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O.S.T.IELECTRODIALYSIS TECHNOLOGY FOR SALT RECOVERY  
FROM ALUMINUM SALT CAKE

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Electrodialysis technology for recovering salt from aluminum salt cake is being developed at Argonne National Laboratory. Salt cake, a slag-like aluminum-industry waste stream, contains aluminum metal, salt (NaCl and KCl), and nonmetallics (primarily aluminum oxide). Salt cake can be recycled by digesting with water and filtering to recover the metal and oxide values. A major obstacle to widespread salt cake recycling is the cost of recovering salt from the process brine. Electrodialysis technology developed at Argonne appears to be a cost-effective approach to handling the salt brines, compared to evaporation or disposal. In Argonne's technology, the salt brine is concentrated until salt crystals are precipitated in the electrodialysis stack; the crystals are recovered downstream. The technology is being evaluated on the pilot scale using Eurodia's EUR 40-76-5 stack.

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## Introduction

Salt cake is a waste stream generated by the aluminum industry. It consists of entrained aluminum metal, spent salt fluxes (mainly NaCl and KCl, with small amounts of MgCl<sub>2</sub> and CaCl<sub>2</sub>), and an oxide-rich fraction called NMP (non-metallic product) consisting primarily of alumina and spinel. We estimate that over 1,000,000 tons of salt cake are landfilled annually in the United States, and this number is growing with the increasing use of aluminum, particularly recycled aluminum. Salt cake can be recycled by crushing salt cake, screening to recover the coarse aluminum metal fraction, leaching the salts from the fines fraction, and recovering the salts from the leach solution using evaporation technology. The remaining non-metallic product (NMP) is disposed of in non-hazardous-material landfills. Our analysis of such a technology indicates that salt recovery is the most energy- and cost-intensive unit operation [1].

To address this issue, we identified several alternative processes that may be technically feasible and economical for salt recovery from salt cake process brines and assessed their economics [2]. Four processes were assessed for salt recovery from salt cake: (1) *base case*: leaching in water at 25°C, with evaporation to crystallize salts; (2) *high-temperature case*: leaching in water at 250°C, with flash crystallization to precipitate salts; (3) *solvent/antisolvent case*: leaching in water at 25°C, concentrating by evaporation, and reacting with acetone to precipitate salts; and (4) *electrodialysis*: leaching in water at 25°C, with concentration and recovery of salts by electrodialysis. Preliminary economic analysis indicated that all test cases for salt recovery had a negative present value, given the pricing structure and 20% return on investment. Although manufacturing costs (variable plus fixed) could reasonably be recovered in the sales price of the salt product, capital costs could not. Our analysis also indicated that recovering only the aluminum fraction from salt cake (i.e., landfilling the aluminum depleted salt cake – salt and NMP) would be profitable as long as the aluminum recovered equaled at least 4-5% of the original salt cake weight.

The results of the preliminary economic study have charted the direction for research on salt cake recycling at Argonne. The economic analysis indicated that, of the potential processes assessed, a less-capital-intensive electrodialysis-based technology may be more cost-effective than an evaporation technology for salt recovery [2]. Therefore, we focussed our efforts on electrodialysis process development.

## Background

Electrodialysis (ED) is a separation process in which salt is transferred from one aqueous solution to another. Separation occurs by ion migration through semi-permeable, ion-selective membranes under the influence of an electric field. This process results in a salt-concentrated stream (concentrate or brine) and a salt-depleted stream (diluate). The two solution compartments are separated by alternating cation- and anion-selective membranes. The compartments adjacent to the electrodes contain a recirculating electrode-rinse solution.

Salt cake leach solutions contain primarily chloride salts (NaCl, KCl, and a small amount of MgCl<sub>2</sub> and CaCl<sub>2</sub>). Because no sulfate impurities are present, we did not expect membrane fouling to be a significant problem in our ED process; we have not experienced membrane fouling problems to date. In our proposed process, salt is precipitated in the ED

stack and no crystallizers or evaporators are needed. We envision a process in which salt is leached from salt cake, transferred by electro dialysis from the salt cake leach solution (diluate stream) to a salt-saturated solution (concentrate stream), and recovered (See Figure 1).

