Salt Extraction from Hydrogen-Sulfide Scrubber Solution Using Electrodialysis

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The buildup of undesirable sulfur compounds (sulfates and thiosulfates) reduces the scrubbing effectiveness of the LO-CAT I autocirculation sulfur recovery process from acid-gas stream. Among various processes, withdrawing and disposing of a portion of the scrubber solution and replacing this "blowdown" with fresh solution have been the practice in the industry. The application of the electrodialysis system to recycle the blowdown is presented. Experiments were carried out using electrodialysis to separate salts (sulfates and thiosulfates) from the LO-CAT I autocirculation scrubber solution containing organic chelating agents, iron, and various alkali-metal inorganic salts. The results indicated that the electrodialysis was successful in removing 50% of the salts from the scrubber solution with less than 8% loss of organic and 8% loss of carbonates. The fluxes of the undesired salt species were high even at low current densities (200 to 400 A/m²).

Introduction

LO-CAT I autocirculation process

Sour natural gas produced from reservoirs contains a significant amount of impurities such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2). Such a gas must be treated before marketing. In a sour-natural-gas sweetening facility, the natural gas is treated directly by an amine process to remove H_2S and CO_2. The amine solution is regenerated in an amine regenerating unit. The regenerated amine solution is recycled in the amine process, and the H_2S and CO_2 concentrated stream from the amine regeneration unit, called acid gas, is either processed for sulfur recovery or incinerated, depending on the concentration of H_2S in the acid gas.

There are several commercial processes available for sulfur recovery, including the Claus process, which is suitable only for sulfur recovery of 10 tonne/day or more. Liquid-redox processes are ideal for sulfur recovery of less than 30 tonne/d. LO-CAT I autocirculation process is an iron-based liquid-redox process that is licensed by ARI Technologies Inc. (Meuly, 1977; Hardison, 1977; Thompson, 1980a; Primak, 1983; 1984; McManus and Kin, 1986) and that uses a proprietary mixture of "Type A" (ethylenediaminetetraacetic-acid (EDTA) -like) and "Type B" (sorbitol-like) chelating agents to hold iron in solution at high pH.

The liquid reduction-oxidation or redox process is used to scrub hydrogen-sulfide (H_2S)-containing gas streams. In this process, the gas containing H_2S is contacted with an alkaline liquid phase (usually at pH 7.0 to 9.0) containing a dissolved metal-organic chelate reagent. While any polyvalent transition metal can be employed in this process, iron is most commonly used. The H_2S from the gas stream is absorbed into the alkaline solution, forming hydrosulfide ions.

$$H_2S_{(g)} \rightleftharpoons H_2S_{(aq)} \rightleftharpoons H^+_{(aq)} + HS^-_{(aq)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}. \quad (1)$$

The ionic distribution of sulfur anions is predominantly HS^-, or hydrosulfide ions, at the process pH. The hydrosulfide ions react with the polyvalent metal, oxidizing the hydrosulfide to elemental sulfur and reducing the oxidation state of the metal:

$$2(Fe^{3+}\cdot \text{chelate})_{(aq)} + S^{2-}_{(aq)} = 2(Fe^{2+}\cdot \text{chelate})_{(aq)} + S^0_{(s)} + H^+_{(aq)}. \quad (2)$$

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The metal is then oxidized with dissolved oxygen in the same vessel:

$$2(\mathrm{Fe}^{2+}\cdot\mathrm{chelate})_{(aq)}+\mathrm{H_2O}+1/2\mathrm{O}_{2(aq)} = 2(\mathrm{Fe}^{3+}\cdot\mathrm{chelate})_{(aq)}+2\mathrm{OH}^-_{(aq)}. \quad (3)$$

The overall sulfur-producing reaction is

$$\mathrm{H_2S}_{(g)}+1/2\mathrm{O}_{2(g)}=\mathrm{H_2O}_{(l)}+\mathrm{S}^0_{(s)}. \quad (4)$$

Side reactions oxidize a portion of the dissolved hydrosulfide ions to acidic sulfur compounds, primarily sulfate (SO_4^{2-}) and thiosulfate ($S_2O_3^{2-}$). Walter (1977) indicated that above pH 7.0 from 2 to 9% of the H_2S fed to a liquid redox scrubber was converted into acidic sulfur compounds. These sulfur compounds tend to lower the pH of the scrubber solution, reducing its scrubbing effectiveness. It is normal practice in these processes to maintain the pH of the scrubber solution above 7.0 by the continuous or periodic addition of alkaline chemicals such as the ammonium or alkali-metal salts of the carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), or hydroxide (OH^-) anions. The neutralization of the acidic sulfur compounds results in a steady buildup of the corresponding ammonium or alkali metal salts. Overall chemical equations are given below for the two most common species formed:

$$2\mathrm{H_2S}_{(aq)}+2\mathrm{O}_{2(aq)}+2\mathrm{MOH}_{(aq)}\Rightarrow \mathrm{M_2S_2O}_{3(aq)}+3\mathrm{H_2O} \quad (5)$$

$$\mathrm{M_2S_2O}_{3(aq)}+2\mathrm{MOH}_{(aq)}+2\mathrm{O}_{2(aq)}\Rightarrow 2\mathrm{M_2SO}_{4(aq)}+\mathrm{H_2O} \quad (6)$$

where M stands for an ammonium or alkali-metal cation.

The presence of excess dissolved salt in the scrubber solution can contaminate the elemental sulfur produced. In scrubbers where the sulfur is removed by settling, high concentrations of dissolved salts can lead to poor sulfur settling because of the high specific gravity of the solution. If no action is taken, the concentration of these salts will increase until the solution becomes saturated. The salts will then precipitate, potentially plugging the piping of the unit.

Several approaches have been taken to solve the problem of salt buildup in liquid-redox processes. Thompson (1980b) recommended withdrawing and disposing of a portion of the scrubber solution and replacing this "blowdown" with fresh, salt-free solution to undersaturate the system. When a blowdown is taken, it eliminates all components of the solution, including those that are beneficial or necessary for the operation of the scrubber.

