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Managing Water in the West

Desalination and Water Purification Research
and Development Program Report No. 135

Pilot Testing of Zero-Discharge Seawater Desalination – Application to Selenium Removal from Irrigation Drainage



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14. ABSTRACT (<i>Maximum 200 words</i>) The soil in some areas of the San Joaquin Valley is rich in selenium, which is leached from the soil during irrigation. The selenium level in irrigation drainage from the test site in the Panoche Water District contains about 450 micrograms per liter (µg/L); whereas, the level allowed for irrigation or drinking water is 10 µg/L. Reverse osmosis (RO) is effective for removal of selenium, but yields of good water are less than 50 percent due to high levels of calcium sulfate (CaSO ₄) leached from the soil. The zero-discharge desalination process tested in this project utilizes electro dialysis metathesis (EDM) to produce two concentrated streams—one rich in calcium chloride (CaCl ₂), and the other rich in sodium sulfate (Na ₂ SO ₄) (also containing all of the selenium, 4,700 µg/L) and which are subsequently mixed to precipitate calcium sulfate (CaSO ₄). The salt-depleted solution from the EDM is returned to the RO to increase the yield of usable water. The supernatant from the precipitation can be processed by electro dialysis to recover sodium chloride (NaCl) for the EDM and produce a waste that is substantially concentrated in selenium. Processing of the supernatant was not performed due to time constraints and malfunction of the apparatus.					
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Pilot Testing of Zero-Discharge Seawater Desalination – Application to Selenium Removal from Irrigation Drainage

Prepared for Reclamation Under Agreement No. 04-FC-81-1036 Task G

by

**University of South Carolina
Research Foundation**



**U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Water and Environmental Services Division
Water Treatment Engineering Research Team
Denver, Colorado**

April 2008

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The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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Acronyms

Ca	calcium
CaCl ₂	calcium chloride
CaSeO ₄	calcium selenate
CaSO ₄	calcium sulfate
Cl ₂	chlorine gas
cm ²	square centimeter
CO ₂	carbon dioxide
ED	electrodialysis
EDM	electrodialysis metathesis
g	gram
gpd	gallons per day
HCl	hydrochloric acid
HNO ₃	nitric acid
H ₂ O	water
H ₂ SO ₄	sulfuric acid
meq/L	milliequivalent per liter
Mg	magnesium
Mg(OH) ₂	magnesium hydroxide
mL	milliliter
mS/cm	millisiemens per centimeter
MW	megawatt
NaCl	sodium chloride
NaOH	sodium hydroxide
Na ₂ SO ₄	sodium sulfate
OVP	over voltage protection
ppm	parts per million
PVC	polyvinylchloride
Reclamation	Bureau of Reclamation
RO	reverse osmosis
SeO ₄ ⁼	selenate
SO ₄ ⁼	sulfate ion

Acronyms (continued)

TDS	total dissolved solids
Wh	watthour
ZLD	zero-liquid discharge
ZZD	zero-discharge desalination
°C	degrees Celsius
µg/L	micrograms per liter
µS/cm	microsiemens per centimeter
%	percent

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Executive Summary

As population grows, the strain on the world's freshwater supplies will increase. By 2025, about 2.7 billion people, nearly one-third of the projected population, will live in regions facing severe water scarcity according to the International Water Management Institute (Smith 2001). Many prosperous and fast growing regions—the American Southwest, Florida, Asia—have inadequate freshwater supplies. But other factors such as a pleasant climate, mineral resources, job growth and rising incomes drive growth in these regions nevertheless. The needs of municipalities, industry, and citizens must be met, even as the difficulty and cost of developing new water resources increases. Desalination has become a popular option in regions where there is abundant water that is unsuitable for use due to high salinity, and there are opportunities for desalination plants that utilize thermal, electrical, or mechanical energy to recover potable water from salty solutions. The choice of the type of desalination process depends on many factors including salinity levels in the raw water, quantities of water needed, and the form and cost of available energy. Reverse osmosis (RO) is gaining increasing acceptance as the process of choice for desalination of seawater and brackish ground water.

Modern RO membranes have such high salt rejection that they are capable of producing potable water (less than 500 parts per million salinity) from seawater in a single pass, and brackish water membranes are designed to operate with remarkably low pressures. However, the yield of freshwater from RO is still constrained by the presence of sparingly soluble salts in the water, most notably calcium sulfate (CaSO_4). Some ground water in the United States has such high levels of CaSO_4 that it is difficult to recover as much as half of the feed as RO permeate. The University of South Carolina has developed technology called the zero-discharge desalination (ZDD) technology that removes CaSO_4 from the RO concentrate so that additional water can be recovered.

Reported herein are the results of a program to construct a pilot plant based on the ZDD technology and demonstrate it on feed water that is of great concern to the Bureau of Reclamation. The subject feed water is irrigation drainage from the San Joaquin Valley in California. The irrigation drainage is of concern because it contains troublesome levels of selenium leached from the soil. RO membranes reject greater than 90 percent of the selenium, but recovery of permeate is limited due to the presence of high levels of CaSO_4 leached from the soil. Consequently, RO treatment of this water leads to the issue of how to dispose of large volumes of concentrate with even higher levels of selenium than in the drainage water.

The approach of this zero-liquid discharge study is to remove CaSO_4 from the RO concentrate and then send the CaSO_4 -depleted water back to the RO for more

recovery of permeate. The CaSO_4 is removed in an electro dialysis metathesis (EDM) process that is a variant of ordinary electro dialysis. EDM utilizes four ion-exchange membranes and four process streams in a repeating unit. There are two depleting streams (the CaSO_4 -rich RO concentrate and a stream of sodium chloride [NaCl]) and two concentrating streams (one rich in sodium sulfate [Na_2SO_4] and the other rich in calcium chloride [CaCl_2]). In essence, the major salts in the two depleting streams change partners to form concentrated solutions of highly soluble salts of the ions that are problematic in RO. The two highly concentrated streams are mixed to precipitate CaSO_4 . The supernatant from the precipitation tank is treated in a second electro dialysis process (with the usual arrangement of two membranes in a repeating cell) to recover NaCl for reuse in the EDM process.

A pilot plant was constructed in the Department of Chemical Engineering at the University of South Carolina, transported to the Panoche Water District in California, and installed in a shed on a local farm. Drainage water from the farm was treated in the pilot plant. The EDM process did, indeed, transfer the calcium, sulfate and selenium to the concentrated streams as expected. Analytical data indicated that the calcium level was 18 times higher in the CaCl_2 -rich concentrate than in the irrigation drainage water fed to the process. Sulfate was 16 times higher, and selenate was 11 times higher in the Na_2SO_4 -rich concentrate than in the irrigation drainage. Mixing of the two concentrate streams produced a precipitate of CaSO_4 that contained very little selenate. Selenate in the supernatant was eight times higher than in the irrigation drainage. It is anticipated that the selenate in a liquid effluent stream will be concentrated by a factor of more than 100 when the process is fully implemented.

The major problems encountered in the pilot demonstration were oxidation damage to the anion-exchange membrane adjacent to the cathode in the EDM stack and reduction of flow in the CaCl_2 -rich concentrate streams in the EDM. Because of these problems, the total onstream time for the pilot plant was limited to 16 days, and the longest sustained run was 5 days. Resolution of these problems is expected with minor modifications to the process. In fact, a ZDD pilot plant implementing lessons learned from the Panoche experience was operated for 18 days and was shut down while still in good working order.

It is reasonable to conclude from this pilot study that the ZDD process has good prospects for dealing with the selenium and the calcium sulfate present in the irrigation drainage water of the San Joaquin Valley. It is recommended that the pilot plant be operated again at the same site after modifications to resolve the problems of membrane damage and precipitation in the CaCl_2 -rich concentrate compartments of the EDM stack.

Background and Introduction

In the last half century, global demand for freshwater has doubled approximately every 15 years (Abramovitz 1996). This growth has reached a point where today existing freshwater resources are under great stress, and freshwater resources have become both more difficult and more expensive to develop. One especially relevant issue is the fact that, in addition to producing a stream of potable water, desalination produces a waste stream containing, in concentrated form, the salts that were removed from the feed stream. In most cases, the disposal of the concentrate from desalination plants is regulated to avoid adverse effects on the environment.

Concentrate disposal imposes significant costs:

- Direct disposal costs, such as injection wells, pipelines, water quality sampling, instream biodiversity studies, can represent between 10 and 50 percent (%) of the total cost of freshwater production (Mickley, private correspondence).
- Time and expense required to obtain discharge permits can be substantial.

Deep well disposal is often used for hazardous wastes, and it has been used for desalination brines in Florida. Published estimates of capital costs are on the order of \$1 per gallons per day (gpd) of desalination capacity. The applicability and sustainability of deep well injection for large desalination plants is questionable because of the sheer volume of the brine and the possibility of ground water contamination.

Zero-liquid discharge (ZLD) systems are widely used in other industrial situations where liquid wastes cannot be discharged. These systems usually include evaporative brine concentration followed by crystallization or spray drying to recover solids. Common ZLD processes include the thermal brine concentrator and crystallizer (manufactured by Ionics-RCC and Aquatech). This technology can be used to separate reverse osmosis (RO) concentrate into freshwater and dry salt. However, the capital costs and electrical consumption, \$23-34 per gallon of daily capacity (gpd) and 114 wathours (Wh) per gallon of freshwater produced, is so high that it has not been used to achieve “zero-discharge” from RO desalination plants. Water removal from dilute brines is usually accomplished by vapor compression or high-efficiency, multiple-effect evaporators. The vapor then condenses in the heat exchanger that contacts the brine to form potable water with less than 10 parts per million (ppm) of total dissolved solids (TDS). Heat for evaporating water from saturated brines is usually provided by steam. Even with the efficiencies of vapor compression, the capital and operating costs of existing ZLD processes are substantial. The

ZLD process in this study shares some similarities to the Ionics RCC brine concentrator, but that process lacks the capability of isolating the salts so that individual salts can be recovered and sold as high-value products.

