bulk bleach stocks. The hydraulic loading rates used in this evaluation were 5, 7.5, 10 and 11.8 gpm/sf. The hydraulic loading rate evaluations were conducted at IL. The TR testing was conducted at a loading rate of 10 gpm/sf. A plot of the loading rate data is shown in Figure 5.3. The pressure drop across a clean filter bed was shown to range from approximately 4.1 to 6.1 psi for the range of hydraulic loading rates specified above. The data demonstrated good linearity and resulted in a correlation coefficient of 0.992.
It was the intention of UCF to obtain operational data in order to predict pressure drop over time for this filter media. However, on-site hydraulic limitations disallowed for the extended run times necessary to see appreciable increases in pressure drop for a given hydraulic loading rate. To obtain this data, further testing should be conducted in parallel to the existing treatment system to obtain longer term process operations data. The equipment would become permanent to the facility after acceptance of testing.

The results of MnO₂ media evaluations at the IL WTP are shown in Table 5.3. The methylene blue method was used here to perform an absence/presence test on the post treated water. This data indicated no significant variation in performance at the different hydraulic loading rates for the conditions tested. Also, a feed dose of approximately 10 mg/L Cl₂ was
observed for operation of the MnO₂ filter to achieve comparable FAC residual levels typically experienced by the full-scale system. However, it was noted that the bleach dose ahead of the MnO₂ filter was well below the 14-15 mg/L Cl₂ demand observed at the Imperial Lakes WTP. This suggests that the MnO₂ bed was providing some benefit in the oxidation of sulfide as is supported by observations made in Table 5.3. This Cl₂ dose is also lower than that required for the Electromedia® filter. As previously noted, the results for the Electromedia® testing at IL were most likely subject to some over-estimation because of the type of bleach initially used in those experiments. There was also a design difference between these two pilot skids. The Electromedia® pilot-filter had a built in contact chamber with a baffled static mixer ahead of which the bleach is fed, while the MnO₂ pilot-filter had its injection quill just ahead of the actual media bed with little to no contact time. The oxidation of sulfide is a relatively rapid reaction. The impetuous for the use of an oxidative MnO₂ media, typically employed for iron and manganese removal, is that the filter media itself will provide some benefit in the sulfide oxidation reaction. In which case, the bleach oxidant acts equally as a regenerate as it does a sulfide oxidant (keeping the bed in an oxidative state). It is possible that a portion of the total sulfide was being converted to colloidal sulfur or sulfate by the bleach because of excess contact time ahead of the bed, which may have negated some of the oxidative benefits that the MnO₂ media may provide. Regardless, the data would indicate that the combined effects of a bleach and oxidative media filtration process is effective a sulfide removal.
<table>
<thead>
<tr>
<th>Hydraulic Loading Rate (gpm/sf)</th>
<th>Cl₂ Feed Concentration (mg/L)</th>
<th>Post Treated Total Sulfide (mg/L)</th>
<th>Cl₂ (FAC) Residual Average (mg/L)</th>
<th>2hr Range (mg/L)</th>
<th>Average Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.2</td>
<td>&lt;0.1</td>
<td>1.06 - 1.52</td>
<td>1.23</td>
<td>0.09</td>
</tr>
<tr>
<td>7.5</td>
<td>5.6</td>
<td>&lt;0.1</td>
<td>0.80 - 1.41</td>
<td>1.15</td>
<td>0.06</td>
</tr>
<tr>
<td>10</td>
<td>5.4</td>
<td>&lt;0.1</td>
<td>0.94 - 1.28</td>
<td>1.06</td>
<td>0.12</td>
</tr>
<tr>
<td>10</td>
<td>10.0</td>
<td>&lt;0.1</td>
<td>3.42 – 3.90</td>
<td>3.59</td>
<td>0.10</td>
</tr>
<tr>
<td>11.8</td>
<td>5.3</td>
<td>&lt;0.1</td>
<td>0.32 - 1.28</td>
<td>0.72</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The results of media pilot testing at the Turner Road site are presented in Table 5.4. This data indicates that there is an increase in the bleach demand at the TR site as compared to the IL site. This is attributed to the increased raw water total sulfides levels at the Turner Road WTP, as the raw water concentration was 2.6 mg/L versus 1.6 mg/L at the Imperial Lakes WTP. Also, the 13.2 mg/L dose concentration required for the MnO₂ filter seems to be similar to the 12.9 mg/L dose concentration required with the Electromedia® filter. Given standard error and the slightly lower free available chlorine (FAC) residual for the Electromedia® system, the two numbers would be considered to be of the same magnitude.

<table>
<thead>
<tr>
<th>Hydraulic Loading Rate (gpm/sf)</th>
<th>Cl₂ Feed Concentration (mg/L)</th>
<th>Post Treated Total Sulfide (mg/L)</th>
<th>Cl₂ (FAC) Residual Average (mg/L)</th>
<th>2hr Range (mg/L)</th>
<th>Average Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>13.2</td>
<td>&lt;0.1</td>
<td>1.16 - 1.51</td>
<td>1.38</td>
<td>0.77</td>
</tr>
<tr>
<td>10</td>
<td>14.3</td>
<td>&lt;0.1</td>
<td>---</td>
<td>3.05</td>
<td>0.20</td>
</tr>
</tbody>
</table>
The schematic presented in Figure 5.4 is representative of a full-scale bleach and manganese (IV) oxide process. It should be noted that additional pumping would be required to carry the treated water from the filter vessels to the GST and a backwash disposal and conveyance system would be required, but is not shown in the schematic.

![Figure 5.4: Schematic of Manganese (IV) Oxide Filter Process](image)

**Media Filtration Reduces Post-Filtration Turbidity Formation**

During the pilot testing phase, it was noted that the existing IL and TR plants produced elevated turbidity (> 6 NTU) in the GST. It was theorized that a majority of this turbidity was colloidal sulfur formed in the bleach oxidation process. The turbidity levels of the post-treated water from the pilot filters was significantly lower, less than 1.0 NTU in most cases. However, the data for the turbidity of the post-treated water was measured at time zero. In order to draw a more valid comparison between pilot and full-scale treatment systems, the turbidity formation over time would need to be observed. The elevated turbidity readings for the existing system were taken from the GST, hydro tanks and POE. In order to evaluate the turbidity formation potential of the treated water from the pilot system, an attempt was made to simulate the existing
plant treatment sequence (i.e. add simulated tray aeration). This would allow UCF to assess the turbidity of the post-treated water from the pilot filter and make comparisons to the water being produced by the existing treatment process.

The results of this turbidity study, using the manganese (IV) oxide filter, are presented graphically in Figures 5.5 and 5.6. The data suggest that the oxidation/filtration technique reduced the turbidity formation over time in dark conditions where no sunlight was present. After a 20-hr bleach contact time, the turbidity of the post media filtrate remained below 0.6 NTU. However, water from the existing IL water treatment system produced turbidity in excess of 6 NTU after a 20-hr contact time. These results are reasonable because the average turbidity observed in the GST at the IL WTP was also in excess of 6 NTUs (illustrated in Figure 2.2 and 2.3). The study demonstrated the effectiveness of MnO₂ filters for the oxidation of sulfide and subsequent prevention of post-treated turbidity formation.