In the LO-CAT I autocirculation process, various organic chemicals (such as "Type A," "Type B" chelating agents) are added to the solution in order to complex the polyvalent metal reagent (such as iron) and increase its solubility at the pH of the system. Additional chemicals are added to the scrubber solution to promote sulfur settling (flocculants, surfactants, antifoam agents), to control bacteria (biostats), and to control pH (including KOH, $KHCO_3$, K_2CO_3, NaOH, $NaHCO_3$, Na_2CO_3). In removing and replacing scrubber solution, all of these beneficial chemicals are sacrificed in order to bleed the offending salts. The preferred approach would be to withdraw only the salts and recycle all of the active chemicals back to the scrubber.

Grinstead (1989) suggests that a polymeric chelating agent with molecular weight between 500 and 1,000,000 be used to complex the reactive metal (such as iron). He claims that it is then possible to use ultrafiltration or diffusion dialysis to remove water and all ions (both organic and inorganic) having a molecular weight less than 500. Any beneficial chemicals dissolved in the scrubber solution with a molecular weight of less than 500 (such as those that control pH), however, will also be removed with the salts and degraded organics. In addition, this process restricts the practitioner to the use of only polymeric chelating agents with suitably high molecular weights.

Results of nanofiltration to separate salts from the solution of the LO-CAT I autocirculation process have been published (Jamaluddin et al., 1993). It is reported that nanofiltration membranes retain organic materials and iron but allow ionic species to permeate. It is also reported that nanofiltration membranes preferentially remove carbonates and bicarbonates over sulfates and thiosulfates. The authors concluded that an excessive amount of carbonates would have to be removed in order to reach a steady-state removal of sulfates from the LO-CAT I autocirculation system. This, in turn, would require the addition of more KOH into the LO-CAT I autocirculation system. This addition of KOH would make the process prohibitively expensive.

The objective of this work was to test an electrodialysis system that will:

1. Selectively remove the alkali-metal salts of thiosulfate ($S_2O_3^{2-}$) and sulfate (SO_4^{2-}) anions from hydrogen sulfide (H_2S) scrubber solutions of the liquid-redox type
2. Retain in the scrubber solution for subsequent recycle:
   - Polyvalent metal reagent (such as iron)
   - Organic chelating agent, without placing any restriction on the nature (molecular weight) of the chelating agent to be used in the H_2S scrubber
   - pH-Adjusting chemicals.

Background and application of the electrodialysis process

Electrodialysis (ED) is an electromembrane process in which ions are transported through ion-exchange membranes from one solution to another under the influence of an electrical potential (Porter, 1989). The electrical charges of these ions allow them to be driven through solutions and water-swollen membranes when a voltage is applied across these media. Since pressures are usually balanced across the membranes, the requirements for strength and support of the membranes and containment vessels are less demanding in electromembrane processes than in pressure-driven membrane processes. Instead, design emphasis is directed toward maintaining a uniform distribution of solution flow and minimizing electrical resistance and current leakage.

Electrodialysis is used mainly for desalination of sea and brackish water (Strathmann, 1985). Other applications include the recovery of water and valuable metal ions from industrial effluents. The removal of salts and acids from pharmaceutical solutions and in food-processing industries have also gained a lot of interest. Selective recovery and concentration of acids from an acidic nickel sulfate stream containing copper, arsenic, bismuth, and antimony has recently been carried out by electrodialysis (Baltazar et al., 1992).

The use of electrodialysis to remove inorganic ions from solutions containing chelated polyvalent transition metals has also been reported. Walker and Pennline (1988) reported the use of electrodialysis to regenerate SO_2–NO_x scrubber solutions containing Fe^{2+}(EDTA) by the removal of sulfite (SO_3^{2-}), bisulfite (HSO_3^-), and dithionate ($S_2O_6^{2-}$) ions. Ono and Watanabe (1980) described a process to remove silver (Ag^+) and silver (thiosulfate) complex ions from solutions containing both Fe^{2+}(EDTA) and Fe^{3+}(EDTA). Grenda (1980) disclosed an electromembrane process to regenerate electromembrane copper-plating baths by the removal of formate (HCO_2^-) and sulfate (SO_4^{2-}) ions through an anion-selective membrane, from solutions containing Cu^{2+} chelated by a variety of organic chemicals.

In this article, we present results of the electrodialysis process to remove sodium (Na^+), potassium (K^+), thiosulfate ($S_2O_3^{2+}$), and sulfate (SO_4^{2-}) ions and to recycle the LO-CAT I autocirculation scrubber solution containing "Type A" (EDTA-like) and "Type B" (sorbitol-like) organic complexes.

Experimental Studies Using Electrodialysis

Electrodialysis mechanisms

The electrodialysis "stack" consists of alternating anion- and cation-selective membranes assembled together using suitable gaskets and flow distributers and placed between two electrodes as shown in Figure 1 (letters A and C (Figure 1) stand for anion- and cation-selective membranes, Naf stands for the Dupont Nafion 324 membrane, and ACM stands for Tokuyama Soda ACM membranes). The solution from which the ions are to be removed enters the dilute compartments, while the solution that is intended to collect the ions is circulated through the concentrate compartments. Special solutions are used in the electrode compartments to avoid side reactions. These solutions are referred to as electrode-rinse solutions. The various solutions are never physically contacted with each other, but electrical continuity is maintained in the stack through the membranes.

When an electrical potential is applied to the electrodes, one (the anode) becomes positively charged and the other (the cathode) negatively charged. Electrostatic forces cause positive ions (cations) to migrate toward the cathode and negative ions (anions) to migrate toward the anode. During this migration process, anions that encounter anion-selective membranes will pass through while those that encounter cation-selective membranes are blocked. If the central compartment in Figure 1 is examined, it will be seen that anions migrating toward the anode will pass through the anion-selective membrane on the left side of the compartment. These anions are trapped in the next compartment because they are unable to pass through the next cation-selective membrane. Cations will behave the opposite way; they will move into the compartment on the right through the cation-