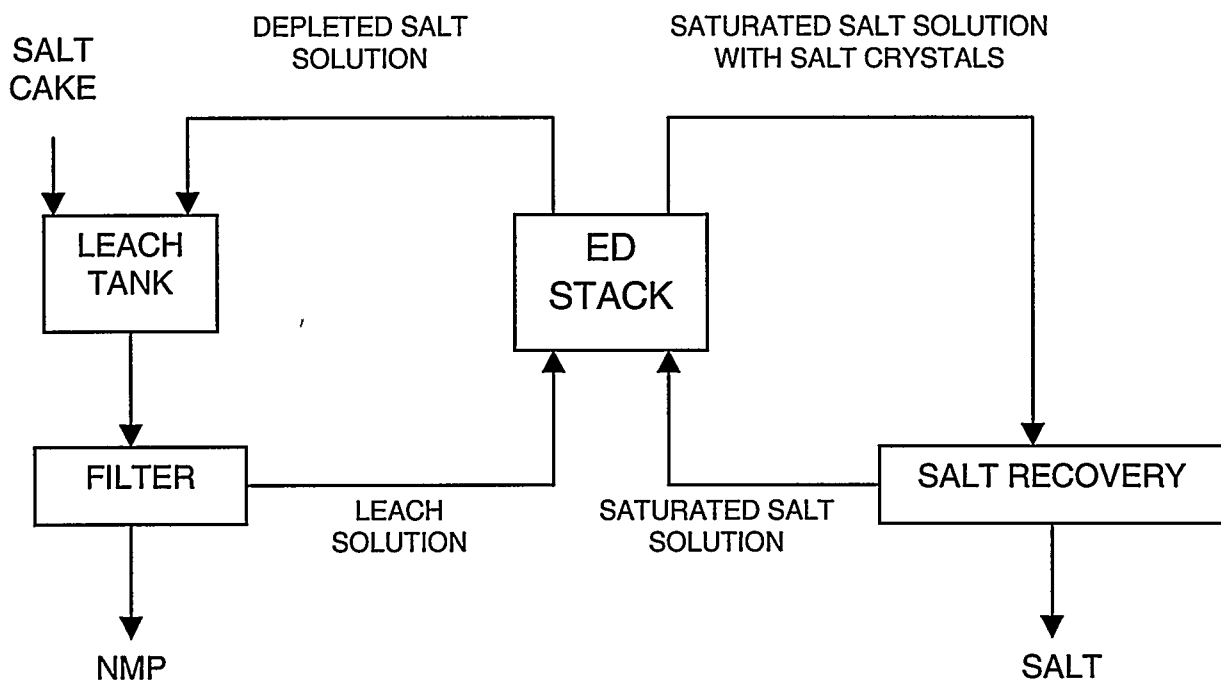


Figure 1. Electro dialysis-based process for salt recovery from salt cake leach solutions.

To determine whether ED is a viable technology for salt recovery from salt cake leach solutions, we first had to characterize ED operation in high-salt-concentration solutions. Our biggest concern was with water transferring through the membranes from the diluate stream to the concentrate stream, diluting it. Ions in aqueous solution are surrounded by a hydration shell of water molecules. In ED, ions migrating through the membranes carry water with them in the hydration shell. This causes the concentrate stream to build up in water and decreases the efficiency of salt recovery. Because the membranes are semipermeable, water also moves through them by osmosis, causing further process inefficiency. Our objectives were to determine whether salt precipitation can occur in an ED stack, measure water transfer rates through the membranes, and determine how the rates vary with current density and solution concentration.