The addition of caustic to the post-treated water was shown to increase turbidity. In the IL experiments, a higher dose of NaOH was added which resulted in a greater increase in turbidity than experienced in the TR study. However, after approximately 30-50 minutes, the turbidity began to decrease. It is believed that this increased turbidity was caused by the formation of calcium carbonate and that the decrease in turbidity was caused by the adherence of calcium carbonate to the amber bottle surface, or sedimentation, thus removing it from suspension. The turbidity formation of the post-treated water at IL remained below one over the duration of testing. Turbidity peaked at around 0.6 NTU after 43 hours of formation time. For the TR system, the turbidity of the post-treated water peaked at around 3.9 NTU after 56 hours of formation time.
In this pilot study, it was also noted that the finish water turbidity levels would rise at a greater rate when exposed to sunlight. It is postulated that calcium carbonate formed as the water was heated by the sunlight. Additional studies should be conducted to investigate this phenomenon. No additional work was conducted because the treated water was to be stored in tanks and distributed in pipes absent of sunlight.

Figure 5.5: Imperial Lakes Turbidity Study Data – Well #1
Figure 5.6: Turner Road Turbidity Study Data

Additional Observations

In Figure 5.7, a representative sample of the average daily recorded turbidity levels is displayed as they varied over time. This figure clearly shows a significant drop in system turbidity between the dates of 6/25/09 and 6/30/09. The drop in turbidity throughout the existing system coincided with a change in the method of pilot operation. Prior to that time, the pilot was run when the system was operating in its normal operation pattern. In order to provide the pilot system with better sustained run times, the pilot system was transferred to the smaller of the two wells (Well #1), and the PRV was opened to allow greater flow to leave the plant. Altering the process configuration minimized water production (using a smaller well) and maximized flow into the distribution system. This decreased system retention time and reduced available turbidity
formation at the points of sampling. System limitation at the TR WTP did not allow for an analogous reconfiguration to increase the pilot filter run time. The TR treatment facility is at a lower elevation in the distribution system relative to the IL WTP and increasing flow (i.e. pressure) into the system could cause damage to the distribution system piping. Also, there was only one well available at the Turner Road WTP, and it had a fixed pumping rate that could not be easily altered.

![Figure 5.7: Average Daily Turbidity at the Imperial Lakes WTP](image-url)
6.0 CONCEPTUAL COST CONSIDERATIONS

General Considerations

It is important in utility deliberation and planning activities that process engineers develop opinions of probable construction cost. Employing processes that properly address Safe Drinking Water Act (SDWA) compliance often requires the use of several interrelated processes or includes integration of newer processes into existing facilities. Hence, a conceptual opinion of probable capital and chemical costs was prepared using the findings of the pilot study and was based on manufacturers’ estimates, existing WTP operational data and best available chemical cost data. The opinions of probable costs presented in this chapter are preliminary and are intended to be used for planning purposes only, as they do not represent design-based engineering evaluations. These conceptual capital costs opinions presented herein are based on an overview of major equipment selection and conceptual flow diagrams.

Costing data was evaluated for both of the oxidation/filtration techniques studied in this work. Design data was generated based on flow estimates provided by one of the County’s consultants, Jones Edmunds and Associates, Inc. and is, in-part, based on the County’s Water Quality Master Plan (Jones Edmunds and Associates, Inc., 2009). The flow projections for the IL WTP are presented in Table 6.1. The values in Table 6.1 represent the projected water demand in units of million gallons per day (MGD) and the numbers in parenthesis are the design flow rate in units of gallons per minute (gpm).
Table 6.1: Imperial Lakes WTP Projected Flow Rates (Based on Demand)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Initial (Year 2011)</th>
<th>Ultimate (Year 2028)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AADD</td>
<td>1.69 MGD</td>
<td>2.30 MGD</td>
</tr>
<tr>
<td></td>
<td>1,170 gpm</td>
<td>1,597 gpm</td>
</tr>
<tr>
<td></td>
<td>(use 1,170 gpm)</td>
<td>(use 1,600 gpm)</td>
</tr>
<tr>
<td>MDD</td>
<td>3.37 MGD</td>
<td>4.60 MGD</td>
</tr>
<tr>
<td></td>
<td>2,341 gpm</td>
<td>3,194 gpm</td>
</tr>
<tr>
<td></td>
<td>(use 2,350 gpm)</td>
<td>(use 3,200 gpm)</td>
</tr>
</tbody>
</table>

The IL WTP currently has two wells installed: Well #1 and Well #2. These wells have design flows of 1,000 and 2,200 gpm, respectively. In order to provide adequate flow for the projected increase in demand, the county is planning on installing a third well with a design flow of 2,200 gpm. These design flows are shown in Table 6.2. No more than two wells are to be operating at once and the designed peak flow is 3,200 gpm. Therefore, when two wells are operating in tandem, it will either be a combination of wells 1 and 2 or 1 and 3 (Jones Edmunds and Associates, Inc., 2009).

Table 6.2: IL WTP Well Flows

<table>
<thead>
<tr>
<th>Well No.</th>
<th>Design flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,000 gpm</td>
</tr>
<tr>
<td>2</td>
<td>2,200 gpm</td>
</tr>
<tr>
<td>3 (Proposed)</td>
<td>2,200 gpm</td>
</tr>
</tbody>
</table>

The numbers in Table 6.3 are based on the county’s Water Quality Master Plan projected facility demand (Jones Edmunds and Associates, Inc, 2009). As noted the county expects demand to gradually increase at the TR WTP. However, the Water Quality Master Plan calls for an eventual shift of drinking water supply capacity from the TR WTP to the IL WTP. Part of the
reasoning for the change is that the TR WTP is a lower elevation and must pump “uphill” to reach many of its customers. The IL WTP is at a higher elevation and does not need to expend as much energy to create the same system pressure. Also, the IL raw water appears to be of slightly higher quality with respect to sulfide content.

Table 6.3: Turner Road WTP Projected Flow Rates (Based on Demand)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Year 2014</th>
<th>Year 2018</th>
<th>Year 2028</th>
</tr>
</thead>
<tbody>
<tr>
<td>AADD</td>
<td>1.05 MGD</td>
<td>1.10 MGD</td>
<td>0.95 MGD</td>
</tr>
<tr>
<td>MDD</td>
<td>2.10 MGD</td>
<td>2.21 MGD</td>
<td>1.90 MGD</td>
</tr>
</tbody>
</table>

Conceptual Process Design

UCF worked with the vendors in order to determine a preliminary system design and provide a rough estimate of probable costs. These costs are based solely on the treatment system additions. In Table 6.4, some of the design parameters for the manganese (IV) oxide (MnO₂) filter are shown. It is suggested that two, 32 ft straight sideshell, horizontal filters be used at both sites. The filter vessels are 10 ft in diameter and have 3 internal cells. The media bed is comprised of a 21 inch layer of anthracite and greensand plus (MnO₂), followed by a 16 inch layer of support gravel. The design hydraulic loading rate is 5.0 gpm per square foot. As noted in the Table 6.4, a reaction vessel has not been included in the bed design. Costs associated with a backwash storage and pump station for sanitary disposal are not included in these cost evaluations.
Table 6.4: Preliminary Design for Manganese (IV) Oxide Filtration System