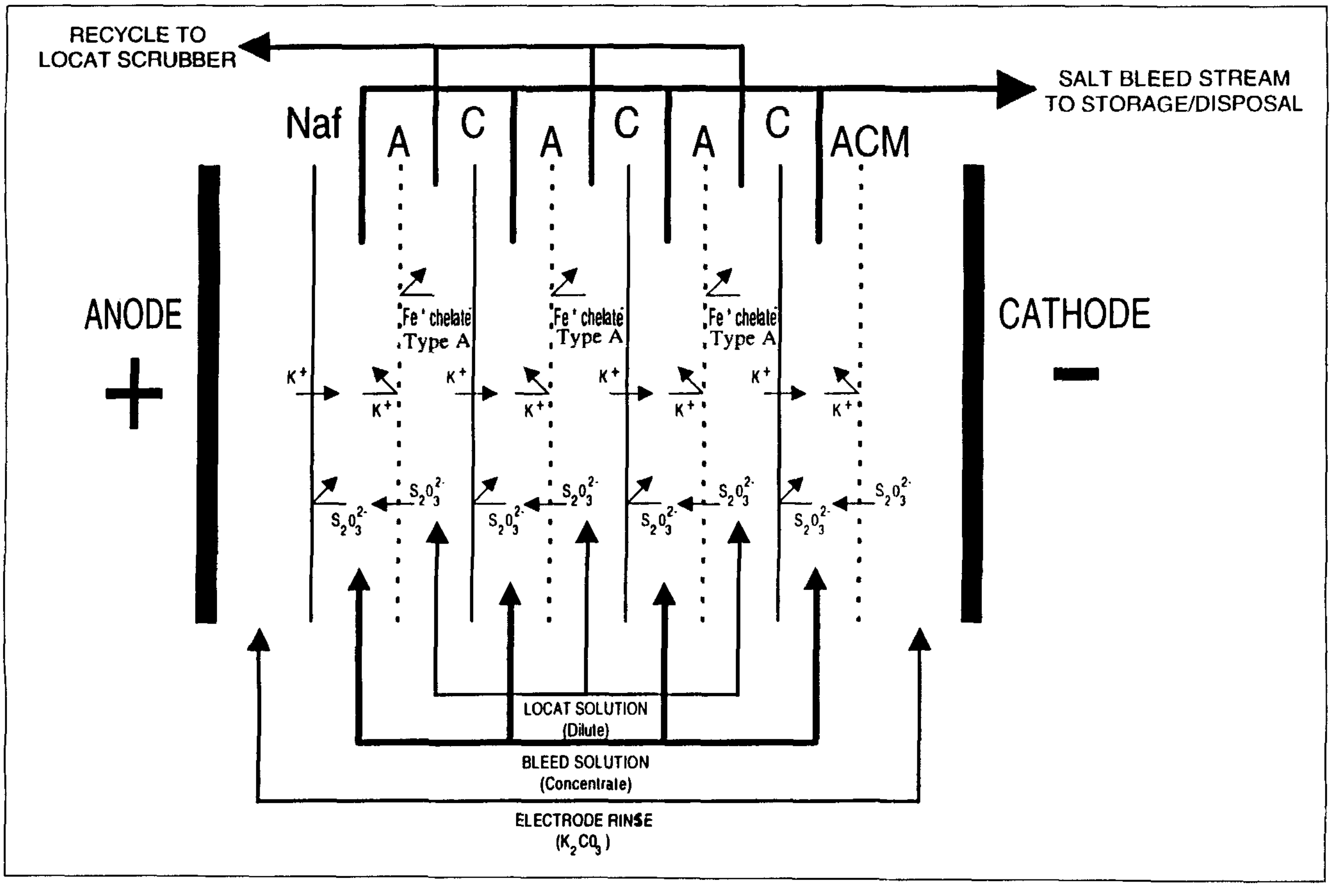

Figure 1. Electrodialysis cell schematic.

selective membrane. In this manner it is possible to remove nearly all the ions from the solution in the dilute compartments.

In the ED process, if large organic molecules are present in the solution, they may be sterically hindered from entering the membranes; they subsequently accumulate on the membrane surface. These organics build up on the membrane surface and cause blockage of the ion- transport process through the membrane, a process called *fouling*. The Type A chelating agents keep iron in solution and form negatively charged organic complexes. These organic complexes accumulate on the anion-selective membranes and cause membrane fouling. The Type B chelating agent is a neutral species at the normal operating pH of 9 to 11 in the solution of the LO-CAT I autocirculation system. Therefore, diffusion is the only means by which the Type B chelating agent can transfer through the membranes, unless it is complexed with some charged species. If the Type B chelating agent is complexed with iron, it forms a cationic complex and either passes through the cation-selective membrane or fouls the membrane.

The fouling problem can be overcome by using a process called electrodialysis reversal (EDR), developed by Ionics. In this process, the polarity of the electrodes and the dilute and concentrate streams are reversed periodically. Walker and Pennline (1988) reported that the implementation of EDR can avoid membrane fouling.

Experimental equipment and procedure

The ED unit used in the experiment was supplied by Tokuyama (model TS-2-10) of Japan. The ED stack was equipped with 10 pairs of alternating monovalent cation-selective (Tokuyama CMS) and medium cross-linked anion-selective (Tokuyama AM 2) membranes. These cell pairs were placed between a platinum-coated anode and a 316-stainless-steel cathode. Special membranes (Dupont Nafion 324 and Tokuyama Soda ACM or CM 2) were used to isolate the two electrode (cathode and anode) compartments. A total of 24 membranes were used in the stack. Each membrane was 18 cm by 28.4 cm with an effective membrane area of 0.02 m^2 for a total area of 0.4 m^2 (0.2 m^2 of anionic and 0.2 m^2 of cationic membrane area). The space between the individual membranes in the stack was 0.7 mm.

In a typical ED experiment, 20 to 30 L of prefiltered LO-CAT I solution was transferred to a polypropylene tank and circulated through rotameters to the stack by magnet-driven sealed-plastic pumps at a rate of 4 L/min. Inside the stack, this flow rate resulted in a fluid velocity of about 6.3 cm/s. The Reynolds number corresponding to this velocity is about 100. All piping (PVC schedule 80) in the apparatus had a diameter of 1.27 cm. All solutions were filtered on-line through plastic cartridge filters (5 micron) to avoid fouling of the membranes. Dilute and concentrate solutions were filtered through additional filters (1 micron). During the experiments, no residue buildup was experienced.

