5-2015

Electrocoagulation for sulfate removal

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Recommended Citation

Layton, Michael A., "Electrocoagulation for sulfate removal" (2015). *Chemical Engineering Undergraduate Honors Theses*. 64.
http://scholarworks.uark.edu/cheguht/64

Electrocoagulation for Sulfate Removal

An Undergraduate Honors College Thesis
in the

Department of Chemical Engineering
College of Engineering
University of Arkansas
Fayetteville, AR

By

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April 23, 2015

This thesis is approved.

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Thesis Committee:

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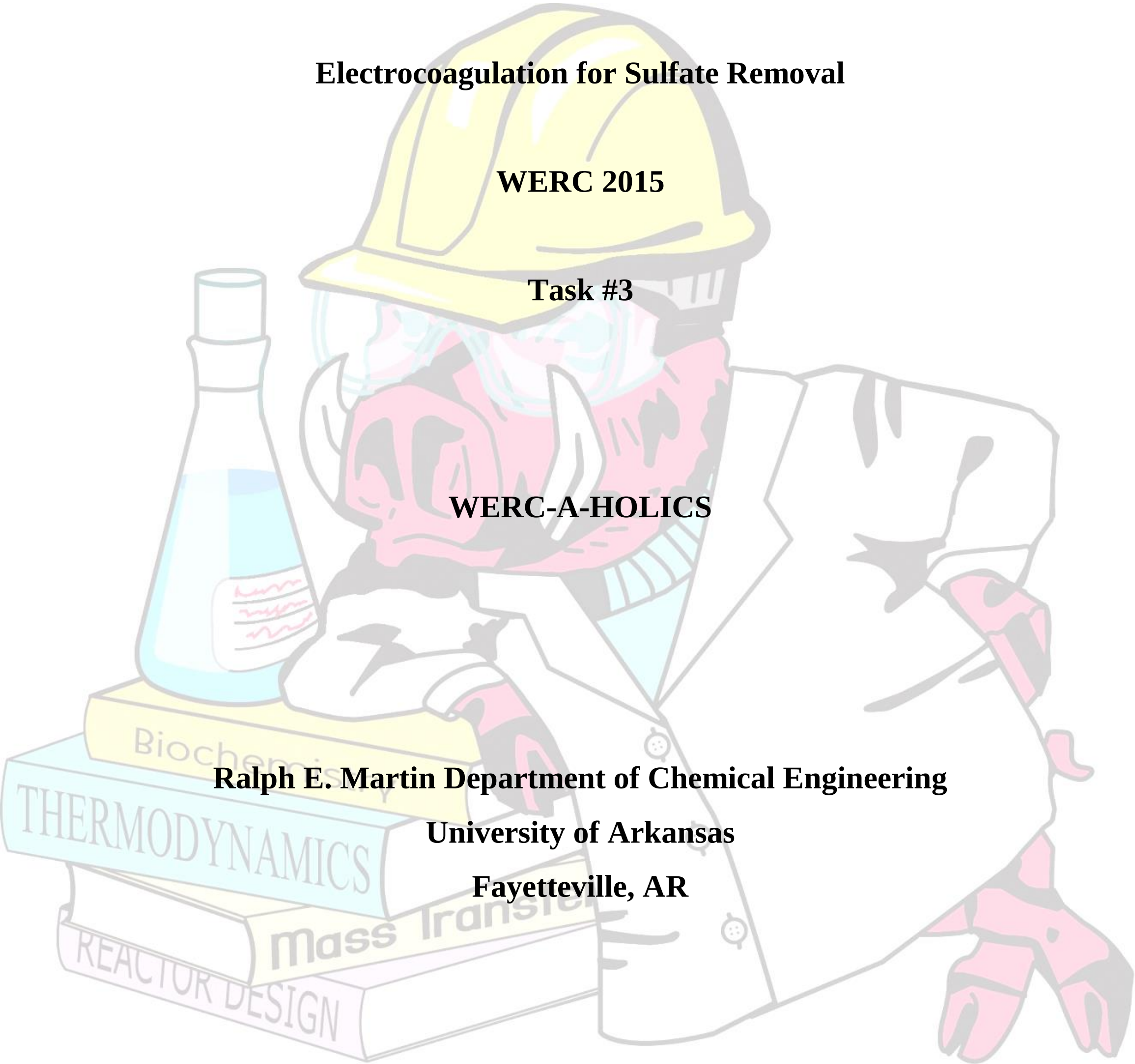
As a participant in the 2015 International Environmental Design Contest (also known as WERC), my Honors College thesis is on our group's WERC task: Electrocoagulation for Sulfate Removal. The purpose of this task was to remove sulfate and other anionic contaminants from contaminated well water using electrocoagulation, a separations technology that utilizes electric current to generate metal ions in situ for removal of contaminants, for a bench-scale process. Our group decided to utilize electrocoagulation as pre-treatment for reverse osmosis to produce potable water for the community on an industrial, economic scale. Because of our group's practical approach, we won first place at the 2015 WERC Competition. As team coordinator of this task, I worked on several aspects of this project.

My main area of expertise was electrocoagulation. In the beginning, I researched the chemistry of electrocoagulation and consulted with Dr. Bill Durham of the chemistry department in expanding this knowledge. After I felt comfortable in my knowledge of how electrocoagulation works on a scientific basis, I designed our first (and later second) electrocoagulation chamber, which included parameters such as plate material, spacing, and arrangement, electrical set-up, and size. After this design was constructed, I helped run experiments on the well water to determine the optimal bench-scale parameters to be used for scale-up. Parameters researched included current density, electrical arrangement, residence time, inlet flow rate, and initial sulfate concentration.

After a sufficient number of experiments were conducted, I created a scale-up model based on the behavior of the well water to the current density in the system. Since the amount of water in the electrocoagulation unit was determined based on the size and water use of Tularosa, New Mexico (a small town near the contaminated water wells) and the plate size was known based on a scale-up factor, then the current in the industrial-scale system would be known. If current is known, then electricity costs can be calculated and plate replacement rates can be determined. From this data, I was also able to perform a complete economic analysis for the electrocoagulation unit. The sections of the technical paper sent to the WERC Competition concerning electrocoagulation chemistry, scale-up, and economics were written by me. As team coordinator, I also assisted in revising the entire paper and educating myself on the other topics in our set-up, including reverse osmosis theory and scale-up and other filtration and separation technologies.

At the competition, I was one of the four presenters for our project (my section was on the bench-scale system and experimental data). I also assisted in answering judges' questions at our bench-scale demonstration sessions. Being the team coordinator also carried some leadership responsibilities, such as organizing experiment times, assigning duties to other members, and making sure that everyone was contributing to the project. I also helped in assessing our progress each week and determining what we should focus on individually and as a group. I did my best in balancing trusting my teammates to do their work and checking on their progress. I also made sure to make myself available to any of them if they needed assistance on their work. Overall, my experiences being a team coordinator and participating in the 2015 WERC Competition were extremely beneficial, and I'm glad to have contributed in all the areas outlined above.

For reference to our project, our formal WERC report is attached.



Electrocoagulation for Sulfate Removal

WERC 2015

Task #3

WERC-A-HOLICS

Ralph E. Martin Department of Chemical Engineering
University of Arkansas
Fayetteville, AR

Electrocoagulation for Sulfate Removal

WERC 2015

Task #3

March 13, 2015

WERC-A-HOLICS

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1.0 EXECUTIVE SUMMARY

In the United States, one of the major rising issues is water shortage, especially in Western, inland states with arid climates. Not only do deficiencies exist for potable water, but for irrigation and agricultural purposes as well. Currently, the Brackish Groundwater National Desalination Research Facility in Alamogordo, New Mexico has four separate wells that are being used for experimentation. A major concern is that a considerable amount of this water is currently wasted by being sent to evaporation ponds without any sort of treatment for human consumption. The WERC-A-HOLICS have identified two possible methods to alleviate this problem.

Electrocoagulation (EC) is a technology useful for the removal of sulfate and other anions from brackish groundwater. The process charges concentrated water through an EC chamber in a serpentine pathway, and uses an applied voltage to flow current through the system. By identifying the ideal combination of current density and residence time, it is possible to achieve approximately 40% sulfate removal by EC alone. In addition to this technology, reverse osmosis (RO) was also considered as a means of water desalination. This is a very attractive option, and has been extensively implemented in other parts of the world, especially Europe and the Middle East. RO is extremely effective in reducing salt concentrations, within EPA limits, suitable for human consumption.

The WERC-A-HOLICS performed experiments to determine if EC was a viable means of removing sulfate from brackish water (well 2). On a purely scientific level, EC as pretreatment for RO produced potable water; however, this system is not economical long term on an industrial scale due to its high yearly operating costs. If implemented on a smaller scale or using brackish water feed with a lower sulfate concentration, such as the other three research wells, EC as pretreatment has potential to be economical due to its lower yearly operating and waste disposal costs.

