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REPORT OF INVESTIGATIONS/1989

Alumina Recovery From Copper Dump Leaching Liquors Using a Supported Liquid Membrane

By S. P. Sandoval and L. E. Schultze

BUREAU OF MINES

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb	pound
cm^2	square centimeter	$\mu g/(cm^2 \cdot h)$	microgram per square centimeter per hour
ft^2	square foot	μm	micrometer
g	gram	min	minute
gal	gallon	mL	milliliter
g/L	gram per liter	pct	percent
h	hour	rpm	revolution per minute
in	inch	st/d	short ton per day
in^2	square inch	vol pct	volume percent
L	liter		

ALUMINA RECOVERY FROM COPPER DUMP LEACHING LIQUORS USING A SUPPORTED LIQUID MEMBRANE

By S. P. Sandoval[1] and L. E. Schultze[2]

ABSTRACT

The U.S. Bureau of Mines investigated the separation of aluminum from copper dump leaching liquors using a supported liquid membrane. Aluminum was selectively transported through porous polypropylene impregnated with di (2-ethylhexyl) phosphoric acid in an aliphatic diluent. The effects of variables, such as solution composition, temperature, and extractant concentration, were measured with a three-level fractional factorial experimental design. Experimental results were used to derive equations for predicting transport rates for aluminum, iron, and copper. The major variables influencing aluminum transport were solution temperature, feed solution pH, aluminum concentration in the feed solution, and extractant concentration. Copper and iron transport rates were almost zero when aluminum transport rates were high. Measured aluminum transport rates under the best conditions of 55° C, pH 3.0, 16 g/L Al^{3+}, and 65 pct extractant solution confirmed the predicted value of 210 $\mu g/(cm^2 \cdot h)$. Transport rates for iron and copper were less than 5 $\mu g/(cm^2 \cdot h)$ under these conditions.

Aluminum was recovered from the stripping solutions by sparging with gaseous hydrogen chloride to crystallize aluminum chloride hexahydrate, which was calcined to alumina. Sparging crystallization regenerated the stripping acid for recycle.

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INTRODUCTION

To make maximum use of domestic resources, the U.S. Bureau of Mines has investigated the possibility of recovering aluminum from copper dump leaching liquors. These solutions contain up to 15 g/L Al and represent more than 2,000 st/d Al_2O_3 (alumina). Earlier efforts to recover the aluminum evaluated solvent extraction (*1*)[3] and ion-exchange methods (*2*). Solvent extraction successfully recovered an aluminum product, but the need to maintain pH control necessitated additions of a base to the circuit. To minimize reagent costs, lime was added, resulting in the formation of a gypsum precipitate. Traps were designed in the settling chambers to remove the gypsum, but operation of a mixer-settler in the presence of fine solids was very difficult because of organic phase entrainment (*1, 3*). (This technique was not applied commercially.) The ion-exchange method also recovered aluminum but yielded low organic loading and poor selectivity. Stripping solutions contained iron, magnesium, and aluminum.

Recent developments in membrane technology (*4-5*) suggest a means to avoid the problems associated with previous research. Microporous hydrophobic polymeric membranes were developed that can be loaded with an extractant solution and used to transport metal ions from a feed solution to a stripping solution without two-phase mixing and phase disengagement (fig. 1). The metal ion is extracted at the membrane surface, transported through the membrane by the extractant solution, and released to the stripping solution. Avoidance of two-phase mixing allows solutions containing fine solids to be treated, provided the solids do not adhere to the membrane.