Anolyte (solution in the anode compartment) and catholyte (solution in the cathode compartment) were made up with either sodium sulfate or potassium carbonate to a conductivity of about 20 mS and added to two 20-L polypropylene tanks. A schematic diagram of the ED set-up is shown in Figure 2. Two sets of experiments were carried out. In the first set, concentrate solution was made up with potassium carbonate to 20 mS and placed in a 2-L tank (11 in Figure 2). The salts carried some hydration water when passing from the dilute stream to the concentrate stream through the membranes. As a result, after a short time the solution in the concentrate tank began to overflow into a 50-L holding tank (1 in Figure 2). This mode of operation minimized the production of concentrate, and hence, disposal costs. In the second set, the 2-L tank was eliminated, and 20 L of concentrate was added to the 50-L reservoir tank at time zero. The volume of the concentrate in the tank slowly increased with time. This mode of operation maximized the concentration difference between the dilute and concentrate streams. Operating in this fashion, mass transport by diffusion was also maximized. This mode of operation yielded the highest current efficiency when operating with a high total-salt content.

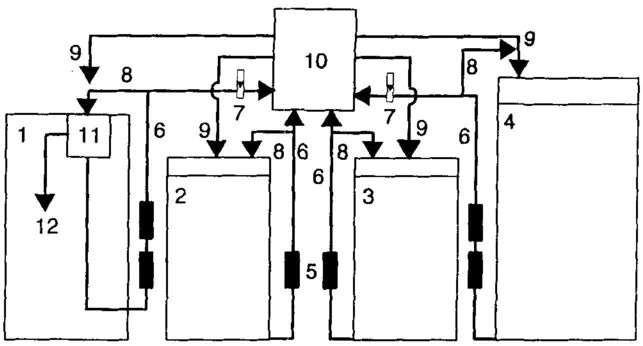

Figure 2. Electrodialysis equipment setup.

1. Concentrate; 2. anolyte; 3. catholyte; 4. dilute; 5. filters; 6. feed solution; 7. flowmeter — normally closed solenoid; 8. backflow; 9. return; 10. electrodialysis cell; 11. holding cell; 12. spillover.

A total of seven runs (A to F) were carried out using solutions from Norcen's Carbondale LO-CAT I autocirculation plant. The initial concentrations of the various chemical species in the dilute compartment of the ED system are summarized in Table 1. The experimental conditions for all the runs are tabulated in Table 2. In run E, the solutions were heated to 40°C using bayonet heaters prior to the start of the experiment. The other runs were carried out at room temperature. There was no temperature control in the system. As the experiments progressed, the temperature of the solution increased because of the resistive-heating effect. The system temperature eventually equilibrated to temperatures tabulated in Table 2 within about 2 to 4 hours. Runs A, B, C, D, D′, and E were carried out with a total-dissolved solids content (TDS) of 9.17% (w/w), while run F was carried out at a TDS of 29.5% (w/w). The high TDS was achieved by doping the solution with anhydrous K_2CO_3 and $Na_2S_2O_3$ (technical grade).

During the experiment, power was applied across the membranes using a 70-A generator (Lamda, Model LT 864) with a maximum potential of 60 V. The current remained constant throughout the experiment for all runs, unless otherwise stated. The process variables (temperature, voltage, current, pH, and conductivity) were logged every five minutes using a Cole-Parmer Mac-14 data-acquisition unit and recorded on an IBM hard disk. Some electrical interfer-

Table 1. Initial Composition of the Dilute Stream of the ED System (Original Solution)

Run No.	Concentration of Dilute Stream (g/L)								
	Fe^{X+}	Na^+	K^+	SO_4^{2-}	$S_2O_3^{2-}$	CO_3^{2-}	Type A Chelating Agent	Type B Chelating Agent	Type A Chelating Agent Byproduct
A	0.48	8.02	25.10	19.40	14.43	3.90	15.85	2.29	3.92
B	0.45	6.76	25.40	20.40	12.07	3.90	16.30	2.33	4.08
C	0.49	6.62	25.40	18.60	13.27	3.90	16.80	2.36	4.18
D	0.58	7.58	28.60	19.40	16.84	3.90	—	—	—
D′	0.54	6.67	25.80	17.50	14.97	3.60	15.23	2.16	3.80
E	0.50	3.94	16.00	13.70	6.07	3.40	14.32	2.24	3.59
F	0.49	79.08	76.78	24.60	175.00	38.90	14.98	2.16	4.24

ence was observed when the voltage of the generator increased above 25 V. Therefore, critical experimental data were verified manually.

On-line conductivity measurements were carried out to monitor the salt concentrations in the recyclable-solution stream. Experimental runs were terminated when the conductivity of the solution reached a sufficiently low value (usually below 50 % of the initial value).

Analytical procedures

Samples collected during the experimental runs were analyzed for inorganics and organics. Potassium and sodium were analyzed using flame-emission spectrophotometry (FE); iron was determined using atomic absorption (AA); and sulfate and total sulfur were determined using gravimetric precipitation. Carbonate and bicarbonate concentrations were determined using double-derivative titration on a 20-mL sample using a Metrohm 686/665 autotitrator and 0.1 N HCl as the titrant. Organics were analyzed using liquid chromatography (LC).

Experimental Results and Discussions

The experimental results for all the runs are summarized in Tables 3 and 4. As an example, the results of run F are shown graphically in Figures 3 to 5. In all electrodialysis runs, the pH was monitored in the feed, permeate, and concentrate streams. All pH values were identical and did not show any variation with time. The pH values varied between 9.2 and 9.7 for all the runs except for run F, where the pH values varied between 10 and 10.8 because of doping.

Extraction of salts and organics

The percent extraction of each ionic species is calculated using the following expression:

$$\%\text{Extraction} = ((M_i^0 - M_i^T)/M_i^0)^* 100, \qquad (7)$$

where M_i is the mass of species i and superscripts 0 and T denote the start and end times of the experiment, respectively. The extraction calculation was carried out using the concentration of the dilute stream of the ED system.