2.0 PURPOSE

As the result of a continually evolving global condition, one major issue that has recently been identified is water scarcity. Scarcity is characterized as a mismatch between water supply and demand. Desalination has been identified as an attractive option to supplement fresh water resources. With the limited availability of fresh water resources, the growing population is putting a significant amount of stress on the water resources and causing a demand for new water treatment technologies. One way to alleviate the stress is to utilize brackish groundwater. Though the number of brackish groundwater sources are considerably larger than the fresh water sources in New Mexico, these sources often go unused because the water is too concentrated for drinking or agricultural purposes and has to be treated to remove the salt before it can be used. RO has been a very popular technique used to treat brackish water, however desalination is an expensive process and has several technological, operational, and regulatory issues that have to be considered, so it is only implemented in areas where brackish water is the main source of water.[1] The greatest concern associated with desalination, especially in inland areas such as New Mexico, is in regard to the disposal of the waste concentrate. High costs associated with RO waste disposal are often the limiting factor in determining economics of the process.

3.0 INTRODUCTION TO WATER PURIFICATION TECHNOLOGIES

3.1 Electrocoagulation

EC is a separation technology that generates coagulant in situ by oxidation of metal anodes when electric current is applied.[2] Iron was chosen as the sacrificial anode material because it generates inexpensive, efficient coagulating agents and is less toxic than the alternative, aluminum. There are three stages of EC: (i) formation of coagulations by electrolytic oxidation of the sacrificial anode, (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions, and (iii) aggregation of the destabilized phases to form flocs.[3] Anode oxidation releases cations that form metal hydroxide complexes which destabilize the electrical double layers around colloid particles and reduce their net surface charge. The reduction of net surface charge causes van der Waals forces to overcome electrostatic repulsion forces as negatively charged colloidal particles are carried toward the anode via electrophoretic motion, resulting in floc formation. Hydrogen gas is produced due to the electrolysis of water, which helps bubble the flocculent to the top of the chamber. The chemistry that occurs during the electrocoagulation process is described in the following breakdown.[2]

For an iron anode, the reaction occurring at the anode is:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}(aq) \tag{1}$$

At alkaline conditions, the following reaction occurs:

$$Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_2(s) \tag{2}$$

Hydrogen gas is generated at the cathode as follows:

$$2H_2O(l) + 2e^{-}(aq) \rightarrow H_2(g) + 2OH^{-}(aq) \tag{3}$$

The overall reaction is:

$$Fe(s) + 2H_2O(l) \rightarrow Fe(OH)_2(s) + H_2(g) \tag{4}$$

Another mechanism proposed for the production of iron hydroxide is outlined in reactions 5-9.

On the anode, the reaction is:

$$4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^{-}(aq) \tag{5}$$

At acidic conditions, not only does precipitation occur, but oxygen evolution occurs:

$$4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 8H^{+}(aq) \tag{6}$$

Hydrogen gas is generated at the cathode as follows:

$$8H^{+}(aq) + 8e^{-}(aq) \rightarrow 4H_2(g) \tag{7}$$

The overall reaction is:

$$4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 4H_2(g) \tag{8}$$

Reaction 9 shows the formation of gelatinous iron hydroxide suspensions that are capable of removing pollutants from wastewater by complex formation. The pollutants act as organic ligands (such as cyanide, fluoride, nitrate, nitrite, phosphate and sulfate) and are abbreviated as L in the Reaction 9.

$$L - H(aq) + (OH)OFe(s) \rightarrow L - OFe(s) + H_2O(l) \tag{9}$$

Instead of forming ferrous hydroxide complexes, ferrous ions can be oxidized to ferric ions, which can form monomeric ions, $Fe(OH)_3$, and polymeric hydroxy complexes, namely: $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^{+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, and $Fe_2(H_2O)_6(OH)_4^{4+}$, depending on the pH of the solution.[3]

In the EC process, the colloids are not technically precipitated, but sequestered. Iron oxide/hydroxide complexes have an isoelectric point at a pH of 7.7, and since the pH of the water solution is below 7.7, the complexes have a positive zeta potential. Zeta potential is a measure of the magnitude of colloidal stability, and in the presence of sulfate, the zeta potential of iron oxide/hydroxide complexes decreases without a shift in the isoelectric point. This indicates there is no chemical interaction between these ions and metal hydroxyl complexes, but suggests an electrical interaction.[3] As a result of these interactions, efficiency of capture is the rate limiting step. On a molecular level, iron hydroxide must be able to sequester sulfate ions randomly in a lattice. Iron electrodes produce a particularly good environment because of the open lattice structure (particularly at pH of approximately 6) and inexpensive cost of material. Ferrous hydroxide is also capable of enmeshing the other anions and cations in the well water, such as bicarbonate, chloride, sodium, magnesium, and calcium, ensuring the resulting sludge and treated water are electrically neutral.[4]

The only approach to overcoming the removal limit would be to lower overall temperature of the process, however this would be uneconomical for large scale water treatment. Cooling would be beneficial since a lower liquid temperature would reduce circulation. Water then becomes more viscous at the molecular level, and the rate of capture would improve. Therefore, the observed sulfate removal limit is independent of process design, and is purely a result of the nature of the EC technology.

3.2 Reverse Osmosis

RO provides a means to utilize brackish water otherwise not accessible for irrigational, industrial and municipal use. All forms of desalination technologies fall under two main categories, thermal and membrane based desalination. The former separates salt from water by evaporation and condensation, while membrane based desalination technologies diffuse water through a membrane, almost completely separating salts. Thermal desalination processes can treat up to 100,000 ppm salt content, but are more energy intensive than membrane based separations. Therefore, this technology was not considered as a possible means for study. RO (RO) is the most commonly used form of membrane based water purification technology. Arid and semi-arid countries in Europe and the Middle East have begun implementing RO systems to overcome regional water scarcity. As such, RO will be considered as both a technology to supplement EC and as a stand-alone water treatment system.

In order to understand RO, it is crucial to study the fundamentals of its counterpart, osmosis. Osmosis is the natural process in which water permeates though a membrane that excludes suspended solids, dissolved salts and larger organic molecules. The size of the pores in the semipermeable membranes are approximately 0.0005 microns. In a direct osmosis configuration (Figure 1), pure water resides on the left side of the membrane, and the concentrated solution is on the right. The same hydrostatic pressure exists on both sides, and the chemical potential of the concentrate is less than the chemical potential of pure water because the mole fraction of water on side 2 is less than the mole fraction of water on side 1. As a result, the driving force for permeation induces a flux of water from left to right until chemical potentials are equalized. After equilibrium has been reached (Figure 2), the chemical potential of water on both sides are equal to each other and there is no flux present. The observed difference in height (and therefore pressure) is known as the osmotic pressure, the pressure difference needed to stop the flow of solvent across a membrane. In RO (Figure 3), additional pressure is applied to the concentrated side of the membrane to force water flow through to the right, the dilute side. The applied pressure must be high enough to overcome the osmotic pressure. Large feed pressure requirements, which increase with salt concentration in the feed, are one of the limiting factors of the RO process; however, this technology is considered to be an efficient and economical means of water desalination.[5]

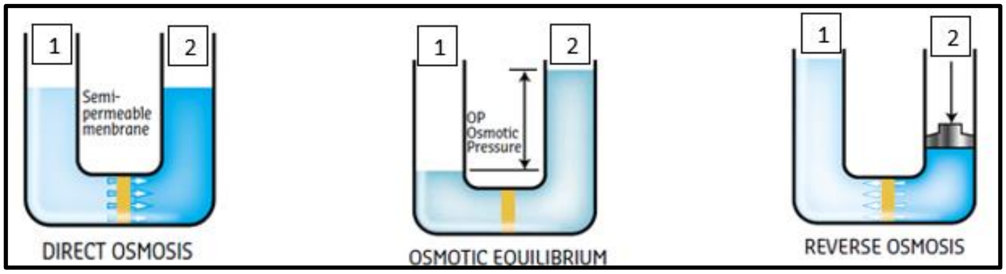


Figure 1 Figure 2 Figure 3

4.0 TASK PREMISES

The purpose of this task was to utilize electrocoagulation to design and build a small water treatment system that removes sulfate and other anionic contaminants. The design considerations for this task were as follows:

1. Demonstrate the process efficacy through the bench-scale apparatus
2. Estimate the total energy required for the full-scale process
    a) Theoretical power cost per mole of sulfate removed
3. Identify the amount of waste produced from the process
4. Address system operation parameters
5. Compare EC to other methods for removing sulfate
6. Provide process details including:
    a) Chemical reactions taking place
    b) Solids formed
    c) Gases formed
    d) The roles of the solids and gases in separation
7. Address health and safety issues

Additionally, the bench-scale demonstration must process no more than 5 gallons of the provided water and must be flexible enough to address real world variations, such as the compositions in the feed varying from the provided analysis.

5.0 METHODS CONSIDERED

Sulfate removal from ground water in New Mexico is an important and economical means to acquire potable water using natural resources. The Environmental Protection Agency (EPA) determined the maximum allowable concentration of sulfate in drinking water to be 250 parts per million (ppm). Most wells have sulfate concentrations in the thousands ppm, therefore making sulfate removal the first priority in producing potable water from brackish well water. There are several treatment methods available for the removal of sulfate from ground water. For this report, two methods of sulfate removal were researched and compared to EC, in addition to RO: treatment with hydrated lime[6] and multiple effect evaporation.

Treatment with hydrated lime, also known as cost effective sulfate removal (CESR)[6], is a process that was successfully used in numerous European plants before implementation in the United States. Hydrated lime is introduced to the feed water and combines with the sulfate, as well as other metals and hydroxides, to precipitate gypsum. This process occurs through a series of pH changes, lime reduction, and recarbonation. While this method produces low sulfate concentration, minimal liquid waste, and allows high flow rates, it requires large quantities of lime, and long residence times. Another significant disadvantage is the production of aluminum hydroxide, a toxic solid, in the recarbonation step of the process.