### Experimental

For our experiments, we used a bench-scale Tokuyama ED unit, model TS2-5. Our ED stack consisted of five cells (anion-selective and cation-selective membrane pairs) with an effective area of 0.02 m<sup>2</sup> per membrane. Membrane pairs used in the experiments were Tokuyama Soda's Neosepta ACM/CMS, ACM/CMX, AMX/CMX, AFN/CM-1, AM-1/CM-1, AM-2/CM-2, and Raipore's R4030/R4010. We prepared concentrate and diluate solutions

using reagent-grade NaCl and KCl. Concentrate solution were close to saturation, while the diluate solution concentration varied from 12 to 22 wt%. Diluate solutions were also prepared using actual salt cake leach solutions at similar concentrations. NaOH (5 wt%), Na<sub>2</sub>SO<sub>4</sub> (10.8 wt%), and NaNO<sub>3</sub> (5 wt%) solutions were used as electrode rinse solutions.

Before each experiment, the ED unit was thoroughly cleaned with distilled water and drained. Test solutions were then added to the tanks and allowed to circulate through the unit for 5 minutes at high flowrates before adjusting flowrates to lower levels. Power was supplied to the stack at constant current and at various current densities held constant throughout an experiment. Experiments typically lasted 4 hours, during which time the solution temperature rose, and volumes and salt concentrations of the concentrate and diluate streams changed. We monitored solution concentrations continuously with in-line conductivity meters and solution temperatures with thermistors. At discrete time intervals, we measured the specific gravity of the solutions with hydrometers and collected samples of the solutions for analyses. The specific gravity of the solution was measured to ascertain the concentration of NaCl and KCl and to verify the conductivity measurements and chemical analyses of the solutions by ICP. From the change in solution salt concentrations, we determined current efficiency, defined as current required for ion transfer per current used. Throughout each experiment, we also monitored the stack voltage and anode-to-cathode voltage to determine energy consumption (kWh/lb salt) for salt recovery.

## Results

The voltage drop across the ED stack was caused by the resistances of the solutions and of the membranes. Values varied from 2.0 to 7.0 V, corresponding to 0.4 to 1.4 V per cell (membrane pair), depending primarily on the types of membranes used. As expected, more resistive membrane pairs, ACM/CMS and ACM/CMX, yielded larger voltage drops than less resistive membrane pairs, AM-1/CM-1, AM-2/CM-2, and Raipore R4030/R4010. We found that the voltage drop did not depend on solution concentrations because the salt concentration of our solution was high, resulting in negligible resistances when compared to the membrane resistances. Voltage drops were also found to be independent of solution flowrates because the solutions were so conductive. The three different electrode rinse solutions used (NaOH, Na<sub>2</sub>SO<sub>4</sub>, and NaNO<sub>3</sub>) also had no effect on the voltage drop. Chemical analyses indicated negligible sulfate or nitrate permeation through the membranes, and pH measurements indicated negligible hydroxide ion permeation as the pH of the concentrate and diluate solution rose from 5 to 10 during the 4-hour experiments. Volumes of all solutions varied from 4 to 6 liters.

The resistive drop across the stack resulted in a rise in the temperature of the solutions. The initial temperature of the solutions was 25°C, but as the experiments progressed, the temperature rose, and leveled off at 40°C, for current densities of 900 A/m<sup>2</sup>. For higher current densities, the temperature rise was higher. For example, for current densities of 1350 A/m<sup>2</sup>, the temperature leveled off at 45°C.

We measured the effect of current density on stack voltage. Although the membranes were rated at 1000 A/m<sup>2</sup>, we were able to achieve a value of 2500 A/m<sup>2</sup> (the limit of our power supply) with no adverse effects, except a dramatic rise in temperature. Because our solutions were so concentrated, we never approached the limiting current density, where

ion starvation at the membrane/solution interface causes membrane damage and high voltage drops.

Energy consumed due to the stack voltage drop ranged from 0.25 to 0.72 kWh/(lb. salt precipitated) at current densities of 1350 A/m<sup>2</sup>. Lower resistance membranes (AM-1/CM-1, AM-2/CM-2, and Raipore R4030/R4010) consumed lower energy as expected. The energy consumption required to precipitate salt decreases with decreasing current density. However, the total cost (operating + capital) required for salt recovery would not necessarily decrease with decreasing current density. There is an optimum current density at which the total cost of salt production by electrodialysis is a minimum. For our test conditions, the optimum current density was 1350 A/m<sup>2</sup>.

