

THE DESIGN OF A DESALINATION PRETREATMENT SYSTEM FOR
BRACKISH GROUNDWATER

A Major Qualifying Project Report
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1. Drinking water
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ABSTRACT

The goal of this project was to design an affordable, low-energy, and cost effective pretreatment process for brackish water that would subsequently be treated by reverse osmosis or electro dialysis reversal desalination to produce potable drinking water. The focus of the project was the removal of hardness, iron, manganese, and aluminum, which are primary contributors to membrane fouling. Alternatives for the removal of these constituents were tested at the bench scale. Based on results, a flow-through prototype system consisting of precipitative softening and ion exchange was constructed, and a full scale pretreatment system was designed.

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This project was completed as a part of the Waste-management, Education, and Research Consortium (WERC) environmental design competition sponsored by New Mexico State University in Las Cruces, New Mexico. Contestants design solutions for real-world problems while developing fully operational bench-scale solutions that are presented to a panel of judges comprised of environmental professionals. The contest is held every spring, and consists of several environmental problems that participants develop solutions to. Brackish water pretreatment was one of these problems. The project was presented and the prototype treatment system was demonstrated at New Mexico State University from April 5 – 8, 2009.

MQP CAPSTONE DESIGN STATEMENT

For this project, our group designed a pretreatment system for brackish groundwater to be used in conjunction with membrane desalination processes. The pretreatment system was intended to remove iron, manganese, aluminum and hardness. In order to determine the most suitable removal processes, bench scale experiments were performed to test the effectiveness of several removal options. To remove hardness, precipitative softening experiments were performed using lime, soda ash and caustic soda. For iron and manganese removal, oxidation with chlorine, potassium permanganate and ozone were tested. Ion exchange was also tested using a strong cation exchange media for removal of all constituents. Results were evaluated in order to determine which treatment options were most suitable for the given feed water parameters and effluent quality specifications.

After selecting appropriate constituent removal mechanisms, our group designed a prototype flow-through pretreatment system to continuously treat a feed stream at a flow rate of 2.5 gallons per hour. The system consisted of a mixing tank, settling basin, rapid sand filter and ion exchange column with in-line static mixers for chemical addition. After testing the prototype for effective reduction of contaminants, the system was scaled up to the size of a small municipal groundwater system with a total capacity of 1 million gallons per day (MGD). In order to scale up the treatment system, standard water treatment design equations and loading rates were used. Multiple treatment trains were provided in the full scale design to accommodate for units to be taken off-line for maintenance and repairs. Finally, a cost analysis of the full-size system was performed, including capital and operation and maintenance costs. It was concluded that the high capital cost of the pretreatment system was offset by the decrease in operational costs and increase in the lifespan of membrane processes.

EXECUTIVE SUMMARY

Reverse osmosis (RO) and electro dialysis reversal (EDR) are membrane processes for the removal of dissolved constituents from a water source. Both technologies are employed for drinking water desalination because of their ability to remove sodium ions. RO is a pressure driven system and its efficiency is greatly reduced by foulants precipitating within its pores, requiring higher energy input. On average, existing brackish water desalination facilities require 1,300 – 3,250 kWh of energy per acre-foot² (1 acre-foot = approximately 326,000 gallons). Although EDR is not pressure driven, organic and inorganic fouling is a concern for EDR systems as well. Therefore, removing constituents that contribute to fouling prior to RO and EDR extends the lifespan of membrane processes and decreases operating costs.

In this project, our goal was to provide an affordable, low-energy and cost effective pretreatment process for the Tularosa Basin Pilot Desalination Facility (TBPDP) in Alamogordo, New Mexico. The facility currently utilizes RO and EDR to treat brackish groundwater. The primary foulants that contribute to membrane fouling found in the TBPDP feed water are hardness, iron, manganese, and aluminum. Initial and target contaminant concentrations are presented in Table 1. Aluminum, iron, and manganese target concentrations were provided by TBPDP, while the hardness target of 300 ppm as CaCO₃ was selected as a concentration that does not cause excessive fouling of membranes.

Table 1 Initial and Target Contaminant Concentrations

Constituent	Untreated Influent Concentration (ppm)	Target Concentration for RO (ppm)
Aluminum	0.4	0.1
Iron	0.5	0.1
Manganese	0.3	0.05
Hardness as CaCO ₃	2649	300

Multiple unit processes for removal of hardness, Fe, Mn and Al were investigated. The treatment options are provided in Table 2 and briefly described in the following sections. Each process was tested independently at the bench scale and qualitatively evaluated based on cost and efficiency.

Table 2 Treatment Options

Alternatives	Constituent	Advantages	Disadvantages
<i>Precipitative Softening</i>			
Lime/ Soda ash	Hardness	- Inexpensive - Decreases total dissolved solids	- Both chemicals needed when carbonate and non-carbonate hardness present - More sludge generated - Storage and feeding problems (lime)
Caustic soda	Hardness	- Removes both types of hardness - Generates less sludge - Easy to store	- Expensive - Increases total dissolved solids
<i>Oxidation</i>			
Chlorine	Fe and Mn	- Inexpensive - Easy to dose	- Long reaction time - Trihalomethane formation
Potassium Permanganate	Fe and Mn	- Efficient - Lower capital costs - Short reaction time	- More expensive - Need careful dose control - May compromise filter performance
Ozone	Fe and Mn	- Effective in presence of humic materials - Short reaction time - No chemicals	- High energy - Onsite generation - Need careful dose control
<i>Activated Carbon Adsorption</i>			
GAC	Al	- Acts as filter - Organics removal	- Requires regeneration
PAC	Al	- Organics removal	- Filtering required
<i>Ion Exchange</i>			
Ion Exchange	Hardness Fe, Mn, and Al	- Removes all constituents - Can handle fluctuating flows - High quality effluent - Many resins available - Low energy	- Al removal requires slightly acidic feed water - Highly concentrated waste - Low efficiency with high total dissolved solids

The water at the TBPFD contains 2650 ppm of hardness as CaCO₃, 1400 ppm of which is in the carbonate form. Lime and soda ash were tested to remove carbonate and non-carbonate hardness, respectively. Caustic soda was also tested as an option that removes both hardness types at a pH of 10. After performing laboratory experiments, it was concluded that lime or soda ash did not significantly reduce hardness beyond that achieved through pH adjustment. In addition, precipitative softening with caustic soda reduced iron and manganese concentrations simultaneously with hardness removal.

For iron and manganese precipitation, oxidation with chlorine, potassium permanganate and ozone were tested. Chlorine was effective at reducing both contaminants after a significant contact time. Potassium permanganate proved ineffective in this application, potentially due to the form of KMnO_4 from which the stock solution was produced. Ozone effectively reduced iron to the desired concentration after a relatively short contact time, but not manganese. After evaluating oxidation results, it was concluded that oxidation can be expensive and can be omitted from the pretreatment process.

Ion exchange was also tested as a hardness removal alternative. Ion exchange is a reversible chemical reaction where an ion in solution is exchanged for a similarly charged ion attached to ion exchange media. It effectively reduces hardness as well as iron and manganese at low concentrations and aluminum at slightly acidic conditions. From testing a strong cation exchange resin, it was concluded that ion exchange is a practical pretreatment technology for the TBDF, however, at the initial hardness level of 2650 ppm, frequent regeneration of resin is cost prohibitive.

After extensive research and evaluation of laboratory testing results, it was concluded that ion exchange is the most practical pretreatment option because it has the potential to remove all constituents of concern from the feed stream. To increase the efficiency of ion exchange in this application, precipitative softening using caustic soda was chosen as a preliminary treatment step. Reducing the hardness to 1000 ppm with NaOH prior to ion exchange increases the bed capacity from 38 to 100 bed volumes.

A prototype pretreatment system consisting of a mixing tank, settling basin, rapid sand filter and ion exchanger was developed for a flow rate of 2.5 gallons per hour. pH of the feed water is adjusted to 10 with NaOH in the mixing tank to allow for precipitation of some hardness, iron and manganese. After settling and filtration of the precipitates, the pH was lowered to approximately 6.5 with HCl prior to ion exchange to allow for effective removal of aluminum, which requires slightly acidic conditions. The system was tested using a prepared water sample with constituent concentrations similar to those of the TBPDF. The results of the test run are presented in Table 3. According to the test run results, the prototype system was successful at reducing all constituents to below the desired concentrations listed in Table 1.

Table 3 Prototype Test Run Results

Constituent	Initial Conc. (ppm)	Conc. after Sand Filter (ppm)	Final Conc. after Ion Exchange (ppm)
Hardness (as CaCO ₃)	2650	~500	~50
Iron	0.50	< 0.1	< 0.1
Manganese	0.37	< 0.1	<0.05
Aluminum	0.59	<0.05	<0.05

Using the results of the pretreatment system, a full-scale system with a capacity of 1 million gallons per day (MGD) was designed. In the full-scale system, multiple treatment trains were utilized to allow units to be taken off-line for backwashing, maintenance or repairs. Design parameters of the full-scale system are listed in Table 4.

Table 4 Full-Scale Design Parameters

Unit	No. of units	Flow rate	Det. Time (min)	Dimensions (ft)	Potential Material	Design considerations
Mixing tank	2	694 gpm	10	Diameter – 10 Height – 12	Concrete; HDPE	NaOH addition/storage
Settling basin	4	1 gpm/ft ²	90	Length – 30 Width – 7.8 Depth – 12	Concrete; HDPE	Manual/automatic sludge removal; Sludge disposal
Sand filter	4	4 gpm/ft ²	N/A	Length – 9 Width – 6.5	Concrete	Backwash system/waste
Ion exchange	12	N/A	5	Diameter – 4 Height - 5	Concrete; HDPE; Fiberglass	HCl addition/storage; Backwash system

Disposal of the concentrated waste is a serious concern for all water systems, but even more so for those treating brackish water. Irresponsible discharges of concentrated salt wastes contaminate receiving waters, such as rivers and lakes, make soil much less fertile, and raise concerns for long-term environmental effects of salt accumulation. Several brine disposal options were considered including municipal sewers and deep well injections. Another option suitable for arid climates is pumping the brine into solar evaporation ponds. Although this disposal method requires a large area and impervious ground cover to protect the groundwater from contamination, evaporation ponds are a suitable option for the New Mexico climate with low rainfall and steady evaporation rates.

Potential public concerns associated with construction and operation of the full-scale facility were also addressed in this project. Desalination technologies raise several concerns including energy consumption, waste disposal, and social and environmental impacts. Overall, the primary advantages of the pretreatment system are the enhanced performance and reduced operating costs of membrane processes. Factors such as meeting all federal and state regulations and providing responsible waste disposal solutions serve as additional ways to justify the need for brackish water pretreatment in the eyes of the public.

In conclusion, precipitative softening in conjunction with ion exchange was determined to be a suitable pretreatment process for brackish water desalination. The system provided high removal of fouling constituents ensuring optimum performance of membrane processes. Reducing foulants significantly increases the lifespan of RO membranes and reduces energy requirements for their operation. Although the initial capital cost of the pretreatment system was estimated to be relatively high, it was concluded that this cost was offset by the decrease in operational costs and increase in the lifespan of the membrane process. Membrane pretreatment systems such as our design help make desalination a more attractive alternative for producing potable drinking water.

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1. INTRODUCTION

Water demand in the United States has increased due to population growth, economic development, and agricultural needs. Historically, surface waters have served as the primary supply of drinking water in the country; however in arid and semi-arid inland areas with limited access to surface waters, groundwater has been recognized as a more abundant and convenient water source. In these areas, groundwaters often contain higher levels of salinity and are considered brackish. Brackish water may result from the mixing of sea water and freshwater, as in estuaries, or it can occur in brackish fossil aquifers. Whether brackish waters are used for drinking or agricultural use, salt concentrations have to be reduced using membrane processes.

Membrane processes used in desalination include reverse osmosis (RO) and electro dialysis reversal (EDR). Although membrane processes are extremely effective at removing dissolved constituents and producing a high quality effluent, they are often expensive due to high fouling rates and energy demand. An effective pretreatment system that provides constituent removal and reduces fouling potential can significantly increase the efficiency of membrane processes and reduce operation and maintenance costs. Pretreatment can encompass chemical processes, such as coagulation and oxidation, and physical processes, such as clarification and filtration. The type of pretreatment is highly dependent upon the composition of the source water.

The Tularosa Basin Pilot Desalination Facility (TBPDF) located in Alamogordo, New Mexico, is a facility that utilizes RO and EDR to treat brackish groundwater for drinking water and irrigation. This facility could benefit from a pretreatment process to improve effluent quality and extend membrane life. The main contaminants of concern at this facility are carbonate and non-carbonate hardness, aluminum, manganese, iron, and particulates. The goal of this project was to design a pretreatment process to treat brackish water at the TBPDF by removing these contaminants, thereby optimizing subsequent membrane processes.

2. BACKGROUND

Water for human consumption and daily use comes from a variety of sources, including surface waters such as lakes, rivers and oceans, and groundwaters. Most raw waters require some degree of treatment depending on their initial quality and intended application. Fresh waters typically undergo a conventional treatment process, which consists of coagulation, flocculation, sedimentation, filtration, and disinfection. In areas where fresh water supplies are limited, alternative processes can be employed for treating saline waters. This chapter presents information on source water quality, treatment regulations, and the use of membrane technologies for treatment of saline waters. The need for partial treatment of feed waters prior to entering membrane processes, as well as some pretreatment options, are also discussed.

2.1 WATER SOURCES

Public water supplies in the U.S. come mainly from surface or ground sources. In the year 2000, water withdrawals for human use in the U.S. approximated 408,000 million gallons per day (MGD), of which 85,000 MGD came from fresh groundwater sources and 323,000 MGD from surface water sources. Fresh ground and surface water withdrawals made up 85% of the total 408,000 MGD, whereas the remaining 15% came from saline sources (Hutson, 2008). Figure 1 presents the breakdown of water sources used in the U.S.

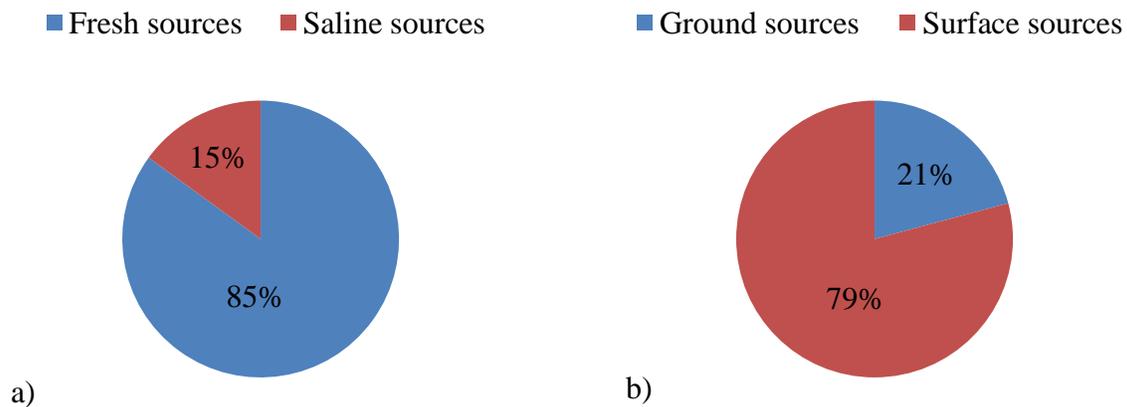


Figure 1 Breakdown of Water Sources in the United States

Historically, surface water sources served as primary suppliers of drinking water in the U.S. However, in the last fifty years, groundwater has been recognized as a more abundant and in some cases more convenient water source and its use has increased (USGS, 2000).

2.1.1 BRACKISH WATER

Brackish water contains a level of salinity between fresh and sea water. While undiluted seawater contains approximately 35,000 mg/L of total dissolved solids (TDS), brackish water contains approximately 1,000 to 15,000 mg/L TDS. Brackish water may result from the mixing of sea and fresh water, as in estuaries, or it can be produced through the engineering of dikes. Brackish water can be found in rivers, lakes, estuaries and underground; however, specific locations which contain brackish water are not easily identified (Corbitt, 1999).

The largest source of brackish water is underground. Brackish groundwater reserves are found in many parts of the world, including the United States, Canada, Mexico, Southern and Western Europe, North Africa, the Middle East, Australia, Western Africa, and South America. Well over half of the land area of the United States is underlain by saline waters, containing total dissolved solids concentrations between 1000 mg/L and 3000 mg/L (Corbitt, 1999). In coastal areas, salt water intrusion occurs primarily by lateral encroachment and by vertical upconing near discharging wells. In locations where groundwater is pumped from aquifers that are in hydraulic connection with the sea, the induced gradients may cause the migration of salt water toward a well. Groundwater withdrawals also change the patterns of groundwater flow and discharge to coastal ecosystems, which may alter the nutrient concentrations and salinity of the coastal waterways and wetlands (USGS, 2000).

Whether brackish waters are used for drinking or agricultural use, they need to be treated in order to alleviate health and environmental concerns. The treatment of saline water, referred to as desalination, utilizes membrane processes (Section 2.5 Membrane Processes for Drinking Water) that remove excess salt and other constituents from the water. In 2002, there were approximately 12,500 desalination plants in operation worldwide, 70% of them located in the Middle East (USGS, 2008). The world's largest plant in Saudi Arabia produces 128 MGD of desalted water. Currently, 12% of the world's desalinized water is produced in the Americas, with most of the plants located in the Caribbean, Florida, and California (Pantell, 1993). Although desalination treatment is relatively expensive, the demand for fresh water for both

human consumption and agricultural purposes is increasing and designing efficient brackish water treatment processes is becoming a priority (USGS, 2008).

2.2 PROBLEM STATEMENT

The goal of this project was to create a pretreatment system for brackish water to enhance the efficiency of reverse osmosis (RO) and electro dialysis reversal (EDR) by removing particulates and inorganic foulants. Specifically, the pretreatment process was designed to reduce levels of aluminum, manganese, iron, and other particulates. The project was designed to meet state and federal regulations, as well as be applicable to rural treatment systems, adaptable to various size systems, and address responsible disposal of removed contaminants. The pretreatment system was also designed to be low cost, energy efficient, and reliable, and to produce a high quality effluent with minimum reject water.