A ZLD process with no chemical recovery was installed at the 665-megawatt (MW) Doswell Combined Cycle Facility in Virginia to treat liquid waste, including RO concentrate and mixed-bed regenerate waste from a makeup demineralizer. The ZLD process includes preconcentration of feedwater by electro dialysis reversal, a step that saved \$900,000 in capital and \$682 per day in operating cost compared to evaporation without preconcentration (Seigworth et al. 1995).

Evaporation ponds can also be characterized as part of a ZLD process; but they are not broadly applicable, because they require unique climatic conditions and dedicated land area.

The Selenium Problem

Selenium is sometimes present in ground water and surface water in concentrations that make the water unsuitable for human consumption, for contact with wildlife, and even for irrigation. Concentrations of even a few ppm of selenium are considered toxic. The agricultural operations in the Central Valley of California have a huge problem of selenium leaching into the drainage waters that prevent reuse of the water for irrigation. A means of removing the selenium would be an economical benefit to the region.

Analysis of the drainage water at a farm in the Panoche Drainage District showed that the water contains appreciable concentrations of sodium, chloride, calcium, magnesium, and sulfate ions as well as a low but toxic concentration of selenium.

Ion	mg/L	meq/L
Na ⁺	1843	80.17
Ca ⁺⁺	529	26.40
Mg ⁺⁺	241	19.78
Σ Cations		126.35
Cl ⁻	1446	40.79
HCO ₃ ⁻	270	4.42
SO ₄ ⁼	3867	80.51
NO ₃ ⁻	287	4.62
Se/SeO ₄ ⁼	0.553	0.0077
Σ Anions		130.35

Results of previous studies on desalination of this water demonstrated that RO effectively rejects the selenium species, but the levels of calcium and sulfate in the water are too high to allow high recovery of RO permeate. Even 50% recovery is problematic.

Selenium is positioned just below sulfur in the Periodic Table of the Elements, and its chemistry is similar in many respects to that of sulfur. That similarity contributes to the difficulty of isolating selenium that is present at low concentrations in water that contains appreciable concentrations of sulfate. Selenium is

generally present in water as the selenate ion (SeO_4^-), analogous to sulfate (SO_4^-) ion. Fortunately there are some differences in the properties of the two ions that can be exploited to make the SeO_4^- ions accessible to removal and recovery. In particular, calcium selenate (CaSeO_4) is substantially more soluble than CaSO_4 . RO is known to be effective for removal of SeO_4^- ions, but its use is limited when the feed water contains appreciable concentrations of calcium sulfate, which is the case in the Central Valley. The zero-discharge desalination (ZDD) process (proprietary to the University of South Carolina) can be used for removal of sulfate ions (SO_4^-) from water as solid sulfate salts prior to removal of SeO_4^- ions. This concept allows recovery of selenium and CaSO_4 separately as solid materials, so that virtually all of the water would be available for beneficial use.

The New ZDD Process

The concept that was investigated in this study is called zero-discharge desalination. ZDD is similar to a ZLD system, but ZDD differs from other ZLD processes in that the ZDD process allows separation of the salts into salable products. The ZDD concept as practiced in this project utilizes the energy-saving feature of a special electro dialysis (ED) technique to remove the CaSO_4 from the concentrate stream of reverse osmosis and recovers it as a solid, potentially salable byproduct of the desalination process. Figure 1 illustrates what would happen if one would attempt to concentrate the divalent salts by conventional ED with ordinary ion-exchange membranes. The SO_4^- ions would migrate through the anion-exchange membrane designated by A, and Ca^{++} ions would migrate through the cation-exchange membrane designated by C. Substantial buildup in the concentrations of these divalent ions would result in precipitation of CaSO_4 in the concentrating stream of the ED process, and such precipitation would cause deterioration in the performance of the ED process.

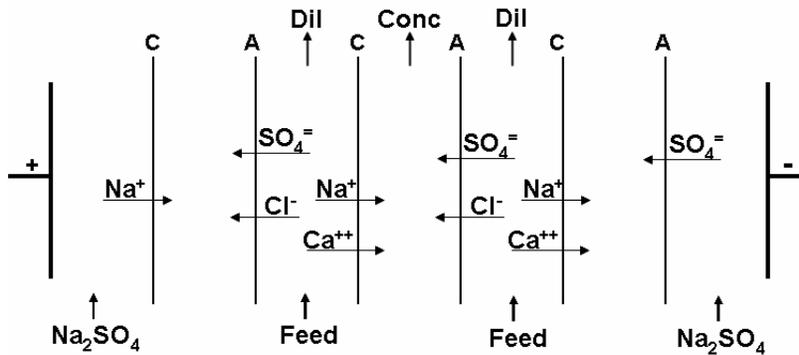


Figure 1. Conventional electro dialysis with ordinary membranes concentrates CaSO_4 .

Precipitation of sparingly soluble CaSO_4 is avoided in the ZDD process by the application of a variant of ED called electro dialysis metathesis (EDM). In EDM, the ions of CaSO_4 in the RO reject stream are separated to make two separate streams of highly soluble salts sodium sulfate (Na_2SO_4) and calcium chloride (CaCl_2). The EDM technique utilizes four ion-exchange membranes in a repeating unit cell of the ED stack. Such an arrangement can be used to change partner ions of two salts. In this example, the two salts, CaSO_4 and sodium chloride (NaCl) in two separate diluate streams change partners to form Na_2SO_4 and CaCl_2 in two separate concentrate streams. The EDM technique is illustrated in figure 2. The designations A and C are used for the ion-exchange membrane bounding the diluate stream containing CaSO_4 , and the designations A' and C' are used for the ion-exchange membrane bounding the diluate stream containing NaCl . A repeating unit cell has the sequence A, C, A' C' when the anode is to the left, as illustrated in figure 2. The solution containing CaSO_4 , in this example RO concentrate solution, flows between the A and C membranes. When an electric potential is applied to the electrodes, portions of all of the anions migrate through the A membrane, and portions of all of the cations migrate through the C membrane. A solution comprising monovalent salt (called the NaCl supply in figure 2) flows between the A' and C' membranes. When an electric potential is applied to the electrodes, Cl^- anions migrate through the A' membrane, and Na^+ cations migrate through the C' membrane. Thus, the solution flowing between the C' and A membranes becomes concentrated with Na_2SO_4 , and the solution flowing between the C and A' membranes becomes concentrated with CaCl_2 . Since the Na_2SO_4 and CaCl_2 salts are substantially soluble in water, these salts can be concentrated appreciably by recirculating the solutions through their respective ED compartments as shown in figure 2.

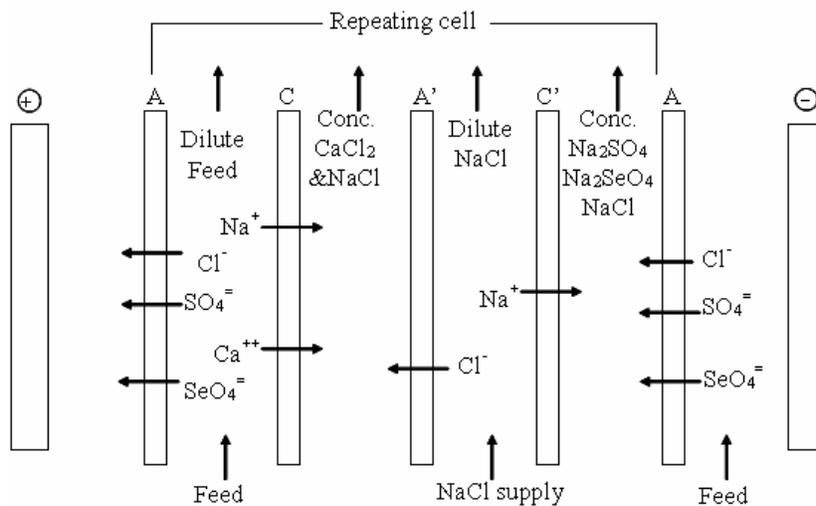


Figure 2. Membrane arrangement and transport of ions in electro dialysis metathesis.

The separate CaCl_2 -rich and Na_2SO_4 -rich concentrated streams produced by the EDM stack are combined in a continuously stirred conical contactor. This arrangement allows for the precipitation of CaSO_4 to occur. The CaSO_4 slurry is removed from the tank and allowed to settle. The precipitate is then collected, and the supernatant is used as the feed solution to the ED stack.

The ED stack contains special ion-exchange membranes that are selective to the transport of monovalent ions, in contrast to conventional membrane that selectively transport divalent ions. The predominant monovalent ions and their relative transport through the special membranes are Na^+ : 1, K^+ : 0.8, Cl^- : 1, Br^- : 3.8 and HCO_3^- : 0.5. The predominant divalent ions and their relative transport through the special membranes are Mg^{++} : 0.05, Ca^{++} : 0.11, and SO_4^{--} : 0.03 (Davis 2005).¹

The use of ED to recover NaCl from seawater to produce edible salt has been applied on a large scale in Japan for about 40 years. In recent years, ED plants have been installed by Japanese companies in Kuwait and South Korea to recover NaCl from seawater for use in chlor-alkali plants. It has been reported that the energy consumption of salt manufacture with seawater reverse osmosis reject as the feed is 80% of that with seawater as the feed (Tanaka et al. 2003).