Percent-extraction values for all components are plotted as functions of time in Figures 3 through 5 and also tabulated in Tables 3 and 4. As seen in these figures, at 18.6 h, 50% of the salts (Na^+, K^+, SO_4^{2-}, and $S_2O_3^{2-}$) is extracted with a coextraction of only 7.5% of the organics (Type A chelating agent and Type A by-products), 7.5% of the carbonates, and 8.8% of the Type B chelating agent. The salt percent-extraction value increased linearly with time, while the organic and carbonate percent-extraction values showed little increase with time. The results for individual inorganic and organic species are plotted in Figures 4 and 5 as functions of time. As seen in Figure 4, the extraction of CO_3^{2-} is much lower than that of the other inorganic anions. No specific reason has been identified for the low percent extraction of carbonates. Lounis and Gavach (1990) reported that this phenomenon may be

Table 2. Summary of Electrodialysis Experimental Runs

Run No.	Run Time (h)	Starting Vol. of Dilute (L)	Stack Current Dens. (A/m^2)	Solution Temp. (°C)	Equip Set up	Common Electrode Rinse	Comments
A	15.5	20.8	200	33.4	1	Yes	New $K_2CO_3^*$
B	6.0	30.6	385	32.7	1	No	New $Na_2SO_4^*$
C	2.0	23.4	385	NR	1	No	Used $Na_2SO_4^*$
D	16.0	30.2	200	27.3	2	Yes	New $K_2CO_3^*$ Flow Reversal
D′	4.0	23.4	200	29.0	2	Yes	New $K_2CO_3^*$ Flow reversal
E	5.0	22.4	400	39.3	2	Yes	Solution from D′
F	44.5	26.9	400	31.3	2	Yes	High salt conc.

*Electrode rinse solution.

Table 3. Electrodialysis Experimental Results: Inorganic Analysis

Run No.	Time to 50% Salt Extraction (h)	Extraction (%)						Average Fluxes (g/m²/h)					
		Fe^{X+}	Na^+	K^+	SO_4^{2-}	$S_2O_3^{2-}$	CO_3^{2-}	Fe^{X+}	Na^+	K^+	SO_4^{2-}	$S_2O_3^{2-}$	CO_3^{2-}
A	6.3	5.0	33	49	32	86	11.7	0.4	44	207	97	214	9.29
B	4.6	5.7	43	48	39	77	10.0	0.9	103	409	270	316	14.45
C	4.3	−4.6	39	49	31	84	15.6	4.1	152	366	174	338	10.34
D	8.0	7.4	46	47	33	79	12.2	0.8	66	255	120	250	8.97
D′	5.5	12.6	46	51	31	73	15.4	1.8	67	267	107	185	10.3
E	2.0	12.4	33	48	47	74	21.7	3.4	77	439	364	263	37.5
F	18.6	3.50	40	47	25	59	7.5	0.2	272	284	50	907	19.2

Table 4. Electrodialysis Experimental Results: Organic Analysis

Run No.	Time to 50% Salt Extraction (h)	Extraction (%)			Average Fluxes (g/m²/h)		
		Type A Chelating Agent Byproduct	Type A Chelating Agent	Type B Chelating Agent	Type A Chelating Agent Byproduct	Type A Chelating Agent	Type B Chelating Agent
A	6.3	4.0	5.0	1.0	1.0	6.0	0.2
B	4.6	10.0	11.0	3.0	14.0	63.0	3.0
C	4.3	12.0	10.0	4.0	18.0	98.0	11.7
D	8.0	N/A	N/A	N/A	N/A	N/A	N/A
D′	5.5	13.0	10.0	4.0	9.0	31.0	0.8
E	2.0	19.0	19.0	2.0	38.0	150	2.7
F	18.6	11.1	6.3	8.8	5.3	14.3	1.0

due to an acid-base reaction that takes place inside the membrane phase, presumably related to dissociation of water.

The Type B chelating agent at operating pH of 9 to 11 acts as a neutral compound. It can be seen from Figure 5 that a significant amount of the neutral organic Type B chelating agent was lost. Table 4 shows that more Type B chelating agent was lost by diffusion in Experiment F, because of the much longer processing time.

Flux

At constant current density, the flux of an individual species is proportional to its rate of electrodialytic transport and to its rate of diffusion. The relative current carried by an ionic species (transport number) can be calculated using published electrochemical data (Robbins, 1979). The flux of an ionic species is then calculated using the total current and its transport number. This approach assumes infinite dilution and is generally applicable up to a normality of 1. The presence of nondissociated species or the formation of complexes invalidates the application of a rigorous model. As a result, an approximate model was adopted for the calculation of relative fluxes at high salt concentrations. Since the data were extremely limited, it was decided to model the fluxes of the individual species as functions of their fraction of the total normality of ions in solution at time zero. This modeling ef-

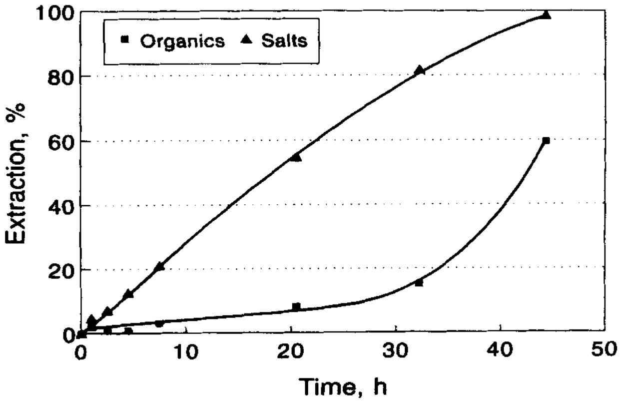

Figure 3. Percent extraction as a function of time (run F).

Organics: Type A chelating agent and Type A by-product. Salts: sodium, potassium, sulfate, and thiosulfate.

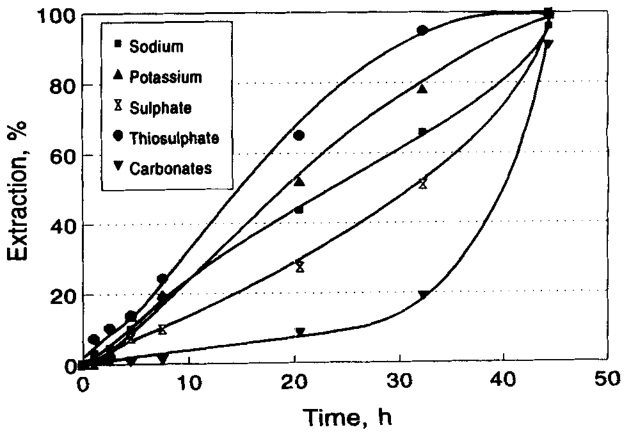

Figure 4. Percent extraction of individual ions as a function of time (run F).