<table>
<thead>
<tr>
<th>Filter Design- Imperial Lakes WTP</th>
<th>Filter Design- Turner Road WTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Filters</td>
<td>2</td>
</tr>
<tr>
<td>Design Flowrate (gpm)</td>
<td>760</td>
</tr>
<tr>
<td>Filter Type</td>
<td>Horizontal</td>
</tr>
<tr>
<td>Diameter (ft)</td>
<td>10</td>
</tr>
<tr>
<td>Straight Cell (ft)</td>
<td>32</td>
</tr>
<tr>
<td>Cells/Filter</td>
<td>3</td>
</tr>
<tr>
<td>Capacity/Unit (%)</td>
<td>50.0</td>
</tr>
<tr>
<td>Flowrate (gpm/sf)</td>
<td>5.0</td>
</tr>
<tr>
<td>Cl₂ Reaction Vessel</td>
<td>N/A</td>
</tr>
<tr>
<td>Media Packing</td>
<td></td>
</tr>
<tr>
<td>Anthracite (in)</td>
<td>21</td>
</tr>
<tr>
<td>Greensand Plus (in)</td>
<td>21</td>
</tr>
<tr>
<td>Gravel (in)</td>
<td>16</td>
</tr>
</tbody>
</table>

In Table 6.5 some of the design parameters for the Electromedia® filter are shown. This filter is of a different design than the greensand filter. Aside from the obvious differences in media type, the filter vessel is smaller at just over 17 ft in length compared to the 32 ft filter vessel with the greensand filter. However, the Filtronics Electromedia® filter includes a reaction vessel in addition to the filter vessel.

Table 6.5: Electromedia® Filter Design for the Imperial Lakes WTP

<table>
<thead>
<tr>
<th>Filter Vessel Design, IL WTP</th>
<th>Reaction Vessel Design, IL WTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Filters</td>
<td>2</td>
</tr>
<tr>
<td>Diameter, in (ft)</td>
<td>84 (7)</td>
</tr>
<tr>
<td>Straight Cell, in (ft)</td>
<td>208 (17.3)</td>
</tr>
<tr>
<td>Max Flowrate, gpm</td>
<td>3200</td>
</tr>
<tr>
<td>Operating Pressure, psi</td>
<td>60</td>
</tr>
<tr>
<td>Test Pressure, psi</td>
<td>78</td>
</tr>
</tbody>
</table>
Conceptual Opinion of Probable Capital Costs

Capital cost estimates for the filtration equipment were provided by Filtronics, Inc. and H&T, Inc. A breakdown of these costs is presented in Table 6.6. These costs are representative of both the IL and TR systems. Most of the differences come from the sulfides loading which will call for more frequent backwashes at the TR WTP.

Table 6.6: Opinion of Probable Capital Cost for Sulfide Filtration Systems

<table>
<thead>
<tr>
<th>Estimated Capital Cost</th>
<th>Range ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Cost\textsuperscript{a,b}</td>
<td>$573,000 - $750,000</td>
</tr>
<tr>
<td>Masterplan Construction Costs</td>
<td>10%</td>
</tr>
<tr>
<td>Contingencies, Installation, etc.</td>
<td>35%</td>
</tr>
<tr>
<td><strong>Total Estimated Capital</strong></td>
<td><strong>$831,300 - $1,088,000</strong></td>
</tr>
<tr>
<td>$/gpd</td>
<td>$0.36 - $1.15</td>
</tr>
<tr>
<td>$/kgal Capital (installed)*</td>
<td>$0.10 - $0.32</td>
</tr>
</tbody>
</table>

\textsuperscript{a} This cost does not include installation, exterior plumbing, exterior wiring, concrete or concrete design, freight. 
\textsuperscript{b} Capable of treating 0.95 – 2.3 MGD

* At 8% interest over 20 years

Conceptual Opinion of Probable Chemical Costs

The projected chemical costs for a filtration process at the Imperial Lakes and Turner Road treatment facilities are presented in Table 6.7. These costs are based on the range of operating bleach doses used in the field which produced a Cl\textsubscript{2} residual between 1 and 3.5 mg/L.

Table 6.7: Opinion of Probable Chemical Costs for the IL and TR WTPs

<table>
<thead>
<tr>
<th></th>
<th>Imperial Lakes WTP</th>
<th>Turner Road WTP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>On-Site NaOCl 50% NaOH</td>
<td>On-Site NaOCl 50% NaOH</td>
</tr>
<tr>
<td>AADF (MGD)</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Dose (mg/L)</td>
<td>5 – 14</td>
<td>0.5</td>
</tr>
<tr>
<td>Feed Rate (lb/day)</td>
<td>96 - 270</td>
<td>9.6</td>
</tr>
<tr>
<td>Chemical Cost ($/lb)</td>
<td>$0.10</td>
<td>$0.26</td>
</tr>
<tr>
<td>$/ year</td>
<td>$3,500 - $9,800</td>
<td>$920</td>
</tr>
</tbody>
</table>
7.0 SUMMARY AND CONCLUSION

Summary

Reduced sulfide is a concern for many water purveyors relying on groundwater supplies. If sulfide is left untreated it can impact finished water quality, corrosivity, create undesirable taste and odor, and oxidize to form visible turbidity. Polk County Utilities (County) has been in the process of expanding its drinking water capacity to meet the demands of its Turner Road (TR) and Imperial Lakes (IL) water treatment facilities. As a result, refurbishment and expansion will be required that involves the installation of a new groundwater well or facility modifications at these two WTPs. This action will necessitate compliance with existing regulatory rules.

Currently, the County’s treatment practice consists of bleach disinfection preceding tray aeration. The Turner Road and Imperial Lakes water treatment plants (WTPs) both rely upon groundwater sources containing hydrogen sulfide that ranges between 1.4 to 2.6 mg/L as total sulfide (as $S^{2-}$). It is anticipated that the new well(s) planned to be constructed will possess a similar water quality to that existing, such that, the raw water will require treatment for sulfide per Florida Department of Environmental Protection (FDEP) “sulfide” rule 62-555.315(5)(a). In its current form, the rule disallows the use of the County’s existing sulfide treatment process (tray aeration) at the current sulfide levels.

As part of the County’s planning process, the County retained the University of Central Florida (UCF) to assist in evaluating available alternative treatment methods that could reduce sulfide content and meet the intent of FDEP’s sulfide rule. The County was concerned with the provisions of FDEP 62-555.315(5)(a) because the identified treatment (i.e. forced-draft aeration)
would not adequately fit within the confines of the existing sites and could negatively impact neighboring residents. The County, seeking assistance, challenged UCF to research alternative treatment scenarios that offered a low profile, did not necessitate the need for additional complex chemical feed systems, minimized the extent of electrical infrastructure upgrades and were inexpensive to construct and operate.

The purpose of this document was to present a summary of the research effort and associated findings developed as part of this work. Several alternative technologies were evaluated at the desktop-, bench- and pilot-scales and included anion exchange, various oxidation methods and alternative media filtration processes.