We were able to precipitate significant amounts of salts in the concentrate compartments of ED stack. The salts collected in the solution tanks. We precipitated salts from NaCl solutions, KCl solutions, mixtures of NaCl and KCl solutions, and from solutions obtained from leaching two industrial salt cakes.

### Discussion

In our lab-scale experiments, we were able to precipitate salts from various salt solutions, and we found that ED is a robust method for salt recovery [3]. Membrane fouling did not occur with the salt solutions we evaluated. However, we did experience flow reductions and stoppages attributed to salt clogging in entry and exit ports to concentrate chambers. We found that reversing flow and using unsaturated solutions in the concentrate loop could clear the clogging salt crystals without damage to membranes.

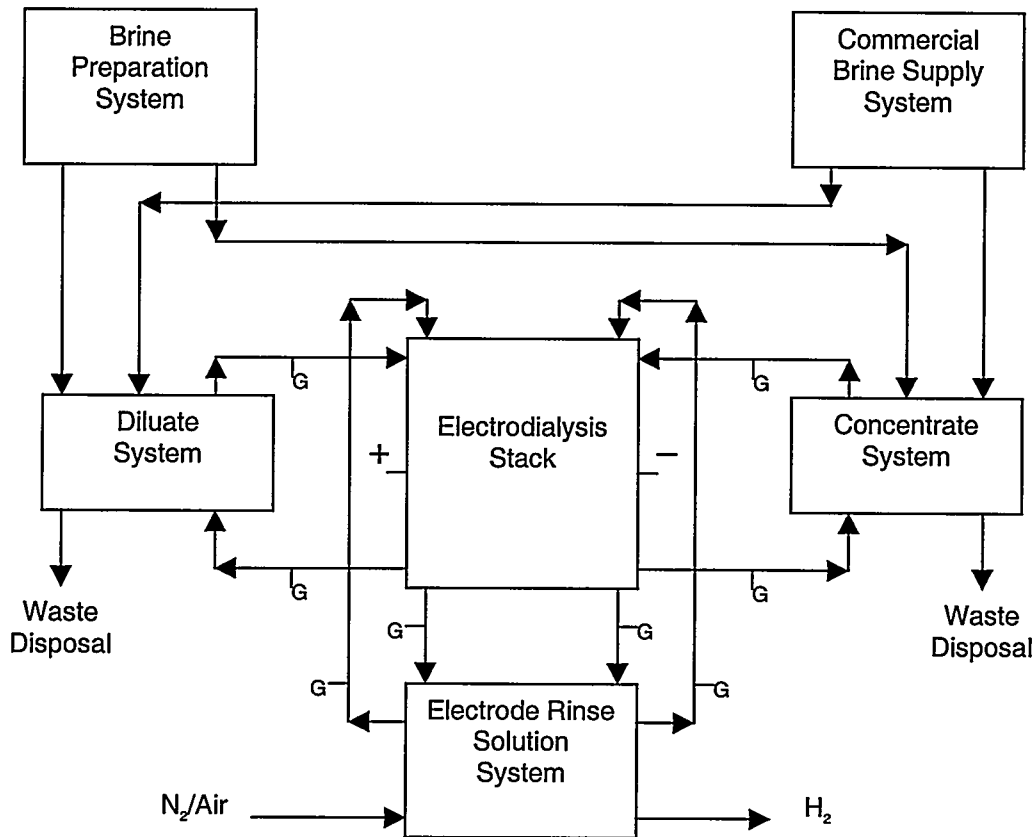
We also found that water migrating through the membranes presented a serious problem to the economics of salt recovery by ED. To this end, we developed operating conditions and membrane arrangements to overcome this issue. Patent applications describing these modifications have been filed.