Work Performed and Results

The original plan was to operate the ZDD pilot plant at a seawater desalination facility, but no suitable location was identified. Moreover, there was a strong incentive to utilize the ZDD technology in the treatment of irrigation drainage in the San Joaquin Valley. The drainage water from irrigation there is problematic in that it contains too much selenium to be discharged and contains too much CaSO_4 to be treated effectively by RO. The ZDD technology had evolved in the direction of treating CaSO_4 -rich ground water, so it was decided to change the scope of the pilot plant to investigate the applicability of ZDD technology to the treatment of irrigation drainage in the San Joaquin Valley. Consequently, the tasks were modified for this new application.

¹ The following are introduced as positive and negative ions. Na^+ = sodium; K^+ = potassium; HCO_3^- = bicarbonate; Mg^{++} = magnesium; Ca^{++} = calcium; SO_4^{--} = sulfate; Cl^- = chloride; Br^- = bromide.

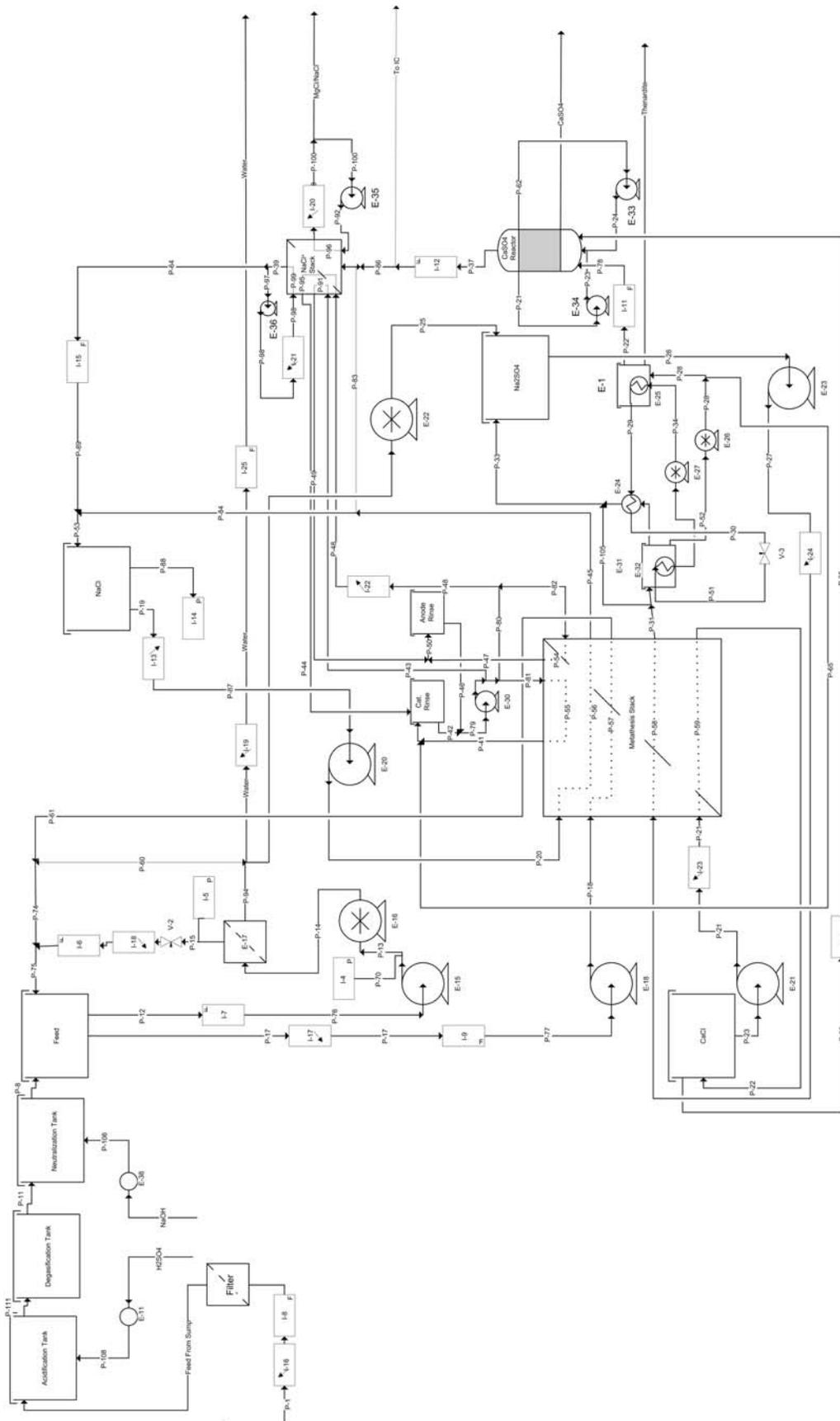


Figure 4. Flow diagram of pilot plant for Panoche.

Task 1. Prepare Skid Layout, Select and Order Materials

A schematic of the skid is shown in figure 4. The EDM stack was purchased from Ameridia, Inc. Each membrane had an exposed area of 500 square centimeters (cm^2) (Matsunaga 2003). The membrane arrangement was like that shown in figure 2. All membranes were of the Neosepta trademark of Tokuyama Corp. The membranes in the 20 repeating units were A = AMX, C = CMX, A' = ACS and C' = CMS. The cation-exchange membrane next to the anode was CMB, and the anion-exchange membrane next to the anode was AHA.

The ED stack designated in figure 4 as the “NaCl Stack” was purchased from Electrolytica, Inc. The end plates of the purchased stack were modified to provide two entry ports for each gasket spacer. Steel-rule dies were purchased, and gaskets, spacers, and membranes were cut in a hydraulic press. The membranes used in the 20 repeating cell pairs of the NaCl stack were ACS and CMS. CMB membranes were used next to the anode and the cathode.

The flow diagram in figure 4 shows how the process works. The pretreatment section of the pilot plant utilizes gravity flow between the tanks in the pretreatment portion, which eliminates the need to actively control the level in the tanks with valves and float switches. The feed water flows through a cartridge filter before it enters the system. Sulfuric acid is added to the filtered water in a stirred tank to maintain a pH of 4. Acidification converts carbonate or bicarbonate into dissolved carbon dioxide. The water then flows into a second tank that is packed with high surface area packing (Vexar netting) to disengage the carbon dioxide (CO_2) from the water. Sodium hydroxide is then added to the solution in a stirred tank to bring the pH back to neutral.

The neutralized feedwater goes to a feed tank that supplies both the RO, which removes water, and the EDM, which removes salts from the feed solution. The cations from the feed go to a concentrate stream where they join Cl^- ions from a supply stream of NaCl to form what is called the chloride-salt stream. The anions join Na^+ ions from the NaCl to form a concentrate stream that is called the sodium-salt stream. The salinity of each of those concentrate streams is roughly 100 times the feed salinity. Stoichiometric (with respect to Ca^{++} and SO_4^- ions) amounts of the two concentrate streams are mixed to precipitate CaSO_4 .

The feed contains more SO_4^- ions than Ca^{++} ions. Excess sulfate is removed by cooling a side stream of the circulating sodium-salt concentrate to crystallize Na_2SO_4 . The crystals that form are $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The decahydrate crystals (Glauber's salt) are subsequently heated to form the

anhydrous salt (thenardite) and a saturated Na_2SO_4 solution that goes to the precipitation tank along with the overflow from the sodium-salt concentrate.

The supernatant from the precipitation is analyzed for sulfate concentration, and the analytical data are used to determine the rate of addition of sulfate to the precipitation tank in order to achieve the desired stoichiometric balance. In a full-scale operation, the entire overflow stream from the circulating chloride-salt stream would enter the precipitation tank. Over the long term, all of the Na_2SO_4 that is not removed as thenardite would enter the precipitation tank; and thenardite production will be dictated by the flow rate of the side stream.

The supernatant from the precipitation of CaSO_4 goes to the second ED stack that contains univalent-ion-selective membranes that produce a concentrated NaCl stream for return to the EDM stack. Since the NaCl stream also passes between univalent-ion-selective membranes in the EDM stack, there is an opportunity for accumulation of divalent ions in the circulating NaCl loop. The accumulation of Mg^{++} or SeO_4^- in the NaCl loop is not a problem, but accumulation of Ca^{++} and SO_4^- could lead to supersaturation in one or both concentrate streams, because the rate of transport is proportional to the concentration of the ions. To avoid buildup of Ca^{++} and SO_4^- ions, a purge stream flows from the NaCl loop to the feed tank. Similarly, since there is no transport of non-ionized solutes like silica through the RO or EDM membranes, some solution is purged from the feed tank.

The diluate stream from the second ED contains most of the magnesium (Mg^{++}) and SeO_4^- ions. The flow rate of that stream is small, because much of the water in the supernatant is transported through the membranes as hydration of the Na^+ and Cl^- ions. Because of the small flow rate, treating it continuously is impractical for the pilot test.

Task 2. Construct Skid and Assemble Components

The skid was constructed in a work area of the Department of Chemical Engineering at the University of South Carolina in Columbia, South Carolina. The framework for the skid was constructed of Dynaform® extruded, fiberglass-reinforced polyester channel, and angle attached with ¼-inch stainless-steel bolts. Horizontal surfaces were ¼-inch-thick polyvinylchloride (PVC) sheet, and vertical surfaces for mounting instruments were ¼-inch-thick acrylic. The skid was mounted on casters. Piping was solvent-welded PVC. All of the pumps used for circulating solutions are Iwaki Model MD30RLZT.

