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Abstract

Electrodialysis was investigated as a possible technology for the cost-effective recovery of salt from salt cake leach solutions. We used a pilot-scale electrodialysis stack consisting of five membrane pairs, each with an effective area of 0.02 m^2. The diluate stream contained synthetic NaCl, KCl, mixtures of NaCl and KCl, and actual salt cake leach solutions (mainly NaCl and KCl, with small amounts of MgCl$_2$). We concentrated and precipitated NaCl and KCl salts from the concentrate stream when the initial diluate stream concentration was 21.5 to 28.8 wt% NaCl and KCl. We found that water transferring through the membranes was a significant factor in the overall efficiency of salt recovery by electrodialysis.

Introduction

Salt cake is a waste stream generated by the aluminum industry during the treatment of aluminum drosses and scrap. It consists of entrained aluminum metal, spent salt fluxes (mainly NaCl and KCl), and residue-oxides (mainly alumina and spinel). We estimate that 800,000 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. The increasing cost of landfilling salt cake presents a potential threat to the economics of aluminum recycling. Also, the leachable chloride content in landfilled salt cake poses an environmental concern. Several salt cake treatment technologies have been developed in response to a prohibition on landfilling salt cake in several European countries [1-2]. These technologies are based on 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. These European technologies are not cost-effective in the United States because landfilling of salt cake is permitted here. Our analysis of these technologies indicates that salt recovery is the most energy- and cost-intensive unit operation [3]. Our analysis also suggests that, for cost-effective salt cake recycling, NMP must be converted to higher-value-added products [3]. That aspect of our work is addressed elsewhere [4].

Efficient recovery of aluminum from skim and dross and from post-consumer and other aluminum-containing scrap requires the use of salt fluxes [5]. During scrap melting, the molten salt aids in aluminum recovery by dissolving and entraining dirt and oils present in the aluminum scrap, and by acting as a physical barrier between the air and aluminum, thereby minimizing oxidation of the aluminum. One solution to the problem of future salt cake disposal is to develop a cost-effective aluminum recovery technology that does not use salt. However, even if a salt-free technology proves to be cost-effective, its use would be limited to some clean scrap and white drosses that initially would not contain salt. Salt would still be used in treating dirty, post-consumer scrap, and a salt cake waste stream would still be generated. There is a need, therefore, to develop a cost-effective salt cake processing technology for use in the United States.

To address this issue, we identified several alternative processes that may be technically feasible and economical. Our bench-scale experiments and economic analysis indicated that, of the potential solutions, an electrodialysis-based technology may be more cost-effective than an evaporation technology for salt recovery [6]. This paper presents the preliminary results of our ongoing work to determine the suitability and limitations of electrodialysis for salt recovery.

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. Figure 1 is a schematic of an ED stack.

C: Cation transfer membrane
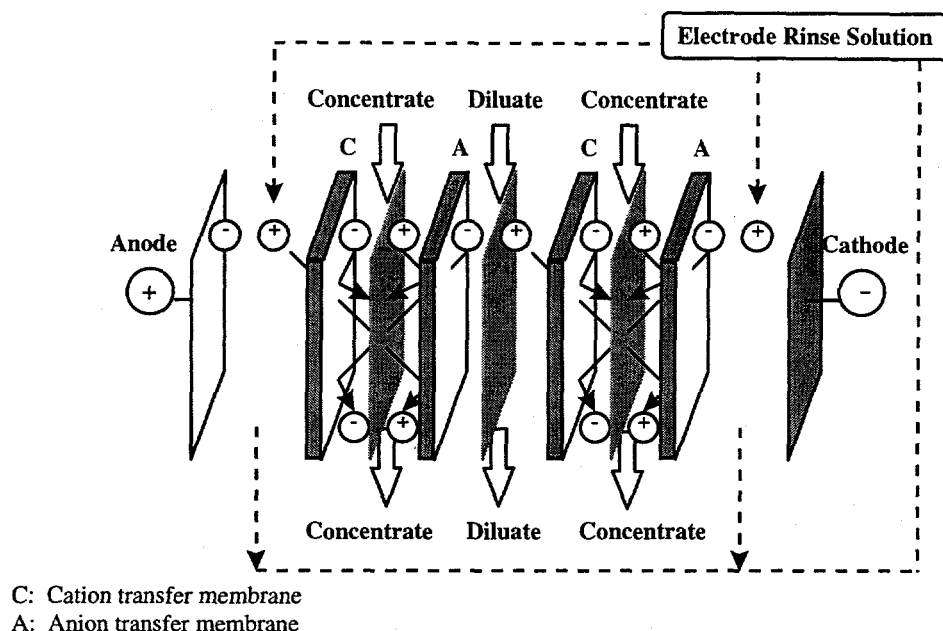A: Anion transfer membrane