Conclusions

Both chlorine bleach oxidation/filtration systems were shown to effectively remove sulfide without the accompanying finished water turbidity common to existing methods. This research has demonstrated that bleach oxidation followed by the use of manganese (IV) oxide or electromedia filters, historically used for iron and manganese removal, show promise for use by water purveyors having elevated (0.6 to 3.0 mg/L) levels of total sulfide in their groundwater supplies. Specific results obtained during the conduct of the study include:

- Media filtration, historically used to treat for iron and manganese, was shown to be effective for total sulfide treatment in water having low iron and manganese content. Bleach oxidation prior to media filtration (either electromedia or manganese (IV) oxide media) removed total sulfide to below detection levels (0.1 mg/L) for groundwater supplies containing as high as 2.6 mg/L total sulfide. The use of bleach oxidation ahead of media filtration produced
finished water with low turbidity (< 1.0 NTU) as compared to traditional tray aeration & chlorination processes (6-16 NTU, as observed in this study). It was determined that the media filtration approach (MnO₂ or electromedia) for sulfide treatment met the County’s objectives that were established at the outset of the project.

- Bleach consumption was reduced in the modified filtration process as compared to tray aeration processes alone. Both the modified filtration process and tray aeration process contained a bleach component. The values presented for the existing process assume a 15% degradation of the County’s bulk bleach stock (~10.3% Cl₂ by wt.). Specifically:

  ✓ Existing IL WTP process: 14-15 mg/L Cl₂ (monthly averages June-August 09)
  ✓ Existing TR WTP process: 17.5-18.5 mg/L Cl₂ (monthly averages June- August 09)
  ✓ Manganese (IV) oxide filter, IL WTP: ~ 10 mg/L Cl₂
  ✓ Manganese (IV) oxide filter, TR WTP: ~ 14 mg/L Cl₂
  ✓ Electromedia filter, IL WTP: ~ 14 mg/L Cl₂

- An opinion of probable capital costs for installing a sulfide oxidation/filtration process at either the Imperial Lakes or Turner Road WTP is provided in the table below:

<table>
<thead>
<tr>
<th>Estimated Capital Cost</th>
<th>Range ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Cost*</td>
<td>$573,000 - $750,000</td>
</tr>
<tr>
<td>Masterplan Construction Costs</td>
<td>10%</td>
</tr>
<tr>
<td>Contingencies, Installation, etc.</td>
<td>35%</td>
</tr>
<tr>
<td>Total Estimated Capital</td>
<td>$831,300 - $1,088,000</td>
</tr>
<tr>
<td>$/gpd</td>
<td>$0.36 - $1.15</td>
</tr>
<tr>
<td>$/kgal Capital (installed)*</td>
<td>$0.10 - $0.32</td>
</tr>
</tbody>
</table>
An opinion of probable chemical costs for a sulfide oxidation/filtration process is provided in the table below:

<table>
<thead>
<tr>
<th></th>
<th>Imperial Lakes WTP</th>
<th>Turner Road WTP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk NaOCl 50% NaOH</td>
<td>Bulk NaOCl 50% NaOH</td>
</tr>
<tr>
<td>AADF (MGD)</td>
<td>2.3</td>
<td>0.95</td>
</tr>
<tr>
<td>Dose (mg/L)</td>
<td>5 – 14</td>
<td>12 - 20</td>
</tr>
<tr>
<td>Feed Rate (lb/day)</td>
<td>96 - 270</td>
<td>95 - 160</td>
</tr>
<tr>
<td>Chemical Cost ($/lb)</td>
<td>$0.10</td>
<td>$0.10</td>
</tr>
<tr>
<td></td>
<td>$0.26</td>
<td>$0.26</td>
</tr>
<tr>
<td></td>
<td>$/ year</td>
<td>$/ year</td>
</tr>
<tr>
<td></td>
<td>$3,500 - $9,800</td>
<td>$920</td>
</tr>
<tr>
<td></td>
<td>$3,500 - $5,800</td>
<td>$380</td>
</tr>
</tbody>
</table>

**Recommendations**

Based on the findings of this project, it is recommended that the County pursue installation of a manganese (IV) oxide media filtration process for sulfide treatment of the Imperial Lakes (IL) and Turner Road (TR) raw water supplies. The low profile manganese (IV) oxide process should be placed between the well field and the tray aeration process atop the ground storage tank. Should a new ground storage tank be constructed, it would also require a tray aerator for removal of carbon dioxide for corrosion control and addition of oxygen for palatability requirements. In addition, the media process will require a backwash pumping station and a backwash water transmission line for disposal of backwash water to the nearest wastewater conveyance system. Because the electromedia process tested by UCF is proprietary, it is recommended that the construction contract documents be prepared such that the manganese (IV) oxide media process (of which there are several available manufacturers) serve as the base bid and the proprietary process serve as an alternative bid option.
The County should provide provisions in the design for these sites space for additional unit operations in an effort to master plan for future needs. As an example, the County should plan for the possibility that the system(s) will in the future have problems in meeting requirements associated with disinfection by-products (DBPs). The formation of DBPs in a water distribution system is a function of contact time, water age, disinfection dose, temperature, bromide concentration, dissolved organic carbon and concentration. For this reason design considerations can include master planning for processes that can deal with many of the factors that impact DBP formation. Consequently, UCF recommends that the County provide master planning within the final design (that is, provide blind flanges at critical locations and allocate room on the site for future process additions) to allow for the installation of alternative processes (such as chloramines or granular activated carbon (GAC)). Moreover, the County should also incorporate provisions for future advanced corrosion control to include in the design additional chemical injector quills post-aeration for inhibitor (blended phosphate chemical) addition.

The County should also further research the use of ferrate as an alternative form of oxidation and disinfection for other facilities. Although one of the County’s objectives for this study included a requirement to limit treatment to technologies that did not require significant investment in electrical infrastructure, the limited ferrate work herein suggested that ferrate is an ideal treatment because of its ability as an oxidant, coagulant and a disinfectant. Ferrate has been shown to reduce disinfection by-product formation and could be used as an alternative to bleach oxidation; however, the use of ferrate ahead of the filtration process would require that the County conduct additional studies to evaluate the removal of floc that forms in the process, either via sedimentation, traditional filtration or a combination thereof.
8.0 APPENDIX: DATA
Table 9.1: Filtronics Electromedia® Pilot Filter Run Data