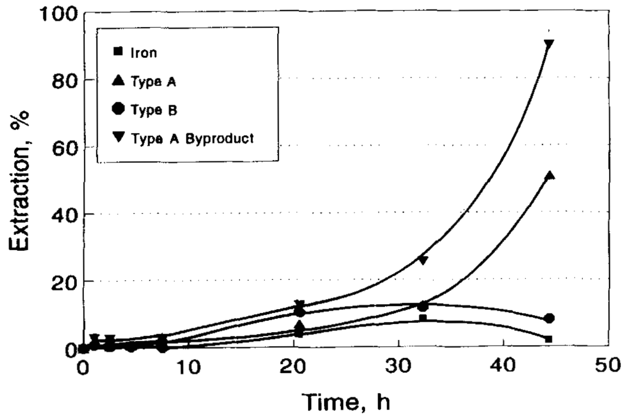

Figure 5. Percent extraction of iron and individual organics as a function of time (run F).

fort was for purely practical purposes. The mathematical expression to calculate flux at 400 A/m^2 is given as follows:

$$F_i = m_i X_i, \tag{8}$$

where F_i and X_i are the fluxes (averaged between 0 and 50% extraction) and ionic fractions of species i, respectively, and m_i are the slopes of the calculated values for the individual species. The values of the regressed parameter, m_i, and the squares of the correlation coefficients are tabulated in Table 5. As seen in this table, the flux of all the species except CO_3^{2-} can be modeled at constant current density in this simple fashion.

The fluxes reported in Tables 3 and 4 are the average flux between 0 and 50% salt extraction for each experiment. As seen in these tables, the fluxes vary with the salt concentrations in the dilute stream. For instance, the sodium and thiosulfate fluxes for run F are higher because of the higher initial salt concentrations, providing larger driving forces.

It was also observed that, compared to the various inorganic ions (Na^+, K^+, $S_2O_3^{2-}$, and SO_4^{2-}), the organic materials (Type A and Type B chelating agents and Type A by-product) and iron showed low fluxes.

To minimize the loss of organics it was necessary to minimize the ratio of organic to inorganic ions in solution. This can be accomplished by using the ED unit when the salt content is large. In other words, the ED process is most effective when the salt concentration reaches its saturation value.

Proper process control could reduce the loss of organics. The actual plant solution used in these experiments had excess amounts of Type A chelating agent. The data in Tables 3 and 4 indicate that a lower percentage of iron was lost than organics in all tests. The most likely explanation is that when iron is chelated by the Type A chelating agent or by a Type A chelating agent by-product, the much larger complex molecule is less able to pass through the membrane than the free excess chelating agents. By maintaining the organic concentration at a level such that all the organics are complexed with iron (mole ratio Type A chelating agent:Fe of 1:1 to 2:1), the organic losses could be reduced by over 50% (run F).

Table 5. Regression Parameters (400 A/m^2)

Species	Slope, m_i	R^{2*}
Potassium (K^+)	1,275	0.442
Sodium (Na^+)	823	0.897
Thiosulfate ($S_3O_3^{2-}$)	3,049	0.994
Sulfate (SO_4^{2-})	1,299	0.744
Carbonate (CO_3^{2-})	233	0.040
Type A chelating agent	984	0.833
Secondary chelating agent byproduct	622	0.708

*R^2 = (variance of data − variance of residual)/variance of data.

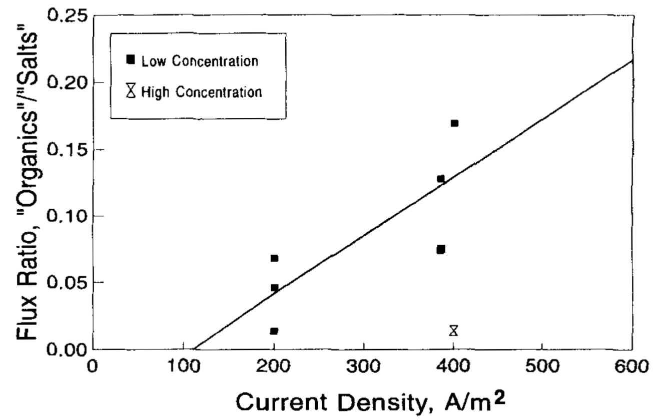

Figure 6. Organic-to-salt flux ratio as a function of current density.

Organics: Type A chelating agent and Type A by-product. Salts: sodium, potassium, sulfate, thiosulfate.

Increasing current density increases the overall flux. The increase in current density, however, also increases the overall energy consumption. As seen in Tables 2, 3, and 4, the fluxes for both inorganics (salts) and organics do indeed increase with an increase in current density. The ratio of organic flux to inorganic flux also increases with the increased current density as shown in Figure 6. The average flux ratios of organics to salts shown in Figure 6 are for two current densities: 200 and 390 A/m^2, calculated from the average flux ratios of runs A, D, and D′ (all at 200 A/m^2), and those of runs B, C (385 A/m^2), and E (400 A/m^2).

An additional point is plotted in Figure 6 to represent the results of Experiment F, which was carried out using the same organic concentration, but at a much higher salt concentration, than in Experiments A to E. The fluxes of the organic ions are lower at higher salt concentrations, which explains the reduced value of the organic-to-salt flux ratio in Figure 6. In Experiments A to E, organic ions carried 37% of the anionic charges, while in Experiment F, they carried less than 5%.

A detailed charge balance for all the experimental runs is tabulated in Table 6. The charge balance is the product of molar flux and the charge of the species. Ideally, positive ions should balance the negative ions. However, due to the use of an industrial solution, which carries unknown anions (additional organic degradation products), a perfect charge balance was difficult to obtain. Overall, the charge balance varied between +13% and −33% for all the experimental runs. It is important to note that in all but one experiment (run E) the ionic species were underreported.