Figure 1.   Schematic of ED stack.

ED is used for desalination and potable water production world-wide, in the production of table salt in Japan, and most recently in the production of acids and bases from salt solutions using bi-polar water splitting membranes [7]. In Japan, seawater is concentrated to near saturation by employing ED, but evaporation technology is used for salt precipitation. We assume that evaporation technology rather than ED is used for salt recovery because impurities build up in the concentrate stream at high salt concentrations. These impurities, mainly sulfates, may form precipitates on the membranes, causing fouling. Salt cake leach solutions contain primarily alkali chloride salts (NaCl, KCl, small amount of $MgCl_2$). Because no sulfate impurities are present, we did not expect membrane fouling to be a significant problem in our process; we have not experienced membrane fouling problems to date. In our proposed process, salt is precipitated in the ED stack and no crystallizers are needed. We envision a process in which salt is leached from salt cake, transferred by electrodialysis from the salt cake leach solution (diluate stream) to a salt-saturated solution (concentrate stream), and recovered (Figure 2).

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 initial 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.
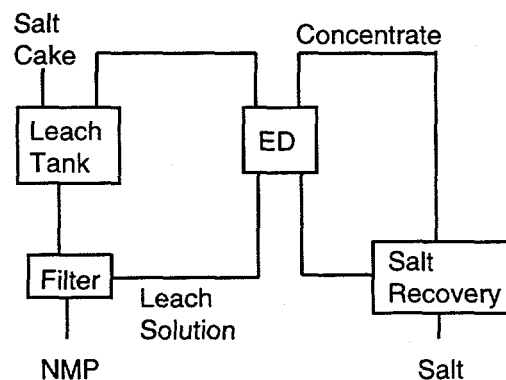

Figure 2.   Electrodialysis-based process for salt recovery from salt cake leach solutions.

For our experiments, we used a pilot-scale ED unit, model TS2-5, manufactured by Tokuyama Soda and supplied by Graver Water (now Aqualytics). Our ED stack consisted of five cells (anion-selective and cation-selective membrane pairs) with an effective area of 0.02 m^2 per membrane. We used Tokuyama Soda's Neosepta ACM/CMX, AMX/CMX, and AM-2/CM-2 membrane pairs. Their relevant properties are listed in Table I.

Table I. Selected Properties of Neosepta Membranes [8]

Grade	Type	Electrical Resistance Ω/cm^2
ACM	Anion permeable	4.0 - 5.0
CMX	Cation permeable	2.5 - 3.5
AMX	Anion permeable	2.5 - 3.5
AM-2	Anion permeable	2.0 - 3.0
CM-2	Cation permeable	2.0 - 3.0

Our ED circuit, shown schematically in Figure 3, contains three separate solutions: concentrate, diluate, and electrode rinse solution. We prepared concentrate and diluate solutions using reagent-grade NaCl and KCl. Diluate solutions were also prepared using actual salt cake leach solutions. NaOH (5 wt%) and Na$_2$SO$_4$ (10.8 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. The solution flowrate was then adjusted to 1.6 L/min, and power was supplied to the stack at constant current such that the effective current density was 900 A/m^2. 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 concentations, 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 power consumption for salt recovery.
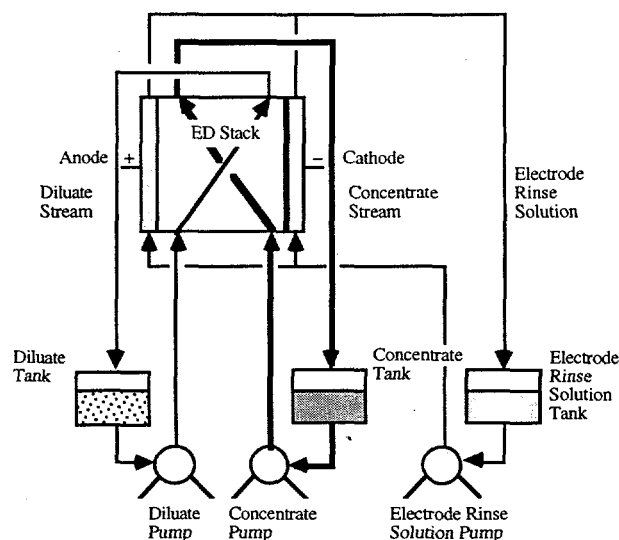