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Test Site</strong></td>
<td>IL WTP</td>
<td>IL WTP</td>
<td>IL WTP</td>
<td>IL WTP</td>
<td>TR WTP</td>
</tr>
<tr>
<td>Hydraulic Loading (gpm/sf)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Feed Cl₂ (mg/L)</td>
<td>12.4</td>
<td>13.8</td>
<td>11.0</td>
<td>11.1</td>
<td>12.9</td>
</tr>
<tr>
<td>Cl₂/S²⁻ (Molar Ratio)</td>
<td>6.4</td>
<td>7.3</td>
<td>5.5</td>
<td>5.8</td>
<td>4.5</td>
</tr>
<tr>
<td>Raw Water Total Sulfide (mg/L)</td>
<td>1.8</td>
<td>1.7</td>
<td>1.8</td>
<td>1.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Post-Treated Total Sulfide (mg/L)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cl₂ Residual [FAC] (mg/L)</td>
<td>1.78</td>
<td>2.33</td>
<td>0.85</td>
<td>0.94</td>
<td>1.02</td>
</tr>
<tr>
<td>Cl₂ Residual [TAC] (mg/L)</td>
<td>3.28</td>
<td>7.56</td>
<td>1.42</td>
<td>1.27</td>
<td>1.18</td>
</tr>
<tr>
<td>Raw pH</td>
<td>7.07</td>
<td>7.23</td>
<td>7.45</td>
<td>7.45</td>
<td>7.50</td>
</tr>
<tr>
<td>Post pH</td>
<td>7.25</td>
<td>7.30</td>
<td>7.48</td>
<td>7.49</td>
<td>7.68</td>
</tr>
<tr>
<td>Raw Temperature (°C)</td>
<td>25.8</td>
<td>24.6</td>
<td>25.2</td>
<td>25.5</td>
<td>29.5</td>
</tr>
<tr>
<td>Post Temperature (°C)</td>
<td>26.9</td>
<td>24.5</td>
<td>25.9</td>
<td>26.5</td>
<td>29.2</td>
</tr>
<tr>
<td>Raw Turbidity (NTU)</td>
<td>0.35</td>
<td>0.20</td>
<td>0.20</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>Feed Turbidity (NTU)</td>
<td>0.68</td>
<td>0.60</td>
<td>0.76</td>
<td>0.38</td>
<td>1.21</td>
</tr>
<tr>
<td>Post Turbidity (NTU)</td>
<td>0.25</td>
<td>0.10</td>
<td>0.28</td>
<td>0.14</td>
<td>0.69</td>
</tr>
<tr>
<td>Date</td>
<td>Feed Cl₂ (mg/L)</td>
<td>Cl₂/S²⁻ (Molar Ratio)</td>
<td>Total Sulfide (mg/L)</td>
<td>Cl₂ Residual (mg/L)</td>
<td>pH</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>-----------------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>Raw</td>
<td>Post</td>
<td>FAC</td>
<td>TAC</td>
<td>Raw</td>
</tr>
<tr>
<td>6/2/2009</td>
<td>-</td>
<td>5.03</td>
<td>1.3</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>IL WTP</td>
<td>8.35</td>
<td>2.1</td>
<td>&lt;0.1</td>
<td>7.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Well #2</td>
<td>9.71</td>
<td>2.4</td>
<td>0.2</td>
<td>7.3</td>
<td>0.2</td>
</tr>
<tr>
<td>18.18</td>
<td>4.6</td>
<td>&lt;0.1</td>
<td>0.29</td>
<td>7.3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>22.69</td>
<td>5.7</td>
<td>&lt;0.1</td>
<td>1.75</td>
<td>7.4</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>27.16</td>
<td>6.8</td>
<td>&lt;0.1</td>
<td>0.35</td>
<td>7.5</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>30.57</td>
<td>7.7</td>
<td>&lt;0.1</td>
<td>0.75</td>
<td>7.5</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>6/4/2009</td>
<td>-</td>
<td>2.23</td>
<td>0.6</td>
<td>1.6</td>
<td>0.5</td>
</tr>
<tr>
<td>IL WTP</td>
<td>6.27</td>
<td>1.8</td>
<td>0.7</td>
<td>0.49</td>
<td>0.03</td>
</tr>
<tr>
<td>Well #2</td>
<td>10.68</td>
<td>3.0</td>
<td>&lt;0.1</td>
<td>2.25</td>
<td>0.64</td>
</tr>
<tr>
<td>16.51</td>
<td>4.7</td>
<td>&lt;0.1</td>
<td>2.61</td>
<td>0.24</td>
<td>1.61</td>
</tr>
<tr>
<td>20.04</td>
<td>5.7</td>
<td>&lt;0.1</td>
<td>3.72</td>
<td>0.19</td>
<td>4.75</td>
</tr>
<tr>
<td>24.88</td>
<td>7.0</td>
<td>&lt;0.1</td>
<td>0.71</td>
<td>0.19</td>
<td>0.72</td>
</tr>
<tr>
<td>28.89</td>
<td>8.2</td>
<td>&lt;0.1</td>
<td>1.60</td>
<td>0.23</td>
<td>13.0</td>
</tr>
<tr>
<td>33.24</td>
<td>9.4</td>
<td>&lt;0.1</td>
<td>0.63</td>
<td>0.24</td>
<td>15.2</td>
</tr>
<tr>
<td>6/11/2009</td>
<td>-</td>
<td>4.98</td>
<td>1.3</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>IL WTP</td>
<td>9.03</td>
<td>2.4</td>
<td>0.6</td>
<td>0.14</td>
<td>0.85</td>
</tr>
<tr>
<td>Well #2</td>
<td>12.40</td>
<td>3.3</td>
<td>&lt;0.1</td>
<td>3.06</td>
<td>0.52</td>
</tr>
<tr>
<td>13.36</td>
<td>3.6</td>
<td>&lt;0.1</td>
<td>0.70</td>
<td>0.39</td>
<td>0.56</td>
</tr>
<tr>
<td>14.59</td>
<td>3.9</td>
<td>&lt;0.1</td>
<td>0.63</td>
<td>0.23</td>
<td>1.77</td>
</tr>
<tr>
<td>19.14</td>
<td>5.1</td>
<td>&lt;0.1</td>
<td>0.68</td>
<td>0.11</td>
<td>4.53</td>
</tr>
<tr>
<td>6/16/2009</td>
<td>-</td>
<td>4.91</td>
<td>1.1</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>IL WTP</td>
<td>9.73</td>
<td>2.2</td>
<td>0.80</td>
<td>0.30</td>
<td>0.09</td>
</tr>
<tr>
<td>Well #2</td>
<td>11.12</td>
<td>2.5</td>
<td>&lt;0.06</td>
<td>0.01</td>
<td>0.35</td>
</tr>
<tr>
<td>13.42</td>
<td>3.0</td>
<td>&lt;0.1</td>
<td>0.69</td>
<td>0.16</td>
<td>0.22</td>
</tr>
<tr>
<td>16.99</td>
<td>3.8</td>
<td>&lt;0.1</td>
<td>0.36</td>
<td>0.11</td>
<td>2.15</td>
</tr>
<tr>
<td>20.21</td>
<td>4.6</td>
<td>&lt;0.1</td>
<td>0.52</td>
<td>0.13</td>
<td>3.25</td>
</tr>
<tr>
<td>21.61</td>
<td>4.9</td>
<td>&lt;0.1</td>
<td>0.25</td>
<td>0.14</td>
<td>1.59</td>
</tr>
<tr>
<td>6/16/2009</td>
<td>-</td>
<td>15.56</td>
<td>3.9</td>
<td>1.8</td>
<td>1.0</td>
</tr>
<tr>
<td>IL WTP</td>
<td>20.37</td>
<td>5.1</td>
<td>0.34</td>
<td>0.03</td>
<td>1.80</td>
</tr>
<tr>
<td>Well #2</td>
<td>24.64</td>
<td>6.2</td>
<td>0.34</td>
<td>0.13</td>
<td>3.15</td>
</tr>
<tr>
<td>29.28</td>
<td>7.4</td>
<td>&lt;0.1</td>
<td>0.17</td>
<td>0.16</td>
<td>8.20</td>
</tr>
<tr>
<td>6/18/2009</td>
<td>-</td>
<td>1.2</td>
<td>1.9</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>IL WTP</td>
<td>2.44</td>
<td>0.6</td>
<td>0.06</td>
<td>0.11</td>
<td>1.4</td>
</tr>
<tr>
<td>Well #2</td>
<td>4.81</td>
<td>1.1</td>
<td>0.42</td>
<td>0.04</td>
<td>1.2</td>
</tr>
<tr>
<td>6.56</td>
<td>1.6</td>
<td>0.34</td>
<td>0.06</td>
<td>0.25</td>
<td>0.85</td>
</tr>
<tr>
<td>9.86</td>
<td>2.3</td>
<td>0.34</td>
<td>0.07</td>
<td>0.51</td>
<td>0.6</td>
</tr>
<tr>
<td>10.52</td>
<td>2.5</td>
<td>&lt;0.05</td>
<td>1.27</td>
<td>0.04</td>
<td>0.27</td>
</tr>
<tr>
<td>14.18</td>
<td>3.4</td>
<td>&lt;0.05</td>
<td>0.56</td>
<td>0.07</td>
<td>2.68</td>
</tr>
<tr>
<td>16.61</td>
<td>4.0</td>
<td>&lt;0.05</td>
<td>0.39</td>
<td>0.04</td>
<td>3.33</td>
</tr>
</tbody>
</table>
### Table 9.3: H&T, INC. Manganese (IV) Oxide Pilot Filter Run Data