The current efficiencies for all the experimental runs are calculated as the ratio of the average current density of the

Table 6. Charge Balance and Current Efficiencies

Run No.	Σ Cations	Σ Anions	Error (%)	Avg. Current Eff. (%)
A	7.21	6.26	−13	90
B	14.94	12.96	−13	97
C	15.97	11.86	−26	96
D	9.39	7.26	−23	111
D′	9.74	6.50	−33	109
E	14.58	16.49	13	104
F	19.09	18.17	−5	125

Σ = sum of ions = $N_i Z_i$ (N_i = molar flux of species i; Z_i = charge of species i). Current Efficiency = I_T/I ($I_T = F\Sigma N_i Z_i$; I = circuit current density).

positive and negative ions to the circuit current density and summarized in Table 6. The current efficiencies of all the experimental runs vary between 90 and 125%. In runs A, B, and C, experimental setup 1 (Table 2) was used. This mode gave the highest concentration of ions in the concentrate stream. This operation minimized the concentration gradient between the dilute and concentrate streams and resulted in lower current efficiencies. On the other hand, in runs D through E, experimental setup 2 (Table 2) was used. In this mode, current efficiencies exceeded 100% because of a lower concentration of ions in the concentrate stream. This concentration difference provided a positive driving force for molecular diffusion to occur from the dilute stream to the concentrate stream and resulted in greater than 100% current efficiencies. An extreme case is shown in run F, where the dilute stream was doped with additional salt, giving a large concentration gradient that resulted in current efficiencies of 125%.

The large scatter in the experimental data could be due to one or a combination of the following factors:

- Initial solution compositions
- Electrodialysis reversal
- Slight temperature variations
- Different degrees of fouling
- Changes in the solution volumes
- Errors in the analytical procedure.

Among these factors, the major contribution came from variations in initial solution compositions, electrodialysis reversal, and temperature variations.

Voltage vs. current density.

When current is passed through an electrolyte, it can be carried by either anions or cations. The proportion of current carried by cations or anions depends on the transport properties of the ions in question. For example, in the case of NaCl, sodium ions carry 40% of the current and chloride ions carry 60% of the current. At the surface of the anion-selective membrane, 100% of the current is carried by anions, and at the surface of the cation-selective membrane, 100% of the current is carried by cations. This change in the proportion of current carried by any given ion induces a net depletion of this type of ion at the surface of the membrane selective to that ion. This depletion sets up concentration gradients within the compartment that result in additional ions being transferred to the surface of the membranes by diffusion. The concentration gradient increases as the current density increases. At some point, the concentration of ions at the surface of the membranes approaches zero. This point is referred to as the limiting current density.

As the limiting current density is being approached, the voltage rises sharply because of the increasing concentration gradient (concentration polarization). Beyond the limiting current density, current will be carried mainly by hydroxyl ions formed by the hydrolysis of water, and this will result in even larger increases in voltage with current. In normal electrodialysis practice, 50 to 80% of the limiting current density is taken as the limit below which concentration polarization is not a problem. The limiting current density at 1-normal concentration is greater than 6,000 A/m^2. In the absence of membrane fouling, it should be possible to operate the stack at current densities above 3,000 A/m^2. Therefore, at the salt concentrations that will be encountered for a LO-CAT I autocirculation bleed (>5 N), the limiting current density is not expected to be an issue in the absence of fouling.

For the experimental ED stack, the increased voltage resulting from the increasing current densities is shown in Figure 7. This figure can be used to determine the power supply required by a pilot unit for any current density up to about the one-half of the limiting current density. It was observed that voltages across membranes decreased very little with increasing salt concentrations above 1 N. For instance, the initial stack and overall voltages for Experiment F (salt concentration greater than 5 N) were measured to be 14.8 V and 30.3 V, respectively. Plots of these voltages are very close to those shown in Figure 7 (salt concentration of 1 N).

The effect of temperature on stack voltage should also be noted: for an increase of 1°C, the resistance of the membranes decreased by about 2%.

Membrane-fouling phenomenon

It is most likely that the ED membranes will foul during electrodialysis of the LO-CAT I autocirculation bleed solution. The key mechanisms that are likely to play a role are fouling by organic poly-acids, and fouling by surface-active chemicals such as surfactants. Organic poly-acids such as the

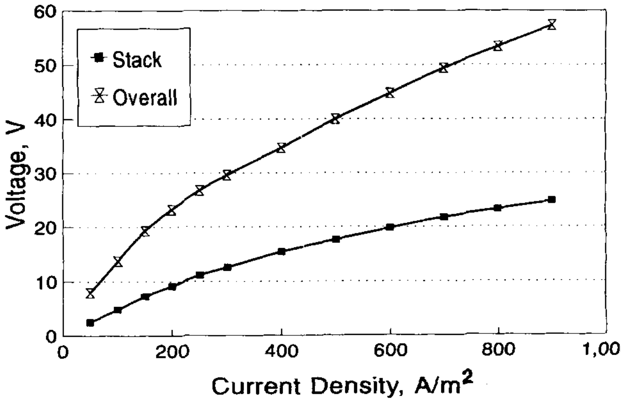

Figure 7. Voltage as a function of current density.

Temperature = 25.7°C; concentrate conductivity = 20 mS; fresh LO-CAT I solution conductivity = 80 mS; composition: run D, Table 1.

Type A chelating agent are generally insoluble in their acid form.

As stated previously, large anionic organic molecules such as the Type A chelating agent will try to pass through the anion-selective membrane but will remain on the surface because of the small pore sizes of the membrane (a small pore size is required to keep the organics). These negatively charged molecules effectively create a cation-selective membrane on the surface of the original anion-selective membrane. This "membrane" has the effect of denying other small anions access to the anion-selective membrane. As a result, the voltage required to operate the stack at a constant current will tend to increase with time. As the concentration of mobile anions at the surface of the anion-selective membrane approaches 10^{-7}, the anion/cation-selective membrane begins to decompose water to form OH^- and H^+ ions [water-splitting ability of anion-selective membranes is well documented (Lounis and Gavach, 1990)]. The OH^- ion will easily pass through the anion-selective membrane, leaving behind the H^+ ion, which will move away from the anion-selective membrane through the organic layer. If this condition becomes severe, the pH in the layer of organic molecules will become lower than the pKa of the organic acid and the insoluble acid form of the organic will precipitate on the membrane, making it impermeable.