We believe that we could not adequately address the issue of salt clogging in small ED stacks. Therefore, we are currently building a pilot-plant using a Eurodia stack (model number EUR-40-76-5) with AM-1 and CMX membrane pairs. The membranes were selected both on the performance in experiments and ease of handling. We had hoped to use thin low-resistance membranes for both cation- and anion-selective membranes, but the cation-selective CM-1 membranes proved to be too fragile for this application.

The stack was selected primarily on the basis of size. We wanted a stack that was large enough to adequately reproduce salt crystal flows through the entry and exit ports to the concentrate compartments that could occur in large stacks used in commercial operation. After investigating several options, we decided on a stack manufactured by Eurodia. The stack has 76 cell pairs with membranes of 0.4 m<sup>2</sup> effective surface area and has the capacity to transfer ~1000 moles/hr of monovalent salts (such as NaCl and KCl) from diluate to the concentrate solution at a current density of 1350 A/m<sup>2</sup>. The stack will be used to evaluate Argonne's ED-based salt recovery technology on a pilot scale. A pilot plant has been constructed and experiments are in progress.

## Pilot Plant Description

The pilot plant is composed of several systems: Brine Preparation System, Commercial Brine System, ED Diluate and Concentrate Systems, Electrode Rinse System, Electrodialysis System, and Waste Brine System. Each of these systems is described in this section. Other systems in the pilot plant are dedicated to the storage and periodic preparation and handling of commercial, prepared, and waste brines. Pilot plant control alarms, shutdowns and safety interlocks are handled by a dual computer control and data acquisition system. Major systems and isopotential grounding fingers are shown in Figure 2.



G = Isopotential Grounding Finger

Figure 2. Argonne's Electrodialysis Pilot Plant showing major systems and locations of isopotential grounding fingers.

### Brine Preparation System

The Brine Preparation Tank is a 1500-gallon HDPE multipurpose mixing tank for use to (1) generate synthetic brines for the ED diluate and ED concentrate, (2) generate saturated commercial brine for the ED concentrate, and (3) provide intermediate storage or brine transfer capability. Consequently, it is equipped with the capability to add DI water,



commercial brines, and solid salts. The solid salts are transported to the top of the tank by a screw conveyor with a ground level hopper.

Diluate brines prepared in the Brine Preparation Tank will be 10-25 wt% salt solutions of NaCl, KCl or both, occasionally spiked with other components – e.g.  $MgCl_2$  and  $CaCl_2$ . Concentrate brines prepared in this tank will be saturated solutions of NaCl, KCl or both, again occasionally spiked with other chloride salts.

#### Commercial Brine System

The pilot plant is designed to process two types of feed streams: (1) synthetic brines produced in the pilot plant; and (2) commercial brines generated at our industrial partner's facility. The Commercial Brine System provides storage and handling facilities for this second feed stream.

Commercial brine will be transported to ANL in a tanker truck and stored in the 10,000 gallon, flat-bottom, FRP Commercial Brine Tank. The tank is equipped with an ultrasonic level transmitter and has an overflow line open to the Brine Sump. The Brine Sump is an 18" high concrete dike encompassing all the brine tanks and their associated equipment.

The brine stored in the Commercial Brine Tank will be periodically pumped through an in-line filter system, to the ED Feed Tank (to supply feed for the ED system) or to the Brine Preparation Tank (to mix with salt to generate a saturated 'commercial' brine for the ED concentrate loop). A valved bypass line is provided for brine transfers not requiring the filter (i.e. when emptying the tank for disposal).

#### ED Diluate and Concentrate Systems

The ED Diluate System (or Diluate Loop) and the ED Concentrate System are designed for continuous, computer-controlled operation and monitoring of the diluate and concentrate feeds and effluents of the ED Stack.

The ED Diluate Tank is a 1500-gallon HDPE tank, while the ED Concentrate Settling Tank is a 1250-gallon, cone bottom, HDPE tank design to collect salt crystals produced in the ED stack. The tank is also equipped with a mixer to provide the capability of operating with solids in the ED concentrate feed and to re-disperse settled solids after shutdown of the system.