This project was completed as part of the annual WERC Environmental Design Contest, which brings together industry, government, and academia in the search for improved environmental solutions. Our particular project was to design a pretreatment process for brackish water that can be used at the Tularosa Basin Pilot Desalination Facility, located in Alamogordo, New Mexico, prior to electro dialysis reversal or reverse osmosis. In arid and semi-arid areas, such as the Tularosa Basin, there are not enough fresh water resources available to meet the population growth, economic development, and agricultural needs. The project results have the potential to enhance the performance of the Tularosa Basin Pilot Desalination Facility, and also provide further research for the Brackish Groundwater National Desalination Research Facility (BGNDRF). The mission of this facility, which opened in 2007, is to study renewable energy technologies to reduce the costs associated with desalination, develop cost effective techniques for small portable systems, and address environmental concerns for the disposal of concentrated wastes from desalination. The BGNDRF is a joint partnership between the Bureau of Reclamation, Sandia National Laboratory, and New Mexico State University. The BGNDRF was sited in the Tularosa Basin of New Mexico because of its extensive saline and brackish groundwater supply as well as the solar, wind, and geothermal potential of the region.

In this project, a pretreatment system for reverse osmosis and electro dialysis reversal was specifically designed to treat brackish water at this facility and optimize the subsequent treatment

processes at Tularosa. The contaminant levels in sample water at the Tularosa Basin Pilot Desalination Facility are provided in Table 5. Our pretreatment process was designed to reduce contaminants to the stated target treatment levels.

Table 5 Sample Water Parameters at Tularosa Basin Facility

Constituent	Untreated Concentration in Well (ppm)	Target Concentration after pretreatment (ppm)	
		EDR	RO
B	0		0.05
Ba total	0.01		
Ca total	500		
Al total	0.4	0.1	0.1
Cu total	0.058		
Fe dissolved		0.3	0.1
Fe total	0.5		
Mn dissolved		0.1	0.05
Mn total	0.3		
Hardness total as CaCO ₃	2649		
K	2.3		
Mg	340		
Na	780		
SiO ₂ reactive	22		
SiO ₂ total			
Chloride	9.5		
Sulfate	530		
Nitrite	3000		
Nitrate			
Fluoride	8.8		
Total inorganic PO ₄			
P/M alkalinity as CaCO ₃ *	1250		
Total dissolved solids	5500		
Total Organic Carbon			
pH	7.2		

* The alkalinity defined by the P alkalinity test (measure of the amount of carbonate and hydroxyl alkalinity) and the M alkalinity test (measure of the amount of carbonate, bicarbonate, and hydroxide) through titration using phenolphthalein and methyl orange indicators respectively.

2.3 U.S.EPA REGULATIONS

The following sections describe the evolution, provisions, and standards of federal drinking water regulations and the state regulations of New Mexico. A brief overview of the regulations relevant to this project is presented in this section, with an emphasis on those dealing with safe drinking water, surface water and groundwater treatment, membrane processes, and disinfection. These regulations focus on control of pathogens by setting standards and techniques for removal and inactivation, as well as mitigating by-products of disinfection.

2.3.1 SAFE DRINKING WATER ACT

The Safe Drinking Water Act (SDWA), established in 1974, was the first set of regulations that applied to all public drinking waters in the United States. It empowered the Environmental Protection Agency (EPA) to pass national drinking water regulations to ensure safe, clean public drinking water supplies. It required local, state, and federal cooperation to reduce chemical and microbial contaminants to safe levels. States retain primacy, or the right to set and enforce their own standards, as long as the EPA's national regulations are met.

Drinking water regulations include primary and secondary regulations. Primary regulations are enforceable and are designed to ensure the safety of the water and address health risks. Secondary regulations cover aesthetic characteristics of drinking water such as taste and odor and are not enforceable. Contaminant concentrations below which they have no known adverse effects on human health are termed Maximum Contaminant Level Goals (MCLGs). The primary regulations are based on concentrations that are technologically and economically feasible to achieve and are known as Maximum Contaminant Levels (MCLs). The MCLs are kept as close to MCLGs as possible. However, if the cost is too high or the technology is not efficient enough to reach a MCLG, the MCL regulation may be higher.

In addition to MCLs, the regulations may define a treatment method for a contaminant in cases where measuring the contaminant is not practical. Water systems are also required to monitor water quality in the distribution system and in consumer taps for certain contaminants. If an MCL is exceeded, the water treatment facility is obligated to notify the public of the potential health risk. Some regulations apply to certain water systems based on type, size, and water source. The EPA can issue variances to a treatment facility, allowing the effluent to contain

different concentrations of contaminants than the standard MCLs. For example, less stringent standards may be allowed for a system if it serves fewer than 3,300 people (small system variance) or if inherent characteristics of the water source make compliance with regulations unachievable (general variance). A variance or exemption cannot be issued if it poses an unreasonable risk to public health (EPA, 1974).

2.3.2 SURFACE WATER TREATMENT RULES

The Surface Water Treatment Rule (SWTR) of 1989 was promulgated to control microbial contaminants in drinking water, especially *Giardia* and viruses. The SWTR requires all treatment facilities using surface water or groundwater under the direct influence of surface water to disinfect and filter their effluent. The rule requires 4-log removal/inactivation of viruses and 3-log removal/inactivation of *Giardia lamblia*. Systems that have filtration receive a log credit for the treatment process (see Table 6; AWWA, 1999), and other water system activities can also receive credit, such as 0.5-log credit for watershed protection. The remainder of the log removal/inactivation that is not achieved through these means must be achieved through disinfection.

Table 6 Log Credits for Removal Of Pathogens By Filtration Under The Surface Water Treatment Rule (AWWA, 1999)

Filtration Type	Viruses	Giardia	Cryptosporidium
Conventional	2.0	2.5	3.0
Direct	1.0	2.0	2.0
Slow Sand	2.0	2.0	2.0
Diatomaceous earth	1.0	2.0	2.0

*Must meet turbidity and HPC requirements (or demonstrate turbidity/particle count performance) to receive credit

The SWTR also includes treatment technique and plant management requirements. To ensure adequate microbial protection in water distribution systems, water systems are required to provide continuous disinfection of the drinking water entering the distribution system and to maintain a detectable disinfectant level within the distribution system. The water entering the distribution system must contain 0.2 mg/L or higher of residual disinfectant and the disinfectant must be detectable throughout the distribution system. The SWTR also requires finished water

storage facilities to be covered and the treatment plant staff to be qualified. Systems using conventional or direct filtration must also monitor individual filters and establish Combined Filter Effluent (CFE) limits (EPA, 1989).

The Interim Enhanced Surface Water Treatment Rule (IESWTR) was built on the SWTR to protect public health against microbial contaminants, particularly *Cryptosporidium*, which can cause the gastrointestinal illness cryptosporidiosis. It was published in 1998 and applied to all water treatment systems serving 10,000 people or more. The major provisions of the IESWTR included more stringent turbidity requirements, disinfection profiling and benchmarking, an MCLG of zero for *Cryptosporidium*, and 2-log removal of *Cryptosporidium* for systems that filter (EPA, 1998). The Long Term 1 Enhanced Surface Water Treatment Rule (LT1 ESWTR), published in 2002, extended the IESWTR to small systems serving fewer than 10,000 people (EPA, 2002). The Long Term 2 Enhanced Surface Water Treatment Rule (EPA), published in 2006, focused on water systems that have a greater risk of *Cryptosporidium* contamination. It requires treatment facilities to monitor the average concentration of *Cryptosporidium* in the source water, unless 5.5-log removal is achieved in the system, to determine if the source is at risk and if additional treatment is necessary. If required, the additional treatment is determined by the source water concentration of *Cryptosporidium* (EPA, 2006a).

2.3.3 GROUNDWATER RULE

Groundwater was thought to be free of common microbial contaminants until recent concerns arose based on waterborne disease outbreaks in groundwater systems. The Groundwater Rule (GWR) targets the removal of bacteria and viruses from groundwater sources and establishes methods of determining which systems are at risk for fecal contamination. The GWR requires systems that have detected fecal indicators to take corrective action. It also requires states to conduct sanitary surveys every three years and systems serving over 3,300 people must continually monitor disinfection (EPA, 2006b).

2.3.4 DISINFECTION REGULATIONS

Disinfection byproducts (DBPs) are products of reactions between organic matter and chemical disinfectants. These byproducts pose health risks and are suspected carcinogens. DBPs were first regulated in 1989 when the MCL for total trihalomethanes (THMs) was set to 0.10 mg/L. The Stage 1 Disinfectants and Disinfection Byproducts Rule (1998) was promulgated to control the concentration of DBPs in drinking water, which could rise with increased disinfectant levels to meet the IESWTR. The regulated DBPs include total trihalomethanes (TTHM) at 0.08 mg/L, five haloacetic acids (HAA5) at 0.06 mg/L, bromate and chlorite. These regulations also establish maximum concentrations of chlorine, chloramines and chlorine dioxide disinfectants (EPA, 1998b). In 2006, the Stage 2 Disinfectants and Disinfection Byproducts Rule further controlled TTHM and HAA5 exposure by requiring locational running annual averages (LRAA) rather than system wide averages for disinfection byproduct monitoring (EPA, 2006c).

2.3.5 MEMBRANE REGULATIONS

Regulations pertaining to membrane processes are included in the Long Term 2 Enhanced Surface Water Treatment Rule, published in 2006. The LT2ESWTR awards *Cryptosporidium* log removal credit to facilities that use membrane filtration under certain conditions that require continuous testing of the membranes to verify their performance. EPA requires membrane facilities to conduct the following testing procedures to verify compliance with the LT2ESWTR:

1. Challenge Testing
2. Direct Integrity Testing
3. Continuous Indirect Integrity Monitoring

Challenge testing is only performed once in order to demonstrate the product's ability to remove *Cryptosporidium* and assign its maximum log removal credit. Direct Integrity Testing and Continuous Indirect Integrity Monitoring are conducted every day to verify and monitor the pathogen barrier is functioning properly throughout the operation period of the membrane. Descriptions and key points of each testing procedure are summarized in Table 7 (EPA, 1996).

Table 7 Membrane Testing Procedures for *Cryptosporidium* Log Removal (EPA, 1996)

Test	Description	Purpose	Applicability	Frequency
Challenge Testing	One-time, product-specific test event designed to demonstrate <i>Cryptosporidium</i> removal ability	<u>Demonstrate</u> <i>Cryptosporidium</i> removal efficiency of the product and establish the maximum removal credit the product is eligible to receive	Membrane product	Once
Direct Integrity Testing	Physical testing applied directly to the pathogen barrier associated with a membrane unit in order to identify and isolate integrity breaches	<u>Verify</u> that the membrane pathogen barrier has no integrity breaches that would compromise the ability to achieve the <i>Cryptosporidium</i> removal credit awarded by the State on an ongoing basis during operation	Membrane units in a site-specific membrane filtration system	Once per day
Continuous Indirect Integrity Testing	Monitoring some aspect of filtrate water quality that is indicative of the removal of particulate matter	<u>Monitor</u> a membrane filtration system for significant integrity problems between direct integrity test applications	Membrane units in a site-specific membrane filtration system	Continuous

2.3.5 OVERVIEW OF NEW MEXICO STATE REGULATIONS

New Mexico has primacy to implement and enforce the primary and secondary regulations put forth by the EPA under the SDWA. While New Mexico follows all of the federal regulations, it also has several additional regulations for water treatment facilities. Many of these regulations apply to the permitting process, construction, maintenance, and repair of treatment systems, as well as defining the powers of the secretary who can take any action necessary to protect public health. Regulations of note include the responsibility of the water supplier to notify the public served of any potential health risk associated with the water provided. All parts of the water system, including storage and distribution, must be secured from unauthorized entry, flooding, and contamination. All groundwater wells must be protected from storm water contamination. Finally, any substance added to the water shall be certified by an independent third party and the use of iodine as a disinfectant has been banned (Environmental Improvement Board, 2002).

2.4 DRINKING WATER TREATMENT

Drinking water treatment plants are designed to produce safe and aesthetically pleasing water at a reasonable cost. Treatment processes remove particulates, organic matter, and microorganisms, among other constituents, and also inactivate pathogens. A conventional drinking water treatment plant consists of several unit processes presented in Figure 2 and described in the following sections.



Figure 2 Conventional Drinking Water Treatment Process

2.4.1 SCREENING/PRECLARIFICATION

Preliminary treatment is used when a water source contains coarse debris such as gravel, sand, and grit. Removal of these large particles prevents equipment damage and overburden of downstream treatment processes. Three commonly used pretreatment methods include screening, presedimentation, and microstraining (AWWA, 2003).

Screens and bar racks are physical processes that are usually located at the intakes of rivers, lakes, and reservoirs for water treatment plants (Droste, 1997). The type and size of screens depends on the location where the raw water is collected. When water is withdrawn from the surface of a river, coarse screens of 3 inches or larger are used. For a submerged intake from a reservoir or lake, smaller coarse screens can be used (Droste, 1997).

Presedimentation is used to remove gravel and sand, which can jam equipment and wear down pump impellers, as well as silt, which causes increased loads on the coagulation and sedimentation processes. Presedimentation systems are intended to remove up to 60% of settleable material (AWWA, 2003).

Microstraining utilizes a fine screen to reduce suspended solids from raw waters that contain high concentrations of algae, other aquatic organisms, and small debris that can clog filters. It is usually made from a fine fabric or screen that is wound around a drum. The drum, which is usually 75% submerged, rotates in a circle as water flows from the inside to the outside of the drum. The thin fabric collects the debris as the water passes through the drum. The

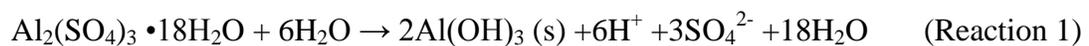
openings in the microstrains vary from 20 to 60 microns. This process removes suspended solids but not bacteria. The solid deposits are removed by water jets, which force the deposited material into a channel where they are then collected (Droste, 1997).

2.4.2 COAGULATION AND FLOCCULATION

Coagulation and flocculation are used in conjunction with clarification (Section 2.4.3) and filtration (Section 2.4.4) to remove colloidal particles which cause turbidity and color. The objective of coagulation and flocculation is to turn small, stable particles into larger flocs that can be settled or filtered out of solution in subsequent processes (Davis, 2008).

Most colloidal particles in natural waters have a negative surface charge that causes them to be stable in solution and repel each other. They are too small to settle in a reasonable time period and will pass through filters as they repel filter media. Coagulation is a chemical process used to reduce the surface charge of colloids. When a positively charged coagulant is added, destabilized particles are able to collide and stick together, forming larger flocs that can be settled or filtered. Coagulants must also be nontoxic and insoluble in the neutral pH range to prevent high concentrations of ions from remaining in the water (Davis, 2008).

Metal salts such as aluminum and iron salts can be used as coagulants. The most common aluminum salt coagulant is aluminum sulfate, or alum. If alum is added at a high enough concentration, some of the aluminum ions may form aluminum hydroxide by Reaction 1:



Aluminum hydroxide assists in solid clarification of the water because it settles in a reasonable time period. When colloidal particles come in contact with aluminum hydroxide, they adhere to one another, forming large positively charged molecules with aluminum ions at their center. This product results in large precipitates that can assist in the removal of many colloids from solution (Weiner, 2003).

Flocculation is a process that follows coagulation. After particles are destabilized, they must make contact in order to form progressively larger flocs. The rate and extent of particle aggregation depends on the velocity gradients and the time of flocculation. The process takes place in a basin equipped with a mixer that provides gentle agitation. The mixing must be fast

enough to encourage inter-particle contact, but gentle enough to prevent the breakup of existing flocculated particles due to sheer stress (Davis, 2008).

2.4.3 CLARIFICATION

Clarification is a solid-liquid separation process used to reduce the solids content of the water. The goal of clarification is to reduce turbidity to below 10 NTU before the water enters a filter. In less turbid waters, the clarification step may be omitted from the treatment process. In addition to removing inorganic and organic particles, clarification also plays an important role in the removal of pathogens such as *Giardia* and *Cryptosporidium* (Betancourt, 2004). The two most commonly used clarification options in a conventional treatment process are sedimentation and dissolved-air flotation.

Sedimentation of flocculent particles depends on properties of the particles, basin depth and surface area, overflow rates, and flow conditions at the inlet and outlet of the basin. The overflow rate can be determined using Equations 1 and 2 (HDR Engineering, Inc., 2001):

$$v = \frac{Q}{A} \quad \text{(Equation 1)}$$

$$t_0 = \frac{V}{Q} \quad \text{(Equation 2)}$$

where:

v = settling velocity of particle that settles the depth of the basin in detention time t_0 (ft/s)

Q = rate of flow through the basin (ft³/s)

A = surface area of the basin (ft²)

V = volume of the settling zone (ft³)

t_0 = basin detention time (s)

These equations describe the settling behavior of particles in ideal settling conditions, where settling is only dependent on flow rate, basin surface area, and properties of the particle and liquid. Ideal conditions cannot be attained, however, in practical applications. Therefore, basin characteristics affecting detention time, as well as various types of currents occurring in the basin, need to be considered. In addition, the type of coagulant used and water temperature also

affect settling velocities. Typically, higher overflow rates are used in warm waters because higher temperatures decrease the kinematic viscosity of fluids, which increases the settling velocity of particles. For example, raising the water temperature from 50 to 86°F increases the settling velocity by a factor of 1.63. Conversely, decreasing the temperature from 50 to 32°F reduces the settling velocity by a factor of 0.73. Typical overflow rates for alum floc are 600 to 1,000 gpd/ft² and for lime floc are 1,400 to 2,100 gpd/ft². Horizontal velocities in sedimentation basins must be kept relatively low in order to prevent floc breakup. Typical influent velocities are 0.5 to 1.0 ft/s (HDR Engineering, Inc., 2001).

Flotation can be used as an alternative to sedimentation. The most common flotation method used in drinking water applications is dissolved-air flotation (DAF). During DAF, dissolved air is bubbled into the bottom of the clarification tank, and the bubbles attach to floc particles as they rise. The bubble-floc aggregates are carried to the surface of the flotation tank and removed with a scraper. One of the benefits of DAF systems is their ability to remove smaller, low-density particles that are difficult to settle such as algae. These particles, if not removed sufficiently, may reduce the efficiency of filters. Other benefits of DAF are lower coagulant dose and shorter flocculation time than those required for conventional sedimentation (HDR Engineering, Inc., 2001). DAF also has an advantage over sedimentation in pathogen removal. Although EPA does not assign clarification processes log removal credits for *Cryptosporidium* and *Giardia*, bench-scale studies have shown that DAF is more effective than sedimentation in removing protozoan cysts from the water under certain conditions (Plummer *et al.*, 1995).