Multiple effect evaporation is a process that utilizes evaporator stages in series, where the pressure at each stage decreases in succession. This configuration allows for the vapor produced in earlier stages to be used as thermal energy downstream, aiding in evaporation. Ultimately, this process still requires a large amount of energy for startup and can be quite expensive in terms of capital, thus discarding it as a viable option.[7]

6.0 DESIGN THEORY

6.1 Electrocoagulation

When designing the original EC chamber, several parameters were considered and analyzed in order to optimize the removal of sulfate from the brackish well water. These parameters included: electrode material, electrode spacing, number of electrodes, electrode configuration, electrical set-up, residence time, fluid flow rate, and current density. Research was done to determine which parameters would be optimal to be used in bench scale experiments. Numerous experiments were conducted while varying one parameter each time. Results were then analyzed to better optimize a full-scale process. Each of the design considerations are discussed below.

6.1.1 Electrode Design

The electrode material was chosen on the basis of minimal cost and level of toxicity. Research showed aluminum and iron to be the most common and effective metals in removing sulfate.[8, 9] Iron (mild steel) was selected because it is less toxic than aluminum. In order to maximize the contact area of the water with the metal ions, 18 electrodes with a height and width of 4 inches and a thickness of 1/16 inches were used for the EC cell design. These plates were attached to a polycarbonate chamber in a serpentine arrangement to allow for sufficient mixing and multiple changes in polarity along the path, allowing complete treatment in a single pass.[9] The spacing between each electrode is 3/8 inches. This was chosen to minimize the resistance while ensuring adequate fluid flow. Figure 4 is a photograph of the experimental apparatus.

Figure 4. Experimental EC apparatus.

6.1.2 Electrical Arrangement

For an EC cell, there are three arrangements in which to arrange the battery connections, allowing current to run through the cell. These arrangements include monopolar parallel, monopolar series, and bipolar series. The cell was originally designed in bipolar series and then as a monopolar parallel system. A monopolar series arrangement (see Figure 5) was chosen for the final design because the total current in the system was equivalent to the current through each plate and provided the least resistance of the three designs. In addition, the experimental results proved monopolar series arrangement to be the most efficient in removing sulfate from the brackish water. On average, approximately 40% of the original sulfate concentration was removed with the monopolar series design, as opposed to negligible removal with the other two electrical arrangements.

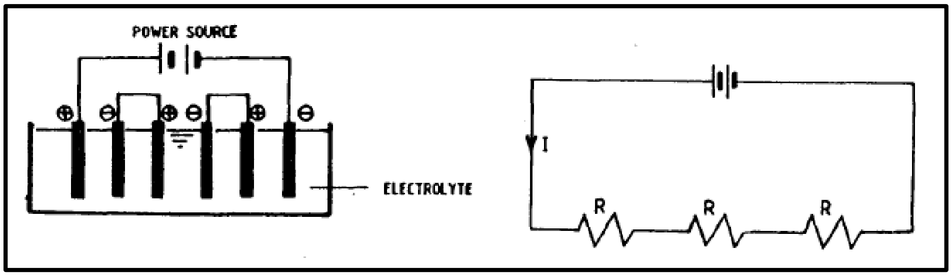


Figure 5. Monopolar series electrical arrangement.[8]

6.1.3 Current Density

The current density of each plate determines how many iron ions are released from the anodes. It is equal to the current divided by the cross-sectional area of the electrode. Several experiments were conducted, varying current density, to find the optimal value for sulfate removal. Results of all bench scale EC testing revealed a sulfate removal limit between 40-47%, which correlated with the theory of capture efficiency. The current density for the industrial scale design was chosen to minimize the number of times the electrodes needed to be replaced in a year; since a higher current density required a faster replacement time, the metal ions would be released at a faster rate.

6.1.4 Residence time

The residence time refers to the amount of time the water spends being treated in the EC chamber. As the current is run through the electrodes, iron will be continuously released into the water. Residence time was varied during experimentation to determine the optimal time interval. The resulting data concludes that after a certain amount of time (depending on current density), the sulfate will go back into solution due to enmeshing caused by the electrical environment. Figure 6 below shows the experimental data for sulfate concentration (ppm) of the water versus residence time (minutes).

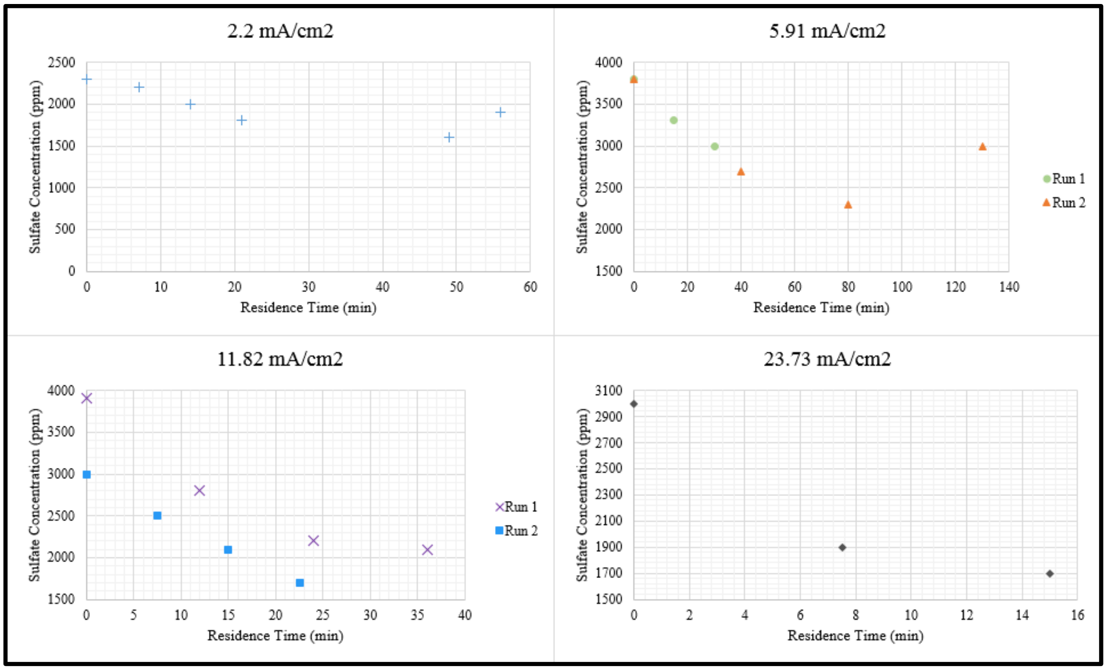


Figure 6. Sulfate concentration versus residence time.

6.2 Sedimentation

Following the EC chamber, the water is sent to a sedimentation unit. Sedimentation is a physical water treatment purification process that utilizes gravity to remove suspended solids and particulates from water. There are two common types of sedimentation chambers: settling basins and clarifiers. Settling basins, which can be large tanks or ponds, are constructed for the purpose of removing entrained solids by simple sedimentation. Clarifiers are tanks built with mechanical means for continuous removal of flocculent and solids being deposited via sedimentation. Settling basins and clarifiers are often large, open tanks that may be rectangular in shape where water flows from end to end, or circular where flow is from the center of the chamber outward. It is important that the sedimentation basin is located close to the flocculation chamber so the transit between the two processes does not permit settlement or flocculent to disassociate.[10]

In the sedimentation process, the water passes through a relatively quiet and still basin. In these conditions, the floc particles settle to the bottom of the basin while the outflow passes over a weir or baffle, allowing only a thin layer of “clean” water to exit. In properly designed clarifiers, the velocity of the water is reduced so that gravity is the predominant force acting on the water/solids suspension. The key factor in this process is speed—the rate at which the flocculent drops out of the water must be faster than the flow rate at which the water passes from the tank inlet to outlet; otherwise, proper settling will not occur and the mechanical integrity of further purification processes will be compromised.[11] Once the solids have collected at the bottom of the basin, a mechanical sludge collection device scrapes the solids to a collection point within the basin, from which it is pumped to a disposal site (i.e., an evaporation pond) or a sludge treatment process.