Both tanks are mounted on a weigh system with 4 load cells for material balance determinations. Ultrasonic level transmitters installed in each tank will provide the signals for continuous level monitoring during ED operation for diagnostics, data acquisition, and high level alarms. The tanks have overflow lines open to the Brine Sump.

The ED diluate is fed to the ED Stack under mass flow control. The mass flow, density, and temperature of the ED diluate feed and effluent are measured by Micro-Motion Coriolis instruments to provide data for material balance calculations. The diluate effluent from the ED stack is recirculated to the ED Diluate Tank. The ED concentrate effluent is routed from the ED stack through a heat exchanger to the Concentrate Settling Tank. In this tank, any solid salts generated in the ED cells or heat exchanger settle to the bottom where they are either allowed to temporarily build-up or are removed from the tank as a slurry (with 25-40 wt% solids).

### Electrodialysis System

The heart of the pilot plant is the Electrodialysis System. In this system, salts (NaCl and KCl) are transported from a dilute brine (10-25 wt% salts) into a saturated brine (30-40 wt% salts) by the current-assisted transfer of ions (Na<sup>+</sup>, K<sup>+</sup> and Cl<sup>-</sup>) through anion- and cation-selective membranes. The dilute and saturated brines (ED diluate and ED concentrate, respectively) are recirculated continuously through dedicated cells in the electrodialysis stack. The ED Diluate and ED Concentrate Systems provide storage, control, and monitoring of these recirculation loops.

The ED Stack is supplied by Eurodia. The stack, EUR-40-76-5, contains 76 active cell pairs and is equipped with membranes of 0.4 m<sup>2</sup> effective area. To protect the membranes, the operating temperature will be maintained below 50° C (122° F).

Sample points are provided for the ED diluate inlet and outlet streams and the ED concentrate feed, effluent prior to cooling and effluent after cooling. Grounding fingers supplied by Eurodia, the ED stack vendor, are installed in the ED diluate and concentrate feed and effluent lines to dissipate stray currents. The ED diluate inlet and outlet piping is configured to allow flexibility in upflow versus downflow operation of the ED system.

The DC rectifier was supplied by Rapid Power and is specified to provide up to 575 amps and 100 volts (changeable to 210 volts). Platinum wire probes are installed in the ED stack near the cathode, anode and both sides of the mid electrode chamber, and at cells 14, 28, 52 and 66 to allow monitoring of voltages across the stack.

To provide automatic start-up and shutdown capability of the ED system, automatic open/shut valves are installed in each of the four brine feed and effluent lines and in the electrode rinse catholyte and anolyte feed lines. These fail-closed valves on the main lines will close to block solution supply sources to the stack.

### Electrode Rinse System

Another component of the electrodialysis process is the Electrode Rinse System. Rinse solution is circulated through the anode and cathode chambers of the ED stack to purge accumulating ions and gases in these chambers. The electrode rinse system also incorporates equipment to isolate and purge the hydrogen gas generated at the cathode from oxygen gas generated at the anode.

The Electrode Rinse System is also designed for continuous, computer-monitored operation of the catholyte and anolyte feeds and effluents to the ED Stack.

The Electrode Rinse Tank is a 500-gallon HDPE tank equipped with an ultrasonic level indicator to provide volume data for solution preparation and for diagnostics of the electrode rinse system. Electrode rinse flow rates to the cathode and anode are set manually upstream of the ED stack, individually via globe valves. These flows will each be maintained at 15 GPM.

Downstream of the ED stack, flow meters in the catholyte and anolyte return lines provide a signal for Bridgeview monitoring. The temperature of the anolyte is measured as a diagnostic of the anode's integrity. Grounding fingers supplied by Eurodia, the ED stack

vendor, are installed in the ED catholyte and anolyte feed and effluent lines to dissipate stray currents.. A probe in the tank continually monitors the pH of the electrode rinse solution.