2.4.4 FILTRATION

Filtration is used in water treatment to remove pathogens and suspended particles that do not settle. Various filtration methods are available, typically capable of handling influent turbidities in the range of 10-20 NTU. Filtration plays an important role in meeting *Cryptosporidium* log removal requirements described in Section 2.3. Another significance of filters is the removal of organic matter, which forms disinfection byproducts (DBPs) when it reacts with chlorine during disinfection. Removal of precipitated organic matter by filtering reduces disinfection costs and prevents some DBPs from forming (AWWA, 1999).

Filtration is a combination of physical and chemical processes and therefore filterability is influenced by a number of water properties. Water temperature affects filterability in that cold waters are more difficult to filter than warm waters. However, size and surface chemistry of the suspended particles have the most impact on filterability. The type and amount of coagulant used influences physical (adsorption) and chemical (electrochemical and van der Waals forces) properties of suspended particles. Therefore, considering the relationship between coagulation and filtration can help maximize the efficiency of filtration systems (HDR Engineering, Inc., 2001).

Filtration technologies can be broken down into two categories: gravity and pressure filtration systems. Pressure systems include rapid rate, diatomaceous earth, membrane, and cartridge filtration (National Drinking Water Clearinghouse, 1996). From these, membrane technologies have received significant attention recently and have a wide variety of applications in water treatment. Membrane processes are discussed in detail in Section 2.5, while this section focuses on gravity filtration systems.

Gravity filters employ a fundamental principle of a porous medium that water passes through to remove suspended solids. Rapid rate gravity filtration is the most common technology used in conventional water treatment. In this process, contaminants attach to the granular media as the water flows downward through the filter bed. Over time, backwashing is necessary as the void spaces between filter media fill with deposited particulates. Granular filters include monomedium (silica sand), dual media (anthracite coal and sand) or trimedia (coal, sand, and garnet). Using granular activated carbon (GAC) as filter media is beneficial for the removal of organic material because of its adsorptive properties. In conjunction with coagulants and filter aids, rapid rate granular filters achieve 2-log removal of *Giardia* and *Cryptosporidium* (LeChevallier, 2004). Slow-sand filters are similar in principle to rapid rate filters. However, they use biological mechanisms, have smaller pores between media particles, and do not require backwashing. Slow-sand filters provide over 3-log removal of *Giardia* and *Cryptosporidium* (AWWA, 1999).

2.4.5 DISINFECTION

Disinfection is used to inactivate pathogens, making them incapable of reproducing and transmitting diseases. Disinfection effectiveness depends on the disinfectant type and dose, the

type of organisms present in the water, contact time, and other water quality parameters (pH, temperature, and turbidity). Because many pathogens are difficult to measure in a laboratory, disinfection effectiveness is not measured by quantifying pathogens in the influent and effluent. Rather, CT values have been established for various types of disinfectants to represent disinfection requirements. CT is a product of residual concentration of disinfectant in mg/L (C), and the contact time in minutes (T). The contact time is the T₁₀ value, representing the amount of time it takes for 10% of the water to pass through the contact basin. Tables 8 and 9 provide example CT values for inactivation of viruses and *Giardia* respective to different disinfectant options (HDR Engineering, Inc., 2001).

Table 8 CT Values for Inactivation of Viruses (AWWA, 1999)

Disinfectant	Units	Inactivation		
		2-log	3-log	4-log
Chlorine ¹	mg min/L	3	4	6
Chloramine ²	mg min/L	643	1,067	1,491
Chlorine dioxide ³	mg min/L	4.2	12.8	25.1
Ozone	mg min/L	0.5	0.8	1
UV	mW s/cm ²	21	36	N/A

¹ At temperature of 10°C, pH range of 6 to 9, and a free chlorine residual of 0.2 to 0.5 mg/L

² At temperature of 10°C and a pH of 8

³ At temperature of 10°C and a pH range of 6 to 9

Table 9 CT Values in mg-min/L for Inactivation Of *Giardia* (AWWA, 1999)

Disinfectant	Inactivation					
	0.5-log	1-log	1.5-log	2-log	2.5-log	3-log
Chlorine ¹	17	35	52	69	87	104
Chloramine ²	310	617	930	1,230	1,540	1,850
Chlorine dioxide ³	4	7.7	12	15	19	23
Ozone ³	0.23	0.48	0.72	0.95	1.2	1.43

¹ At temperature of 10°C, pH of 7, and with a free chlorine residual of less than or equal to 0.4 mg/L

² At temperature of 10°C and a pH range of 6 to 9

³ At temperature of 10°C and a pH of 7

Two types of disinfection are used in drinking water treatment: primary and secondary disinfection. Primary disinfection in the treatment plant is used to inactivate pathogens to meet log inactivation requirements of the Surface Water Treatment Rule (SWTR). Primary disinfection requires a relatively high disinfectant dose and short contact time. Secondary disinfection refers to the maintenance of disinfectant residual to ensure water quality in the distribution system. Selection of a disinfectant depends on cost, desired inactivation strength, DBP formation, and control of other water quality parameters such as iron, manganese and tastes and odors. Table 10 provides a summary of available disinfectants along with the benefits and drawbacks of their use (HDR Engineering, Inc., 2001).

Table 10 Comparison of Disinfection Options

Disinfectant	Primary Disinf.	Secondary Disinf.	Fe, Mn Control	Taste & Odor	Biofilm Control	Relative Cost	Inactivation Strength	DBP Formation
Chlorine	Yes	Yes	Yes	Yes	Yes	Low	High	High
Monochloramine	No	Yes	No	No	Yes	Low	Low	Moderate
Chlorine Dioxide	Yes	Yes	Yes	Yes	Yes	Moderate	High	Low
Ozone	Yes	No	Yes	Yes	No	High	High	Low
UV	Yes	No	No	No	No	Moderate	High	Low/None

2.5 MEMBRANE PROCESSES FOR DRINKING WATER

Membrane processes are used in drinking water treatment to separate dissolved and colloidal particles by using pressure, electrical potential, or a concentration gradient. Some membrane processes are effective in treating sea and brackish water. However, membrane fouling is of concern and can make the process cost prohibitive. Fouling of membranes is caused by several constituents in the waters, resulting in low permeability. To address this concern, pretreatment options are available to reduce fouling potential. Disposal of desalination byproducts, known as brine, also presents a problem due to the environmental impacts of its high salt concentration. This section gives a brief introduction to the types of membranes used in drinking water treatment, causes of membrane fouling, pretreatment alternatives, and brine disposal options.

2.5.1 SUMMARY OF MEMBRANE PROCESSES

This section discusses the five main membrane processes typically used for drinking water treatment: microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and electro dialysis. Table 11 gives an overview of these processes and their applications.

Table 11 Membrane Processes and Applications

Process	Membrane Type	Pore Size (μm)	Objective	Driving Force	Water Type
Membrane Filtration	Microfiltration	0.1-10	Particle and microbial removal	Straining/size exclusion	Fresh water only
	Ultrafiltration	0.001-0.1			
Reverse Osmosis	Nanofiltration	0.0005-0.03	Brackish/seawater desalinization, softening, pathogen removal	Pressure (diffusion)	Brackish and sea water
	Reverse Osmosis	0.0001-0.001			
Electrodialysis Reversal	Ion-permeable membranes	N/A	Brackish/seawater desalinization	Electrical potential	Brackish and sea water

Micro- and ultrafiltration are two common membrane processes which remove particulates and microorganisms from the water. Microfilters have pore sizes ranging from 0.1-10 μm , and thus can exclude large colloids and microorganisms such as algae, protozoa, and bacteria, but not viruses. They are typically used to remove chlorine-resistant pathogens such as *Cryptosporidium* oocysts and *Giardia* cysts. Ultrafiltration uses membranes with smaller pore sizes of 0.001 to 0.1 μm . Both processes remove constituents from the water through straining, or size exclusion. Micro- and ultrafilters are manufactured in several configurations including tubular, capillary, hollow fiber and spirally wound sheets. Some configurations are more favorable in certain applications due to larger surface area (LeChevallier, 2004).

Reverse osmosis (RO) and nanofiltration (NF) are both pressure-driven membrane processes used to remove salts, pathogens such as viruses and bacteria, turbidity, disinfection byproduct (DBP) precursors, synthetic organic compounds (SOCs), and hardness from water. High-pressure RO membranes are typically constructed of dense material with pore sizes ranging from 0.0001 to 0.001 μm . Nanofiltration membranes utilize porous material with typical pore size between 0.0005 and 0.03 μm . RO and NF function by forcing water through a semi-

permeable membrane from a more concentrated solution into a more dilute solution. Operating pressures for RO membranes range from 1550 – 3200 kPa, while the operating pressures for nanofiltration range from 500 – 1000 kPa. Compared to RO systems, nanofiltration membranes operate at much lower pressures but yield higher flow rates of permeate. Although they do not produce water of the same quality as RO, the use of nanofiltration membranes is becoming more frequent in applications where ultrafiltration is not sufficient (Gray, 2005).

RO technology is widely applied in brackish and sea water treatment. Because the solubility of salt ions in the membrane is much less than the solubility of salt ions in water, dissolved salt ions do not diffuse through the membrane. As the water's velocity through the membrane increases, the salt and water will separate, leaving the salt on the membrane layer. Since pressure is the driving force in RO systems, concentration differentials do not dominate, allowing an increase in pressure to increase the flow of water without increasing the flow of salt through the membrane (AWWA, 1996). RO systems, when functioning with high efficiency, can remove up to 99% of all dissolved materials.

Electrodialysis, unlike other membrane processes, is not a pressure driven system. It uses an electric field to separate ions of opposite charges, primarily removing salts and other ionic compounds from the water. Electrodialysis is typically applied where deionization of aqueous solutions is necessary, such as in production of potable water from brackish sources. The process can separate a waste stream containing 1,000 to 5,000 mg/L inorganic salts into a dilute stream of 100 to 500 mg/L salt and a concentrated stream of up to 10,000 mg/L salt (Davis, 2008).

The electrodialysis system is composed of a matrix of ion permeable membranes, each having a fixed charge group. This configuration allows ions to be attracted to the membrane of opposite charge, thereby separating the anions from the cations in solution. The unit is comprised of many flat membrane sheets, with cation- and anion-exchange membranes alternately arranged between an anode and a cathode on each side. Anion membranes are permeable to anions and impermeable to cations, while cation membranes are permeable to cations and impermeable to anions. Applying a voltage between the two end electrodes generates an electric potential which allows the ions to be driven toward their corresponding electrode: cations to the cathode and anions to the anode. The ion selective membranes, however, restrict the movement of the

charged particles, capturing the anions and cations. This results in two separate solutions: an ion-enriched brine and a desalinated water effluent (Gray, 2005).

2.5.2 MEMBRANE FOULING AND SCALING

Depending on the water source and membrane type, several constituents can cause contamination of membranes reducing their efficiency. Contamination of membranes, typically called fouling, causes higher energy use, more frequent cleaning, and shorter life span of membranes. Three main types of fouling can occur in membrane processes: plugging, scaling, and biofouling.

Membrane **plugging** occurs due to high concentrations of suspended and colloidal matter in the feed water. These solid particles physically plug the membrane pores, requiring higher pressures to keep the same level of performance. Plugging results in higher energy costs for treatment systems. **Scaling** is caused by precipitation of inorganic salts from the water on the membrane. Nanofiltration (NF) and reverse osmosis (RO) are especially prone to membrane scaling. Deposition of precipitates from water-insoluble salts, such as calcium carbonate, causes the flux to decrease. As a consequence, more frequent cleaning cycles and higher pressures must be applied. **Biofouling** is also of concern for NF and RO membranes. The growth of bacteria depends on the temperature and pH, dissolved oxygen, and the presence of nutrients in the feed water. Biofouling causes extensive damage to the membranes and is often irreversible (Lenntech Membrane Technology, 2008). Microbiological growth can be attributed to the feed water not going through disinfection before entering most membrane processes. High concentrations of chlorine needed to control biofilm formation reduce the flux of membranes and reduce their performance (Buch, 2007). Recently developed chlorine resistant membranes may be able to mitigate this problem, making desalination processes more efficient (Freeman, 2007).

One way to predict the amount of fouling during a membrane process is through the Silt Density Index (SDI) of the feed water. SDI can be defined as the amount of time it takes to filter a certain amount of water through a 0.45 μm microfiltration membrane at a pressure of 2.07 bar (206.84 kPa). To determine the SDI of feed water, one time measurement is taken using a clean filter. Another time measurement is taken after 15 minutes of continuous filtration. Using this data, the SDI can be calculated using Equation 3 (WaterTech, 2003). Membranes show the most

efficient operation at the SDI of less than 5. Various physical and chemical pretreatment options are available to reduce the SDI, thereby reducing membrane fouling potential.

$$SDI = 100 \times (1 - \frac{T_i}{T_f}) / T_i \quad \text{(Equation 3)}$$

Where:

T_i = initial time required to obtain an arbitrary volume of sample (s)

T_f = time required to obtain same volume of sample after 15 min. of continuous filtration (s)

2.5.3 PRETREATMENT

With all membranes, fouling is inevitable. Application of chemical, physical or a combination of the two types of pretreatment processes before the feed water enters a membrane may reduce fouling potential and extend membrane life (Lenntech Membrane Technology, 2008). Table 12 presents the typical fouling causes and appropriate pretreatment options.

Table 12 Pretreatment Options and Applications

Fouling	Cause	Pretreatment
Biological	Bacteria, microorganisms, viruses, protozoan	- Chlorination
Particle	Sand, clay (turbidity, suspended solids)	- Filtration
Colloidal	Organic and inorganic complexes, colloidal particles, micro-algae	- Coagulation, filtration - Optional: Flocculation, sedimentation
Organic	Natural Organic Matter (NOM) : humic and fulvic acids, biopolymers	- Coagulation, filtration, activated carbon adsorption - Coagulation, ultrafiltration
Mineral	Calcium, magnesium, barium or strontium sulfates and carbonates	- Anti-scalant dosing - Acidification
Oxidant	Chlorine, ozone, potassium permanganate	- Oxidant scavenger dosing: sodium (meta) bisulfite - Granulated Activated Carbon

Chemical pretreatment processes, such as coagulation and disinfection, are effective in preventing some types of fouling but can be problematic because they alter the water characteristics. For example, acid dosing is often used to prevent precipitation of sulfates and carbonates which cause scaling. Strong acids, such as sulfuric or hydrochloric acids, prevent calcium and magnesium bicarbonate precipitation but also alter the pH of the water, an important property that affects subsequent treatment processes. Therefore, post pretreatment adjustments may be necessary to bring the pH back to a suitable range for subsequent treatment steps, including the membrane process itself. For example, cellulose acetate membranes function poorly outside the pH range of 4-6, resulting in increased salt passage (Porteous, 1983).

Unlike chemical pretreatment, physical pretreatment options, such as clarification and filtration, are often preferred as they do not significantly alter water characteristics. Filtration is the most common physical pretreatment process. Traditional filtration techniques including single- and multi-media filters can be used to pretreat waters entering membranes. Membrane technologies with larger pore sizes, such as micro- or ultra-filtration, have also become popular pretreatment options. Clarification methods such as DAF may also be included in a pretreatment process as a way to remove light organic particles (HDR Engineering, Inc., 2001).

For several years, membrane research has focused on replacing some of the chemical pretreatment options with physical processes. Over time, RO technology has also improved to require less chemical conditioning of the feed water. For example, open channel modules, such as Rochem RO DT module, were developed to prevent biofouling and control scaling without acid dosing. Its fluid dynamics and construction of the disk membrane stack create an open channel, which allows for unrestricted, turbulent flow through the system. This means less deposition of foulants within the membrane. These modules operate at a moderate SDI of around 15 and are known for their energy efficiency and low environmental impact (Rochem Separation Technologies, 2008).

2.5.4 BRINE DISPOSAL

Several concerns exist for desalination facilities, including desalination efficiency, cost of operation, and disposal of salts and other concentrates. Typically, the efficiency for brackish water membrane processes is 75 to 80 percent, meaning 15 to 20 percent of all the water that enters the membrane process leaves as waste (Brandhuber, 2007). Disposal of the concentrated

waste is a serious concern for all water systems, but even more so for those treating brackish water. Irresponsible discharges of concentrated salt wastes contaminate receiving waters, such as rivers and lakes, make soil much less fertile, and raise concerns for long-term environmental effects of salt accumulation. Fortunately, many different brine disposal options are available.

One option is to discharge brine into public sewers. An advantage of this approach is that the brine can be blended with the sewer flow, reducing the concentration of total dissolved solids and other contaminants. However, if the wastewater flow is also relatively high in salt content, the brine will not dilute sufficiently. Also, wastewater treatment system capabilities of the area need to be considered. Although some dilution with domestic and industrial wastewater will occur, highly concentrated solutions, even in low volume, can produce a large strain on the wastewater treatment facility operations (Brandhuber, 2007).

Another option is deep well injection, during which brine is pumped into a deep underground aquifer of undrinkable water. This method is presently applied worldwide for disposal of industrial, municipal, and liquid hazardous wastes (Glater, 2003). Deep well injection has been applied successfully for brine disposal from several membrane plants in Florida as well (Skehan, 2000). Although 800 wells are in operation throughout the United States for disposal of solutions of toxic and hazardous wastes, disposal of brine from desalination facilities is not currently in practice in this country with the exception of Florida. According to Mickley (2001), deep well injection is a reasonable method for brine disposal, as long as there can be long term operation and maintenance in order to dispose large volumes of process fluid. Disadvantages include high costs for conditioning the waste brine, possible leakages in the well casing, and other activities that could cause contamination of clean or relatively clean groundwater sources (Mickley, 2001).

Pumping brine into evaporation or solar ponds is a possibility for some locations. The brine is left to evaporate from shallow ponds leaving salt precipitates. Evaporation ponds are primarily used in the Middle East. This disposal method is especially effective in regions with low rainfall, where climates favor steady and relatively fast evaporation rates (Glater, 2003). However, evaporation ponds use a large area and require an impervious ground cover or a lining to prevent infiltration into the groundwater. Due to the amount of land required for evaporation ponds, the land value must be relatively low or this disposal option would not be cost effective (Glater, 2003). All of these disposal options have benefits and potential risks to the environment.

The best disposal method is site dependent and should be as inexpensive and environmentally sound as possible.