Instrumentation for measurement of pH and conductivity of solutions was built around the SC1000 system of Hach Company. Toroidal conductivity sensors were inserted into tees in the solution lines or mounted in the walls of tanks.

Sensors for RO concentrate pressure and for current and voltage to the ED stack were also used. Data from the Hach SC1000 system was sent to a signal processor that was monitored by a program written in Lab View (National Instruments). Data from the sensors were recorded every 10 seconds, averaged with values from the previous six measurements to avoid effects of noise, displayed on a computer monitor, and stored in a spreadsheet.

Task 3. Perform Shakedown in Lab with NaCl Solution

Shakedown testing of the RO-ED system was done with a synthetic feed solution of NaCl in tap water. Using this feed that was free of potential fouling materials allowed more flexibility in the initial testing. Experimental data from the operations with NaCl feed allowed establishment of baseline values for operating parameters so that deviations from those baseline data would be recognized and quantified during the experiments with the irrigation wastewater.

Task 4. Make Preparations at Test Site

The test site was on a farm in the Panoche Water District of California's San Joaquin Valley. The pilot plant was housed in a shed that measured approximately 10 feet by 30 feet. Since the RO and ED processes imparted heat to the water being treated, it was necessary to set up a chiller to provide cooling. The condenser was air-cooled, and the evaporator was placed inside a 45-gallon drum that contained circulating water. A water coil was installed inside the building to augment the existing air-conditioning system. A shell-and-tube heat exchanger was also connected to the chilled water circulation loop to remove heat accumulated in the circulating solutions in the pilot plant. An air compressor was installed outside the shed to supply air to actuate the RO backpressure control valve.

Task 5. Move Skid to Test Site and Set Up

After assembly and shakedown testing at the University of South Carolina, the skid was rolled onto an automobile-transport trailer, and a plywood box was constructed around it for protection. A motor home was used to pull the trailer from South Carolina to California. A photograph of the installed pilot skid is shown in figure 5.

The water supply for the tests came from a 1,000-gallon outdoor storage tank that contained irrigation drainage water.



Figure 5. ZDD pilot skid installed at Panoche farm.

Task 6. Perform Shakedown at Site

Because there was no freshwater available at the site, feed solutions for the process streams were made up with permeate from the RO system used to treat the irrigation drainage. Deionized water was prepared by filtering the RO permeate with a mixed-bed cartridge from Cole-Parmer. In a shakedown test, RO permeate was circulated for all streams to ensure that no leaks developed during transport of the skid. The NaCl solution for the EDM NaCl was prepared with deionized water and commercial-grade salt used to regenerate water softeners. Electrode rinse solution was prepared with deionized water and Na_2SO_4 purchased from Uni-Var. The initial solutions in the concentrate streams of the EDM were deionized water. Their conductivity increased rapidly as soon as direct current potential was applied to the electrodes of the EDM stack.

Task 7. Modify Equipment

No modifications were made to the skid after it arrived at the Panoche site. Several deficiencies in the system design were noted during operation of the system. Those deficiencies are noted here, and suggestions for improvements are described under “Conclusions and Recommendations.” Contact with the Vexar screen was insufficient to remove all of the CO_2 from the acidified feed. The 20-gallon tanks provided for collection of the CaCl_2 -rich and Na_2SO_4 -

rich concentrated product streams were too small. Using larger tanks would allow larger quantities of the concentrated streams to accumulate, which would permit analyses of the streams prior to mixing in the precipitation tank. The digital flow meters were not sufficiently accurate and reliable to allow detection of changes in flow rates that would be an early indicator of problems in the flow channels of the EDM stack. The absence of pressure gauges in the process streams where the solutions entered the stack made it difficult to detect increases in hydraulic resistance in the EDM stack.

Task 8. Operate for Month-Long Test

Five attempts were made to operate the system for an extended period of time. Each attempt was terminated when the operator detected symptoms that indicated a malfunction that necessitated maintenance to the system. In each of the attempts, lessons were learned about the system behavior. The recorded operating data and comments by the operator are presented in Appendix A

Run 1

In Run 1, which was started on June 26, 2006, at 12:00 p.m., NaCl for the EDM salt supply was prepared by dissolving water softener salt obtained from Lowes with deionized water produced using an under-the-sink RO unit and a mixed-bed ion exchange column. The electrode rinse solution was prepared by dissolving sodium sulfate obtained from UNIVAR with deionized water as noted above. The EDM CaCl₂ and the EDM Na₂SO₄ tanks were partially filled with deionized water prepared as noted above. The EDM feed was irrigation drainage water from Panoche Drainage District sump DP 25 that was stored in a large, black tank. Only the EDM stack was operated at the beginning of Run 1 until the conductivity of the feed solution had dropped significantly. This was done to prevent the formation of CaSO₄ on the RO membrane. The RO system was started after the conductivity of the EDM RO feed tank had dropped to about 10 millisiemens per centimeter (mS/cm). The RO feed pressure was adjusted regularly to maintain the conductivity of the EDM RO feed tank at approximately 15 mS/cm. The concentrated solutions in the CaCl₂ and Na₂SO₄ tanks were withdrawn and mixed in the agitated, conical precipitation tank to produce CaSO₄ precipitate. A slurry of the precipitate was withdrawn from the conical tank and allowed to settle in a 5-gallon bucket, and the supernatant was decanted from the bucket and stored for processing in the ED2 stack. After 3.5 days of operation, it was noticed that flow had stopped in the EDM CaCl₂ solution compartments. The system was shut down, and the EDM stack was disassembled. Examination revealed that the CaCl₂ compartments were full of a white solid, shown in figure 6. Also it was noticed that the solids were adhered very firmly to the ACS membrane. There was no obvious reason why the solids had formed. The



Figure 6. Photographs from left to right of the CMX membrane above the CaCl_2 compartment, the spacer in the CaCl_2 compartment, and the ACS membrane below the CaCl_2 compartment

compartment that shares the ACS membrane is the EDM NaCl compartment of which the NaCl solution was prepared with water-softener salt, which would appear to eliminate the NaCl supply as the source of the problem. It was also noted that while the solids did not dissolve in RO permeate water or in dilute sulfuric acid (H_2SO_4), they did dissolve in the presence of hydrochloric acid (HCl). The solids were removed from the stack components by rinsing the membranes and spacers with dilute HCl solution, and the stack was reassembled and put back into service.

Run 2

Run 2 was started at noon on July 8, 2006. Again the system was started up in the same manner as in Run 1. The NaCl supplied to the EDM was recovered in the ED2 stack from the supernatant that was collected from the CaSO_4 precipitator in Run 1. After 0.5 day of operation, it was noticed that the EDM CaCl_2 stream appeared to be cloudy, so about 5 gallons of RO permeate was added to the CaCl_2 solution tank to dilute the stream and, hopefully, dissolve the precipitate that seemed to be forming. The flow rate in the CaCl_2 seems to improve after about 15 minutes, and the solution was less cloudy. Adding RO permeate to the EDM CaCl_2 stream was done frequently in Run 2 to prevent the formation of the solids that was observed in Run 1. Despite the efforts made to keep the system running by dilution of the CaCl_2 solution, after 3.75 days, the EDM stack once again was exhibiting an unusually low current—4.3 amperes at 35 volts compared to 13.7 amperes at 30 volts at the beginning of the run. The system was shut down again, and the EDM stack was disassembled. Upon disassembly, the white solids were again found in the CaCl_2 compartment. Again, the solids were found to be insoluble in just RO permeate but soluble in a 1% HCl solution. Substantial gas was evolved when the solids were contacted with HCl. After the solids had been dissolved, the EDM stack was reassembled and prepared for Run 3.

The evolution of gas when the precipitate was mixed with HCl solution indicated that perhaps the scale contained CaCO_3 . The likely source of the carbonate could

be the feed water. Although the feed was acidified to convert bicarbonate to CO_2 , there was no provision for ensuring that the dissolved CO_2 was actually removed from the feed water before it was neutralized with sodium hydroxide (NaOH). A reasonable solution to this problem would have been to bubble air through the acidified feed to reduce the partial pressure of CO_2 in the solution before neutralization with NaOH converted it to bicarbonate.

Run 3

Run 3 was started at 9:30 a.m. on July 21, 2006. Again, the system was started up in the same manner as in Run 1. The decision was made to operate the EDM stack on water-softener salt that had been purified in the ED2 stack. Use of purified NaCl from the ED2 stack would, hopefully, ensure the purity of the EDM NaCl stream. After 1.6 days of operation, the level in the Na_2SO_4 tank was observed to be dropping when it should have been rising. A plausible explanation was an internal leak in the stack. The presence of an internal leak between the EDM rinse compartment and the EDM Na_2SO_4 compartment was confirmed 12 hours later, 2.06 days into the experiment. This also explained the odor of chlorine (Cl_2) gas in the building, because Cl_2 gas would be generated if Cl^- ions were in contact with the anode. To alleviate the internal leak, the flow rates of both streams were adjusted so that the electrode rinse compartment was at a higher pressure than the Na_2SO_4 compartment. The system continued to operate in this manner until it was shut down to determine the source of the leak. The system operated continuously for 4.1 days during Run 3. Disassembly and inspection of the EDM stack revealed discoloration and a tear in the AHA membrane that separated the cathode compartment from the first Na_2SO_4 concentrating compartment. Since no replacement membrane was on hand, several attempts were made to repair the membrane using a small piece of AHA membrane; however, no suitable adhesive was found to bind the small piece of membrane to the larger membrane. A new CMB membrane was shipped from USC and arrived at the test facility on August 2, 2006. It should be noted that there were no signs of solid formation in any of the solution compartments at the end of Run 3. However, it is likely that the HCl added to prevent the fouling of the CaCl_2 compartments could have diffused into the electrode rinse solution where it was oxidized to Cl_2 that lead to degradation of the AHA membrane. The stack was reassembled, and the system was prepared for Run 4.