With guidance from a technical consultant from WesTech Engineering, a company specializing in municipal water treatment, the WERC-A-HOLICS chose to use a solids contact clarifier (see Figure 7) as the sedimentation chamber. A solids contact clarifier combines slow mixing, flocculation and sedimentation in a single basin and is very popular in municipal water treatment facilities due to its high efficiency. Other benefits of this clarifier are that it has low power requirements, leaves a smaller footprint than conventional treatment, provides more flexibility than a settling basin (i.e., polymer can be added to the center well of the clarifier to improve flocculation), and has lower installation and operational costs than most other sedimentation chambers.[12]

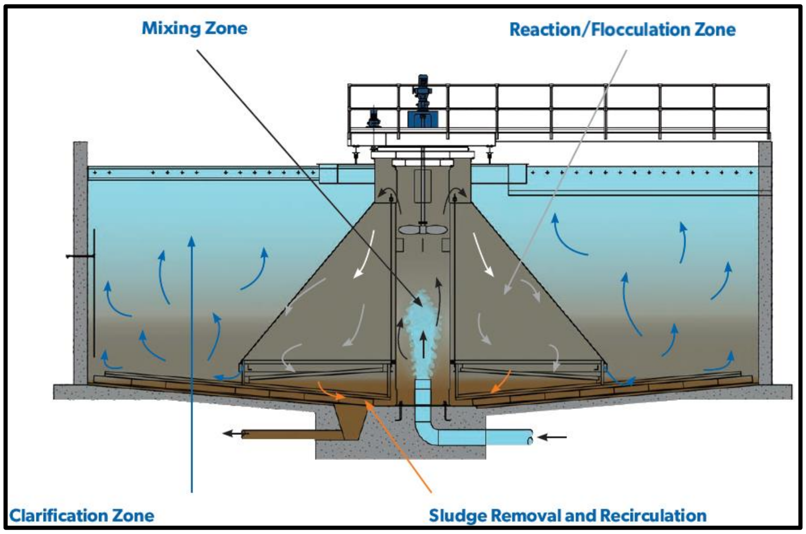


Figure 7. Solids contact clarifier.[12]

6.3 Filtration

The purpose of filtration following the clarifier is to provide a final step in purification in order to further protect the RO membrane. The osmotic pressure required to push the feed through the membrane varies based on concentration of solids in the feed stream. The more solids present in the feed, the higher the osmotic pressure. Pre-filtering the feed allows for some of the excess solids to be removed, helping to lower the required osmotic pressure and ultimately decreasing the size of the pump required. RO membranes are spiral shaped and are difficult to backwash with water or air, which can lead to potential fouling and high cleaning and replacement costs. Pretreating the inlet stream to the RO through a filter removes unwanted and excess solids from the feed, prolonging the life of the membrane and reducing the amount of membranes purchased.[13] A depth filter was used for the bench scale design because of its capability to remove suspended solids and particulates from the water, as well as its relatively cheap cost.

6.4 Reverse Osmosis

In order to achieve the desired sulfate concentration of 250 ppm for potable water, a RO system was added to our design. Although the bench scale apparatus only reduced the sulfate concentration to 400 ppm, the industrial design is estimated to reduce the level of sulfate to less than 50 ppm. In designing the bench scale RO system, a single membrane cartridge was chosen. The bench scale apparatus served in demonstrating the impact a RO system would have in removing total dissolved solids (TDS) from water treated at a municipal water treatment facility. This was done in order to determine the effect of the EC pretreatment in regard to the economics of an industrial scale RO system.

Scaling of the membranes is a major consideration in RO study. When scaling occurs on the membrane, the water permeability and purity decrease. The most common species that lead to scaling include calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, and reactive silica [1]. To prevent this from occurring, we performed a solubility limit experiment on both water systems—the brackish water with no EC pretreatment and the brackish water with EC treatment. The experiment concluded that brackish water going directly to an RO system from a well (i.e., no EC pretreatment) would have a solubility limit of only 30%. The water post-EC had a solubility limit of 70%, therefore increasing the potential recovery of the RO system by 40%.

7.0 BENCH SCALE DESIGN

Reference Figures 8-11 for the design of the experimental apparatus.

7.1 Experimental Apparatus Equipment List

1. EC Feed Bucket
    a. Size: 5 gallon
    b. Material: plastic
2. Ball Valve (x2)
    a. Size: ½”
3. Flow Meter
    a. Brand: Gilmont Instruments
    b. Model: 65 MM

4. EC Chamber
    a. Material: polycarbonate
    b. Size: 6.5” x 5.5” x 10”
5. Electrodes
    a. Material: Mild steel
    b. Number: 18
    c. Size: 4” x 4” x 1/16”
    d. Spacing: 0.393”
6. DC Power Source
    a. Voltage limit: 200 V
7. Pump
    a. Brand: GE Commercial Motors
    b. Model: AC-2CP-MD
8. Pump
    a. Brand: GE Commercial Motors
    b. Model: 5KH36KNB633X
9. Pump
    a. Brand: MagneTek
    b. Model: DC-3C-MD
10. Settling Bucket
    a. Size: 5 gallon
11. Piping
    a. ID: ½”
    b. Material: flexible PVC
12. Depth Filter
    a. Brand: AMETEK
    b. Size: 8”
13. RO membrane
    a. Size: TFM 24
    b. Max pressure: 65 psig

Figure 8. DC power supply.

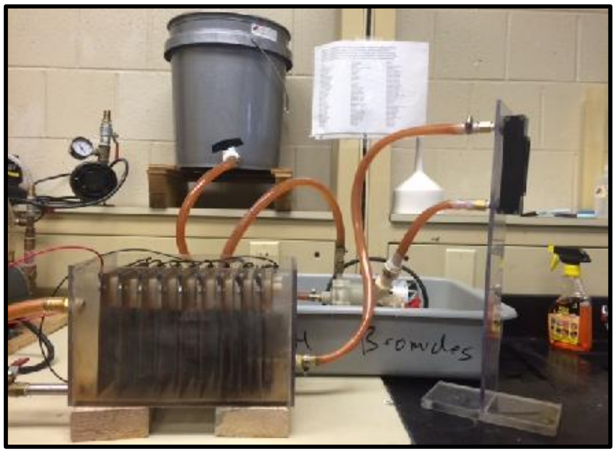


Figure 9. Experimental apparatus.

Figure 10. RO system.

7.2 Experimental Procedure

1. From the DC power source, connect the positive (red) wire to the corresponding wire on the EC cell.
    1. Twist the open ends of the two wires together.
    2. Place the cap on the connection and twist it clockwise until secure.
    3. Repeat the previous steps with the negative (black) wires.
2. With all valves initially closed, pour 10.5 L (2.77 gal) of the brackish well water into the 5 gallon EC feed bucket.
3. Turn on the DC power source.
    1. Adjust the dial until the desired voltage is reached. (NOTE: the ammeter will read little to no current until water is in the EC cell.)
4. Open the ball valve connected to the feed bucket.
5. Open the gate valve upstream from the flowmeter.
6. Turn on the EC pump and set the flow rate at 500 mL/min by adjusting the gate valve.
7. Allow water to fill the EC chamber to the overflow line (3.5 L).
    1. Start the timer when water begins to flow out of the chamber.
8. Discard the first 3.5 L of the processed water as this water has not been treated consistently with the rest, due to start-up.
9. Allow the resulting water to flow into the settling bucket for 14 minutes; periodically recycling the water from the settling bucket back into the EC feed bucket.
10. After 14 minutes, stop the timer.
    1. Turn off the EC pump.
    2. Set the voltage on the DC power source to zero. Turn of the power source.
11. Open the ball valve to allow the water in the EC chamber to drain into the settling bucket.
12. Allow the treated water to settle in the settling bucket for a sufficient time (NOTE: the solids will fall to bottom and water will settle on top).
13. Use a 100 mL beaker to slowly “scoop” the top layer of clear water from the settling bucket to a separate bucket. Be sure to minimize the amount of solids collected in the beaker. Repeat until a minimal amount of water is left in the settling bucket.
14. Vacuum filter the remaining sludge in the settling bucket to remove excess water.

15. Turn on the second and third pumps, which will pump the treated water through the depth filter and into the RO system.
16. Operate the RO system for 10 minutes in a batch process and collect the RO permeate.
17. Turn off all pumps.

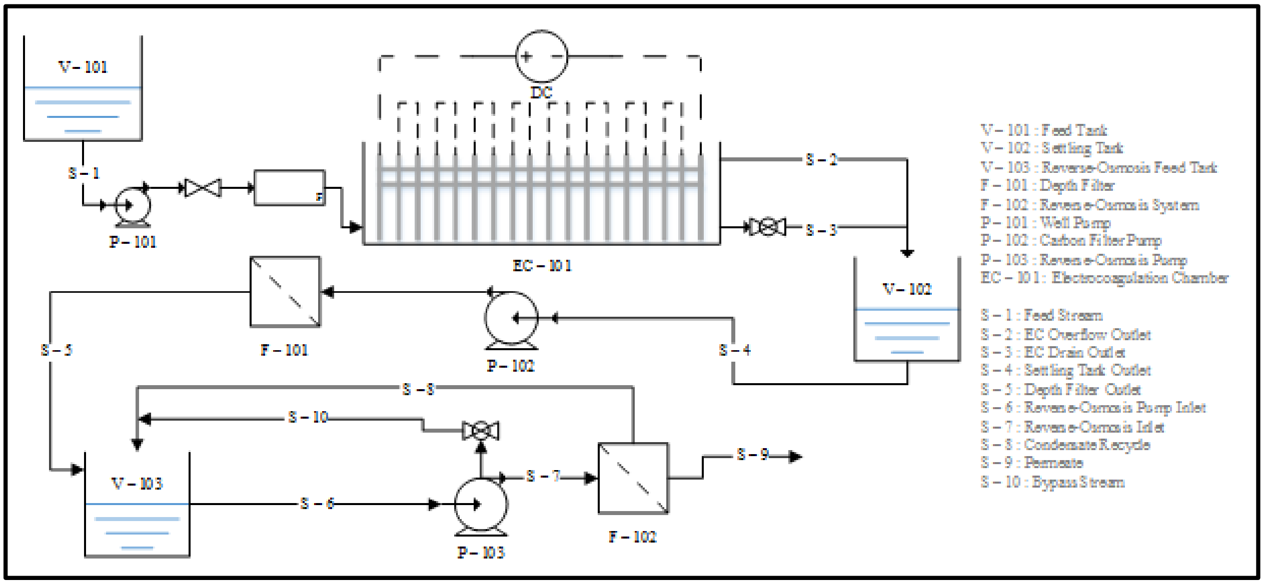


Figure 11. Process flow schematic of experimental apparatus.