2.5.5 CHAPTER SUMMARY

Desalination is a flourishing industry that has the potential to benefit many arid areas around the world, but the concerns of efficiency and waste disposal have to be addressed to make it a cost effective option for large coastal facilities and small inland plants alike. Because of increasing demands for water, along with more stringent regulations, many areas in the United States will be forced to produce higher quality water using lower quality sources, such as brackish water (Brandhuber, 2007). At this time, desalination facilities are not operating at their optimum efficiency due to fouling, and the wastes are not disposed of in the most environmentally sensitive manner. The hopes of this project are to explore potential ways to improve treatment efficiency with a pretreatment system and provide feasible waste disposal options for the Tularosa Basin Pilot Desalination Facility, while minimizing costs and environmental impacts.

3. METHODOLOGY

The goal of this project was to design a pretreatment process to increase the efficiency of brackish water desalination. The objectives of pretreatment were to reduce hardness, iron, manganese, and aluminum concentrations of the feed water prior to treatment using electro dialysis or reverse osmosis. Laboratory experiments were conducted to test different treatment processes and their effectiveness in the removal of these contaminants. Precipitative softening and ion exchange were tested for hardness removal, and oxidation followed by filtration was tested for iron and manganese removal. Although aluminum removal was not tested in the laboratory, aluminum removal options and techniques were researched and analyzed. This chapter presents the methodology used in conducting the laboratory experiments.

3.1 EXPERIMENTAL OVERVIEW

High concentrations of hardness, iron, manganese and aluminum are problematic for membrane treatment processes because of their fouling potential and tendency to decrease the efficiency of the membrane. Hardness can cause scale formation on the membrane surface. While hardness includes all multivalent cations in a water, the two predominant cations are typically calcium and magnesium. Their concentrations tend to be high in groundwaters. To remove hardness, precipitative softening with lime, soda ash, and/or caustic soda was tested, as was ion exchange. High iron and manganese concentrations also contribute to fouling because they are easily oxidized, forming a precipitate. Oxidation was evaluated for the removal of iron and manganese using chlorine, potassium permanganate, or ozone. All three were tested in the laboratory. For both softening and oxidation, a filtration step was included in laboratory testing to remove any precipitate that formed. Aluminum is present in the feed water at the Tularosa Basin Pilot Desalination Facility at a concentration of 0.4 ppm, which is typical of groundwaters. Removal of aluminum depends on whether it is present primarily in a soluble or precipitated form. Literature research was conducted to determine appropriate removal mechanism for aluminum. Lastly, ion exchange was tested as a removal process for all four fouling contaminants. Table 13 summarizes the significance of these contaminants along with removal options that were evaluated.

Table 13 Summary of Removal Options

Contaminant	Why is it a problem for membranes?	Treatment Options Evaluated
Hardness	<ul style="list-style-type: none"> • Scale Formation 	Softening with: <ul style="list-style-type: none"> • Lime • Soda ash • Caustic soda • Ion exchange
Iron and Manganese	<ul style="list-style-type: none"> • Scale Formation • Easily oxidizes and precipitates anywhere within the process 	Oxidation and filtration using: <ul style="list-style-type: none"> • Chlorine • Potassium Permanganate • Ozone
Aluminum	<ul style="list-style-type: none"> • Scale Formation • Insoluble in groundwater • Impurities in pretreatment chemicals 	<ul style="list-style-type: none"> • Activated carbon adsorption • Ion exchange

3.2 SOFTENING

Hardness is defined as the concentration of multivalent cations in a water, of which calcium (Ca) and magnesium (Mg) are typically the two predominant cations. Ca and Mg in concentrations typically found in surface waters present no health or aesthetic concerns. However, hardness in the range of 200-300 mg/L as CaCO₃ produces scale in heaters and other appliances, reducing their efficiency. On the other hand, soft waters with hardness below 75 mg/L as CaCO₃ are corrosive (AWWA, 1999).

Groundwaters tend to be higher in calcium and magnesium content than surface waters. Feed water at the Tularosa Basin Pilot Desalination Facility has a hardness of 2,650 mg/L as CaCO₃, which is extremely high compared to a typical fresh water range of 0 – 300 mg/L. Although no target hardness was provided by the WERC Competition, our pretreatment process goal was to reduce hardness to 300 mg/L as CaCO₃ or lower, a concentration that membrane technologies can handle without excessive fouling (Bartels, 2008). Two treatment processes were tested to remove hardness: precipitative softening and ion exchange. For the former, lime, soda ash, and pH adjustment with caustic soda were tested. Each of these chemical additions precipitates Ca and Mg ions out of solution and the precipitate is subsequently settled or filtered.

For the latter, Ca and Mg ions in solution are exchanged for sodium (Na) ions on a media surface. Sections 3.2.1 and 3.2.2 present the methods used to conduct softening experiments.

3.2.1 PRECIPITATIVE SOFTENING

Both calcium and magnesium were present in the feed water at the Tularosa Basin Pilot Desalination Facility (TBPFD). The total hardness in the feed water was 2,650 ppm as CaCO₃, with Ca and Mg concentrations of 500 ppm and 340 ppm, respectively (Table 5). The alkalinity of the water was 1,250 ppm as CaCO₃, meaning 1,250 mg/L of the total hardness was in the carbonate form while the remaining 1,400 mg/L was in the non-carbonate form. In order to remove hardness, precipitative softening with lime, soda ash, lime and soda ash, or caustic soda was tested in batch experiments. Table 14 summarizes the experiments conducted. Details on the experimental water preparation, dosing, and softening experiments are provided in the following sections.

Table 14 Summary of Precipitative Softening Experiments

Hardness Type		Softening Chemical	Dose Range (mg/L)
Carbonate only	Calcium	Lime	176 – 700 mg/L
	Magnesium	Lime	176 – 700 mg/L
Non-carbonate only	Calcium	Soda ash	560 – 1484 mg/L
	Magnesium	Soda ash	560 – 1484 mg/L
Total hardness	Calcium & Magnesium	Lime	176 – 444 mg/L
		Soda ash	560 – 1484 mg/L
		Caustic Soda	480 mg/L

3.2.1.1 EXPERIMENTAL WATER FOR SOFTENING

Five water samples were prepared as listed in Table 14. For each sample, the appropriate amount of chemical was calculated based on the desired concentration and the molecular weight of the compound used. For example, CaCl₂ was used to create the sample with non-carbonate hardness due to calcium. The desired concentration was 1,400 mg/L as CaCO₃, to mimic the non-carbonate hardness concentration in the TBPFD feed water. To determine how much CaCl₂ to add, first the hardness concentration was converted to molarity:

$$1400 \frac{\text{mg}}{\text{L}} \text{CaCO}_3 * \frac{1 \text{ g}}{1000 \text{ mg}} * \frac{1 \text{ mole CaCO}_3}{100 \text{ g CaCO}_3} = 0.014 \frac{\text{moles}}{\text{L}} \text{CaCO}_3$$

Since CaCO₃ and CaCl₂ have the same number of equivalents per mole, 0.014 moles CaCl₂/L were needed. Then, the molar concentration was converted to grams per liter of CaCl₂:

$$\frac{0.014 \text{ moles CaCl}_2}{\text{L}} * \frac{110.98 \text{ g CaCl}_2}{1 \text{ mole CaCl}_2} = \frac{1.554 \text{ g CaCl}_2}{\text{L}}$$

Thus, 1.554 g of CaCl₂ was used to create 1 L of non-carbonate hardness with a concentration of 1,400 mg/L as CaCO₃. Calculations for the remaining samples were conducted similarly and the values are summarized in Table 15.

Table 15 Sample Water Parameters

Hardness Type	Chemical	Molecular Weight (g/mol)	Desired Concentration (mg/L)	g chemical/ L solution
Carbonate	CaCO ₃	100.09	1250	1.250
	MgCO ₃	84.35		1.053
Non-carbonate	CaCl ₂	110.98	1400	1.554
	MgCl ₂	95.91		1.342

To prepare the experimental water, the appropriate chemical was weighed using a weighing dish on an analytical scale. The chemical was added to a volumetric flask, and the total volume was brought up to 1 liter with reagent grade (E-pure) water. To ensure sufficient mixing, each sample was placed on a stir plate until its contents dissolved completely. The non-carbonate hardness samples completely dissolved by mixing. For the carbonate samples prepared with CaCO₃ and MgCO₃, a small amount of 1+1 HCl was added to aid with dissolution, after which the total volume of the sample was brought up to 1 L with E-pure. This acid addition diminished some of the alkalinity. To account for the alkalinity reduction, 2 g of NaHCO₃ was added to the sample. After all chemicals were dissolved, the pH of the solution was brought to neutral with 6N NaOH.

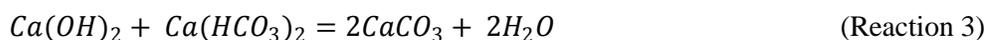
3.2.1.2 SOFTENING CHEMICAL PREPARATION

Prior to testing hardness removal processes, stock solutions of both lime and soda ash were produced. A lime stock solution was made by adding 18.5 grams of CaO to 100 mL of E-pure water, and the soda-ash stock solution was made by adding 2.8 grams of Na₂CO₃ to 50 mL of E-pure water.

To determine the dose of lime required to treat the water, the concentration of CaCO₃ in the experimental water was first converted to molarity:

$$1250 \frac{mg}{L} \times \frac{1 g CaCO_3}{1000 mg} \times \frac{1 mol}{100 g CaCO_3} = 0.0125 \frac{mg}{L}$$

Next, the moles of lime needed to precipitate each mole of carbonate hardness were determined. Reaction 2 shows lime, dosed as CaO, converted to hydrated lime. Then, Reaction 3 shows how hydrated lime reacts with carbonate hardness to form a CaCO₃ precipitate.



Based on Reaction 3, 1 mole of Ca(OH)₂ removes 1 mole of carbonate hardness. Thus, 0.0125 moles/L of lime is needed for the experimental water. Using lime as CaO, the molar concentration of lime was converted to grams per liter of CaO:

$$\frac{0.0125 mol CaO}{L} * \frac{56 g CaO}{1 mol CaO} = \frac{0.70 g CaO}{L}$$

Thus, a 700 mg/L dose of CaO is needed to remove 1,250 mg/L of hardness. Because the initial strength of the stock was 185,000 mg/L, the volume of stock needed for a 100 mL sample of experimental water was calculated as follows:

$$C_{stock} \times V_{stock} = C_{test} \times V_{test}$$
$$185,000 \frac{mg}{L} \times V_{stock} = 700 \frac{mg}{L} \times 100 mL$$

The resulting stock volume of CaO (lime) needed to remove 1,250 mg/L hardness in a 100 mL sample was 2.64 mL. Similar calculations were conducted to determine the required soda ash dose to remove 1,400 mg/L of non-carbonate hardness from a 100 mL sample. The resulting soda ash dose was 1,484 mg/L and the volume of stock required was 26.5 mL. See Appendix A for full calculations for the determination of the soda-ash dose.

An appropriate dose for caustic soda was not measured. Instead, 6 N NaOH was added to the experimental water, and monitored using a pH meter until the pH reached 10.

3.2.1.3 SOFTENING EXPERIMENTS

To conduct a softening experiment, first a sample of the experimental water was tested for total hardness (see Section 3.5.3). Next, a 100 ml sample was measured into a beaker and the pH was raised to approximately 10 using NaOH. Then, the sample was placed on a stir plate and the softening chemical was added at the appropriate dose (for caustic softening, no additional chemical was needed beyond the NaOH). The sample was mixed for 10 minutes and then the precipitate was allowed to settle for 10 minutes. Next, the contents of the beaker were filtered through a Whatman 934-AH 1.5 μm filter, after which the hardness was re-measured. Initial and final hardness values were compared to determine the most effective softening treatment.

3.2.2 ION EXCHANGE

An alternative way of removing hardness is with a strong cation exchange resin arranged in a column. As the water is pumped through the column, the cation resin exchanges positively charged ions, typically sodium or potassium, for the calcium and magnesium which cause hardness in the water. The resin used was a Rohm & Haas Amberlite IR120 Na – Strong Acid Cation resin of the sulphonated polystyrene type, typically used in water softening and demineralization. The total exchange capacity of the resin is 2.00 eq/L. The calcium and magnesium ions remain on the resin and are replaced by the sodium ions which flow with the water out of the column.

The cylindrical column was approximately 1 inch in diameter and 3.8 inches in height. Empty bed contact times (EBCT) for ion exchange softening are typically between 3 and 7

minutes (AWWA, 1999), and therefore we chose to use an average EBCT of 5 minutes during our tests. Using the dimensions of the column, the desired flow rate to achieve this contact time was calculated. First, the volume of the column was determined:

$$V_{cylinder} = \frac{\pi D^2}{4} \times h$$

Where:

D = diameter of the cylinder

h = height of the cylinder

$$V_{cylinder} = \frac{\pi(1 \text{ in})^2}{4} \times 3.8 \text{ in} = 2.98 \text{ in}^3$$

With a bed volume of 2.98 in³ and a desired EBCT of 5 minutes, the flow rate through the column was calculated:

$$Q = \frac{V}{t}$$

Where:

V = volume of the cylinder

t = time

$$Q = \frac{2.98 \text{ in}^3}{5 \text{ min}} = 0.596 \text{ in}^3 / \text{min}$$

The flow rate was then converted to ml/min:

$$Q = \frac{0.596 \text{ in}^3}{\text{min}} \times \frac{\text{ft}^3}{(12 \text{ in})^3} \times \frac{0.02831 \text{ m}^3}{\text{ft}^3} \times \frac{1000 \text{ L}}{\text{m}^3} \times \frac{1000 \text{ ml}}{\text{L}} = 9.7 \text{ ml} / \text{min}$$

Next, the time until the ion exchange resin had to be regenerated and the theoretical volume of water the system was able to treat before regeneration were calculated. Using the flow

rate, the exchange capacity of the bed (2 eq/L), and the initial hardness of 2,650 ppm, the number of bed volumes that can be treated was calculated:

$$V_{Bed} = \frac{2 \text{ eq}}{L} \times \frac{1 \text{ L } H_2O}{2650 \text{ mg as } CaCO_3} \times \frac{50,000 \text{ mg } CaCO_3}{\text{eq } CaCO_3} = \frac{37.7 \text{ vol } H_2O}{\text{vol resin}}$$

The calculations show that 37.7 bed volumes of water can flow through ion exchange resin before the majority of the ions in the resin have been exchanged and the column must be regenerated. With an EBCT of 5 minutes, the maximum amount of time the water can be flowing through the column before backwashing is:

$$t_{Bed} = \frac{5 \text{ min}}{BV} \times 37.7 \text{ BV} = 188.5 \text{ min} \cong 3.15 \text{ hr}$$

3.2.2.1 ION EXCHANGE EXPERIMENTS

A cylindrical glass column, approximately 1 inch in diameter and 3.8 inches in height, was used for the ion exchanger. The exchanger was clamped vertically to a stand. The column was tightly packed with the ion exchange resin and then saturated with E-pure water. The top of the column was connected to a 1-100 RPM peristaltic pump by a plastic tube approximately 1/8 inch in diameter. The pump was used to create a flow-through system in which the feed water with hardness, which was prepared using the same methods as described in the precipitative softening section, Section 3.2.1.1, was pumped through the column at a flow rate of 9.7 mL/min. The effluent traveled out of the column through another small plastic tube and was captured in a beaker. This system was operated for a total of four hours. Effluent samples were collected at 15 minute intervals for the first hour, followed by 20 minute intervals for the next three hours. Prior to our experiments, the ion exchange resin was completely saturated with E-pure water.

The hardness of each effluent sample was tested and compared to the influent hardness. This treatment process continuously ran until the ion exchange resin was no longer effective and the effluent hardness was not reduced sufficiently.

3.3 IRON AND MANGANESE REMOVAL

Iron and manganese occur naturally in water sources and are especially common in groundwaters. Iron and manganese do not show adverse effects on human health. However, their concentrations are often reduced during treatment processes for aesthetic reasons. Primary consumer concerns for iron are staining of household fixtures and industrial products, clogging of pipes, and a “rusty” taste and color of the water. Manganese presents similar aesthetic concerns and at concentrations of 0.2 to 0.4 mg/L can promote the growth of microorganisms in the distribution system. Iron and manganese are typically oxidized to form a precipitate which can then be filtered out of solution. Some of the most common oxidants used for iron and manganese removal are chlorine, potassium permanganate and ozone. Chlorine is effective and economical for iron removal whereas potassium permanganate is more commonly used to remove manganese. For systems removing both constituents, a combination of the two oxidants is often an economical option. Ozone is commonly used for iron and manganese oxidation as well.

3.3.1 IRON AND MANGANESE SAMPLE PREPARATION

Iron and manganese samples were prepared using FeCl_3 and MnSO_4 . The desired starting concentrations were 0.5 mg/L Fe and 0.3 mg/L Mn. The amount of FeCl_3 to add to water was calculated by converting from Fe^{+3} to FeCl_3 using molecular weights:

$$\frac{0.5 \text{ mg Fe}^{+3}}{\text{L}} * \frac{\text{g}}{1000 \text{ mg}} * \frac{\text{mole Fe}^{+3}}{55.8 \text{ g Fe}^{+3}} = 8.96 * 10^{-6} \frac{\text{mole Fe}^{+3}}{\text{L}}$$

Since 1 mole of FeCl_3 will yield one mole of Fe^{+3} when dissolved, $8.96 * 10^{-6}$ moles of FeCl_3 is needed. This value is then converted to a mass in milligrams needed for each liter of solution:

$$\frac{8.96 * 10^{-6} \text{ mole FeCl}_3}{\text{L}} * \frac{162.2 \text{ g FeCl}_3}{\text{mole}} * \frac{1000 \text{ mg}}{\text{L}} = 1.453 \frac{\text{mg}}{\text{L}} \text{FeCl}_3$$

Table 16 summarizes the sample preparation calculations. The iron and manganese concentrations of all samples were verified using an atomic absorption spectrophotometer (AA) prior to conducting experiments (Section 3.5.4).

Table 16 Iron and Manganese Sample Preparation

Contaminant	Desired Concentration (mg/L)	Chemical	Target Concentration (mg/L)	mg chemical/ L solution
Iron	0.5	FeCl ₃	0.1	1.453
Manganese	0.3	MnSO ₄	0.05	0.8246

3.3.2 OXIDANT DOSES

Three oxidants were tested for iron and manganese removal: potassium permanganate, chlorine, and ozone. Theoretical doses of the most commonly used oxidants are summarized in Table 17.