Small amounts of hydrogen gas (max 0.16 CFM) will be generated at the cathode and oxygen gas (max 0.08 CFM) at the anode. To prevent the mixing of these gases, the hydrogen is removed from the catholyte in the Catholyte Rinse Tank by bubbling nitrogen at 1-2 SCFM through retained solution. The hydrogen/nitrogen gas is vented from the tank through an FRP blower into a 3" vent line routed to the outside. Air ingressed through an open ball valve located at the top of the tank will dilute the hydrogen concentration below 10% of its lower explosive limit (hydrogen concentration < 0.4 vol%).

Rinse solution selection is currently underway. Two options likely to be tested are (1) NaOH at 5 wt% concentration and (2) NaNO<sub>3</sub> at 5 wt% concentration and pH of 7-9.

#### Waste Brine System

The Waste Brine Tank is a 10,000-gallon flat-bottom, FRP holding tank for waste brines. All brine tanks can be drained to this vessel. Waste brines from this tank are pumped to transport vehicles for disposal. Like the Commercial Brine Tank, the Waste Brine Tank is equipped with an ultrasonic level transmitter to provide the signal for local level indication and high level alarms. The tank has an overflow line open to the Brine Sump.

#### Data Acquisition System

To facilitate the need for advanced instrumentation and data acquisition but not compromise a reliable control system an integrated, dual stage supervisory control and data acquisition system (SCADA) was developed. The hardware interface consists of an Allen-Bradley SLC 5/05 system running parallel to a National Instruments FieldPoint system. The SLC, interfaced with RSVIEW32 provides robust systems control and safety interlocking capabilities while the FieldPoint system, when interfaced with BridgeView data acquisition software, allows for advanced data acquisition. Seamless integration between systems is achieved utilizing OPC Servers, linked over Ethernet. This allows for the SLC to handle plant operations, like pump control, PID flow loops, and safety interlocks while BridgeView can concentrate on data acquisition.

Complete facility operations are controlled through the SLC. Flow, pressure, and temperature parameters for flow loops are entered through the HMI using RSVIEW32. ED Stack voltage and current can also be entered through the HMI. PID loop tuning is achieved using RSTUNE, to insure reliable process flows. Facility interlocks are also monitored by the SLC. Multi-level system shutdowns are initiated upon upset system conditions to insure operator safety and equipment protection. Using OPC servers, SLC data common to both operations and data acquisition can be accessed by BridgeView.

All critical system parameters are monitored and recorded by BridgeView. Instrumentation surrounding the ED concentrate and diluate flow loops are particularly important. Density, mass flow and temperature are determined using Micro Motion Elite CMF200 meters, with density measurements accurate to ±0.0005 g/cc. Tank weights are obtained via Mettler-Toledo load cells and pressures are acquired with Fisher-Rosemount

pressure transducers. Additional instrumentation monitors the flow and pH of the electrode rinse solution, in addition to detectors monitoring hydrogen and oxygen build-up. Flowline ultrasonic level sensors installed on all tanks provide both level indication and overflow protection. Voltage probes installed between membrane layers provide an image of the voltage distribution throughout the stack. BridgeView also processes the data to insure proper operating conditions and can also initiate a systems shutdown in the event of an emergency.

### Conclusion

We were able to precipitate salts from a wide variety of solutions and concentrations in our lab-scale TS 2-5 ED stack. However, we found that water transferring through the membranes is extremely important to the economics of a salt recovery technology using ED. We found that, apart from the types of membranes used and the difference in salt content between the diluate and the concentrate, no other parameters significantly affected ED performance in concentrated salt solutions. Energy consumed due to the stack voltage drop ranged from 0.25 to 0.72 kWh/(lb. salt precipitated) at current densities of 1350 A/m<sup>2</sup>.

We developed technology that overcomes problems associated with water transferring through membranes, and are evaluating the technology on a pilot scale. The pilot plant is built around a Eurodia EUR 40-76-5 stack containing AM-1/CMX membrane pairs.

### Acknowledgments

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