The voltage drop across the membrane increases as the membrane fouls. As portions of the membrane foul, the effective current density on the remaining areas of the membranes becomes higher. As a result, the rate of membrane fouling is exponential once initiated. Once a precipitate or scale has formed on the membrane, the voltage will not return to normal without chemical treatment. In the case of the LO-CAT I autocirculation solution, strong acid and brine were used against fouling and found to work well. A base such as KOH could be used to dissolve any precipitated organic acid and could then be recycled to the process.

Since membrane fouling and limiting current density are related, it is not surprising that any variable that increases the limiting current density also reduces fouling. These factors include salt concentration, temperature, and liquid flow velocity.

- As the salt concentration increases relative to the organics, the salts carry a higher proportion of the current in the stack. In that case, the stack may still foul, but more slowly. The higher salt concentration allows more salt to penetrate any buildup of organic layer on the surface of the anion-selective membrane. The higher anion concentration at the membrane surface effectively eliminates water splitting and prevents formation and precipitation of organic acids.
- At higher temperatures most chemicals have a higher solubility and are less likely to precipitate. Also, the diffusion coefficients of all species are higher, and it is easier for the salts to diffuse through the fouling layer.
- Finally, a higher solution flow rate will reduce the thickness of the Nernst diffusion boundary layer and effectively increase the concentration of anions at the surface of the anion-selective membrane.

From the preceding, it is clear that the most efficient mode of operation for the LO-CAT I autocirculation system is with a high salt content, a low organic content, a high temperature, and a high solution flow rate. Of these factors, concentration and temperature are the most important.

Experimentally, fouling was encountered only at low salt concentrations. In Figure 8, the resistance of the stack as a function of time was plotted for run A (salt concentration of 1 N) and for run F (salt concentration of 5 N). The temperature profiles were included so that the reader can be assured that temperature is not affecting the membrane resistance. At the high salt concentration (run F), fouling was not apparent. However, it is highly likely that, given a longer period of operation, the membranes would have fouled.

If it becomes apparent at a later stage that fouling is indeed a major problem, the technique of EDR pioneered by Ionics could be used. In EDR, the polarities of the anode and cathode are alternated during equal periods of time. Obviously, the concentrate and dilute streams must also be reversed at the same time as the current reversal.

The use of electrodialysis reversal was demonstrated on the LO-CAT I autocirculation solutions in Experiments D and D′. The dilute solution was changed from Experiment D to D′. The overall voltages of the stack (including the anode and cathode) were plotted in Figures 9 and 10 for these experiments. Electrodialysis reversal was conducted manually each

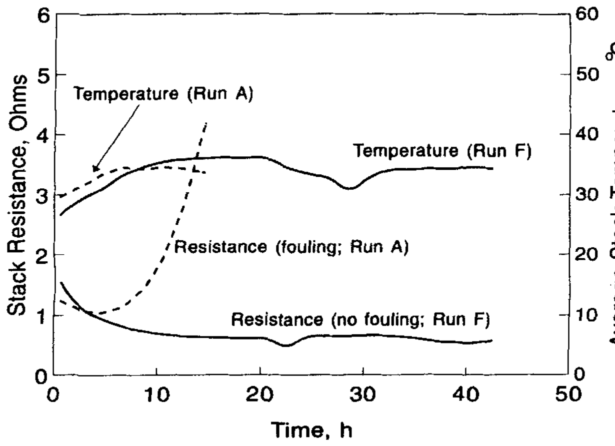

Figure 8. Stack resistance and temperature as a function of time.

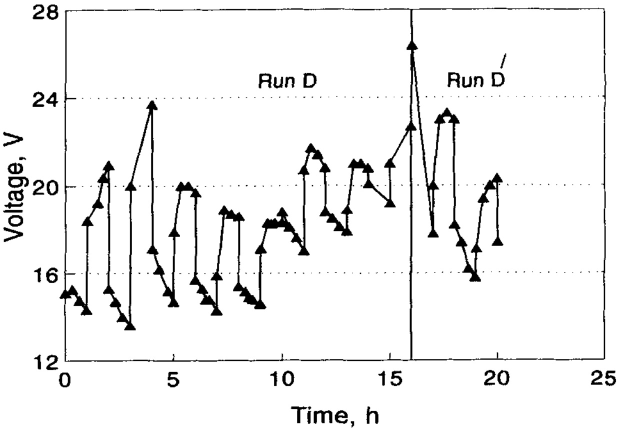

Figure 9. Voltage variation with EDR.

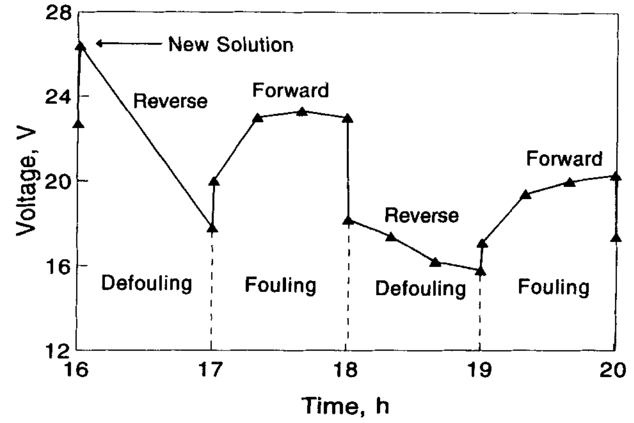

Figure 10. Voltage variation with EDR.

Run D; expanded from Figure 9.

hour. The overall voltage variation as a function of time for the EDR process is shown in Figure 10. As explained earlier, the overall voltage decreases with time during defouling mode and increases with time during fouling mode.

Conclusions

Testing of the electrodialysis process to separate salts from the hydrogen-sulfide scrubber solution (iron-based liquid-redox) indicated that 50% of the salts from the scrubber solution could be removed with less than 8% loss of carbonate (run F). The fluxes of the undesired salt species (50 to 2,000 g/m^2/h) were high even at a low current density (200–400 A/m^2). Current densities higher than 200 A/m^2 may increase organic losses. At low salt concentrations, fouling was encountered, but found to be controllable and reversible. Membrane fouling was not a problem at higher salt concentrations.

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Notation

F = Faraday constant
I = circuit current density, A/m^2
I_T = current density of ions, A/m^2
N_i = molar flux of species i
Z_i = charge of species i

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