Table 17 Oxidant Summary (AWWA, 1999)

Oxidant	Iron oxidation dose (mg/mg Fe ²⁺)	Sludge produced (kg/kg Fe ²⁺)	Manganese oxidation dose (mg/mg Mn ²⁺)	Sludge produced (kg/kg Mn ²⁺)
Oxygen	0.14	1.9	0.29	1.58
Chlorine	0.64	1.9	1.29	1.58
Chlorine Dioxide	1.21	1.9	2.46	1.58
Potassium Permanganate	0.94	2.43	1.92	2.64

Oxidant doses in mg/L for the test waters were calculated based on Table 17. An example calculation for oxidizing Fe with chlorine is provided below. According to Table 17, 0.64 mg of Cl₂ is needed to oxidize 1 mg of Fe²⁺. Therefore, for a solution with 0.5 mg/L Fe²⁺,

$$\frac{0.64 \text{ mg Cl}_2}{1 \text{ mg Fe}^{2+}} * \frac{0.5 \text{ mg Fe}^{2+}}{L} = \frac{0.32 \text{ mg Cl}_2}{L}$$

Similar calculations were performed for each combination of oxidant and contaminant. Then, stock solutions were prepared for chlorine and potassium permanganate. The chlorine stock

solution had a concentration of 1,380 mg/L. Using a 100 mL sample of experimental water with 0.5 mg/L Fe, the necessary volume of chlorine stock was calculated:

$$C_{stock} * V_{stock} = C_{test} * V_{test}$$

$$\frac{1380 \text{ mg}}{L} * V_{stock} = \frac{0.32 \text{ mg}}{L} * 100 \text{ mL}$$

$$V_{stock} = 0.0232 \text{ mL}$$

A summary of the oxidant doses and stock volumes is provided in Table 18.

Table 18 Summary of Oxidant Doses and Stock Volumes

Contaminant	Contaminant Concentration (mg/L)	Oxidant	Oxidant Stock Concentration (mg/L)	Oxidant Dose (mg/L)	Volume Oxidant Stock (mL)
Iron	0.5	Chlorine	1380	0.320	0.0232
		KMnO ₄	1000	0.470	0.0470
Manganese	0.3	Chlorine	1380	0.387	0.0280
		KMnO ₄	1000	0.576	0.0576

3.3.3 CHLORINE AND POTASSIUM PERMANGANATE OXIDANTION EXPERIMENTS

To conduct the oxidation experiments, first a sample of the experimental water was prepared. The initial concentrations of iron and manganese were determined using the atomic absorption spectrophotometer (AA) (see Section 3.5.4). Next, an appropriate volume of sample was measured into a beaker and the pH was raised using NaOH to approximately 8 for oxidation with chlorine. Potassium permanganate oxidation requires a pH of higher than 5.5, so the original pH 7 was sufficient. Next, the oxidant chemical was added at the appropriate dose and mixed to ensure an even distribution. Then, the oxidant was given time to react with the iron and manganese, as shown in Table 19.

Table 19 Summary of Oxidation Conditions

Oxidant	pH	Reaction Time (min)	
		Iron	Manganese
Cl ₂	8 - 8.5	25 - 30	120 - 180
KMnO ₄	> 5.5	60	15

After the appropriate oxidation times, the contents of the beaker were filtered through a 0.45 µm Millipore mixed cellulose ester filter membrane to remove the precipitate, and the final concentration of dissolved iron and manganese was measured using the AA. Initial and final concentrations were compared to determine the most effective oxidation treatment. When using chlorine, the final sample was also tested for total and free chlorine using a spectrophotometer (Section 3.5.5) in order to determine whether a residual was present and whether dechlorination would be necessary.

3.3.4 OZONE OXIDATION EXPERIMENT

Ozone is a powerful oxidant that is becoming more common in iron and manganese removal applications. Some of the advantages of ozone are disinfecting ability and some taste and odor control. Some of the disadvantages are on-site generation and relatively high cost due to power consumption. Ozone reacts with iron almost instantaneously over a wide pH range of 4-10. Manganese reactions require a reaction time of 3-5 minutes and a pH higher than 5 (HDR Engineering, Inc., 2001).

Ozone was tested as an oxidant alternative to chlorine and potassium permanganate. The ozone generator was set to the highest output rate of 10 standard cubic feet per hour (SCFH). A 300 mL sample containing iron and manganese was adjusted to a pH of 8 using 6N NaOH, after which ozone was bubbled into the sample for 5 minutes. The sample was then allowed to settle for 5 to 15 minutes and filtered. Fe and Mn concentrations were measured in the post treatment samples as described in Section 3.5.4.

3.4 ALUMINUM REMOVAL

As an abundant element in the Earth's crust, aluminum is a common constituent in groundwater. Being exposed to and inhaling/ingesting high concentrations of aluminum can cause health problems, such as damage to the central nervous system, dementia, lung damage, and kidney problems. In large quantities, it can also be toxic to aquatic life, and damage plant roots. One of the aluminum removal processes is activated carbon adsorption. Activated carbon is available in two different forms: Powder Activated Carbon (PAC) and Granular Activated Carbon (GAC). Of these, GAC is more widely used. The GAC process is typically set up in a column where the influent water flows through a volume of activated carbon, allowing the constituents to adsorb to the carbon and be removed from the effluent stream (Lenntech, 2008).

Aluminum is present in the feed water at the Tularosa Basin Pilot Desalination Facility at a concentration of 0.4 ppm, which is typical of groundwaters. Removal of aluminum depends on whether it is present primarily in a soluble or precipitated form. Solubility data were consulted to determine whether activated carbon adsorption was necessary for our feed water, or if a sufficient fraction of aluminum would be present in the precipitated form and thus could be filtered. It was concluded that if aluminum is present in solid form, it would be removed during precipitative softening followed by sand filter and the remaining dissolved aluminum will be removed by ion exchange provided slightly acidic conditions. Therefore, activated carbon adsorption was not necessary for its removal and was not tested during this project.

3.5 ANALYTICAL PROCEDURES

In this section, detailed analytical procedures are provided for all laboratory measurements.

3.5.1 PH MEASUREMENT

An Accumet Basic AB15 pH meter was used for all pH measurements. Prior to use, the pH meter was calibrated using the following procedures. First, the electrode was immersed in pH 4 buffer, after which we pressed the *std* button and waited for the reading to stabilize. Once the display screen indicated "STABLE," we pressed *std* again to store the standard. We confirmed that the % slope was in the range of 90 and 100%, indicated by "GOOD ELECTRODE" display

on the screen. Then the process was repeated with a pH 7 and a pH 10 buffer. The calibration steps were repeated each day the pH meter was used. After calibration, the pH meter was used for reading the pH of the experimental water. The electrode was rinsed with E-pure and placed in a sample until the reading stabilized.

3.5.2 ALKALINITY TITRATION

To test the alkalinity of a sample, a titration burette with 0.1N hydrochloric acid was used to titrate the sample while monitoring its pH. For this titration, a sample volume of 100 mL was measured into a beaker and placed on a stir plate. After the initial pH reading was taken, HCl was slowly added to the sample until it reached a pH of 4, ensuring the titration endpoint was reached. The actual endpoint of the titration is pH 4.5, however the sample was titrated to pH 4 to make sure the endpoint was passed. A titration curve can be drawn to identify the endpoint based on an inflection point. Therefore, with a known amount of titrant used to reach pH the inflection point, total alkalinity expressed in mg/L as CaCO₃ was calculated using Equation 4:

$$\text{Alkalinity} = \text{mg} \frac{\text{CaCO}_3}{\text{L}} = \frac{A \times N \times 50,000}{\text{mL sample}} \quad (\text{Equation 4})$$

Where:

A = amount of HCl used in mL

N = normality of HCl

3.5.3 HARDNESS TITRATION

For hardness titrations, standard EDTA titrant, EDTA buffer solution, and calmagite indicator were prepared. The buffer solution for hardness titrations was prepared by dissolving 16.9 g of ammonium chloride (NH₄Cl) in 143 mL of concentrated ammonium hydroxide (NH₄OH). Next, 1.25 g magnesium salt of EDTA was added and the solution was diluted to 250 mL with E-pure water. To prepare 0.001 M standard EDTA titrant, 0.3723 g of analytical reagent-grade EDTA was dissolved in E-pure water and diluted to 1,000 mL. The titrant had an expiration period of four weeks, after which new titrant was made. To prepare the calmagite indicator solution, 0.10 g of Calmagite was dissolved in 100 mL of E-pure.

Because the hardness in the experiments was relatively high, samples were diluted to reduce the amount of titrant used in each titration. To measure hardness, 1 mL of sample was diluted with 99 mL of E-pure in a flask and placed on a stir plate. Next, 1 to 2 mL of buffer was added to the sample to raise the pH to approximately 10, which was verified using a pH meter. Next, approximately 10 drops of calmagite indicator solution were added, which changed the color of the sample to dark pink. Then, standard 0.001 M EDTA titrant was slowly added while the solution turned purple and then blue at the endpoint of the titration. The volume of the titrant used to reach the blue endpoint was recorded in order to calculate the total hardness of the sample using Equation 5. All titrations were performed in less than 5 minutes to ensure a clear color change to signify the endpoint of the titration.

$$\text{Hardness} \left(\frac{\text{mg}}{\text{L}} \text{ as } \text{CaCO}_3 \right) = \frac{A \times B \times 1,000}{\text{mL sample}} \quad (\text{Equation 5})$$

Where:

A = volume of titrant used in mL

B = strength of titrant in g/L (for this calculation, used 0.001 M = 0.1 g/L)

3.5.4 AA MEASUREMENT

To quantify iron, manganese, and aluminum concentrations before and after treatment, the samples were analyzed using the atomic absorption spectrophotometer (AA). The AA uses light produced by a flame to measure the amount of a specific metal in solution. Every time the AA was needed for measurements, a standard curve was prepared using standard solutions of 0.1, 0.5, 1.0, and 3.0 ppm Fe^{+3} and Mn^{+3} . The unknown concentrations of our samples were determined by using the absorbance data and interpolating the values from the standard curve. For aluminum measurements, the graphite furnace was used in order to measure concentrations in the desired range. All AA measurements were conducted by Don Pellegrino, the laboratory manager for the Department of Civil and Environmental Engineering at WPI.

3.5.5 CHLORINE MEASUREMENT

The free and total chlorine concentrations were measured using a Hach DR/3000 Spectrophotometer. Free chlorine was measured by accessing stored program #8 and selecting a wavelength of 530.0 nm. Next, two spectrophotometer cells were filled with 25 mL of sample. One was placed into the cell holder as a zero concentration reference sample. The contents of one DPD Free Chlorine reagent powder pillow were added to the second cell. A stopper was placed in the cell and the cell was shaken for 20 seconds. Within one minute, it was placed in the cell holder and the free chlorine concentration was displayed on the screen in mg/L.

Similarly, the total chlorine concentration was measured. Stored program #8 was accessed and the same wavelength was selected. Two spectrophotometer cells were filled, one of which served as a zero reference concentration. The contents of one DPD Total Chlorine reagent powder pillow were added to the second cell and shaken for 20 seconds, after which the sample was allowed to react for 3 minutes. After zeroing the instrument, the sample was placed in the cell holder and the total chlorine concentration was read on the display screen in mg/L.

4. RESULTS AND DISCUSSION

This chapter presents the results of experiments conducted in the laboratory. These results are compared to theoretical predictions and explanations of any discrepancies between theoretical and experimental results are also provided. Conclusions are drawn as to what treatment methods were more effective. Then, a prototype design for pretreatment of brackish water is provided, along with results of its effectiveness in reducing fouling contaminants. Lastly, a full scale design for a 1 MGD pretreatment facility is presented.

4.1 SOFTENING

The following sections present results on softening experiments including precipitative softening and ion exchange. Precipitative softening was tested using various chemicals: lime, soda ash, and caustic soda. Various chemical doses were tested to determine the optimum dose for the removal of hardness. Ion exchange was also tested for the removal of hardness using a column filled with strong cation resin. The effectiveness of each softening experiment was analyzed and a softening treatment method for the pretreatment system was selected.

4.1.1 LIME AND SODA ASH

Initially, lime and soda ash were tested on individual carbonate and non-carbonate hardness samples. Lime doses ranged from 176 to 444 mg/L and soda ash doses ranged between 560 and 1120 mg/L. Tables 20 and 21 present the results of hardness removal with lime and soda ash, respectively.

In individual samples, lime was effective at removing calcium carbonate hardness at higher doses. At a 444 mg/L dose, approximately half of the hardness was removed. In the case of magnesium, lime was less effective; however, final hardness concentrations did decrease with a respective dose increase. Table 21 illustrates that soda ash was very effective at removing non-carbonate hardness from the calcium sample, however the hardness of the magnesium sample remained the same.

Table 20 Carbonate Hardness Removal with Lime

Sample #	Sample description	Lime Dose (mg/L)	Initial Hardness (mg/L CaCO ₃)	Final Hardness (mg/L CaCO ₃)
1	CaCO ₃	176	1550	1070
2	CaCO ₃	268	1550	880
3	CaCO ₃	361	1550	1170
4	CaCO ₃	444	1550	750
5	MgCO ₃	176	1100	1000
6	MgCO ₃	268	1100	950
7	MgCO ₃	361	1100	810
8	MgCO ₃	444	1100	700

Table 21 Non-Carbonate Hardness Removal with Soda Ash

Sample #	Sample description	Soda Ash Dose (mg/L)	Initial Hardness (mg/L CaCO ₃)	Final Hardness (mg/L CaCO ₃)
1	CaCl ₂	560	1400	720
2	CaCl ₂	1120	1400	280
3	MgCl ₂	560	620	600
4	MgCl ₂	1120	620	600

Experimental results show that lime and soda ash were more effective in removing calcium than magnesium hardness. Mg reactions generally require a higher pH. Although the pH was raised to 10 in both types of samples prior to softening chemical addition, it is possible that the sample pH did interfere with adequate removal. Another problem that arose during softening tests was MgCl₂ sample preparation. As shown in Table 21, the initial hardness of the Mg sample is 620 instead of the desired 1,400 mg/L. It is unknown why preparation of the water according to the theoretical calculations described in Section 3.2.1.1 did not result in the appropriate sample hardness.

Because a successful Mg sample could not be prepared, a combined sample containing both carbonate and non-carbonate hardness was prepared using only CaCO₃ and CaCl₂. Therefore, Mg hardness removal results presented in this report are inconclusive. Table 22 presents hardness removal results from a combined calcium hardness sample. The sample

contained a sufficient amount of alkalinity to ensure the correct distribution of carbonate and non-carbonate hardness. Four different softening trials were conducted: lime alone, soda ash alone, lime and soda ash together, and caustic soda. The doses of lime and soda ash were intended to remove all hardness from the sample.

Table 22 Hardness Removal in Combined Carbonate and Non-Carbonate Sample

Sample #	Softener Added	Dose (mg/L)	Initial Hardness (mg/L CaCO ₃)	Final Hardness (mg/L CaCO ₃)
1	Lime	700	2160	2200
2	Soda Ash	1484	2160	800
3	Lime & Soda Ash	700 1484	2160	1500
4	Caustic Soda (6 N)	Raised pH to 10	2160	1000

Contrary to the results obtained from testing individual samples, in this case lime did not remove any hardness from the sample. The results indicate that hardness was added, however, it may have been the result of the hardness measuring technique not being precise. Inconsistency in softening results using lime could be attributed to the lime stock solution preparation. When the stock was prepared, the non-hydrated form of lime (CaO) was used instead of the recommended Ca(OH)₂. The lime did not dissolve completely, which may have resulted in inconsistent doses when the stock solution was used. Also, a separate step was needed to raise the pH in order to force the precipitate to form. Lastly, the dose of lime was based on the stoichiometric ratio of lime to carbonate hardness, assuming no other competing reactions in the water. However, lime also reacts with constituents such as carbon dioxide, causing an additional demand for lime above what is needed for softening. This was not accounted for and thus the softening dose may have been too low.

A last experiment was conducted in which the pH was raised to 10 using caustic soda but no other softening chemical was added. The residual hardness of the sample treated with caustic soda was 1000 mg/L. Therefore, pH adjustment alone was able to reduce the hardness to a similar or lower level than achieved using soda ash (800 mg/L) or lime and soda ash (1,500 mg/L). Considering the various options, precipitative softening alone did not provide sufficient removal of hardness and thus an additional treatment step was required. In order to keep the

pretreatment process as simple as possible, caustic soda softening (which only requires one chemical addition) was concluded to be the most desirable option. Although caustic soda is usually more expensive than other chemicals, the other options considered required a pH adjustment prior to the chemical addition, which would therefore be more expensive due to the addition of multiple chemicals.

4.1.2 ION EXCHANGE

As an alternative to precipitative softening, ion exchange was tested for hardness removal. As described in the methods, ion exchange was tested with a strong cation sodium exchanger in a flow-through column at a flow rate of 9.7 mL/min. Table 23 and Figure 3 present the results of the ion exchange run tested on sample water with initial hardness of 2,400 mg/L as CaCO₃, and run for a total of 4 hours.

Table 23 Ion Exchange Hardness Removal

Time (min)	Hardness (mg/L as CaCO₃)
0	2400
15	20
30	4
45	4
60	5
80	10
100	11
120	7
140	9
160	6
180	22
200	75
220	274
240	700

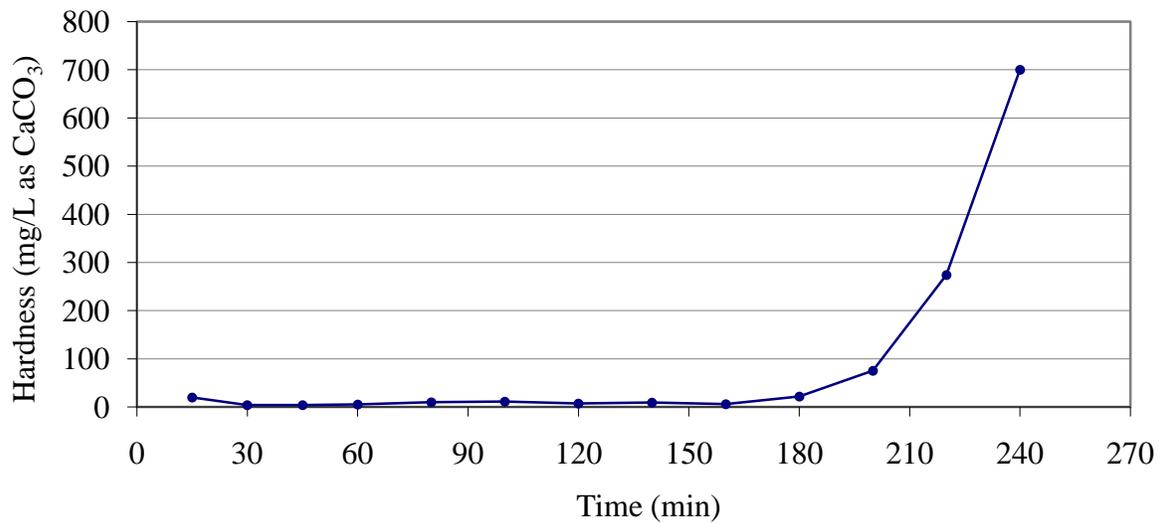


Figure 3 Ion Exchange Hardness Removal

As shown in Figure 3, ion exchange is an effective treatment process for removing hardness. For the first 180 minutes, the residual hardness was less than or equal to 22 mg/L. After 220 minutes, the resin became exhausted and therefore a breakthrough in hardness concentration occurred. The calculated theoretical breakthrough time for an initial hardness of 2,400 mg/L was approximately 210 minutes, which closely matches experimental data.