Using a CMB membrane in place of the AHA membrane on the cathode side of the stack added some complexity to the operation. Because there were trace amounts of Mg^{++} in the Na_2SO_4 streams, Mg^{++} would then be entering into the electrode rinse compartment which deposits as nonconductive magnesium hydroxide ($\text{Mg}(\text{OH})_2$) on the cathode. Allowing $\text{Mg}(\text{OH})_2$ to remain on the cathode would result in the buildup of electrical resistance.

One way to avoid the buildup of $\text{Mg}(\text{OH})_2$ is to maintain the pH of the electrode rinse compartment below 7 pH.

Run 4

Run 4 was started at 12:15 a.m. on August 3, 2006. The system was started up in the same manner as in Run 3, which included a purified water-softener salt from ED 2. Run 4 was unsustainable. The power supplies began to trip the over voltage protection (OVP) circuits built into the power supplies once H_2SO_4 was added to the electrode rinse compartments. There was a strong odor of chlorine in the building during the course of Run 4. Then, 1.34 days into the run, an operational error led to the termination of Run 4. A solution of Na_2SO_4 that had been produced by the EDM stack was mistakenly used to replenish the depleted EDM NaCl stream. Corrective actions taken as soon as the mistake was realized did not prevent scaling of the CaCl_2 and Na_2SO_4 streams and the increase in the stack electrical resistance. The power supply to the EDM stack was turned off, and RO permeate was circulated through the EDM stack and drained three times during the course of approximately 2 days starting on the afternoon of August 4, 2006, and continuing until early in the morning of August 6, 2006. The total operating time for Run 4 was 1.46 days.

Run 5

Run 5 was started at 11:37 a.m. on August 6, 2006. The system was started up in the same manner as in Run 3, including the use of purified water-softener salt from ED 2. There was still a small resistance to flow in the Na_2SO_4 compartment, but it was decided to run the system with the flow restriction, because time available to run the system again was running out. Two days after the beginning of the experiment, the current had dropped to 1.7 amperes at 35 volts compared to 8.9 amperes at 35 volts at the beginning of the experiment. Sulfuric acid was added to the electrode rinse solution to adjust the pH from 8.5 to 5 pH. At 2.17 days into the experiment, the EDM power supply was turned off due to OVP situations; and more H_2SO_4 was added to the electrode rinse. At 2.28 days into the experiment, 6:18 p.m. on August 8, 2006, the EDM power supply was energized; and the EDM stack operated at 11.7 amperes at 35 volts. Early in the morning on August 9, 2007, it was noticed that there had been no significant Na_2SO_4 production from the system. The lack of Na_2SO_4 production was traced back to an internal leak in the EDM stack between the Na_2SO_4 compartment and the electrode rinse compartment. Later at 9:30 a.m. on August 9, 2006, 2.91 days into the run, a flow resistance in the CaCl_2 compartment was noticed. HCl was added to the CaCl_2 stream to dissolve the solids that were forming in the compartment. At 9:30 p.m. on August 9, 2007, 3.41 days into the experiment, samples of all the process streams

were obtained for later analysis. After the samples were obtained, the system was shutdown and prepared for long-term storage.

The system was operated at Panoche for a total of 16.19 days according to the operator logs, which are included in Appendix A. The longest continuous operation was 4.1 days in Run 3, which was terminated due to a damaged AHA membrane next to the cathode. While a long continuous run was not obtained, there were several practical lessons learned that will allow for the process to be improved.

A sequel to this project was carried out with a newly constructed, trailer-mounted ZDD process in El Paso, Texas, in the spring of 2007. A continuous run of 20 days was conducted with CaSO_4 -rich ground water. Some problems of flow restriction in the concentrate compartments occurred, but it was found that the problems could be alleviated by rinsing of the concentrate compartments without disassembly of the stack. Sulfate of unknown origin, possibly from an internal leak, was found in the analysis of the NaCl solution being circulated through the stack. Chloride was also found in the electrode rinse solution, and it was subsequently found to be an impurity listed on the label of the bag of Na_2SO_4 used to make up the electrode rinse. It is worth noting that using a common solution to rinse both electrodes is an optional configuration. An alternative would be to use separate electrode-rinse solutions with the same configuration of membranes—CMB next to the anode and AHA next to the cathode. With no mixing of the rinse streams, problems of chlorine degradation of the AHA membrane should be avoidable.

Sampling and Analytical

Samples were taken on August 9, 2006, at the end of Run 5 that lasted 3 days. Samples of the liquid products and the precipitate were collected and brought back to the University of South Carolina. A review of the operating log revealed that this particular run occurred during a period when the NaCl supply was derived from water-softener salt that was dissolved in RO permeate and treated in the ED2 stack. This run occurred after an episode when the flow rate in the concentrating CaCl_2 stream of the EDM stack was sluggish, a condition that was remedied by adding HCl acid to the tank supplying that stream. Consequently, the pH of the samples collected from the EDM process streams was unusually low. Samples were chosen for a particular point in time where conditions were steady. Those samples were submitted to the analytical laboratory of Dow Chemical Company in Midland, Michigan.

Calcium and magnesium in the solution samples were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin-Elmer 3300DV) and reported as ppm (weight) of the ion. The solutions were diluted 10-fold and

100-fold in 5% nitric acid (HNO_3) before analysis. Sodium, selenium, and total chlorine in solution samples were determined by neutron activation analysis and reported as wt% or ppm (wt). Sulfate in the solution samples was determined by ion chromatography with conductivity detection (Dionex Corp). For solution samples containing less than 0.5% total chlorine, chloride was also determined by ion chromatography. To obtain a calculation of milliequivalent per liter (meq/L), it was necessary to estimate the solution density, which was done by looking up values in the *CRC Handbook*.

The solid sample submitted to Dow was simply the material collected from the precipitation tank. No attempt was made to wash away liquid that adhered to the crystals of CaSO_4 that precipitated. For analysis of the reactor precipitate, selenium in the wetcake as received was determined by neutron activation analysis. Sodium and total chlorine were determined by neutron activation analysis on a small aliquot of wetcake dissolved in dilute HNO_3 . Sodium was also determined on a sample of the wetcake dried overnight at 130 °C. Calcium and magnesium in the reactor precipitate were determined by ICP-OES after weighing out approximately 1 gram of the wetcake as received and dissolving into 50 milliliters of 5% nitric acid. No results were reported for sulfate in the precipitate.

The analytical data are presented in figure 7. Since selenium is a major concern, it will be discussed first. The RO treatment reduced the SeO_4 to undetectable levels (less than 50 parts per billion) in the permeate. Consequently, the SeO_4 level was elevated in the RO concentrate and in the feed tank. The SeO_4 was undetectable in the concentrated CaCl_2 stream. That is not surprising, because anions should only enter that stream from the NaCl supply stream through a univalent-anion-selective membrane (ACS). In contrast, there was abundant SeO_4 in the concentrated Na_2SO_4 stream, because the SeO_4^- ions are similar to SO_4^- ions in their ionic transport properties. The SeO_4 was also abundant in the supernatant with a reported value of 3.6 ppm. The SeO_4 content of the precipitate was 4.5 ppm and Mg was 1,800 ppm, not much higher than that in the supernatant. Evidently, there was little, if any, co-precipitation of SeO_4 or Mg in the formation of the solid CaSO_4 byproduct. This is good news, because it indicates that disposal or utilization of the byproduct will not be hampered by selenium contamination or soluble MgSO_4 .

Again, it should be stated that the pH values of the process streams of the EDM stack were anomalous, because HCl had been added to the tank containing the concentrated CaCl_2 stream. Evidently, that acidity permeated the other process streams. The sample of supernatant from the precipitation was taken at the same time as the other samples, but it was made up of CaCl_2 and Na_2SO_4 streams from a run when there was no acidification.