8.0 INDUSTRIAL SCALE

8.1 Electrocoagulation Scale-Up

The premise of the industrial scale water treatment system was based off of a small town outside of Alamogordo, NM with a population of approximately 2800 people. From this, all industrial scale parameters were determined. For a given current density, the capture rate of sulfate was achieved after a particular residence time. The greater the current density, the shorter the residence time. If the water were left in the chamber for too long, then the sulfate would fall back into solution via Le Chatelier's principle. From this, the relationship between current density and residence time was best modeled with a quadratic equation, $ax^2 + bx + c$, where the "a" and "b" coefficients were plotted against current density, as seen in Figure 12.

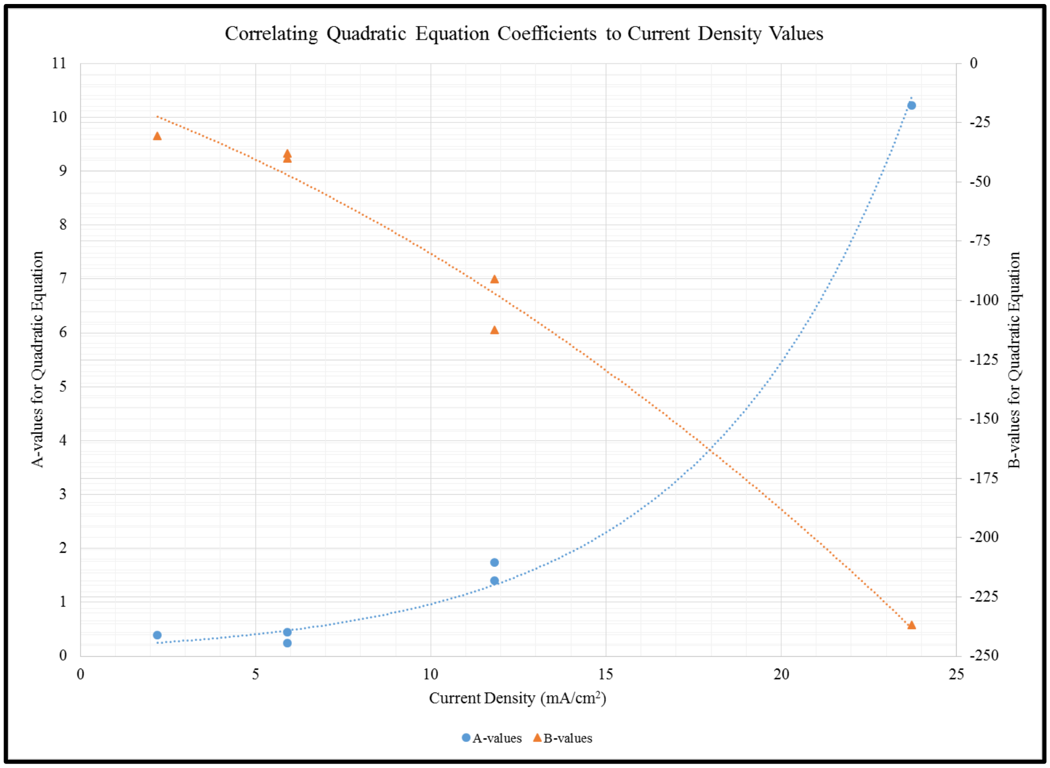
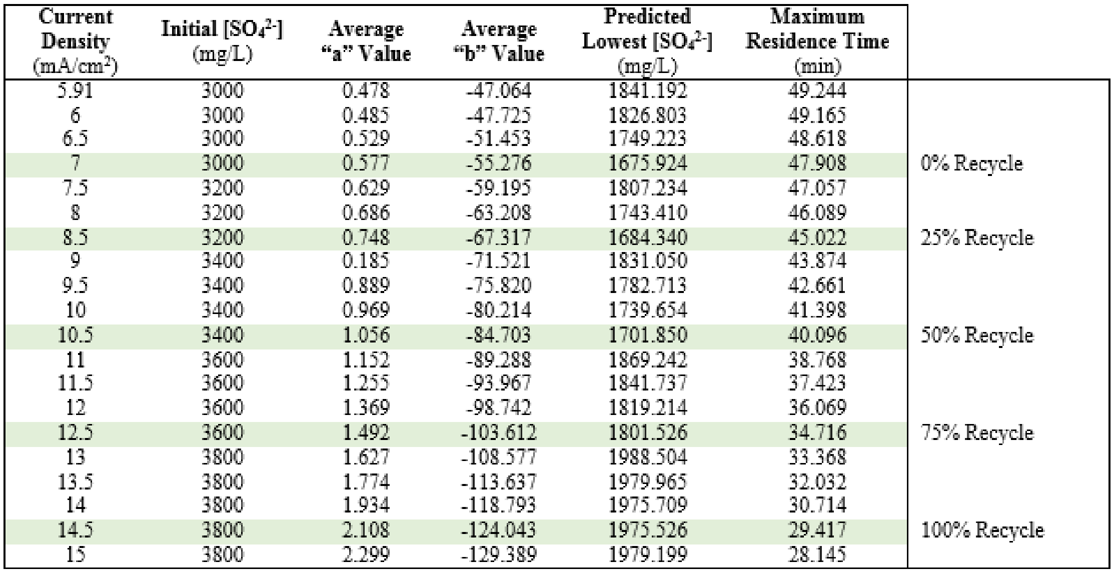


Figure 12. Relationship between quadratic coefficients and current density.

The model trend lines for the “a” and “b” coefficient values correlated the experimental data well; therefore, this model was used to predict a quadratic equation relating any theoretical current density to residence time. This is reported in Table 1.

Table 1. Determining Ideal Current Density for Scale-Up.



Current Density (mA/cm^2)	**Initial [SO$_4^{2-}$]** (mg/L)	**Average “a” Value**	**Average “b” Value**	**Predicted Lowest [SO$_4^{2-}$]** (mg/L)	**Maximum Residence Time** (min)	
5.91	3000	0.478	-47.064	1841.192	49.244	
6	3000	0.485	-47.725	1826.803	49.165	
6.5	3000	0.529	-51.453	1749.223	48.618	
7	3000	0.577	-55.276	1675.924	47.908	0% Recycle
7.5	3200	0.629	-59.195	1807.234	47.057	
8	3200	0.686	-63.208	1743.410	46.089	
8.5	3200	0.748	-67.317	1684.340	45.022	25% Recycle
9	3400	0.185	-71.521	1831.050	43.874	
9.5	3400	0.889	-75.820	1782.713	42.661	
10	3400	0.969	-80.214	1739.654	41.398	
10.5	3400	1.056	-84.703	1701.850	40.096	50% Recycle
11	3600	1.152	-89.288	1869.242	38.768	
11.5	3600	1.255	-93.967	1841.737	37.423	
12	3600	1.369	-98.742	1819.214	36.069	
12.5	3600	1.492	-103.612	1801.526	34.716	75% Recycle
13	3800	1.627	-108.577	1988.504	33.368	
13.5	3800	1.774	-113.637	1979.965	32.032	
14	3800	1.934	-118.793	1975.709	30.714	
14.5	3800	2.108	-124.043	1975.526	29.417	100% Recycle
15	3800	2.299	-129.389	1979.199	28.145	

The possibility of recycling a portion of the RO concentrate back to the original feed stream entering the EC chamber was considered in order to optimize the overall efficiency and cost of the water treatment system. As previously determined by the solubility experiment, the RO system would operate at 70% recovery for water with a maximum sulfate concentration of 1700 ppm. If the sulfate concentration exiting the EC chamber exceeded the 1700 ppm limit, then the percent recovery of the RO system would decrease due to increased salt concentrations in the water. This would result in higher waste production; therefore, the 75% and 100% recycle systems shown in Table 1 were dismissed.

The town of Tularosa, New Mexico was selected as an ideal town for the production of water due to its relatively small population of 2842. Assuming a water usage of 80 gallons per person per day[14], the required production of potable water was approximately 160 gallons per minute. Based on the RO system's 70% recovery, a flow rate of 230 gallons per minute was required for the EC chamber.

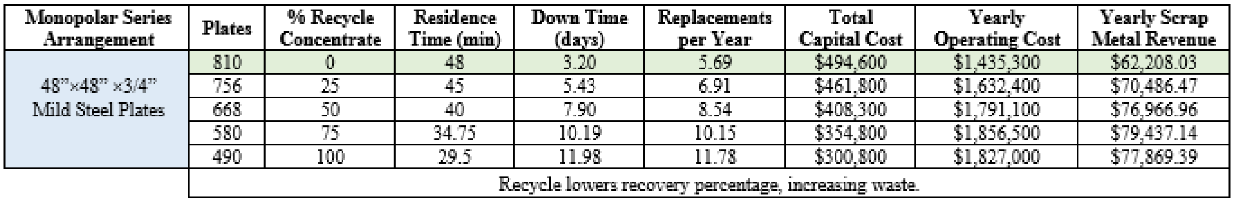
The experimental flow rate of 500 milliliters per minute was changed to the industry scale 230 gallons per minute, resulting in an increase by a factor of 1700. Therefore, the volume of each plate was scaled-up by a factor of 1700. This changed the plate size from 4"x4"x1/16" to 4'x4'x3/4'. The overlap ratio is the ratio of plate overlap to plate length, which on the experimental set-up was 0.792. In order to accurately replicate the serpentine flow in the scale-up chamber, the overlap ratio was applied to the scale-up design. From the overlap ratio, the width of the chamber was determined. Assuming the height of water in the chamber was the height of the plates, the chamber length would be the only unknown dimension. Assuming the experimental plate spacing of 0.9525 centimeters was used, the number of plates were determined since the inner volume of the chamber must match the volume of water calculated from residence time and volumetric flow rate.