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Site</td>
<td>IL WTP</td>
<td>IL WTP</td>
<td>IL WTP</td>
<td>IL WTP</td>
<td>TR WTP</td>
</tr>
<tr>
<td>Hyd. Loading (gpm/sf)</td>
<td>5 10</td>
<td>5 7.5</td>
<td>11.8 10 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw Total Sulfide (mg/L)</td>
<td>1.6 1.7</td>
<td>-</td>
<td>1.5 2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed Cl₂ (mg/L)</td>
<td>5.2 5.4</td>
<td>6.3 5.6</td>
<td>5.3 13.2 14.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂/S²⁻ (mol/mol)</td>
<td>2.9 2.9</td>
<td>3.6 3.2</td>
<td>3.2 4.6   5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post Total Sulfide (mg/L)</td>
<td>&lt;0.1 &lt;0.1</td>
<td>&lt;0.1 &lt;0.1</td>
<td>&lt;0.1 &lt;0.1 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂ Residual [FAC] (mg/L)</td>
<td>1.23 1.06</td>
<td>1.07 1.15</td>
<td>0.72 1.38 2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂ Residual [TC] (mg/L)</td>
<td>1.48 1.63</td>
<td>1.29 1.24</td>
<td>1.47 1.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.09 0.12</td>
<td>0.01 0.06</td>
<td>0.07 0.77 0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed Ca²⁺ (mg/L)</td>
<td>43.3 44.2</td>
<td>45.1 44.7</td>
<td>45.3 45.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post Ca²⁺ (mg/L)</td>
<td>- 44.1</td>
<td>45.0 44.4</td>
<td>44.8 45.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed Mg²⁺ (mg/L)</td>
<td>12.7 12.9</td>
<td>13.1 12.9</td>
<td>12.9 12.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post Mg²⁺ (mg/L)</td>
<td>- 13.0</td>
<td>12.8 13.0</td>
<td>12.8 12.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed Fe²⁺ (mg/L)</td>
<td>0.012 0.011</td>
<td>0.008 0.012</td>
<td>0.023 0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post Fe²⁺ (mg/L)</td>
<td>- &lt;0.0003</td>
<td>0.0003 0.0003</td>
<td>0.0055 0.0007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed Mn²⁺ (mg/L)</td>
<td>0.026 0.0042</td>
<td>0.048 0.0092</td>
<td>0.026 0.0016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post Mn²⁺ (mg/L)</td>
<td>- 0.0040</td>
<td>0.0036 0.0022</td>
<td>0.0038 0.0019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed SO₄⁻ (mg/L)</td>
<td>2.63 2.97</td>
<td>2.84 2.93</td>
<td>3.04 5.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post SO₄⁻ (mg/L)</td>
<td>- 2.63</td>
<td>2.67 3.02</td>
<td>2.61 4.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed TOC (mg/L)</td>
<td>0.80 0.85</td>
<td>0.86 0.84</td>
<td>0.88 1.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post TOC (mg/L)</td>
<td>- 0.79</td>
<td>0.73 0.74</td>
<td>0.89 1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Date</td>
<td>Raw pH</td>
<td>Turbidity (NTU)</td>
<td>Date</td>
<td>Raw pH</td>
<td>Turbidity (NTU)</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
<td>-----------------</td>
<td>------------</td>
<td>--------</td>
<td>-----------------</td>
</tr>
<tr>
<td></td>
<td>Raw</td>
<td>GST</td>
<td>HT</td>
<td>POE</td>
<td>Raw</td>
</tr>
<tr>
<td>6/23/2009</td>
<td>7.4</td>
<td>0.48</td>
<td>7.4</td>
<td>8.9</td>
<td>13.1</td>
</tr>
<tr>
<td>IL WTP Well #1</td>
<td>7.2</td>
<td>1.91</td>
<td>6.8</td>
<td>5.6</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.57</td>
<td>5.3</td>
<td>5.1</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.27</td>
<td>5.0</td>
<td>5.7</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0.89</td>
<td>5.4</td>
<td>5.3</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.36</td>
<td>5.3</td>
<td>4.9</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.29</td>
<td>5.7</td>
<td>4.5</td>
<td>4.9</td>
</tr>
<tr>
<td>Average =</td>
<td>7.3</td>
<td>0.68</td>
<td>5.85</td>
<td>5.70</td>
<td>7.83</td>
</tr>
<tr>
<td>6/25/2009</td>
<td>7.4</td>
<td>0.45</td>
<td>4.9</td>
<td>10.5</td>
<td>10.9</td>
</tr>
<tr>
<td>IL WTP Well #1</td>
<td>6.9</td>
<td>0.28</td>
<td>6.4</td>
<td>7.6</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>0.45</td>
<td>7.4</td>
<td>6.7</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.25</td>
<td>5.8</td>
<td>5.8</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>6.9</td>
<td>0.21</td>
<td>5.5</td>
<td>5.2</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.15</td>
<td>6.0</td>
<td>6.9</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>0.17</td>
<td>4.7</td>
<td>5.4</td>
<td>6.5</td>
</tr>
<tr>
<td>Average =</td>
<td>7.0</td>
<td>0.28</td>
<td>5.66</td>
<td>6.62</td>
<td>8.67</td>
</tr>
<tr>
<td>6/30/2009</td>
<td>7.48</td>
<td>0.11</td>
<td>6.3</td>
<td>8.8</td>
<td>9.4</td>
</tr>
<tr>
<td>IL WTP Well #1</td>
<td>7.31</td>
<td>0.30</td>
<td>4.7</td>
<td>6.3</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>7.29</td>
<td>0.19</td>
<td>4.6</td>
<td>6.4</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>7.23</td>
<td>0.04</td>
<td>4.3</td>
<td>5.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Average =</td>
<td>7.3</td>
<td>0.16</td>
<td>4.96</td>
<td>6.80</td>
<td>6.57</td>
</tr>
<tr>
<td>7/7/2009</td>
<td>7.48</td>
<td>0.11</td>
<td>6.3</td>
<td>8.8</td>
<td>9.4</td>
</tr>
<tr>
<td>IL WTP Well #1</td>
<td>7.31</td>
<td>0.30</td>
<td>4.7</td>
<td>6.3</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>7.29</td>
<td>0.19</td>
<td>4.6</td>
<td>6.4</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>7.23</td>
<td>0.04</td>
<td>4.3</td>
<td>5.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Average =</td>
<td>-</td>
<td>0.33</td>
<td>7.52</td>
<td>7.26</td>
<td>7.00</td>
</tr>
</tbody>
</table>
Table 9.5: Turbidity Summary Statistics - IL WTP Well #1