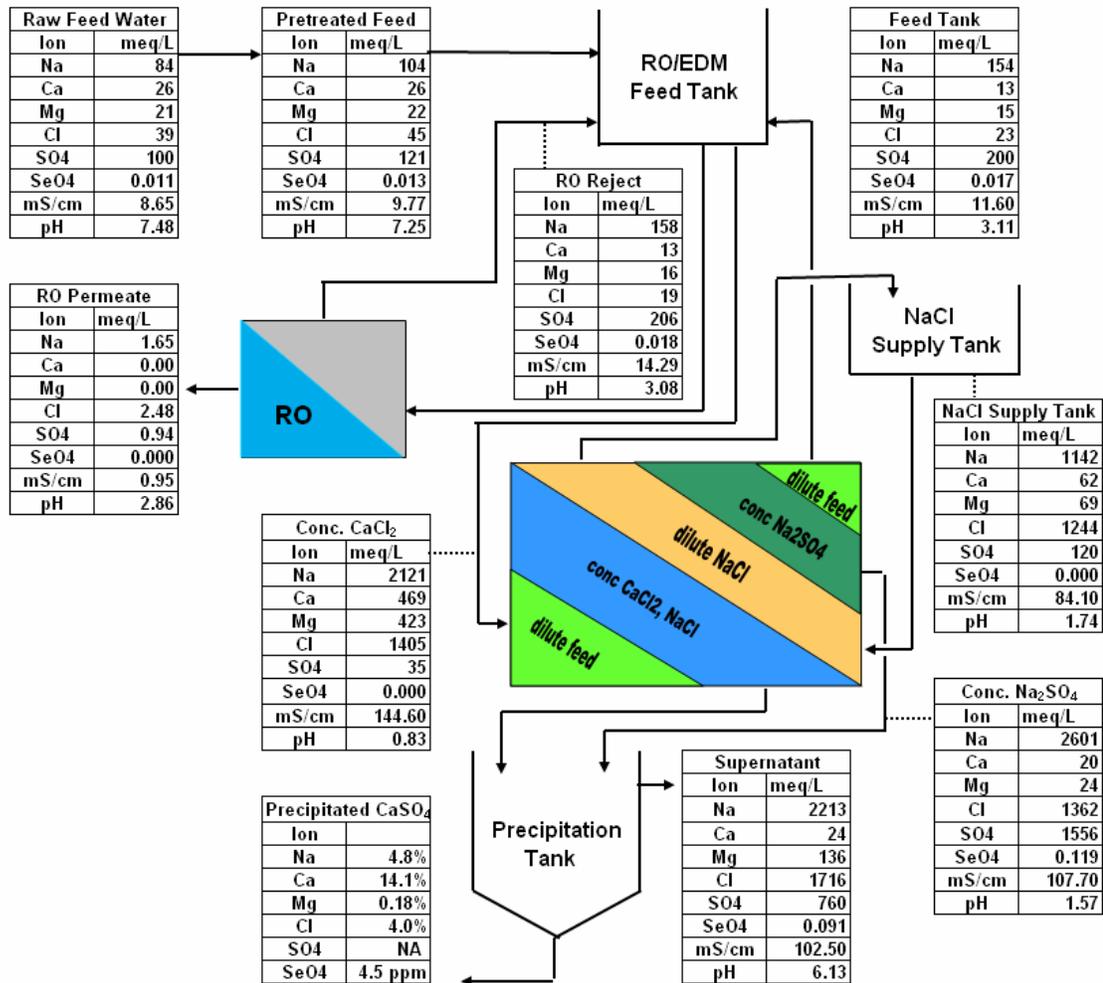


Figure 7. Composition of process streams in Run 5.

Task 9. Dismantle and Ship Equipment

The pilot plant is still located at the Panoche site. There are no current plans for the plant to be moved. There has been some discussion that the plant could be modified and then used to further study selenium removal from the drainage water.

Task 10. Reporting

Discussion

The most persistent problems that limited the duration of experimental runs were the reduction in flow rate of the CaCl₂ stream and damage to the anion-exchange membrane next to the cathode. The system was designed to allow use of a

common solution of Na_2SO_4 to rinse both the anode and the cathode. The membranes next to the electrode rinse compartments were selected to be a cation-exchange membrane (Neosepta CMB) next to the anode to transport Na^+ ions and an anion-exchange membrane (Neosepta AHA) next to the cathode to transfer SO_4^- ions. A concentrated solution of Na_2SO_4 was infused into the electrode rinse stream to make up for the lost ions. Selection of this arrangement for the electrode rinse was based on the presumption that minimal chloride ions would be present in the electrode rinse. However, analysis of a sample of the common electrode rinse solution collected on June 30 revealed a sulfate level of 1,438 meq/L and chloride level of 145 meq/L. It was subsequently learned that commercial Na_2SO_4 has NaCl as a contaminant. Moreover, the data in figure 7 indicate that the Na_2SO_4 -rich concentrate stream contains nearly as much chloride (1,362 meq/L) as sulfate (1,556 meq/L), and that could be the major source of chloride in the electrode rinse.

Figure 8 illustrates what can happen when there is substantial chloride in the solution compartment next to the anode compartment. Although the CMB membrane is selective for the transport of cations (Na^+ ions in this case), that selectivity is not absolute. According to the principles of Donnan exclusion, the selectivity decreases as concentration increases. Thus, there is a mechanism for chloride ions to enter the anode compartment. Chloride ions in the anode compartment can lose an electron at the anode and become oxidized to elemental chlorine, which readily dissolves in the electrode rinse solution. When that common rinse solution enters the cathode compartment, the chlorine reacts with hydroxyl ions generated at the cathode and becomes hypochlorite anions, which readily migrate into and through the AHA membrane. AHA membrane is the only commercial anion exchange membrane that is supposedly resistant to oxidation, but its oxidative resistance in this environment appears to be insufficient.

As mentioned previously, using a common electrode rinse solution is a convenience, not a necessity. An alternative is to operate with two separate electrode rinse solutions and still use Na_2SO_4 as the conducting electrolyte in the rinse solution. For example, infusion of a solution of H_2SO_4 (diluted with deionized or softened water) into the catholyte would neutralize the hydroxyl ions generated at the cathode. That would require pH control, because the catholyte should not become sufficiently acidic to corrode the stainless steel cathode. The infused acid stream should contain a little sodium ion to replenish what is lost in the overflow. A separate anolyte stream would need to be fed with NaOH (diluted with deionized water) with a little sulfate and would require pH control. Perhaps the CMB membrane should be replaced with Nafion, which has even better resistance to oxidation.

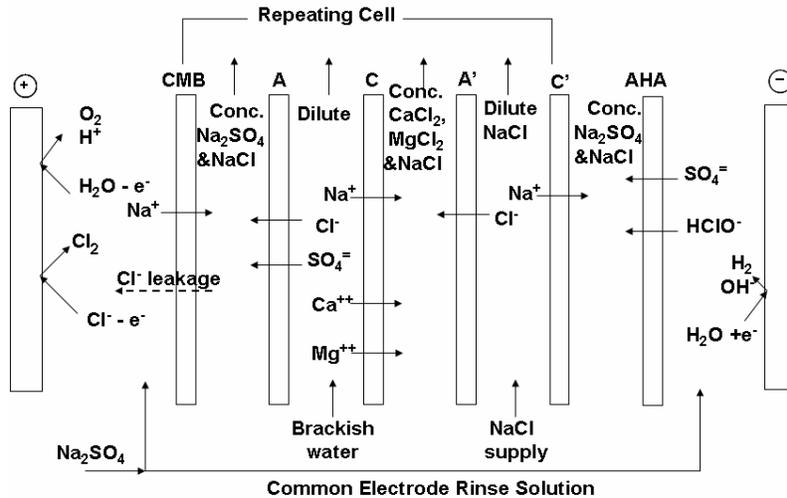


Figure 8. Mechanism for chloride entry into electrode rinse and oxidative damage to the AHA membrane.

The observed flow reduction in the CaCl_2 -rich concentrate streams of the EDM stack is attributed to precipitation of a sparingly soluble calcium salt in the solution compartments. The precipitate might have been CaCO_3 , CaSO_4 , or both. CaCO_3 is suspected because acidification of some precipitate collected from the concentrate compartments dissolved and released bubbles when it was acidified. Although the feed pretreatment included acidification to remove carbonate from the feed solution, the apparatus provided for CO_2 removal (a small tank filled with Vexar) was ineffective. The simplest solution is to blow air into the acidification tank in order to reduce the partial pressure of CO_2 . That approach was successful when the ZDD process was demonstrated in El Paso and in the Brackish Ground Water National Desalination Research Facility in Alamogordo, New Mexico.

Data in figure 7 indicate that the concentration of sulfate in the supernatant of the precipitation tank was substantially higher than the concentration of calcium. This situation occurred because the irrigation drainage had more sulfate than calcium, and none of the concentrated Na_2SO_4 solution was diverted from entering the precipitation tank. It was also observed that the product of concentration of calcium and sulfate ions was higher than that predicted on the basis of reported solubility product for CaSO_4 . The reason for the unexpected solubility is that the presence of NaCl increases the solubility of CaSO_4 (Cameron and Seidell 1901). At the concentrations in the supernatant, the solubility is increased by a factor of 3.

Conclusions and Recommendations

The reason for operating this pilot plant at Panoche was to determine the applicability of the ZDD technology to the problem of selenium in the irrigation drainage that complicates disposal and reuse of the water. Reverse osmosis produces permeate with acceptably low levels of selenium, but the high CaSO_4 of the feed water dictates low recoveries. Consequently, the selenium remains in a large volume of water. The results of this study demonstrated that selenium in the RO permeate was below detectable limits (0.05 ppm). The selenium level was 10 times higher in the concentrated Na_2SO_4 -rich stream (4.7 ppm) than in the drainage water (0.45 ppm) fed to the process. When the Na_2SO_4 -rich and CaCl_2 -rich streams were mixed, they produced CaSO_4 precipitate that contained very little selenium, and the supernatant from the precipitation contained a high concentration (3.6 ppm) of selenium.

It is recommended that modifications listed below be made to the ZDD pilot plant before it is returned to service.

- Install an air dispersion device in the feed acidification tank to improve decarbonation.
- Replace the digital flow meters in process streams with all-plastic rotameters to improve reliability of flow-rate measurement.
- Install pressure gauges between the rotameters and entry points to the stacks to allow balancing of internal pressures in stacks and to detect flow problems.
- Use larger tanks for collection of the concentrate streams so the calcium and sulfate levels can be measured to allow mixing of stoichiometric quantities of these ions in the precipitation tank.
- Install a refrigeration system to crystallize Na_2SO_4 from the concentrate stream to achieve a better balance between the concentrations of sulfate and calcium in the precipitation tank.
- Install an apparatus and establish a procedure for washing the precipitated CaSO_4 to remove soluble salts.
- Modify the electrode rinse system to provide independent, pH-controlled electrode rinse streams for the anode and the cathode of the EDM stack. Control pH by infusion of H_2SO_4 into the catholyte and NaOH into the anolyte.