Figure 3. Solution flow diagram of electrodialysis circuit.

Results

The voltage drop across the ED stack was caused by the resistances of the solutions and of the membranes. Values varied from 2.9 to 4.8 V, corresponding to 0.6 to 1.0 V per cell (membrane pair), depending primarily on the types of membranes used. As expected, more resistive membrane pairs, ACM/CMX, yielded larger voltage drops than less resistive membrane pairs, AM-2/CM-2. 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 two different electrode rinse solutions used (NaOH and Na$_2$SO$_4$) also had no effect on the voltage drop. Chemical analyses indicated negligible sulfate 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.

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^2.

We measured the effect of current density on stack voltage. Although the membranes were rated at 1000 A/m^2, we were able to achieve a value of 2500 A/m^2 (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. Figure 4 shows the effect of current on stack voltage. The voltage drop for anode-to-cathode also includes the drop caused by hydrogen production at the cathode and oxygen production at the anode.
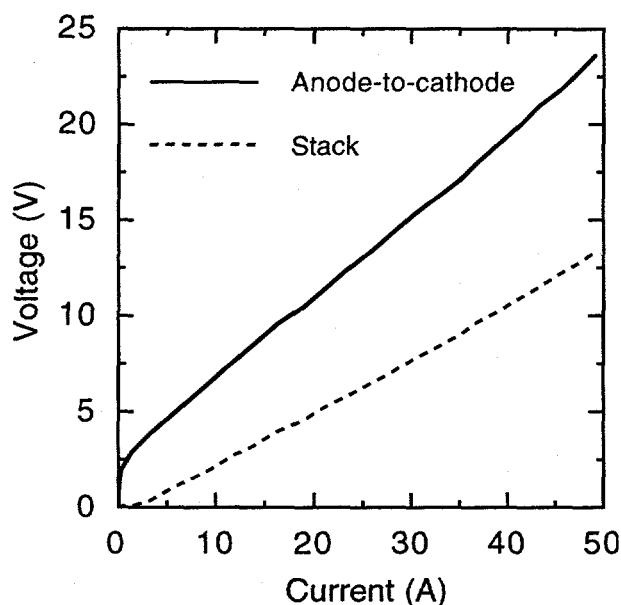

Figure 4. Voltage-current relationship during electrodialysis. Concentration of diluate and concentrate solutions = 23 wt% NaCl. Electrode rinse solution = 5 wt% NaOH. Scan rate = 1 V/min. Membranes: Neosepta ACM and Neosepta CMX.

We were able to precipitate significant amounts of salt in the ED stack. The salt 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. Current efficiencies varied from 80 to 95%, but we were not able to identify the parameters that affected current density. Diluate and concentrate solution concentrations are shown in Table II. In solutions where both NaCl and KCl were present, analyses of salt product indicated that KCl permeated the membranes at a slightly higher rate than NaCl.

We calculated the amount of water transferred from the diluate to the concentrate for each experiment. Results indicated that water transfer rates ranged from 5 to 9 moles of water transferred per mole of salt transferred. The average difference in salt concentration between the diluate and concentrate streams significantly affected water transfer rates, as shown in Figure 5.