For each initial sulfate concentration, the resistivity of the solution was calculated. For each electrical setup, the total resistance, current and voltage of the water was determined. The voltage that produced a current density matching its associated residence time from the models was used as the operating voltage. Over time, the sacrificial anodes would corrode and plate spacing would increase, resulting in a decrease in current density and less efficient sulfate removal. The effects of increasing plate spacing were assumed to be mitigated by a process controls loop that would measure the current in the chamber and increase the voltage over time.

Among the three electrical arrangements, monopolar series generated the least resistance and therefore, had the lowest electricity costs. It also had less wiring installation costs and down time than the monopolar parallel arrangement. Bipolar series was excluded because every plate corroded and had twice the plate replacement down time and costs.

An important parameter that was not encountered in the bench scale apparatus that would be a problem in the industry scale system was the replacement of plates. Assuming that 75% of the plate may corrode before replacement and that all plates corrode at equal rates, the total amount of iron dissolved before replacement was calculated. The coulombs generated in the chamber for a given residence time was determined and then Faraday's Law was used to determine the amount of iron dissolved for each batch of water. The time required to dissolve 75% of the iron could then be calculated by dividing the total mass of iron by the mass of iron dissolved per residence time. As current density increased, the number of replacements per year also increased; therefore, it was important to find the lowest possible current density for each initial sulfate concentration to minimize the cost of purchasing plates (one 4'x4'x3/4" plate costs $606.40).[15] The final EC designs are shown in Table 2. Note that the yearly operating cost includes plate replacement, power, and wiring costs.

Table 2. Comparison of all EC designs.



Monopolar Series Arrangement	Plates	% Recycle Concentrate	Residence Time (min)	Down Time (days)	Replacements per Year	Total Capital Cost	Yearly Operating Cost	Yearly Scrap Metal Revenue
48"×48" ×3/4" Mild Steel Plates	810	0	48	3.20	5.69	$494,600	$1,435,300	$62,208.03
	756	25	45	5.43	6.91	$461,800	$1,632,400	$70,486.47
	668	50	40	7.90	8.54	$408,300	$1,791,100	$76,966.96
	580	75	34.75	10.19	10.15	$354,800	$1,856,500	$79,437.14
	490	100	29.5	11.98	11.78	$300,800	$1,827,000	$77,869.39
	Recycle lowers recovery percentage, increasing waste.							

8.2 Reverse Osmosis Scale-Up

The industrial scale RO system was designed using the Dow Chemical ROSA Software. The RO system was optimized using the composition of the water leaving the EC chamber, a recovery rate of 70%, and an overall permeate flow rate of 160 gpm as input parameters. The optimal design was a single-stage system with 6 pressure vessels and 7 membranes per pressure vessel, a recirculating flow rate of 10 gpm, and an average flux of 12.47 gallons per square foot of membrane per day (gfd). This design proved to be the most economical, producing water at about $3.90/kgal. The maximum recovery rate, maximum permeate flow rate, the maximum feed flow rate per element, and the minimum concentrate flow rate are all limiting parameters that were considered in the optimization.

8.3 Process and Equipment Description

Water from a brackish water well is pumped to the bottom inlet of an electro-coagulation chamber at a rate of 329,000 gallons per day. The EC chamber has 810 plates sized as 4’x4’. The plates are set up in a serpentine pattern like the bench-scale process with a 0.95 centimeter gap and a 38” overlap. A non-conductive bar is threaded through the plates so that when they are removed every 2 months they can be removed as one unit by a hoist. The average power usage is 66 kW. Once water has filled the EC chamber it will exit via the overflow pipe line to a clarifier. After passing through the clarifier, generated waste is sent to an evaporation pond. Clean water from the clarifier is pumped to a depth filter prior to feeding the RO system. Retentate (concentrate) from the RO is sent to evaporation ponds, while the permeate (purified water) is sent to a water treatment center for further disinfection at a rate of 288,000 gallons per day. An overall process flow schematic is presented in Figure 13.

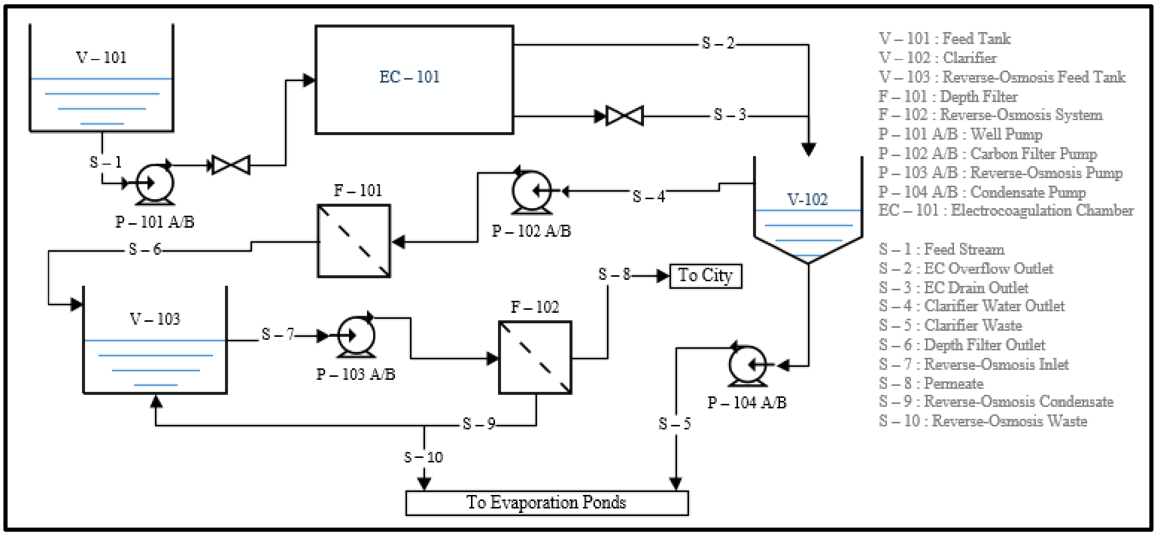


Figure 13. Process flow diagram of industrial scale water treatment system.

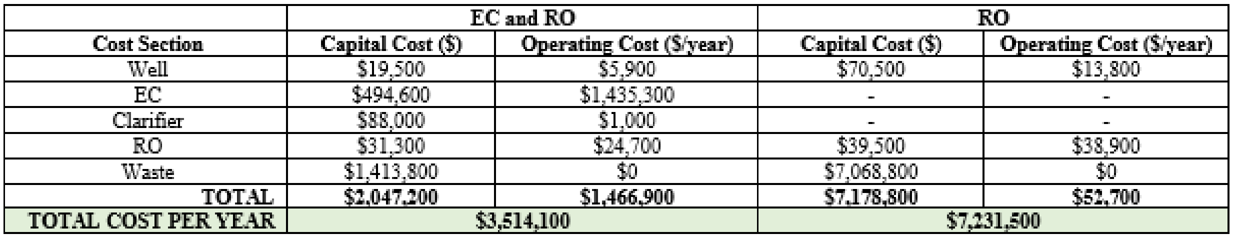
8.4 Waste Disposal

As previously stated, the desalination of brackish groundwater is a promising technology to provide an increased supply of water to arid, inland regions in the southwestern United States. However, as groundwater desalination technology develops, a desire for more sophisticated and efficient disposal methods arises. The concentrate stream from RO systems is disposed of by several means, including discharge to surface water or a sanitary sewer system, deep well injection, land application, and evaporation ponds. From the bench scale experiment, it was determined that approximately 982 mg of waste, mainly green rust and various salts, was produced per 50 mL of processed water. Unlike coastal regions where waste streams high in salt concentrations can be discharged to a larger body of water, inland regions are limited in waste disposal options. Discharge to surface water and sanitary sewers are not an option because the waste discharge exceeds the salt concentration limit. In addition, disposal of the waste water for land irrigation is not a possibility because salt concentrations are unsafe for human consumption. Finally, deep well injection may not be feasible due to high costs and its dependability on geological features.[1] Due to the abundance and relatively cheap costs of land in New Mexico paired with low operational costs, evaporation ponds proved to be a viable waste disposal option.

9.0 ECONOMIC ANALYSIS

The main goal in this analysis was to compare the cost of using EC as a pre-treatment method for RO versus simply using an RO system. The costs were determined by detailing the process differences for each system and calculating the yearly operating and total capital costs for each system as seen in Table 3.

Table 3. Economic analysis of EC as a pre-treatment against RO only.