It is further recommended that, after the modifications have been implemented, the system be operated for several weeks to establish steady-state operating conditions and collect enough CaSO_4 precipitate to allow evaluation of its utility as a component of building materials such as gypsum wallboard, plaster, or cement. It is recommended that the precipitation tank be operated with a slight excess of calcium to suppress sulfate content of the supernatant and that the supernatant be titrated with Na_2CO_3 to remove the residual calcium. During a period of steady-state operation, samples of all process streams should be collected for analysis with particular attention to closing the selenium balance. It is anticipated that this experiment will demonstrate that essentially all of the selenium in the feed stream will end up in a discharge stream that is less than 1% of the flow rate of the feed stream.

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APPENDIX A

Date	Time	Run time, days		Comments
2006		Run	Cumul.	RUN 1
6/26	12:00	0.00	0.00	Started system using feed from DP25
6/27	23:00	1.46	1.46	Added ~ 5 gal of settled supernate to ED2/ supernate, Added ~5 gal of NaCl from ED2 to EDM NaCl tank, removed ~3 gal of Na2SO4 and CaCl2 from Edm tanks
6/28	19:00	2.29	2.29	NaCl form ED overflowing onto floor --> pumped produced NaCl into EDM NaCl tank. Very little ~2 gal of Na2SO4 & CaCl2 produced since 2:00 pm. Added ~5 gal of settled supernate to ED2 feed.
6/29	0:00	2.50	2.50	noticed PPT on CaCl2 tubing walls and low flowrate, removed conc CaCl2 from tank Filled w/ RO perm again, new stream conductivity 60.2 mS/cm. I am concerned that there is a build up of SO4= in EDM NaCl supply. Will drain tank @5:00 am had planned to drain during day of 6/29/06. Added conc CaCl2 and Na2SO4 to reactor.
6/29	5:00	2.71	2.71	Everything looks ok except PPT still on Edm CaCl2 lines. I am not sure about it being SO4= or OH-. Crystals are small, will pull sample of CaCl2 stream and NaCl stream. Hesitate to drain EDM tank b/c I do not have any salt stockpiled. Will drain and refill, will check in 3 hrs
6/29	8:00	2.83	2.83	Found Floor flooded- seems to be a trend RV Floor flooded also! Used wet vac to clean up water. Feed valve was stuck open! Read readings at 8:15am next readings will be @ 11:00 am. Added ~5 gal Na2SO4 and CaCl2 to reactor
6/29	10:15	2.93	2.93	added NaCl from ED2 to NaCl tank for EDM ~2 gal
6/29	14:15	3.09	3.09	adjusted EDM voltage to 25V to reduce conc. of RO/EDM feed, also the RO perm cond is measured after the introduction of RO rej @ 30 mL/min. Installed Dwyer flowmeter 0-50 ml/min after RO BPV and before reject flow meter. The outlet of the rotometer is before the tee to the RO perm conductivity cell. before was using BV to prevent SiO2 build up in EDM/RO feed. Pumped NaCl from ED2 to EDM added approx. 5 gal CaCl2 and Na2SO4 to react.
6/29	19:00	3.29	3.29	Increased EDM V to 30 V to reduce EDM/RO feed cond. Increased ED2 v to 15V to increase production of NaCl, transferred ~5 gal of Na2SO4 and CaCl2 to rect. Added some product water to Erinse b/c level was getting low, but cond was increasing
6/30	0:00	3.50	3.50	Concerned about EDM stack. The current has dropped off which maybe a sign of fouling since conductivities have not changed. Trying to produce as much RO perm as possible so that I can use it to try and soak the stack. Collecting all perm. Collected samples of all EDM, ED2, and RO streams. Noticed no CaCl2 flow. shut system down, will try to reverse flow in the CaCl2 compartment to down flow. Replacing CaCl2 and Na2O4 streams with product water. If I can get CaCl2 to flow will allow to circulate over night to dilute/ rinse any crystals out. will sample solution in AM. man need to disassemble stack. No Flow through CaCl2 compartments. Will call Dr. Davis on the AM to see what needs to be done. 9:00 am Dr. Davis concurred that taking stack apart was a good Idea. Started RO to produce 5 gal of Perm to soak stack in.
				RUN 2
7/8	12:00	0.00	3.50	Started Experiment at 9:00 am on 7/9/06
7/8	15:00	0.13	3.63	Purge rate of RO Reject is 15 ml/min. Approx 5 gal of NaCl from ED2 product was added to EDM NaCl.
7/8	18:00	0.25	3.75	Approx 3 gal of CaCl2 and 3 gal of Na2SO4 were added to CaSO4 reactor.
7/8	21:00	0.38	3.88	
7/9	0:00	0.50	4.00	Observed that ED2 Diluate flowrate is low and scale is forming in the lines. Added ~ 10 Gal of RO perm to Diluate Stream. Will discard all NaCl that has been produced. CaCl2 stream for EDM appears to be cloudy; added ~5 gal of RO Perm to stream. RO Perm seems to be helping. ED2 scale in lines is gone after 15 min and the flowrate has improved. same happened with EDM flowrate appears to be increasing and the PPT seems to be dissolving.
7/9	3:00	0.63	4.13	EDM Current appears to be a little low
7/9	9:00	0.88	4.38	After removing about 3 gal of CaCl2 from the tank, added 2 gal of RO Perm. Also removed ~2 gal of Na2SO4 from tank
7/10	12:00	2.00	5.50	Was collecting RO perm, thus none was moving across the Conductivity probe. Transferred 5 gal of NaCl from ED2 to EDM added 5 gal of supernatant to ED2 diluate. Made up a batch of 10% HCl for acid feed to decarbonization tank.
7/11	9:00	2.88	6.38	
7/11	15:00	3.13	6.63	Drained EDM NaCl tank and refilled with NaCl produced by ED2 from supernatant produced yesterday.
7/11	18:00	3.25	6.75	Shut Down ED2 because there is too much produced NaCl on hand. Drained ~2 gal of CaCl2 from EDM CaCl2 tank
7/11	21:00	3.38	6.88	All is OK
7/11	21:00	3.38	6.88	Added ~2 gal of RO perm to EDM Na2SO4 tank, trying to get EDM current back to ~15 A. Used multimeter and measured 3.3 V between D1 and C2 in the first set of membranes from the cathode and measured 1.2 V between the compartments D2 and C1 in the same cell pair as above
7/12	0:00	3.50	7.00	EDM still problematic. Noticed Black Dots of the EDM feed outlet tubing. BIO-Problem????
7/12	3:00	3.63	7.13	Plan to shutdown system @ 6:00 Am if conditions do not improve
7/12	6:00	3.75	7.25	Shut Down System. Left EDM and E-rinse pumps on. Plan to discuss the possibility of rotating the stack of membranes 180 dgrs so that the membranes closest to the anode are closer to the cathode. Also considering bleaching the feed lines to remove the black scale. The solution compartments inside the stack do not seem to be fouled.