Table II. Diluate and Concentrate Salt Content (wt%)

| Salt | Diluate | | Concentrate | | Salt |
	Initial	Final	Initial	Final	Precipitation
NaCl	16.0	3.3	16.0	21.7	No
NaCl	18.0	1.7	18.0	23.1	No
NaCl	23.0	17.2	23.0	26.0	Yes
NaCl	23.0	17.2	23.0	26.0	Yes
NaCl	23.0	16.9	23.0	26.0	Yes
NaCl	22.2	17.5	21.5	25.8	No
NaCl	22.0	16.6	21.5	26.0	Yes
KCl	22.0	8.0	22.0	24.0	Yes
NaCl	11.0	6.9	13.4	15.0	Yes
KCl	11.0	4.3	13.4	15.9	
NaCl	13.4	11.0	13.4	16.2	Yes
KCl	13.4	7.8	13.4	13.9	
NaCl	13.0	11.6	13.0	15.9	Yes
KCl	15.8	11.5	15.8	14.5	
NaCl*	7.0	3.4	13.5	15.4	No
KCl*	5.8	1.4	11.7	12.1	
NaCl*	11.6	7.6	15.1	16.2	No
KCl*	9.9	3.7	13.1	13.0	
NaCl*	12.7	10.2	14.2	17.1	Yes
KCl*	8.8	5.1	13.3	12.9	

* Indicates actual salt cake solution in diluate, synthetic NaCl and KCl solution in concentrate.

Discussion

We were able to precipitate salts from various salt solutions, and we found that ED is a robust method for salt recovery. However, we also found that water migrating through the membranes presents a serious problem in salt recovery by ED. In saturated salt solutions, the molar ratio of water/salt is approximately 9 in NaCl solutions and 8 in KCl solutions. Clearly, if water is transferred through the membranes at a water/salt ratio greater than 9, salt precipitation cannot occur.
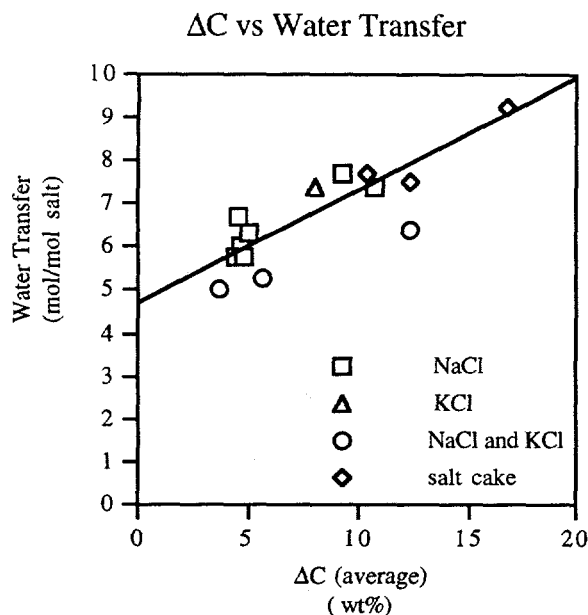
ΔC vs Water Transfer

Figure 5. The effect of the average difference in salt concentration between the concentrate and diluate (ΔC) on the ratio of water/salt transferred through the membranes.

Figure 5 suggests that water transferring through the membranes is made up of 5 moles per mole salt from water transferring in the hydration shell of ions; the remainder (0.24 moles water per mole salt per 1 wt% difference salt content between the concentrate and diluate) is from osmosis. Our data suggest a linear relationship between ΔC and the amount of water transferred, with a slope consistent with theory [9].

The extent of water transferring through the membranes is very important to the economics of salt recovery. Our economic analysis indicates that ED is cost-effective compared to evaporation under certain conditions; for example: 15% or less salt concentration in salt cake leach liquor, 5 moles or less of water transfer, current density of 1000 A/m^2, and a plant with salt production capacity of 50,000 tons/yr or less. Water migration must be reduced to make ED attractive for salt recovery from salt cake leach solutions.

Conclusion

We were able to precipitate salts from a wide variety of solutions and concentrations. 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. Although the membranes

were rated for use with no more than 1000 A/m^2, we were able to operate at 2500 A/m^2 without damaging the membranes.

Because of the amount of water transferring through the membranes, ED is not competitive with evaporation under present operating conditions and economic assumptions. We are investigating new concepts that should reduce the amount of water transferring through the membranes due to both migration with the ions in their hydration shell and osmosis.

Acknowledgments

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