During the laboratory ion exchange run, not all of the resin was saturated with experimental water due to imperfect hydraulic conditions in the column. Because the resin may not have been fully utilized, breakthrough may have occurred more quickly than with ideal flow conditions. One way to improve performance of the resin in the design phase is to ensure that the water runs through the entire volume of the resin. Another way is to design ion exchange columns in series. Arranging columns in series allows for a better utilization of the resin because even after breakthrough occurs, available sites remain. Having the effluent go through a second ion exchanger provides a polishing step while allowing for complete exhaustion of the resin in the first column before regeneration. For a design in series, three columns are typically provided so that adequate treatment is provided by any two of them while the third column is backwashed.

Although ion exchange is generally an effective and energy efficient option, it is not practical for hardness levels as high as 2,650 mg/L as CaCO₃ because the resin is exhausted rather quickly and needs to be regenerated often. To increase the efficiency of this option, we concluded that precipitative softening (with settling and filtration to remove the precipitate) with caustic soda prior to ion exchange would result in the desired hardness removal and extend the life of the ion exchange resin. This combination of processes was used in the final pretreatment design.

4.2 IRON & MANGANESE REMOVAL

To remove iron and manganese, oxidation experiments were tested using chlorine, potassium permanganate, and ozone. Samples were tested using various doses of chemical oxidants, and were ozonated for various lengths of time. The oxidation experiment results were analyzed to determine which oxidant was the most effective for the removal of iron and manganese.

4.2.1 CHLORINE AND POTASSIUM PERMANGANATE OXIDATION

Results of chlorine and potassium permanganate oxidation experiments are shown in Tables 24 and 25, respectively.

From the results summarized in Table 24, it was concluded that chlorine is effective in removing iron and manganese if a sufficient dose is used to provide a residual of at least 0.5 mg/L. In the first three samples, Fe and Mn were not reduced sufficiently because the dose was too low, or because vigorous mixing of the sample caused some of the chlorine to volatilize. In samples 9-13, the dose was adjusted to provide a sufficient residual for the oxidation reactions to go to completion and mixing was reduced. With sufficient time, both iron and manganese were oxidized sufficiently; however, from a practical standpoint, a contact time of three hours is too long to consider the treatment method practical. The residual post-treatment free and total chlorine concentrations were 1.12 and 1.13 mg/L, respectively, for samples 1 through 5. A potential drawback of using chlorine is the need for de-chlorination after the oxidation reactions are complete, as chlorine is known to degrade RO membranes.

Table 24 Chlorine Oxidation Results

Sample #	Sample Description	Oxidant	Oxidant Dose (mg/L)	Initial pH	Contact Time (min)	Initial Conc (mg/L)	Final Conc (mg/L)
1	Fe	Cl ₂	0.29	8.2	15	0.453	0.33
2	Fe	Cl ₂	0.29	8.2	30	0.453	0.31
3	Mn	Cl ₂	1.216	8.2	60	0.943	0.76
4	Mn	Cl ₂	1.216	8.2	120	0.943	0.76
5	Mn	Cl ₂	1.216	8.2	180	0.943	0.81
6	Fe + Mn	Cl ₂	0.7	8.2	30	Fe - 0.261 Mn - 0.416	Fe - 0.11 Mn - 0.22
7	Fe + Mn	Cl ₂	0.7	8.2	120	Fe - 0.261 Mn - 0.416	Fe - 0.11 Mn - 0.23
8	Fe + Mn	Cl ₂	0.7	8.2	180	Fe - 0.261 Mn - 0.416	Fe - 0.16 Mn - 0.3
9	Fe + Mn	Cl ₂	1.205	8.4	15	Fe - 0.27 Mn - 0.20	Fe - <1.0 Mn - 0.14
10	Fe + Mn	Cl ₂	1.205	8.4	30	Fe - 0.27 Mn - 0.20	Fe - <1.0 Mn - 0.16
11	Fe + Mn	Cl ₂	1.205	8.4	60	Fe - 0.27 Mn - 0.20	Fe - <1.0 Mn - 0.15
12	Fe + Mn	Cl ₂	1.205	8.4	120	Fe - 0.27 Mn - 0.20	Fe - <1.0 Mn - 0.11
13	Fe + Mn	Cl ₂	1.205	8.4	180	Fe - 0.27 Mn - 0.20	Fe - <1.0 Mn - <0.1

Table 25 Potassium Permanganate Oxidation Results

Sample #	Sample Description	Oxidant	Oxidant Dose (mg/L)	Initial pH	Contact Time (min)	Initial Conc (mg/L)	Final Conc (mg/L)
1	Fe	KMnO ₄	0.426	5.5	15	0.453	<0.1
2	Fe	KMnO ₄	0.426	5.5	30	0.453	<0.1
3	Fe	KMnO ₄	0.426	5.5	60	0.453	0.13
4	Mn	KMnO ₄	1.81	5.5	1	0.943	1.4
5	Mn	KMnO ₄	1.81	7	1	0.943	1.3
6	Fe + Mn	KMnO ₄	1.045	7.5	15	Fe - 0.261 Mn - 0.416	Fe - 0.2 Mn - 0.67
7	Fe + Mn	KMnO ₄	1.045	7.5	60	Fe - 0.261 Mn - 0.416	Fe - 0.21 Mn - 0.67

In the case of potassium permanganate, manganese concentrations increased in all of the experiments. The additional manganese came from the permanganate itself, and may have been due to the potassium permanganate not being in the correct oxidation state. Iron was not reduced significantly with the use of potassium permanganate. Some of the inconsistencies in iron removal can be explained by the difficulties in preparing the iron sample. Each time the sample was prepared, there were differences in how much of the iron was dissolved, which affected the removal results. Because the iron was not dissolved sufficiently, some of the removal can be attributed to filtration and not necessarily the oxidation method used. In the case of manganese removal in samples where both metals are present, higher removal than in the individual sample can be explained by some of the manganese being adsorbed onto the iron precipitate.

4.2.2 OZONE

Ozone was also tested as an alternative for iron and manganese oxidation. The ozone generator was set to an output rate of 10 standard cubic feet per hour, and the experimental water which contained iron and manganese was ozonated for 5 minutes, settled for 5 minutes or 15 minutes, and filtered. Fe and Mn concentrations were measured before and after ozone treatment, and the results are presented in Table 26.

Table 26 Ozone Oxidation Results

Ozone Time (min)	Settling Time (min)	Initial Fe Conc. (mg/L)	Final Fe Conc. (mg/L)	Initial Mn Conc. (mg/L)	Final Mn Conc. (mg/L)
5 min	5 min	0.60	< 0.1	0.33	0.154
5 min	15 min	0.60	< 0.1	0.33	0.130

From the results summarized in Table 26, it was concluded that ozone is effective in removing iron, however the ozone only oxidized half of the initial manganese concentration. Manganese was not reduced sufficiently because the sample was not ozonated long enough, or because the output rate of the ozone generator was not high enough. Table 17 in Section 3.3.2. illustrates that the removal of manganese requires approximately twice the dose of oxidant than for the removal of iron for oxygen, chlorine, chlorine dioxide and potassium permanganate. Although ozone was not listed as an oxidant on Table 17, it can be predicted that the ozone dose to remove manganese is higher than the dose needed to remove iron. If additional ozone experiments were tested, the sample water would be ozonated for a longer period of time in order to remove manganese.

4.3 ALUMINUM REMOVAL

Options for removal of aluminum were considered based on literature research and the chemical properties of aluminum. The initial concentration of aluminum in the feed water was 0.4 mg/L Al^{+3} . This value was converted to molarity using the molecular weight:

$$\frac{0.4 \text{ mg } Al^{+3}}{L} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol } Al^{+3}}{27 \text{ g}} \times \frac{1 \text{ mol } Al(OH)_3}{1 \text{ mol } Al^{+3}} = \frac{1.5 \times 10^{-5} \text{ moles } Al(OH)_3}{L}$$

Our goal was to reduce the concentration to 3.7×10^{-6} mol/L (0.1 mg/L) through pretreatment. Although aluminum is typically in a soluble state at pH values greater than 7, during precipitative softening, aluminum can sometimes be captured by other precipitates as it settles, thereby removing some of the aluminum concentration in the water (Droste, 1999). Another more reliable option is to remove aluminum through ion exchange. Aluminum can easily be removed through ion exchange at slightly acidic conditions (MWH, 2005). Based on

this information, it was concluded that if aluminum is present in solid form, it would be removed during precipitative softening followed by sand filtration. If it was present in the dissolved form, some removal through softening would be expected, and the remaining dissolved aluminum will be removed by ion exchange provided slightly acidic conditions were maintained. Therefore, other alternatives for aluminum removal, such as activated carbon adsorption, were not necessary for its removal and were not tested during this project. The effectiveness of the pretreatment process for aluminum removal was tested using the prototype (see Section 4.4.1.2) to verify that the aluminum goal concentration was met.

4.4 DESIGN

In addition to the laboratory results presented in Section 4.3, each of the treatment alternatives was qualitatively evaluated based on cost and efficiency as summarized in Table 27. For precipitative softening, although caustic soda is a more expensive softener, it removes both carbonate and non-carbonate hardness together, generates less sludge, and is easy to store compared with lime and soda ash. While oxidants such as chlorine, potassium permanganate, and ozone are all effective at removing iron and manganese, chlorine requires a long reaction time, potassium permanganate is generally expensive, and ozone treatment is not energy efficient. Ion exchange, which is effective at removing hardness, iron, manganese, and aluminum, can produce a high quality effluent, and is energy efficient. Disadvantages of ion exchange include low efficiency with high dissolved solids, requiring frequent backwashing and maintenance.

After evaluating the available options, precipitative softening using caustic soda, sedimentation, rapid sand filtration and ion exchange were selected for the final pretreatment design. The precipitative softening raises the water sample pH to 10, thereby precipitating calcium, magnesium, iron, manganese and aluminum particles. The precipitates are subsequently removed through settling and filtration. Next, the ion exchanger acts as a polishing treatment method, removing any residual hardness and aluminum remaining in the water, but also removing iron and manganese.

The following sections provide details on the bench-scale prototype that was designed, constructed and tested to demonstrate its effectiveness in pretreating brackish waters. Then, a full scale model design for a 1 MGD treatment plant is presented.

Table 27 Summary of Pretreatment Options

Alternatives	Constituent	Advantages	Disadvantages
<i>Precipitative Softening</i>			
Lime/ Soda ash	Hardness	- Inexpensive - Decreases total dissolved solids	- Both chemicals needed when carbonate and non-carbonate hardness present - More sludge generated - Storage and feeding problems (lime)
Caustic soda	Hardness	- Removes both types of hardness - Generates less sludge - Easy to store	- Expensive - Increases total dissolved solids
<i>Oxidation</i>			
Chlorine	Fe and Mn	- Inexpensive - Easy to dose	- Long reaction time - Trihalomethane formation
Potassium Permanganate	Fe and Mn	- Efficient - Lower capital costs - Short reaction time	- More expensive - Need careful dose control - May compromise filter performance
Ozone	Fe and Mn	- Effective in presence of humic materials - Short reaction time - No chemicals	- High energy - Onsite generation - Need careful dose control
<i>Activated Carbon Adsorption</i>			
GAC	Al	- Acts as filter - Organics removal	- Requires regeneration
PAC	Al	- Organics removal	- Filtering required
<i>Ion Exchange</i>			
Ion Exchange	Hardness Fe, Mn, and Al	- Removes all constituents - Can handle fluctuating flows - High quality effluent - Many resins available - Low energy	- Al removal requires slightly acidic feed water - Highly concentrated waste - Low efficiency with high total dissolved solids

4.4.1 PROTOTYPE

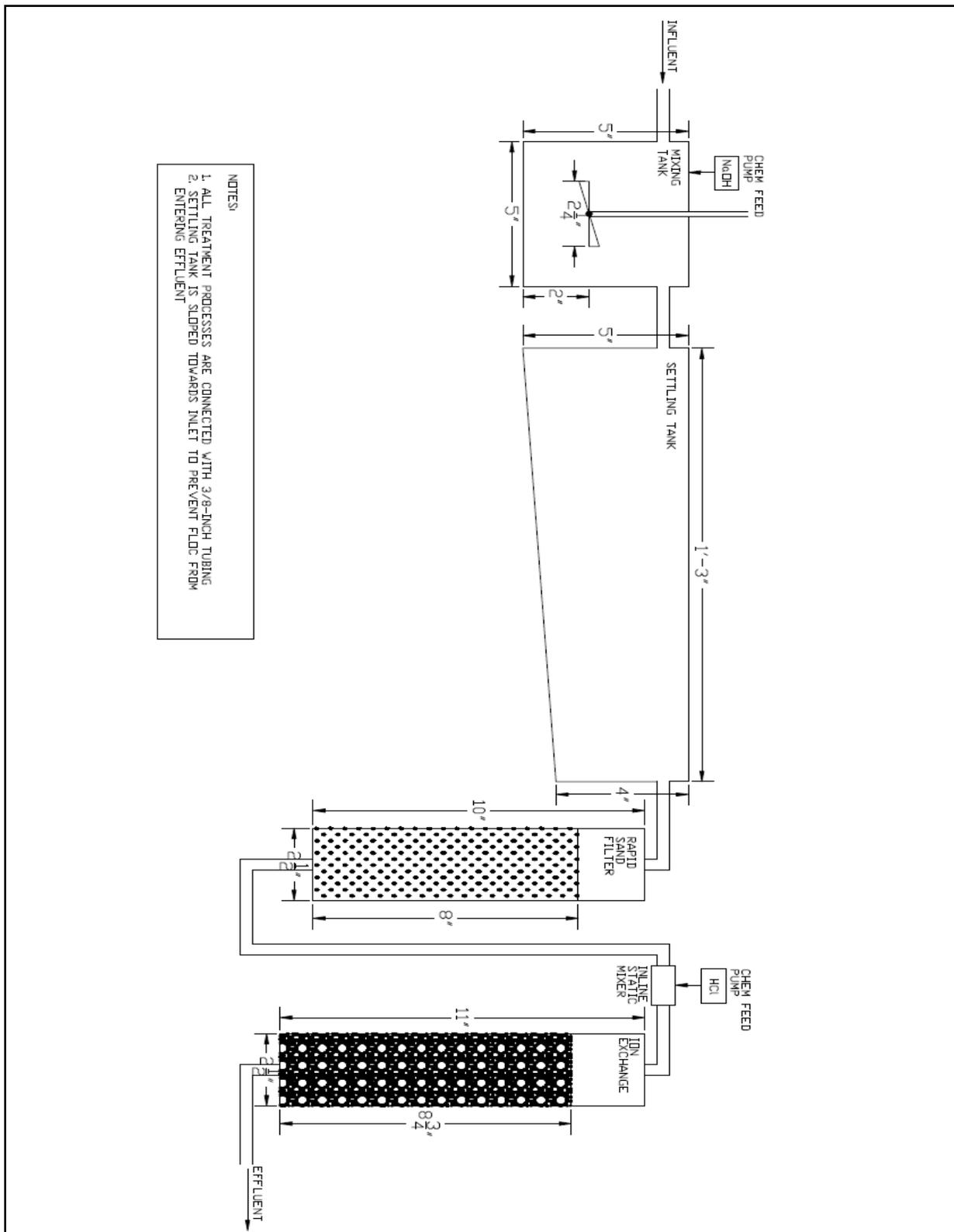
Figure 4 illustrates the prototype pretreatment system, which consists of a mixing tank into which caustic soda is added and precipitation reactions occur, a settling basin and rapid sand filter to remove solids, an inline static mixer to reduce the pH to 6.5 using hydrochloric acid, and ion exchanger. The prototype was designed for a flow rate of 2.5 gallons per hour. For detailed calculations of design parameters, refer to Appendix B.

The first treatment process consists of a mixing tank where caustic soda is added to the influent water, increasing the pH to 10. Typical mixing tanks have a contact time between 5 and 20 minutes, therefore an average contact time of 10 minutes was chosen for the mixing tank (MWH, 2005).

After the caustic soda is fully mixed in the mixing tank, it travels to the sedimentation tank where the precipitate is allowed to settle. The sedimentation tank was designed using a length-to-depth ratio of 15:1, and a width-to-depth ratio of 5:1, which promotes plug flow conditions in rectangular sedimentation basins. In general, long, narrow, and relatively deep basins are preferred to minimize short circuiting. The length of the sedimentation basin is also extremely important to allow the particles sufficient time to settle prior to leaving the tank. For a full-scale water or wastewater treatment plant, sedimentation tanks typically have a detention time of between 1 and 4 hours depending on the size of the facility. A 26-minute detention time was considered sufficient time for the removal of particulate matter for our pretreatment prototype design because pilot-scale sedimentation tanks, depending on the size of the tanks, need at least 20 minutes to allow sufficient settling (calculations are provided in Appendix B) (MWH, 2005).

The sedimentation tank was designed to remove most of the precipitate from the water, and a rapid sand filter was designed as a subsequent process to remove any particulate matter still suspended in solution. Sand was chosen as the filter media because it is inexpensive and easily accessible. Before utilization of the sand filter, experimental water was pumped through the filter in order to accommodate for the ripening period of the sand. The ripening period allowed particulate matter to attach to the sand filter, thereby increasing its effectiveness.

The last treatment process in the prototype design is ion exchange. The pH of the water is lowered by adding hydrochloric acid using an inline mixer prior to ion exchange treatment. A sodium strong cation resin was chosen for the ion exchange media in order to remove any remaining hardness ions, iron and manganese ions, as well as aluminum ions. The pH was adjusted to approximately 6.5 because aluminum can be removed through ion exchange at slightly acidic conditions (MWH, 2005).