RUN 3				
7/21	9:30	0.00	7.25	Will operate the EDM RO Feed at ~20 mS/cm in order to maintain EDM current
7/21	12:30	0.13	7.38	EDM stack appears to be operating well
7/21	15:20	0.24	7.49	
7/21	18:30	0.38	7.63	Found EDM current low. The cause was low level in EDM NaCl tank due to NaCl being siphoned from tank into NaCl storage tank through a transfer pump.
7/21	21:30	0.50	7.75	Had to shut down RO system to allow for the EDM stack to reduce the conductivity of the EDM RO Feed tank. This caused the low EDM current reading.
7/21	12:30	0.13	7.38	Noticed low EDM current, but no obvious explanation. Added ~ 500 ml of HCL to CaCl2 stream to break up possible PPT.
7/22	3:30	0.75	8.00	Still concerned about EDM stack. Will try Diluting EDM CaCl2 tank with RO perm at 6:30 Am
7/22	6:30	0.88	8.13	Flushed both EDM Na2SO4 & CaCl2 tanks with RO permeate water
7/22	9:00	0.98	8.23	Shut RO down to drop EDM/ RO feed Conductivity. Plan to attempt CIP (clean in place) latter to day for the EDM stack. Will attempt after I have collected enough RO permeate. Restarted RO at 11:00 AM to produce water.
7/22	12:00	1.10	8.35	Decided to Hold off on CIP until later, EDM current is recovering. Drained EDM NaCl tank and refilled with fresh solution.
7/22	15:30	1.25	8.50	
7/22	18:30	1.38	8.63	Concerns about EDM still present, but things seem to be reaching a steady state
7/22	21:30	1.50	8.75	
7/23	0:30	1.63	8.88	Where is the Na2SO4 going? It seems to be lost! The Na2SO4 tank volume is dropping!!!!
7/23	3:30	1.75	9.00	Turned ED2 Voltage down to 5 V to slow NaCl production down. Perhaps the Na2SO4 from the EDM stack is entering the E rinse. I smell Cl2 gas. Opened E-rinse valves for EDM to balance the pressure in the E-rinse compartments to prevent Na2SO4 stream from entering the e-rinse compartments.
7/23	6:30	1.88	9.13	
7/23	11:00	2.06	9.31	Drained and refilled EDM NaCl tank. It appears that there is a leak between the EDM Na2SO4 and E-rinse, by restricting Na2SO4 flow the leak seems to have stopped or reversed.
7/23	15:15	2.24	9.49	EDM current has recovered.
7/23	20:15	2.45	9.70	
7/24	6:00	2.85	10.10	EDM NaCl tank became diluted overnight.
RUN 4				
7/24	10:00	3.02	10.27	
1/1	0:00	0.00	0.00	
7/24	18:00	3.35	10.60	
7/25	11:00	4.06	11.31	Shut system down removed EDM stack and replaced the AHA membrane with a CMB.
8/3	0:15	0.00	11.31	
8/3	3:00	0.11	11.43	
8/3	6:30	0.26	11.57	Water on the floor near power supplies/ EDM power is off. OVP light is on. Restarted by pressing standby switch twice. NaCl Mixing tank was almost empty. Remade with permeate. Detected communication between ED2 catholyte and NaCl product. Shut Down ED2.
8/3	9:30	0.39	11.70	ED2 is shut down. 11:45 E-rinse pH was 8.4 added H2SO4 to pH 3.1 12:05 pH 5.4. Added more H2SO4.
8/3	12:12	0.50	11.81	Collected 4.5 gal CaCl2 and 2.5 gal of Na2SO4 from 3:00 am to now, 12:12 pm. Rinse pH=6.9; added 6 ml H2SO4; pH=4.9. Added 6 ml 25% H2SO4; pH=3.6. Added 7 ml of H2SO4; pH=3.3. At 4:30 E rinse pH=4.5. EDM power supply stopped.
8/3	17:05	0.70	12.01	Sulfate analysis with Hach kit: 45 PPM in permeate and 35000 in Supernatant. Rinse pH=6.9 at 7:00 pm.
8/3	20:00	0.82	12.14	10:00 PM Rinse pH 7.0
8/3	23:00	0.95	12.26	RO dP 145 psig
8/4	2:00	1.07	12.39	RO dP 134 PSIG. Stopped purging E-rinse with RP Perm
8/4	5:15	1.21	12.52	Rinse pH=8.4, added 3/5 MI H2SO4; pH 5.8. At 8:00 am transferred about 3 gal of NaCl depleted EDM solution to RO/ED feed tank. Cond. jumped to 23 mS/cm.
8/4	8:30	1.34	12.66	It was discovered that Na2SO4 concentrate had been used to refill the EDM NaCl tank. The remedy employed was to reduce the EDM stack voltage to 12.6 V, 3.8 A, drain the NaCl tank to the pump suction level, refill with 2 gal of NaCl from ED-@, drain and refill twice more, and drain the CaCl2 to suction level and discard the solution. Added 2.5 gal of RO perm to dilute the CaCl2.
8/4	11:20	1.46	12.77	
RUN 5				
8/6	11:37	0.00	12.77	Restarted the system after CIP of all streams in EDM stack using RP Perm w/ cond ~450uS/cm for two days. Na2SO4 stream still has low flowrate.
8/8	12:50	2.05	14.82	Low current Perhaps scale formation on Cathode? Adjusted pH of E-rinse to 5 using H2SO4; pH was originally 8.5
8/8	15:42	2.17	14.94	Turned off EDM power supply and added some more H2SO4 to Rinse.
8/8	18:18	2.28	15.05	RO dP 131 PSIG 12:30, and all looks well!
8/9	3:30	2.66	15.44	RO dP 176 PSIG. Drained EDM NaCl tank and added fresh RO perm/ NaCl to tank. Current returned to 15.9 Amps. No significant Na2SO4 production!! Rinse tank is overflowing! 6:30 Am still no Na2SO4 production and overflowing Rinse. Decided restrict Na2SO4 flow.
8/9	9:30	2.91	15.69	RO dP 280 PSIG. Refilled NaCl tank! Na2SO4 volume increasing, Rinse still extremely full. Added 250 ml HCl to CaCl2 stream, noticed low flowrate in CaCl2 stream prior. By 11:00 AM the flowrate of CaCl2 stream had partially recovered; added 250 ml more of HCl.
8/9	18:33	3.29	16.06	RO dP 317 PSIG
8/9	21:30	3.41	16.19	RO dP 244 PSIG. Shutting it Down! Took samples of all process streams for analysis.

Operating data from pilot plant.

Cumul. days	EDM		ED-2		Feed	Conductivity, mS/cm				
	Volts	Amps	Volts	Amps		Permeate	Reject	NaCl	CaCl ₂	Na ₂ SO ₄
0.00						Run 1				
1.46	30	16.2	12.1	19.9	14.2	0.426	16.0	171	219	172
2.29	29.9	17	11.8	19.9	12.7	0.357	14.5	140	222	153
2.50	30	5.4	12	1.7	15.4	0.583	17.0	34	216	161
2.71	20	7.7	12.1	1.8	13.9	0.412	15.0	69	142	145
2.83	20	7.8	12.1	7.5	11.2	0.230	12.4	103	180	151
2.93	20	7.8	12	12.8	14.0	0.416	15.2	71	189	145
3.09	20	8.9	12	5.1	14.2	1.123	15.7	123	205	168
3.29	25	8	12	9.2	16.1	1.657	17.6	84	218	145
3.50	30	4.8	15	5.8	18.3	3.058	19.5	48	210	147
						Run 2				
3.50	30	13.7	19.9	14.9	6.8	0.875	7.4	107	155	101
3.63	29.9	12	18.2	19.9	7.8	1.087	8.5	22	184	131
3.75	29.9	15.6	16.9	19.9	7.8	0.912	8.5	203	200	148
3.88	30	13.3	15	19.9	7.4	0.793	8.0	177	211	157
4.00	30	12	15.1	15.7	8.0	1.014	8.6	171	213	159
4.13	30	9	15.1	4.2	7.8	0.889	8.4	147	166	161
4.38	30	8.8	15.1	2.2	8.8	1.152	9.4	124	185	165
5.50					7.8		8.4	171	134	143
6.38	30	7.5	15.1	1.7	9.1	1.089	9.7	102	160	151
6.63	20	9.2			11.2	1.274	11.9	152	160	170
6.75	30	6.4			8.3	1.307	8.7	132	173	156
6.88	35	8			10.2	1.135	10.8	112	185	161
7.00	35	4.6			8.2	1.397	8.7	91	187	96
7.13	35	4.2			8.5	1.535	9.0	73	190	110
7.25	35	4.2			9.3	1.893	9.8	58	191	120
						Run 3				
7.25	35	10.8	13.1	19.9	5.5		32.0	257	142	136
7.38	26.1	20	12.8	19.9	23.4	0.981	25.8	220	192	166
7.49	25.2	20	15	15.2	22.4	0.832	25.0	168	216	176
7.63	34.9	4.8	11.2	19.8	27.5	1.666	29.8	128	253	178
7.75	35	7	11.7	19.8	6.3	1.567	8.5	218	238	181
7.38	35	16.6	13.4	19.9	24.6	1.019	27.4	170	240	179
8.00	35	15.1	15	6.3	25.4	1.683	25.7	184	237	186
8.13	35	10.2	15	3.2	15.4	2.058	16.5	149	237	167
8.23	35	7.5	11.8	19.9	14.8	2.096	15.8	171	111	129
8.35	35	11.6	10.7	19.9	25.1		27.9	149	144	143
8.50	35	13.4	9.4	19.8	31.0	2.328	33.8	194	187	162
8.63	35	10.4	9.6	19.8	24.9	3.168	26.5	167	200	165
8.75	35	10.1	10.3	19.8	23.8	2.613	25.4	136	206	166
8.88	35	9	10.3	19.9	23.7	2.743	25.3	164	217	112
9.00	35	8.8	10.6	19.9	23.9	2.734	25.3	142	222	132
9.13	35	8.4	4.9	1.9	24.1	2.853	25.5	116	220	148
9.31	35	8.8	4.9	2.7	24.2	2.798	25.8	59	223	157
9.49	35	10.8	4.9	2.8	23.8	2.294	25.5	173	229	167
9.70	35	9.5	4.9	2.5	24.4	2.647	26.0	124	232	175
10.10	35	12.2	4.9	3	29.4	8.309	30.4	86	215	168

Run 4										
10.27	35	8	4.9	3.1	25.3	3.297	26.6	184	222	179
0.00						0.000				
10.60	35	4.3	4.9	3.4	4.2	9.950	3.2	157	214	167
11.31	35	18.4	4.9	2.2	11.7	1.527	13.6	172	141	143
11.31	35	15.3	10	13.5	12.8			245		38
11.43	35	15.6	10	12.3	12.4	0.476	13.9	217	115	101
11.57	0.01	0.4	8.9	20	27.7	3.926	28.8	211	131	115
11.70	35	15.3	0.3	0.01	13.7	0.665	15.3	168	205	162
11.81	35	14.6			14.7	0.580	16.3	117	221	173
12.01	35	16.1	0.1	0.01	17.8	0.645	19.8	166	225	178
12.14	35	14.5			16.1	0.557	18.0	128	233	183
12.26	35	12.6			17.5	0.000	19.4	75	234	182
12.39	35	12.1			17.7	0.376	19.1	134	237	182
12.52	35	11.1			17.6	0.474	19.4	97	240	183
12.66	35	12.5			20.9	0.780	22.1	127	241	184
12.77	35.1	12.3			21.6	0.688	23.2	195	169	185
Run 5										
12.77	35	8.9			16.7	0.000	18.4	197	5	10
14.82	35	1.7			12.3	0.000		187	19	26
14.94					8.9	0.000		173	32	43
15.05	35	11.7			8.9	0.289	12.5	164	36	56
15.44	35	4.7			21.2	0.402	23.2	19	197	166
15.69	35	10.7			22.6	0.294	24.6	76	219	162
16.06	35	15.6			26.3	1.111	27.9	150	241	179
16.19	35	10			18.5	1.202	20.4	127	240	181