<table>
<thead>
<tr>
<th>Statistical Parameter</th>
<th>Raw pH</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>GST</td>
</tr>
<tr>
<td>IL Well # 1 Average =</td>
<td>7.3</td>
<td>0.33</td>
</tr>
<tr>
<td>IL Well # 2 Geo. Mean =</td>
<td>-</td>
<td>0.26</td>
</tr>
<tr>
<td>IL Well # 1 St. Dev. =</td>
<td>-</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Table 9.6: Existing System Turbidity Data- IL WTP Well #2

<table>
<thead>
<tr>
<th>Date</th>
<th>Raw pH</th>
<th>Turbidity (NTU)</th>
<th>Raw</th>
<th>GST</th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/2/2009</td>
<td>-</td>
<td>-</td>
<td>0.33</td>
<td>7.5</td>
<td>8.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>0.33</td>
<td>7.5</td>
<td>8.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>0.18</td>
<td>6.7</td>
<td>7.0</td>
<td>7.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.23</td>
<td>8.9</td>
<td>9.1</td>
<td>9.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.34</td>
<td>9.2</td>
<td>9.2</td>
<td>9.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.18</td>
<td>8.4</td>
<td>9.0</td>
<td>8.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.18</td>
<td>8.3</td>
<td>7.0</td>
<td>8.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.02</td>
<td>8.2</td>
<td>9.4</td>
<td>7.0</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>7.4</td>
<td>0.22</td>
<td>8.18</td>
<td>8.41</td>
<td>8.38</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Date</th>
<th>Raw pH</th>
<th>Turbidity (NTU)</th>
<th>Raw</th>
<th>GST</th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/4/2009</td>
<td>-</td>
<td>-</td>
<td>0.23</td>
<td>6.4</td>
<td>10.2</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.41</td>
<td>7.8</td>
<td>8.1</td>
<td>8.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.49</td>
<td>8.6</td>
<td>8.9</td>
<td>8.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.50</td>
<td>8.6</td>
<td>8.4</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.24</td>
<td>8.4</td>
<td>9.5</td>
<td>8.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.19</td>
<td>8.5</td>
<td>8.7</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.19</td>
<td>7.7</td>
<td>8.3</td>
<td>9.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.19</td>
<td>7.6</td>
<td>8.9</td>
<td>8.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.24</td>
<td>7.8</td>
<td>8.9</td>
<td>8.3</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>7.5</td>
<td>0.30</td>
<td>7.92</td>
<td>8.89</td>
<td>8.52</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Date</th>
<th>Raw pH</th>
<th>Turbidity (NTU)</th>
<th>Raw</th>
<th>GST</th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/11/2009</td>
<td>7.3</td>
<td>0.70</td>
<td>7.1</td>
<td>10.6</td>
<td>7.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>0.14</td>
<td>7.9</td>
<td>8.4</td>
<td>8.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.12</td>
<td>8.0</td>
<td>9.3</td>
<td>8.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.04</td>
<td>8.5</td>
<td>8.3</td>
<td>8.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>0.39</td>
<td>7.7</td>
<td>8.6</td>
<td>8.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.23</td>
<td>7.9</td>
<td>7.9</td>
<td>8.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.11</td>
<td>9.2</td>
<td>9.2</td>
<td>7.4</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>7.3</td>
<td>0.25</td>
<td>8.04</td>
<td>8.90</td>
<td>8.07</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Date</th>
<th>Raw pH</th>
<th>Turbidity (NTU)</th>
<th>Raw</th>
<th>GST</th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/12/2009</td>
<td>7.3</td>
<td>0.27</td>
<td>6.9</td>
<td>8.6</td>
<td>9.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>0.27</td>
<td>8.1</td>
<td>9.1</td>
<td>9.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>0.01</td>
<td>8.4</td>
<td>9.0</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>0.16</td>
<td>7.9</td>
<td>9.1</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>0.11</td>
<td>8.6</td>
<td>8.5</td>
<td>8.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.13</td>
<td>7.7</td>
<td>8.0</td>
<td>8.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.14</td>
<td>8.2</td>
<td>8.6</td>
<td>8.5</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>7.2</td>
<td>0.16</td>
<td>7.94</td>
<td>8.61</td>
<td>8.62</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Date</th>
<th>Raw pH</th>
<th>Turbidity (NTU)</th>
<th>Raw</th>
<th>GST</th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/16/2009</td>
<td>7.3</td>
<td>0.13</td>
<td>8.5</td>
<td>9.0</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.10</td>
<td>8.1</td>
<td>8.8</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>0.29</td>
<td>8.0</td>
<td>10.8</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.01</td>
<td>8.1</td>
<td>8.1</td>
<td>8.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.03</td>
<td>8.1</td>
<td>9.1</td>
<td>9.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.13</td>
<td>8.6</td>
<td>9.4</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.16</td>
<td>8.7</td>
<td>8.4</td>
<td>11.0</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>7.1</td>
<td>0.12</td>
<td>8.39</td>
<td>9.11</td>
<td>9.21</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Date</th>
<th>Raw pH</th>
<th>Turbidity (NTU)</th>
<th>Raw</th>
<th>GST</th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/18/2009</td>
<td>7.2</td>
<td>0.06</td>
<td>7.5</td>
<td>8.2</td>
<td>8.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>0.06</td>
<td>7.7</td>
<td>9.5</td>
<td>8.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.25</td>
<td>8.1</td>
<td>12.1</td>
<td>8.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.11</td>
<td>7.5</td>
<td>8.2</td>
<td>7.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.04</td>
<td>7.7</td>
<td>8.2</td>
<td>9.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.07</td>
<td>8.2</td>
<td>8.1</td>
<td>8.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>0.04</td>
<td>7.2</td>
<td>7.4</td>
<td>8.3</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>7.2</td>
<td>0.09</td>
<td>7.62</td>
<td>8.89</td>
<td>8.57</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Date</th>
<th>Raw pH</th>
<th>Turbidity (NTU)</th>
<th>Raw</th>
<th>GST</th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/9/2009</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>6.92</td>
<td>7.80</td>
<td>7.24</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>0.27</td>
<td>6.95</td>
<td>7.38</td>
<td>6.96</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>0.31</td>
<td>7.45</td>
<td>7.17</td>
<td>7.18</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>0.19</td>
<td>7.43</td>
<td>6.39</td>
<td>7.12</td>
</tr>
<tr>
<td>Average</td>
<td>-</td>
<td>0.28</td>
<td>7.19</td>
<td>7.18</td>
<td>7.12</td>
<td></td>
</tr>
</tbody>
</table>