- NOTES:
1. ALL TREATMENT PROCESSES ARE CONNECTED WITH 3/8-INCH TUBING
 2. SETTLING TANK IS SLOPED TOWARDS INLET TO PREVENT FLOC FROM ENTERING EFFLUENT

Figure 4 Prototype Pretreatment System

4.4.1.2 PROTOTYPE TEST RUN

The prototype system was tested using prepared sample water with constituent concentrations similar to those of the TBPDF. The system was run in flow-through mode, treating 5 liters of water over a 2-hour time period. The results of the test run are presented in Table 28. Hardness samples were collected periodically throughout a 1.5 hours period, and the concentrations of the other constituents were tested after the prototype was running for approximately 1 hour.

Table 28 Prototype Test Run Results

Constituent	Initial Conc. (ppm)	Conc. after Sand Filter (ppm)	Final Conc. after Ion Exchange (ppm)
Hardness (as CaCO ₃)	2650	500	50
Iron	0.50	< 0.1	< 0.1
Manganese	0.37	< 0.1	<0.05
Aluminum	0.59	<0.05	<0.05

According to the test run results, the prototype system was successful at reducing all constituents to below the desired concentrations listed in Table 5. Therefore, the pretreatment system will significantly increase the performance of RO membranes by reducing the concentration of fouling contaminants, and this in turn reduces operating costs. Using these results, a full-scale pretreatment system with a capacity to treat 1 million gallons of water per day was designed.

4.4.2 FULL-SCALE DESIGN

The full-scale pretreatment system was designed for 1 million gallons per day (MGD) because it is a typical flow rate for a small municipal groundwater treatment system (MWH, 2005). Multiple treatment trains are utilized to allow units to be taken off-line for backwashing, maintenance or repairs. Design parameters are listed in Table 29, and Figure 5 provides the configuration of the pretreatment system. For detailed calculations of design parameters, refer to Appendix C. The subsequent sections discuss each unit process in detail.

Table 29 Full-Scale Design Parameters

Unit	No. of units	Flow rate	Detention Time (min)	Dimensions (ft)	Potential Material	Design considerations
Mixing tank	2	694 gpm	10	Diameter – 10 Height – 12	Concrete; HDPE	NaOH addition/storage
Settling basin	4	1 gpm/ft ²	90	Length – 30 Width – 7.8 Depth – 12	Concrete; HDPE	Manual/automatic sludge removal; Sludge disposal
Sand filter	4	4 gpm/ft ²	N/A	Length – 9 Width – 6.5	Concrete	Backwash system/waste
Ion exchange	12	N/A	5	Diameter – 4 Height – 5	Concrete; HDPE; Fiberglass	HCl addition/storage; Backwash system

4.4.2.1 MIXING TANK

The mixing tank for precipitative softening is designed for the full capacity of 1 MGD or 694 gallons per minute (gpm) with a detention time of 10 minutes. Typical mixing tanks have a contact time between 5 and 20 minutes, therefore an average contact time of 10 minutes was chosen for the mixing tank (MWH, 2005). The tank is 10 feet in diameter and 12 feet in height with an impeller for mixing. A NaOH feed pump and inline mixer are provided to raise the pH of the feed water to 10 prior to entering the mixing tank. A chemically resistant storage area is provided to store dry NaOH as well as a day tank to more accurately monitor daily chemical use.

4.4.2.2 SETTLING BASIN

The settling basin was designed for an overflow rate of 1 gpm/ft² with a detention time of 1.5 hours. These values were chosen because typical design criteria for horizontal-flow rectangular tanks have average overflow rates between 0.5 and 1.0 gpm/ft², and detention times between 1.5 to 4 hours. A shorter detention time was chosen because the flow rate for this groundwater treatment facility is relatively small compared to surface water treatment plants. Each basin is 30 feet in length, 7.8 feet in width and 12 feet in depth. These values were chosen based on width-to-depth and length-to-width ratios of 15:1 and 5:1, respectively. These ratios were necessary in order to allow enough time for the particulate matter to settle in the tank. A depth of 12 feet was chosen because the minimum depth required for a settling tank is approximately 8-10 feet. This depth ensures adequate volume for sludge deposit (MWH, 2005).

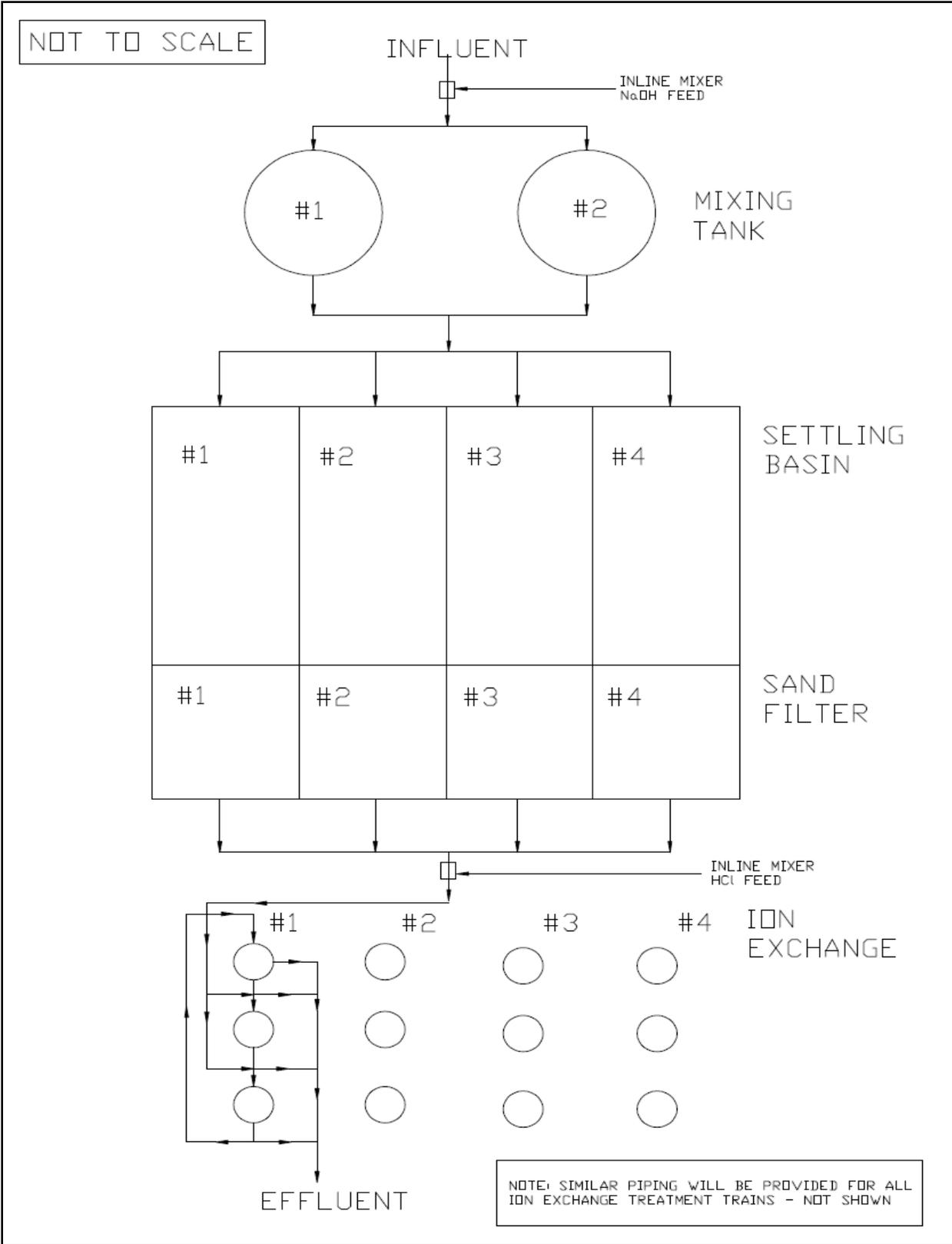


Figure 5 Full-Scale Pretreatment System

A manual or automated sludge mechanism is required. Manual sludge removal is recommended because it is more cost-effective and is typically used at smaller water treatment facilities. Four tanks are provided to handle the full capacity when any three tanks are on-line. This allows the fourth tank to be taken off-line for manual sludge removal if necessary. Upon removal, sludge is transported to the onsite lined lagoons/drying beds.

4.4.2.3 RAPID SAND FILTER

The mono-media rapid sand filter was designed for an average loading rate of 4 gpm/ft². Typical loading rates for rapid sand filtration range between 2 and 6 gpm/ft² (MWH, 2005). Four filters are provided, each with a length of 9 feet and width of 6.5 feet with a typical media depth of 2 feet. Typical bed depths range from 2 – 6 feet, and the other parameters of the sand filter were designed in order to accommodate 1 MGD flow rate (MWH, 2005). This configuration allows for one filter to be off-line at all times. Sand with grain size of 0.5-mm is used as the media, with typical media diameters ranging from 0.5 – 1.2 mm (MWH, 2005). A turbidimeter is used to monitor the turbidity of the sand filter effluent. At a turbidity level of 0.5 NTU, the filter is backwashed because turbidity higher than 1 NTU causes plugging of ion exchange resins (HDR Engineering, 2001). A backwash system is provided, with the backwash water disposed of in the drying lagoons.

4.4.2.4 ION EXCHANGE

Prior to entering the ion exchange column, the pH of the feed stream is adjusted to 7 with HCl via an in-line static mixer and HCl feed pump. Ion exchange columns are designed in series to allow for full utilization of the resin. Four treatment trains are utilized with three columns in each train to allow for resin regeneration. The columns are 4 feet in diameter with a media height of 5 feet. Appropriate dimensions for each column were determined based on a 4 ft diameter, which is a typical dimension for larger ion exchange columns (MWH, 2005). The media is automatically backwashed with a concentrated salt solution every 20 hours to regenerate the resin. A low cost option is to use the waste stream from the RO process at the TBPDF for regeneration. The weak brine regeneration alternative uses 6-7 pounds of salt to regenerate each cubic foot of ion exchange media (NHDES, 2001). To regenerate the ion exchange media, approximately 2,964 lbs of salt are needed. According to the sodium concentration of the feed

stream, in addition to the sodium ions exchanged for hardness ions, the total salt concentration of the RO waste stream is approximately 0.06 lbs/ft³. At an efficiency of 100 bed volumes treated before regeneration, 2,882 lbs of salt are produced, which is comparable to the necessary 2,964 lbs (Note: All calculations were performed using the resin volume contained in 8 ion exchange columns, assuming that one of the three columns in series will always be offline and may be used for maintenance, repairs, and backwashing).

4.4.2.5 PROCESS MONITORING

All process monitoring is done by a Supervisory Control and Data Acquisition (SCADA) system which calculates proper chemical dosing to account for variability of the feed water characteristics. pH is monitored at the inlet of the system, after NaOH addition, prior to and after HCl addition and at the outlet of the system. Turbidity is monitored prior to ion exchange ensuring it does not exceed 0.5 NTU in case the sand filter backwash system is not functioning properly. Hardness concentration of the effluent is monitored to ensure it is low enough not to foul RO membranes. Limits on the parameters are set through the SCADA system and the water stream is sent to appropriate back up treatment units while the primary units are backwashed or serviced.

4.4.2.6 ADHERENCE TO REGULATIONS

The Environmental Protection Agency (EPA) enacted the Safe Drinking Water Act (SDWA) in 1974 to ensure quality drinking water for the general public. The EPA specifies standards for drinking water quality and treatment, and also oversees all states and municipal water suppliers who implement these standards. The New Mexico Environment Department Drinking Water Bureau has the authority to implement and enforce both the primary and secondary SDWA regulations which control contaminants in drinking water based on Maximum Contaminant Levels (MCLs). Some regulated contaminants include *Cryptosporidium*, *Giardia lamblia*, arsenic, copper, lead, fluoride, and nitrite/nitrate. Adhering to these regulations will help ensure safe drinking water for the public (SDWA, 1974).

Our pretreatment process is designed to meet both federal and state regulations. Federal regulations that apply include the Surface Water Treatment Rules, Groundwater Rule, and Membrane Regulations. The Surface Water Treatment Rule (SWTR) of 1989 requires all

treatment facilities using surface water or groundwater under the direct influence of surface water to disinfect and filter their effluent. The Groundwater Rule (GWR) is targeted for the removal of bacteria and viruses from groundwater sources and has established methods of determining which systems are at risk for fecal contamination. The GWR requires systems that have detected fecal indicators to take corrective action (GWTR, 2006). Regulations pertaining to membrane processes are included in the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR), published in 2006, which awards *Cryptosporidium* log removal credit to facilities that use membrane filtration. Continuous testing of membranes is required to verify their performance. EPA requires membrane facilities to conduct Challenge Testing, Direct Integrity Testing, and Continuous Indirect Integrity Monitoring procedures to verify compliance with the LT2ESWTR (2006).

While New Mexico follows all of the federal regulations, it also has several additional regulations for water treatment facilities. Many of these regulations apply to the permitting process, construction, maintenance, and repair of treatment systems, as well as defining the powers of the secretary who can take any action necessary to protect public health. Regulations of note include the responsibility of the water supplier to notify the public served of any potential health risk associated with the water provided. All parts of the water system, including storage and distribution, must be secured from unauthorized entry, flooding, and contamination. All groundwater wells must be protected from storm water contamination. Finally, any substance added to the water shall be certified by an independent third party and the use of iodine as a disinfectant has been banned (NM Drinking Water Bureau, 2009).

4.4.2.7 COST ANALYSIS

The cost of the pretreatment system was estimated from a 2 MGD facility constructed in 2001 with similar design parameters and anticipated chemical costs. As a rough estimate of costs, the 2001 cost was divided by 2 for the 1 MGD system. Then, the values were scaled using the ENR construction cost index where 8534 is the March 2009 index and 6343 is the average annual 2001 index. For example, Equation 6 shows how the site work cost was scaled. The approximate cost analysis is presented in Table 7. Prior to implementation of a brackish water pretreatment system, a more refined cost analysis is recommended.

$$\$84,000 \times \frac{8534}{6343} = \$113,015 \quad (\text{Equation 6})$$

Table 30 Pretreatment Cost Analysis

Capital Costs	Cost of 2 MGD	Cost of 1 MGD	2009 Cost
Site Work	\$ 168,000	\$ 84,000	\$ 113,000
Concrete	\$ 660,500	\$ 330,250	\$ 444,300
Building	\$ 960,500	\$ 480,250	\$ 646,100
Process	\$ 645,000	\$ 322,500	\$ 433,900
Subtotal	\$ 2,434,000	\$ 1,217,000	\$ 1,637,400
10% Contingency	\$ 243,400	\$ 121,700	\$ 163,700
TOTAL	\$ 2,677,400	\$ 1,338,700	\$ 1,801,100
Annual Costs			
O&M	\$ 29,000	\$ 14,500	\$ 19,500
Power	\$ 60,000	\$ 30,000	\$ 40,400
TOTAL	\$ 89,000	\$ 44,500	\$ 59,900

The costs listed in Table 30 are of the pretreatment system, not including the subsequent reverse osmosis membrane process. Table 31 provides comparative capital and O&M costs of existing brackish water desalination systems, obtained by the U.S. Army Corps of Engineers from existing desalination facilities in Florida as of 1997 (IETC, 1997). These costs were scaled to the current year and to the full scale system size (1 MGD flow rate). ENR index values of 8534 for March 2009 and 5826 for 1997 were used to scale the capital and annual costs (Sample calculations are shown in Equations 7 through 10). The resulting costs are presented in Table 32. While the pretreatment process requires a significant capital investment, high O&M costs of the RO process can be significantly reduced due to the increased efficiency and membrane life.

Table 31 U.S. Army Corps of Engineers Cost Estimates of RO Desalination Plants in Florida (IETC, 1997)

Feed water Type	Capital Cost (\$/m ³ /day)	O&M Cost (\$/m ³)
Brackish water	380 - 562	0.28 - 0.41
Seawater	1341 - 2379	1.02 - 1.54

Using a \$471 mean capital cost value per cubic meter of feed water per day, the capital costs for a brackish water desalination plant in 1997 dollars was determined using Equation 7.

$$\$471 \frac{\$}{m^3/day} \times \frac{m^3}{264.17 \text{ gal}} \times \frac{1,000,000 \text{ gal}}{day} = \$1,782,943 \quad (\text{Equation 7})$$

Similarly, typical annual operation and maintenance costs for a 1 MGD facility in 1997 dollars was calculated using Equation 8.

$$\$0.345 \frac{\$}{m^3} \times \frac{m^3}{264.17 \text{ gal}} \times \frac{1,000,000 \text{ gal}}{day} \times 365 \text{ days} = \$476,682 \quad (\text{Equation 8})$$

The cost figures were then scaled to 2009 dollars as shown in Equations 9 (capital) and Equation 10 (O&M).

$$\$1,800,000 \times \frac{8534}{5826} = \$2,636,663 \quad (\text{Equation 9})$$

$$\$477,000 \times \frac{8534}{5826} = \$698,715 \quad (\text{Equation 10})$$

Table 32 Reverse Osmosis Cost Analysis

Costs	1997 Cost	2009 Cost
Capital	\$ 1,800,000.00	\$ 2,636,700
O&M	\$ 477,000.00	\$ 698,700

4.4.2.7 PUBLIC OUTREACH AND EDUCATION

With construction of a new facility, local support and public involvement are necessary for funding and ease of implementation. Desalination technologies have several concerns including energy consumption, waste disposal, and social and environmental impacts. High energy consumption and the environmental impacts of brine disposal have been previously discussed. In addition, social, political, and institutional issues play a key role in regulatory and permitting processes. Desalination technologies are not widely used in the United States and therefore limited permitting experience and the complexity of regulations often make implementation difficult (AWWA, 2009).

The treatment system currently in operation at Tularosa Basin is a pilot-scale facility. A full-scale system servicing an entire community requires high capital costs and a large land area to provide for multiple treatment trains and lagoons for brine disposal. Our pretreatment process improves the desalination process by lowering energy consumption and provides a sensible waste disposal solution. Table 33 presents ways in which our pretreatment technology may alleviate common public concerns with desalination technologies. All pertinent information to the construction of the full-scale facility would be made available to future consumers at town meetings.