	EC and RO		RO	
Cost Section	**Capital Cost ($)**	**Operating Cost ($/year)**	**Capital Cost ($)**	**Operating Cost ($/year)**
Well	$19,500	$5,900	$70,500	$13,800
EC	$494,600	$1,435,300	-	-
Clarifier	$88,000	$1,000	-	-
RO	$31,300	$24,700	$39,500	$38,900
Waste	$1,413,800	$0	$7,068,800	$0
TOTAL	**$2,047,200**	**$1,466,900**	**$7,178,800**	**$52,700**
TOTAL COST PER YEAR	**$3,514,100**		**$7,231,500**	

The well costs included the drilling of additional wells needed in each scenario, the pumping cost for the adequate amount of water needed, and the capital pump cost. The costs for EC included the costs of the plates, electricity, and the capital costs of the tank and pump installation. The theoretical power cost per mole of sulfate removed was determined to be $0.0055. The costs for the flocculating clarifier were determined based on recommendations from WesTech Engineering, a company that specializes in clarifiers. The costs for the RO system were dependent on the composition of the inlet water which dictated not only the osmotic pressure but also the recovery percentage. Based on these two parameters, the number of pressure vessels, membranes, and pumping cost varied and affected the costs accordingly. The costs for evaporation ponds was dependent on the amount of total waste[16]; the costs for disposal decreased as more waste from the RO concentrate was recycled back to the EC chamber as shown in Figure 14.

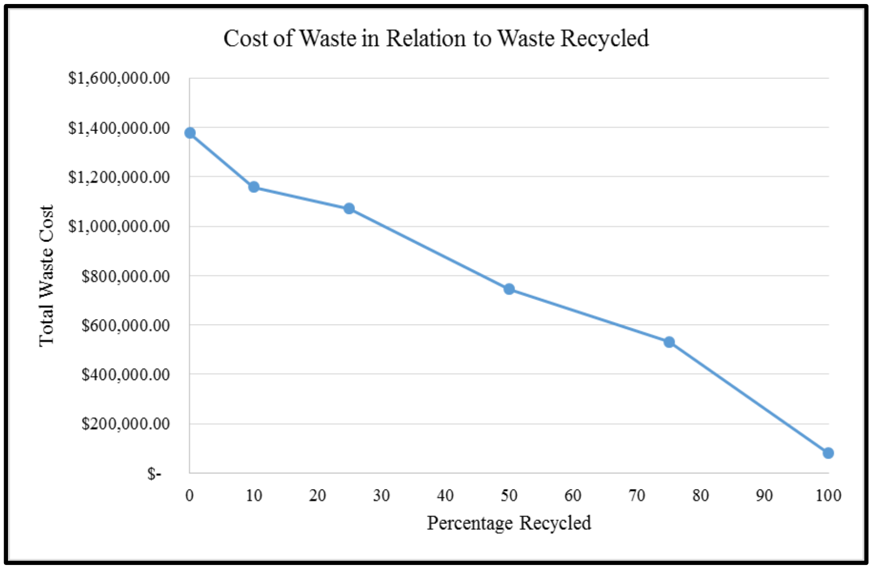


Figure 14. Economic analysis of waste costs in relation to the amount of waste recycled back into the system.

The cost of waste disposal is also dependent upon the size of the evaporation ponds. While using EC as pre-treatment had a lower capital cost, the use of only RO had a lower operating cost. However, the total cost of using only RO by far outweighed the cost of using EC as a pre-treatment by $3.9 million in the first year as shown in Table 2 and Figure 15.

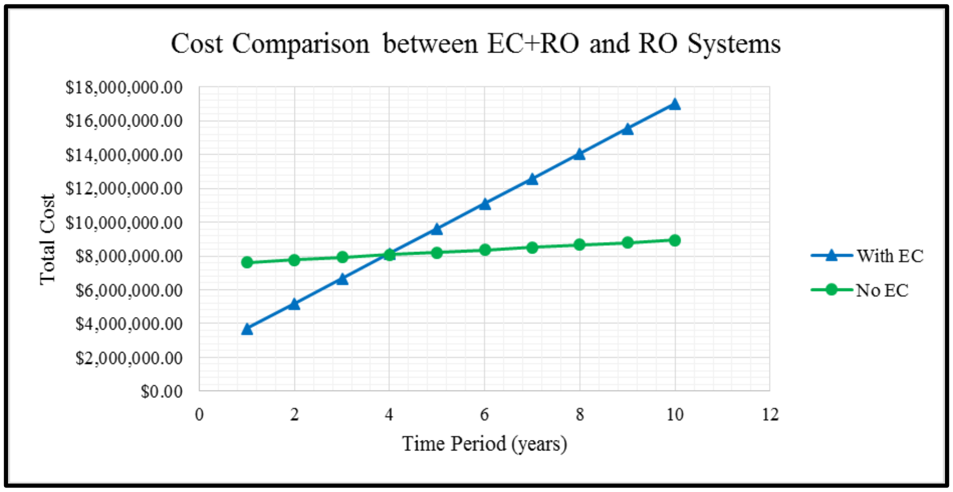


Figure 15. Cost comparison between both systems.

As mentioned above, a problem that was created from recycling the concentrate was the initial sulfate concentration increased coming into the EC chamber. As a result the current density increased, which increased the number of plate replacements and therefore the operating cost. Consequently, recycle proved not to be economical and a zero percent recycle was determined to be the most economical system.

The average household water bill in Tularosa, New Mexico is assumed to be close to the average household water bill in Albuquerque, New Mexico, which is \$1.85/kgal[17] or approximately \$250,000 per year. Assuming the cost of land in New Mexico to be \$540 per acre[18] and the plant to be approximately 100 acres, a discounted cash flow diagram can be constructed as seen in Figure 16.

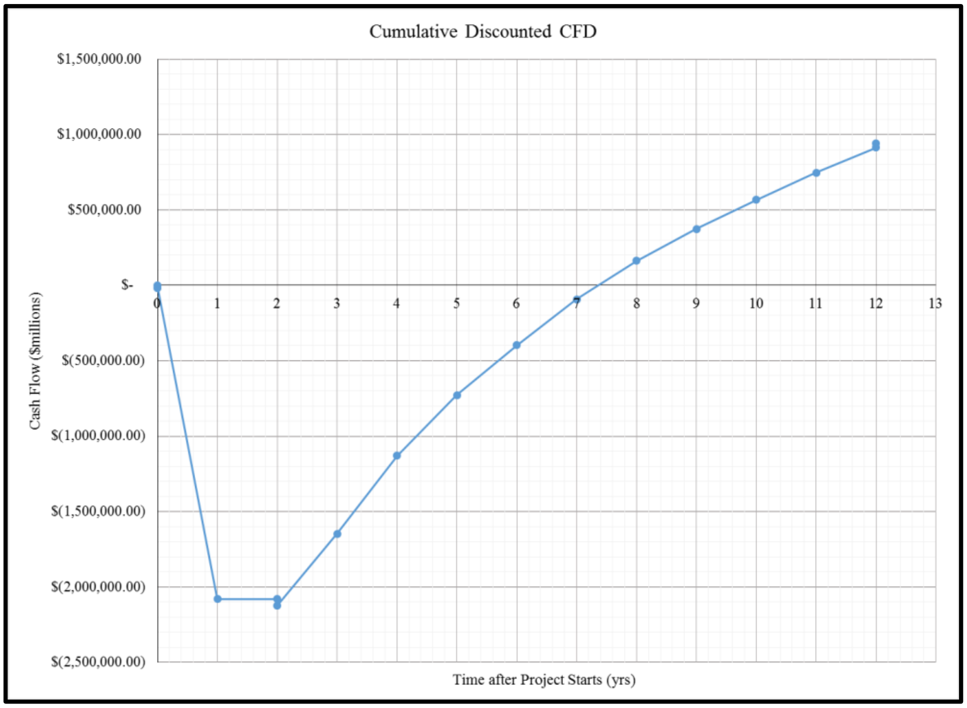


Figure 16. Discounted cash flow diagram.

Due to the high operating costs of the EC unit, selling the water at established prices in Tularosa, New Mexico would not generate enough revenue to break even on the project. Assuming a five year payback period, water would have to be sold at an average price of \$23.58/kgal, which is 12.7 times more expensive than the current cost of water in Albuquerque. Therefore, the use of EC is not economical. Even though EC had shown to reduce waste costs by millions of dollars and increased the RO recovery rates up to 40%, the high operating costs of EC make this process uneconomical from a profit standpoint. It would be economically possible to use EC as pretreatment for smaller commercial units or if EC treated water from the different Alamogordo wells.

10.0 SAFETY AND ENVIRONMENTAL

Electrical: All users were trained on operational safety when using electrical equipment, such as the DC power source and EC cell, in a lab setting. An emergency kill switch was added to the power source for additional safety. The pump was connected to the power source in such a way that adds an on/off switch for safe start-up and shut-down, as well. To protect users from electrocution, the cell was covered in a non-conductive material while in use. In an industrial setting, users must comply by OSHA's *Electrical Safety-Related Work Practices, 29 CFR 1910.331*.[19]

Chemical: Hydrogen gas is produced into the air from the reaction at the cathodes. Hydrogen gas is a flammable gas that must be well ventilated. The flammability limit is 4-75 volume percent.[19] Nitrile gloves and safety glasses were worn at all times by members working in the lab.

Environmental: There are no environmental hazards associated with this process.