Average =
Table 9.7: Turbidity Summary Statistics- IL WTP Well #2

<table>
<thead>
<tr>
<th>Statistical Parameters</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>GST</td>
</tr>
<tr>
<td>IL Well # 2 Average</td>
<td>7.3</td>
<td>0.20</td>
</tr>
<tr>
<td>IL Well # 2 Geo. Mean</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>IL Well # 2 St. Dev.</td>
<td>0.14</td>
<td>0.64</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL Well # 2 Average</td>
<td>8.67</td>
<td>8.46</td>
</tr>
<tr>
<td>IL Well # 2 Geo. Mean</td>
<td>8.62</td>
<td>8.42</td>
</tr>
<tr>
<td>IL Well # 2 St. Dev.</td>
<td>0.98</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Table 9.8: Existing System Turbidity- TR WTP

<table>
<thead>
<tr>
<th>Date</th>
<th>Turbidity (NTU)</th>
<th>Raw</th>
<th>GST</th>
<th>HT</th>
<th>POE</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/14/09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TR WTP</td>
<td></td>
<td>0.25</td>
<td>17.40</td>
<td>17.25</td>
<td>11.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.10</td>
<td>16.64</td>
<td>15.89</td>
<td>10.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>16.34</td>
<td>16.57</td>
<td>10.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td>16.57</td>
<td>15.36</td>
<td>10.54</td>
</tr>
<tr>
<td>Average  =</td>
<td>0.13</td>
<td>16.74</td>
<td>16.27</td>
<td>10.93</td>
<td></td>
</tr>
<tr>
<td>7/16/09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TR WTP</td>
<td></td>
<td>0.11</td>
<td>15.88</td>
<td>15.52</td>
<td>13.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
<td>16.17</td>
<td>16.47</td>
<td>13.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11</td>
<td>15.45</td>
<td>17.12</td>
<td>12.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>16.03</td>
<td>17.27</td>
<td>12.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td>16.10</td>
<td>16.76</td>
<td>12.02</td>
</tr>
<tr>
<td>Average  =</td>
<td>0.12</td>
<td>15.93</td>
<td>16.63</td>
<td>12.97</td>
<td></td>
</tr>
</tbody>
</table>
Table 9.9: Turbidity Summary Statistics- TR WTP

<table>
<thead>
<tr>
<th>Statistical Parameters</th>
<th>Turbidity (NTU)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>GST</td>
<td>HT</td>
<td>POE</td>
</tr>
<tr>
<td>TR Average =</td>
<td>0.13</td>
<td>16.29</td>
<td>16.47</td>
<td>12.07</td>
</tr>
<tr>
<td>TR Geo. Mean =</td>
<td>0.10</td>
<td>16.28</td>
<td>16.45</td>
<td>12.01</td>
</tr>
<tr>
<td>TR St. Dev. =</td>
<td>0.08</td>
<td>0.55</td>
<td>0.73</td>
<td>1.21</td>
</tr>
</tbody>
</table>
Table 9.10: MnO₂ Filter- 24 HR Simulated Distribution System THM Formation

<table>
<thead>
<tr>
<th>Well Site (gpm/sf)</th>
<th>TOC (mg/L)</th>
<th>pH</th>
<th>T (°C)</th>
<th>Cl₂ Dose (mg/L)</th>
<th>t (days)</th>
<th>FAC Residual (mg/L)</th>
<th>CHCl₃</th>
<th>BrCl₂CH</th>
<th>Br₂CICH</th>
<th>Br₃CH</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL WTP (5)</td>
<td>0.7</td>
<td>≈7.4</td>
<td>≈26</td>
<td>6.3</td>
<td>1</td>
<td>0.4</td>
<td>7.8</td>
<td>2.2</td>
<td>4.4</td>
<td>0.22</td>
<td>14.6</td>
</tr>
<tr>
<td>IL WTP (7.5)</td>
<td>0.7</td>
<td>≈7.4</td>
<td>≈26</td>
<td>5.6</td>
<td>1</td>
<td>0.3</td>
<td>10.5</td>
<td>2.8</td>
<td>5.9</td>
<td>0.28</td>
<td>19.5</td>
</tr>
<tr>
<td>IL WTP (10)</td>
<td>0.8</td>
<td>≈7.4</td>
<td>≈26</td>
<td>5.4</td>
<td>&lt;0.10</td>
<td>9.3</td>
<td>2.4</td>
<td>4.6</td>
<td>&lt;0.15</td>
<td>0.29</td>
<td>16.7</td>
</tr>
<tr>
<td>TR WTP (10)</td>
<td>1.0</td>
<td>≈7.5</td>
<td>≈29</td>
<td>13.2</td>
<td>1</td>
<td>0.5</td>
<td>10.1</td>
<td>1.3</td>
<td>3.6</td>
<td>&lt;0.15</td>
<td>15.0</td>
</tr>
<tr>
<td>Well Site (gpm/sf)</td>
<td>TOC (mg/L)</td>
<td>pH</td>
<td>T (°C)</td>
<td>Cl₂ Dose (mg/L)</td>
<td>t (days)</td>
<td>FAC Residual (mg/L)</td>
<td>MCAA</td>
<td>DCAA</td>
<td>TCAA</td>
<td>DBAA</td>
<td>MBAA</td>
</tr>
<tr>
<td>------------------</td>
<td>------------</td>
<td>----</td>
<td>--------</td>
<td>-----------------</td>
<td>--------</td>
<td>---------------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>IL WTP (5)</td>
<td>-</td>
<td>≥7.4</td>
<td>≥26</td>
<td>5.2</td>
<td>1</td>
<td>1.2</td>
<td>5.1</td>
<td>5.2</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>IL WTP (5)</td>
<td>0.7</td>
<td>≥7.4</td>
<td>≥26</td>
<td>6.3</td>
<td>1</td>
<td>&lt;2</td>
<td>5.2</td>
<td>2.9</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
</tr>
<tr>
<td>IL WTP (7.5)</td>
<td>0.7</td>
<td>≥7.4</td>
<td>≥26</td>
<td>5.6</td>
<td>1</td>
<td>&lt;1</td>
<td>4.1</td>
<td>1.9</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>TR WTP (10)</td>
<td>1.0</td>
<td>≥7.5</td>
<td>≥29</td>
<td>13.2</td>
<td>1</td>
<td>0.5</td>
<td>4.6</td>
<td>5.0</td>
<td>4.3</td>
<td>1.6</td>
<td>&lt;0.4</td>
</tr>
</tbody>
</table>
9.0 REFERENCES