Table 33 Public Concerns on Pretreatment Technology

Public Concern	Potential Mitigation
Water quality compared to traditional systems	- Treatment system abides by all state and federal regulations - Reverse osmosis technology used in commercial applications (e.g. Dasani)
High capital costs	- Ensures system reliability - Sustainable water solution due to availability of brackish water - Cost offset by pretreatment process
High energy consumption	- Pretreatment removes iron, manganese, aluminum, calcium and magnesium prior to membrane process - Extends membrane life and reduces energy requirement
Concentrate Disposal	- Drying lagoons suitable for New Mexico climate

5. CONCLUSIONS AND RECOMMENDATIONS

After extensive research and many laboratory experiments, a simple, low-energy pretreatment process prior to reverse osmosis or electro dialysis reversal was designed to remove hardness constituents, as well as iron, manganese, and aluminum. The constituent removal increases the efficiency and reduces the operation costs of the subsequent membrane process.

The process involves precipitative softening by increasing the pH of the water to 10, thereby removing approximately half of the hardness ions, and some of the iron and manganese. The process includes a mixing tank to adjust the pH, followed by a sedimentation tank where the particulates settle out of solution.

The second process in the pretreatment system consists of rapid sand filtration. During this process, the residual particles still suspended in solution are removed inside the filter. Hardness was reduced from 2650 ppm as CaCO_3 to roughly 500 ppm as CaCO_3 . Iron, manganese and aluminum were also reduced to less than 0.1 ppm, which is considered appropriate removal prior to the reverse osmosis process.

Ion exchange is the last process of our pretreatment design. This treatment process acts as a polishing mechanism to remove any residual contaminants still left in solution, including hardness. Reducing the hardness prior to a membrane process will reduce fouling on the subsequent membrane process. Furthermore, the ion exchange resin can be regenerated using the reverse osmosis waste stream, further reducing energy requirements.

In conclusion, the pretreatment system designed effectively removes the primary membrane fouling constituents to below target concentrations. With such extensive contaminant removal during pretreatment, a significant reduction in operating costs of membrane processes can be expected.

To extend the scope of this project, given more time and resources, we recommend performing a more detailed cost analysis of the pretreatment system. This cost analysis should include materials of construction, chemical costs, and energy demands of daily operation. In order to compare the performance of a membrane system without pretreatment to a system that utilizes precipitative softening and ion exchange, a full cost analysis of the entire treatment system is needed. A cost comparison with a net gain would further justify constructing a pretreatment system.

Regarding laboratory bench-scale testing, more softening experiments should be performed with higher doses of lime and soda ash without the use of NaOH for pH adjustment. Because NaOH is an expensive chemical, it may be possible to achieve sufficient hardness removal using a less expensive option. It would also be beneficial to repeat the oxidation experiments with a solution with a higher dissolved concentration of iron and manganese. Because we encountered issues with Fe and Mn dissolution, some of the results obtained during oxidation experiments were inconclusive. However, these results did not influence our pretreatment system design because we concluded that the oxidation was not necessary when using ion exchange. With regard to ion exchange, it may be beneficial to test several different resins to determine the optimum resin for a particular water source.

REFERENCES

- American Water Works Association (AWWA), & American Society of Civil Engineers (ASCE), (1998). *Water Treatment Plant Design*. United States: The McGraw-Hill Companies, Inc.
- Bartels, Craig et. al., "New Generation of Low Fouling Nanofiltration Membranes". *Desalination* 221, 1-3 (158-167, 2008)
- Brandhuber, P. (2007, July). Options for Inland Membrane Concentrate Disposal. *Water and Wastes Digest*.
- DOW Water Solutions: Product Selection Guide – DOWEX Resins for Separation of Aluminum from Liquid Media. Retrieved February 5, 2009 from http://www.dow.com/liquidseps/prod/pt_al.htm
- Droste, R. (1997). *Theory and Practice of Water and Wastewater Engineering*. Danvers, MA: John Wiley & Sons, Inc.
- Glater, J. & Cohen, Y. (2003). *Brine Disposal from Land Based Membrane Desalination Plants: A Critical Assessment*. University of California, Los Angeles: Polymer and Separations Research Laboratory.
- HDR Engineering, Inc. Handbook of Public Water Systems, Second Edition (2001).
- Humphreys, Kenneth and Wellman, Paul. Basic Cost Engineering, 1996.
- Hutson, S. S., Barber, N. L., Kenny, J. F., et al. Estimated Use of Water in the United States in 2000. *U.S. Geological Survey*. Retrieved September 30, 2008, from <http://pubs.usgs.gov/circ/2004/circ1268/>
- International Environmental Technology Centre (IETC), & United Nations Environment Programme. (1997). *Source Book of Alternative Technologies for Freshwater Augmentation in Latin America and the Caribbean*. Osaka/Shiga, Japan: UNEP International Environmental Technology Centre. Retrieved February 19, 2009 from <http://www.oas.org/dsd/publications/Unit/oea59e/ch20.htm>
- Mickley, M. C., Membrane Concentrate Disposal: Practice and Regulation," *Desalination and Water Purification Research and Development Program Report No. 69*, September 2001 (Agreement No. 98-FC-81-0054), Prepared for the U.S. Department of the Interior,

Bureau of Reclamation, Technical Service Center, Water Treatment Engineering and Research Group.

MWH. (2005). *Water Treatment Principles and Design*. Danvers, MA: John Wiley & Sons, Inc.

New Hampshire Department of Environmental Services (NHDES). Environmental Fact Sheet: Ion Exchange Treatment of Drinking Water, 2001.

<http://des.nh.gov/organization/commissioner/pip/factsheets/dwgb/documents/dwgb-2-12.pdf>

New Mexico Environment Department. The Drinking Water Bureau: Laws and Regulations. *New Mexico Environment Department*. Retrieved March 2, 2009, from

<http://www.nmenv.state.nm.us/dwb/regulations/index.htm>

Remco Engineering: Water Systems and Controls – Ion Exchange. Retrieved March 1, 2009 from <http://www.remco.com/ix.htm>

Siemens AG. Energy Efficient Desalination Technology. Research and Development, 2008. Retrieved March 4, 2009 from

http://w1.siemens.com/innovation/en/news_events/ct_pressemitteilungen/index/e_research_news/2008/index/e_22_resnews_0828_1.htm

Skehan, S and P. J. Kwiatkowski, “Concentrate Disposal via injection wells – permitting and design considerations,” *Florida Water Resources J.*, May 2000, 19-22.

Skipton, Sharon. *Drinking Water Treatment: Water Softening (Ion Exchange)*. University of Nebraska – Institute of Agricultural and Natural Resources, 2008.

<http://www.ianrpubs.unl.edu/epublic/live/g1491/build/g1491.pdf>

State of California Department of Water Resources. *Water Desalination: Findings and Recommendations*, October 2003.

<http://www.owue.water.ca.gov/recycle/desal/Docs/Findings-Recommendations.pdf>

U.S. Environmental Protection Agency (EPA). Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) Washington, DC: EPA, 2006. Retrieved November 19, 2008, from

<http://www.epa.gov/OGWDW/disinfection/lt2/index.html>

U.S. Environmental Protection Agency (EPA). Safe Drinking Water Act (SDWA) Washington, DC: EPA, 1974. Retrieved November 19, 2008, from

<http://www.epa.gov/safewater/sdwa/index.html>

U.S. Environmental Protection Agency (EPA). Surface Water Treatment Rules (SWTR)

Washington, DC: EPA, 1989. Retrieved November 19, 2008, from

<http://www.epa.gov/ogwdw/dwa/electronic/swtr.html>

U.S. Environmental Protection Agency (EPA). The Groundwater Rule (GWR) Washington, DC:

EPA, 2006. Retrieved November 19, 2008, from

<http://www.epa.gov/safewater/disinfection/gwr/index.html>

Waterline: Minnesota Department of Health. Winter 2004-05, Volume 12/3.

http://www.health.state.mn.us/divs/eh/water/com/waterline/waterline_winter2004_05.pdf

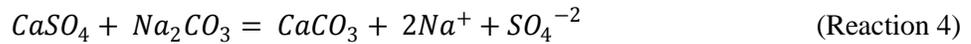
Xu, Pei, et. al., Consider the Pros and Cons of Desalination. American Water Works Association, Opflow (13-3, 2009).

APPENDIX A: SODA ASH SOFTENING CALCULATIONS

A soda ash stock solution was made by adding 5.6 grams of Na_2CO_3 to 100 mL of E-pure water. To determine the dose of soda ash required to treat the water, the concentration of CaCO_3 in the experimental water was first converted to molarity:

$$\text{Hardness} = 1400 \frac{\text{mg CaCO}_3}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol}}{100 \text{ g CaCO}_3} = 0.014 \frac{\text{mol}}{\text{L}}$$

The molar ratio of Na_2CO_3 to hardness was determined from Reactions 4 and 5, assuming the water contains CaSO_4 or CaCl_2 .



For either reaction, 1 mole of soda ash is needed for each 1 mole of non-carbonate hardness removed. Since the initial non-carbonate hardness is 0.014 mol/L, 0.014 mol/L soda ash is required. This was converted to g/L of soda ash.

$$\frac{0.0140 \text{ mol Na}_2\text{CO}_3}{\text{L}} * \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} = \frac{1.484 \text{ g Na}_2\text{CO}_3}{\text{L}}$$

Thus, a 1484 mg/L dose of Na_2CO_3 is needed to remove 1,400 mg/L of hardness. Because the initial strength of the stock was 5,600 mg/L, the volume of stock needed for a 100 mL sample of experimental water was calculated as follows:

$$C_{\text{stock}} \times V_{\text{stock}} = C_{\text{test}} \times V_{\text{test}}$$

$$5,600 \frac{\text{mg}}{\text{L}} \times V_{\text{stock}} = 1484 \frac{\text{mg}}{\text{L}} \times 100 \text{ mL}$$

The resulting stock volume of Na_2CO_3 (soda ash) needed to remove 1,400 mg/L hardness in a 100 mL sample was 26.5 mL.

APPENDIX B: PROTOTYPE DESIGN CALCULATIONS

The prototype design consisted of four main treatment processes: coagulation in a mixing tank, flocculation in a settling basin, filtration in a slow sand filter, and ion exchange in a cylindrical column. Each process was designed based on a flow rate of 2.5 gallons per hour.

Mixing Tank:

The size of the mixing tank was determined using an average detention time of 10 minutes. The volume of the tank was determined from Equation 11.

$$V = Q * t \quad \text{(Equation 11)}$$

Where:

V = Volume of the tank [ft³]

Q = Flow rate [ft³/min]

T = detention time [min]

The tank volume needed to withstand a flowrate of 2.5 gal/hr and a detention time of 10 minutes was calculated:

$$V = \frac{2.5 \text{ gal}}{\text{hr}} * \frac{3.79 \text{ L}}{\text{gal}} * \frac{\text{hr}}{60 \text{ min}} * \frac{0.03532 \text{ ft}^3}{\text{L}} * 10 \text{ min} = 0.056 \text{ ft}^3$$

The tank volume of 0.056 ft³ was needed. Because a circular mixing tank was desired, the radius and height of the tank were chosen based on required total volume using Equation 12:

$$V_{\text{cyl}} = \pi r^2 h \quad \text{(Equation 12)}$$

Where:

V_{cyl} = Volume of the cylinder [ft³]

R = Radius of the cylinder [ft]

H = Height of the cylinder [ft]

With a radius of 2.5 in, the height of the cylinder required to contain 0.056 ft³ was calculated.

$$h = \frac{0.056 \text{ ft}^3 * 12^3 \text{ in}^3 / \text{ft}^3}{\pi * (2.5^2) \text{ in}^2} = 5 \text{ in}$$

The cylindrical mixing tank necessary to withstand a 2.5 gal/hr flowrate must have a radius of 2.5 inches and a height of 5 inches.

Settling Tank:

The size of the settling tank was determined using a length-to-depth ratio of 15:1, and a width-to-depth ratio of 5:1. These ratios are necessary in order to allow enough time for the particulate matter to settle in the tank. With these ratios, a tank size of 5" x 4" x 15" was developed.

$$(5 * 4 * 15) \text{ in}^3 * \frac{1 \text{ ft}^3}{[(12)^3] \text{ in}^3} = 0.1736 \text{ ft}^3$$

The volume of this tank was calculated to be 0.1736 ft³. The detention time for this tank was calculated in order to ensure the particles had at least 20 minutes to settle.

$$\frac{0.1736 \text{ ft}^3}{1} * \frac{\text{gal}}{0.1337 \text{ ft}^3} * \frac{\text{hr}}{2.5 \text{ gal}} * \frac{60 \text{ min}}{\text{hr}} = 26 \text{ min}$$

A 26-minute detention time was considered sufficient time for the removal of particulate matter, therefore, the 5" x 4" x 15" settling tank was constructed.

Rapid Sand Filter:

The size of the rapid sand filter column was determined using an empty bed contact time (EBCT) of 5 minutes and a flowrate of 2.5 gal/hr. The volume of the cylinder was determined using Equation 12.

$$V_{cyl} = \frac{2.5 \text{ gal}}{\text{hr}} * \frac{3.785 \text{ L}}{\text{gal}} * \frac{1000 \text{ ml}}{\text{L}} * \frac{1 \text{ hr}}{60 \text{ min}} * \frac{1 \text{ in}^3}{16.4 \text{ ml}} * 5 \text{ min} = 50 \text{ in}^3$$

With a rapid sand filter volume of 50 in³, an appropriate height and radius were chosen using Equation 12. With a radius of 1.25 in. the height of the cylinder required to contain 50 in³ was calculated.

$$h = \frac{50 \text{ in}^3}{\pi * (1.25^2) \text{ in}^2} = 10.2 \text{ in} \approx 10 \text{ in}$$

The rapid sand filter column needed to withstand a 2.5 gal/hr flowrate must have a radius of 1.25 in, and a height of 10 in.

Ion Exchange:

The size of the ion exchange column was determined using an EBCT of 5 minutes and a flowrate of 2.5 gal/hr, similar to the rapid sand filter. Therefore, the volume of the ion exchange cylinder was calculated to be the same as the volume of the rapid sand filter: 50 in³. The initial cylinder was designed to have a diameter of 2.5 in. and a height of 10 in., which is the same size as the sand filter. However, the column was designed to be 1 inch taller in order to allow for a water level to form above the resin, thereby maintaining a constant head.

APPENDIX C: FULL-SCALE DESIGN CALCULATIONS

The full-scale design consisted of four main treatment processes: coagulation in a mixing tank, flocculation in a settling basin, filtration in a slow sand filter, and ion exchange in a cylindrical column. A flowrate of 1 MGD was used as an appropriate flowrate for a small municipal groundwater treatment system. The design consisted of multiple parallel treatment trains. The system was designed so that not all of the trains are needed for the peak flow capacity.

Mixing Tank:

The size of the mixing tank was determined using an average detention time of 10 minutes. The volume of the tank was determined from Equation 13.

$$V = Q * t \quad \text{(Equation 13)}$$

Where:

V = Volume of the tank [ft³]

Q = Flow rate [ft³/min]

T = detention time [min]

The tank volume needed to withstand a flowrate of 1 MGD and a detention time of 10 minutes was then calculated:

$$V = \frac{1,000,000 \text{ gal}}{\text{day}} * \frac{1 \text{ day}}{1440 \text{ min}} * \frac{0.1337 \text{ ft}^3}{1 \text{ gal}} * 10 \text{ min} = 930 \text{ ft}^3$$

The total mixing tank volume needed was calculated to be 930 ft³. Although two mixing tanks were designed, each tank should be able to handle the total volume. Equation 12 was used to determine an appropriate radius and height for the tank.

$$h = \frac{930 \text{ ft}^3}{\pi * (5^2) \text{ ft}^2} = 12 \text{ ft}$$

With a tank radius of 5 ft, the height of each tank would be approximately 12 ft.

Settling Tank:

The size of the settling tank was determined using a length-to-depth ratio of 15:1, and a width-to-depth ratio of 5:1. These ratios were necessary in order to allow enough time for the particulate matter to settle in the tank. With these ratios, and an average detention time of 1.5 hours, the volume of each tank was determined.

$$V = \frac{1,000,000 \text{ gal}}{\text{day}} * \frac{1 \text{ day}}{24 \text{ hr}} * \frac{0.1337 \text{ ft}^3}{1 \text{ gal}} * 1.5 \text{ hr} = 8360 \text{ ft}^3$$

Because there are four settling tank trains, the total volume was split amongst three trains, with the fourth one available for maintenance or repairs. Therefore, with a total volume of 8360 ft³, each basin needs to handle 2790 ft³. Using the ratios as guidelines, an appropriate settling tank size was determined:

$$(12 * 4 * 60) \text{ft}^3 = 2880 \text{ ft}^3$$

The volume of each settling tank was calculated to be approximately 2880 ft³.

Rapid Sand Filter:

For the full-scale rapid sand filter, the units will be rectangular in shape. A typical surface loading rate for a rapid sand filter was found to be 4 gpm/ft². The surface area needed to withstand a 1 MGD facility was calculated.

$$A = \frac{1,000,000 \text{ gal}}{\text{day}} * \frac{1 \text{ day}}{1440 \text{ min}} * \frac{1 \text{ ft}^2}{4 \text{ gpm}} = 174 \text{ ft}^2$$

Because there are four sand filter trains, the total area was divided among three trains, with the fourth train available for maintenance or repairs or backwashing. Therefore, with a total area of 174 ft², each basin needs to handle 60 ft². Appropriate dimensions for the sand filters were determined using a 60 ft² surface area for each unit.

$$9 \text{ ft} * 6.5 \text{ ft} \cong 60 \text{ ft}^2$$

Four sand filters were designed, each 9 ft x 6.5 ft.

Ion Exchange:

The size of the ion exchange columns was determined using an EBCT of 5 minutes and a flowrate of 1 MGD. The total volume needed to handle the flow in this treatment process was calculated.

$$V_{\text{column}} = \frac{1,000,000 \text{ gal}}{\text{day}} * \frac{1 \text{ day}}{1440 \text{ min}} * \frac{0.1337 \text{ ft}^3}{1 \text{ gal}} * 5 \text{ min} = 464 \text{ ft}^3$$

Although there are 12 ion exchange units in 4 trains, 8 of these units can withstand the flow capacity. Therefore, each of the eight ion exchange columns must have a volume of 58 ft³. Appropriate dimensions for each column were determined based on a 2 ft radius.

$$h = \frac{58 \text{ ft}^3}{\pi * (2^2) \text{ ft}^2} \cong 5 \text{ ft}$$

Twelve ion exchange columns were designed, each 5 ft tall with a 2 ft radius.