Legal Requirements: Disposal of solid waste materials in the state of New Mexico must comply with the New Mexico Environmental Improvement Board's *Solid Waste Rules 20.9.2-20.9.*10.[20] Any plans to construct new disposal sites must comply with the *Solid Waste Plan* 20.9.4 NMAC.[21]

11.0 CONCLUSIONS AND RECOMMENDATIONS

1. The WERC-A-HOLICS have determined that the best conditions for operation of EC technology are to run in a serpentine fluid pattern, a monopolar series power configuration, without recycle, and at an average current density of 7 mA/cm^2. These conditions provided sulfate removal of approximately 40%.
2. The WERC-A-HOLICS have determined that using EC in conjunction with the RO technology would significantly enhance efficiency and reduce waste of the RO system.
3. The WERC-A-HOLICS have determined that due to high operating costs of EC, it would not be economical to implement this system on the current scale.
4. The WERC-A-HOLICS recommend using EC as pretreatment either for a smaller scaled system or for water with a lower sulfate concentration (i.e., the other wells); both of these scenarios would lower the yearly operating costs.

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Memorandum

TO: Gina Densmore
WERC-A-HOLICS Team Member

FROM: Hayden Dwyer
Facilities Engineer
Southwestern Energy Co.

DATE: March 11, 2015

RE: WERC Report Audit

Overall, this is a very well researched and written report. I have a few comments and questions which I will outline in the bullets below.

1. Section 3.1 – It is stated that both Oxygen and hydrogen gas are produced due to the electrolysis of water but in all of the following equations only hydrogen gas is produced and discussed. If the oxygen gas is not shown to be produced and not discussed to help the EC mechanism I would not mention it and just focus on the production of hydrogen gas.
2. Section 3.2 – In the 3rd sentence clarify that "almost completely retaining salts" is in the waste retentate stream. In my initial reading of the sentence it sounds as though the water retains the salt which would be in the permeate stream negating the reason for doing RO.
3. Section 3.2 – In the sentence about thermal desalination, I would word it "can treat up to 100,000 ppm salt content, *but* are more energy intensive…" Since the next sentence says "Therefore, this technology was not considered" you need to introduce a negative point to go with the high concentration it can treat and but provides the contrast instead of "and."
4. Section 6.1.2 – You report that the monopolar series arrangement was tested to be the most efficient with removing approximately 40% of the sulfate concentration. I would like to see what this number was in comparison to with the monopolar parallel and the bipolar series. What was the removal % for the other configurations?
5. Section 6.1.4 – It is stated in this section that the resident time was calculated to a specific time due to the fact that the sulfate will go back in solution. However, the following section discusses the process of sedimentation which involves the water and EC flocculent products being in a very slow moving settling tank with high resident times. Just looking for a little more explanation on how the solids will be able to settle out to be removed at a later time if the sulfur will dissolve back into solution? Is that only capable of happening due to the electrical currents in the EC chamber?

6. Section 7.2 – Procedure step 3, add a word to "(NOTE: the ammeter will read little to no current until water is *in* the EC cell)"
7. In Table 2, what is the Yearly Operating Cost column? Is that due to the electrical consumption for the added plates? I do not see any elaboration of what this column represents. I assume the Total Capital Cost is the cost of the initial metal plates so I do not know what causes the large increase in price to operate the system. Some more explanation on these costs would be nice.
8. Section 9.0 – Above Figure 16, the water bill in Alamogordo, NM is listed as $23.15/month or approximately $200,000 per year. These numbers do not match. If I am reading it right as equivalent numbers for water cost in Alamogordo, $23.15/month X 12 months/year = $27,780/year. Not the $200,000. I do not know what this number represents in reference to all of the information around it.

Few General Question

9. You discuss the effects of pH on the EC process. What is the effect of pH on the RO process downstream of this? Will the membranes perform well in acidic conditions or will there need to be some water conditioning in between the EC chamber and the RO?
10. Background of the premise of the project that might help to understand why this project is important. Why is the pretreatment really necessary? If you tested the RO alone and the EC with the RO, what is the importance of needing the EC before if the RO can handle no pretreatment? I understand that solids will reduce the function of the membrane, but why could you not filter out solids since you have a filter step in the process anyways? Why is EC important? If it is because the sulfur is dissolved and not a solid then what does the dissolved sulfur do to the membrane? I think you cover it briefly when the scaling of a membrane is discussed but if that is the main reason you are doing this entire project and chose EC, I would spend more than just a sentence or two describing the problem that sulfur causes and why your proposed process is necessary and the best option to solve it.

My main thing when reading was making me understand the problem, care about it, and convince me that your proposed solution was the best, be it economical or not. You do a great job of presenting the problem that there is a water shortage in arid areas, and that the best option for water would be brackish ground water and that this has high sulfur content. From that point why is EC coupled with RO the best option? The EC does not reduce the Sulfur concentration to below the 250ppm requirement and unless I missed it does not reduce the salt. So RO is absolutely required to reduce Sulfur concentration and eliminate salt to produce usable water from the permeate. Really give good reasons why it was important to have the EC pretreatment to remove the amount of sulfur that it does. Which I know you state it causes an increase of 40% efficiency but I think it would add to the report to show why sulfur wrecks havoc on the RO membrane and why EC was important instead of another pretreatment such as filtration or something similar. I am sure I just repeated points I made above but that was my rough synopsis of the thoughts I had reading through it. Very good project and well done!

NALCO
An Ecolab Company

1601 W. DIEHL ROAD
NAPERVILLE, IL 60563-1198

Re: Electrocoagulation for Sulfate Removal

Gina,

I did a quick read of the report and have a few comments.

1. It is a nice research project and the report was well written.
2. The title of the report is Electrocoagulation for Sulfate Removal. However, there is no mention of sulfate removal in the conclusions. I think there should be at least one.
3. Section 11 is Conclusions and Recommendations, but I saw only conclusions. I would change that heading to Conclusions. If you want a separate Recommendations section, you can add it and possibly recommend additional experiments to fill in any information gaps.
4. Towards your specific question concerning environmental legal issues with open ponds, state and local laws can be significantly different depending on location. Legal issues can often be addressed by contacting the local Environmental Protection Agency to determine if there would be an environmental issue.

From my practical experience, I have not seen Electrocoagulation (EC) be cost effective (so the one conclusion is on target), and in general I have not seen EC or any other technology be very successful at removing sulfate. Sulfate is just too soluble, a serious environmental concern for many industries, and is very difficult to do on an economical basis as you found in your study and experiment. Reject water from the RO process is always an issue -again something that you found and identified in your study. If there is not a way to dispose of the reject water- sending it back into a receiving stream for example-then disposal costs can become prohibitive. This is something that you found. I would look further at the disposal costs on the RO reject as this was by far the largest expense and while there may not have been other viable options in this particular situation the use of RO has increased significantly in recent years. One of the driving forces is having a lower operating pressure but having less permeate and higher reject- this has significantly reduced the cost of systems but as you found can present other issues. Overall would say a good report- well researched -would encourage you to continue looking at water related projects and processes.

Regards,

John W Sparapany

John W. Sparapany, Ph.D.
Technical Expertise Center
Nalco Co.

Date: March 12, 2015

From: William N. Varnava, NAVFAC EXWC

To: University of Arkansas WERC-A-HOLICS Team

Subject: Review of WERC 2015 Paper titled Electrocoagulation for Sulfate Removal

1. Per your request I have reviewed the paper entitled Electrocoagulation for Sulfate Removal prepared for the WERC 2015 contest. Overall I thought it was well organized and detailed in explaining the principles and theory behind electrocoagulation and reverse osmosis. The design and lab scale tests used to develop the overall parameters appeared to be very thorough and well thought out. The data generated from the bench scale tests were used to project the size, power and economics for a full scale design.

2. I would commend the team for taking an overall systems engineering approach to the problem be examining each of the key subcomponents, electrocoagulation, sedimentation, filtration and reverse osmosis involved in the system design. The engineering economic analysis on the full scale system was good and provided a good example of where a technology may appear to work on a technical level but as this paper indicated it was not practical from an economic standpoint. Engineering at is core is the process of examining the tradeoff between all the system variables but also keeping in mind the practical limits of what can or should be done.

3. I have a few specific comments and suggestions for the paper

    a. Section 6.3, Filtration, page 12, paper states s " *RO membranes are spiral shaped and therefore are difficult to backwash with water or air, allowing them only to be replaced, not cleaned.*

        Comment:
        In my experience with RO membranes, if fouling occurs the membranes can usually be chemically cleaned with a regime of low pH and high pH chemicals to remove the biofouling or contaminants on the membrane surface. Replacement of RO membranes can be costly and should be considered only if production or water quality is impaired to the point of not meeting the project specifications.

    b. Section 9.0 Economic Analysis, pages 21-22. I was unclear as to how the waste disposal costs for the RO process alone in table 3 was determined. This projected waste disposal cost of $7,068,000 for RO only was a key factor in your analysis. I think a better explanation and calculation showing how this number was derived is needed and would be beneficial for the reader. Overall I concurred with the rest of the economic analysis performed.

4. I would like to commend the WERC-A-HOLICS team at the University of Arkansas for their research and work on this project. I wish you all the best of luck in your future endeavors in the engineering field.

5. If you have any further questions or comments please feel free to contact me at 805-982-6640 or by email at William.varnava@navy.mil.

Sincerely yours,

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