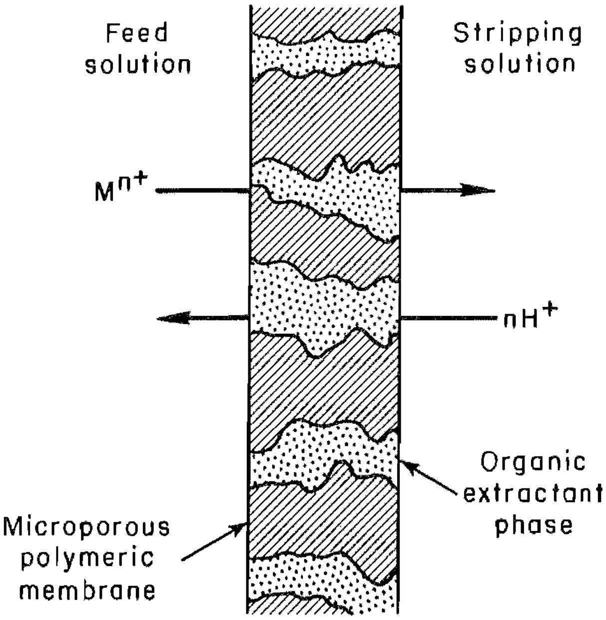

Figure 1.–Supported liquid membrane as extractant for metal ions.

Aluminum concentrates in the acidic stripping solutions, from which it is recovered by existing technology. Aluminum chloride hexahydrate (ACH) is crystallized from a hydrochloric acid (HCl) solution by adding gaseous HCl and is calcined to obtain Al_2O_3 suitable for feed to a reduction cell (*6*). If sulfuric acid (H_2SO_4) is used as the stripping solution, a similar technique can be used to crystallize ACH (*7*), but sulfur contamination occurs. Although sulfur tolerance for reduction-grade Al_2O_3 is not well established, Scott (*8*) estimates that the Al_2O_3 should contain less than 0.25 pct SO_3 (sulfur trioxide).

The objectives of the study described in this report were to select a suitable membrane and extractant solution for aluminum, to determine the effects of variables on extraction and stripping, and to demonstrate methods for recovering Al_2O_3 from solution on a bench scale.

METHODS AND PROCEDURES

Based on a review of solvent extraction methods (*1; 9, pp. 507-509*), an acidic organophosphate was selected as the best extractant for aluminum. Two commercially available extractants, di (2-ethylhexyl) phosphoric acid (DEHPA) and Cyanex 272,[4] an organophosphorus acid, were selected for evaluation in separatory funnel tests. The tests were conducted by mixing 40 mL of a 1:1 mixture of extractant and kerosene with 40 mL of feed solution in 125-mL separatory funnels. The feed solution was prepared with reagent-grade metal sulfate and deionized water to yield a concentration of 7 g/L metal. The distribution coefficients of Al^{3+}, Cu^{2+}, Fe^{2+}, and Mg^{2+} as a function of feed pH were calculated on the amount of metal extracted from the feed solution. H_2SO_4 and sodium hydroxide (NaOH) were used to modify the feed pH. On the basis of these tests, DEHPA was chosen for subsequent tests.

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[3] Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

[4] Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Supported liquid membrane experiments were conducted with the apparatus shown in figure 2. Membrane cells were suspended in a reservoir containing 1 L of feed solution. The acrylic lid supported six membrane cells, a pH electrode, an NaOH addition port, and a motor to stir the feed solution. The membrane cells were constructed by cementing a piece of membrane support onto the end of a polyvinyl chloride (PVC) tube with PVC cement. The clear PVC tubes were 3/4-in, ANSI schedule 40, approximately 4 in long. A one-half section of a 3/4-in coupling was glued on the outside and at the tops of the PVC cells so that the cells could be suspended from the lid. The membrane support was impregnated by soaking the ends of the cells in extractant solution. Excess extractant solution was removed by rinsing with deionized water. The impregnated membrane cells were filled with stripping solution and suspended in the feed solution. The stripping solution inside the cells was stirred with motors fitted with fluorocarbon tubing agitators. The effective surface area of each cell was 3.3 cm^2 (0.5 in^2). Sufficient sodium sulfate to yield 1 g/L Na$^+$ was added to the feed solution in order to detect membrane leaks. Sodium, which was not taken up by the membrane, would report to the stripping solution if a leak occurred. Temperature was controlled by

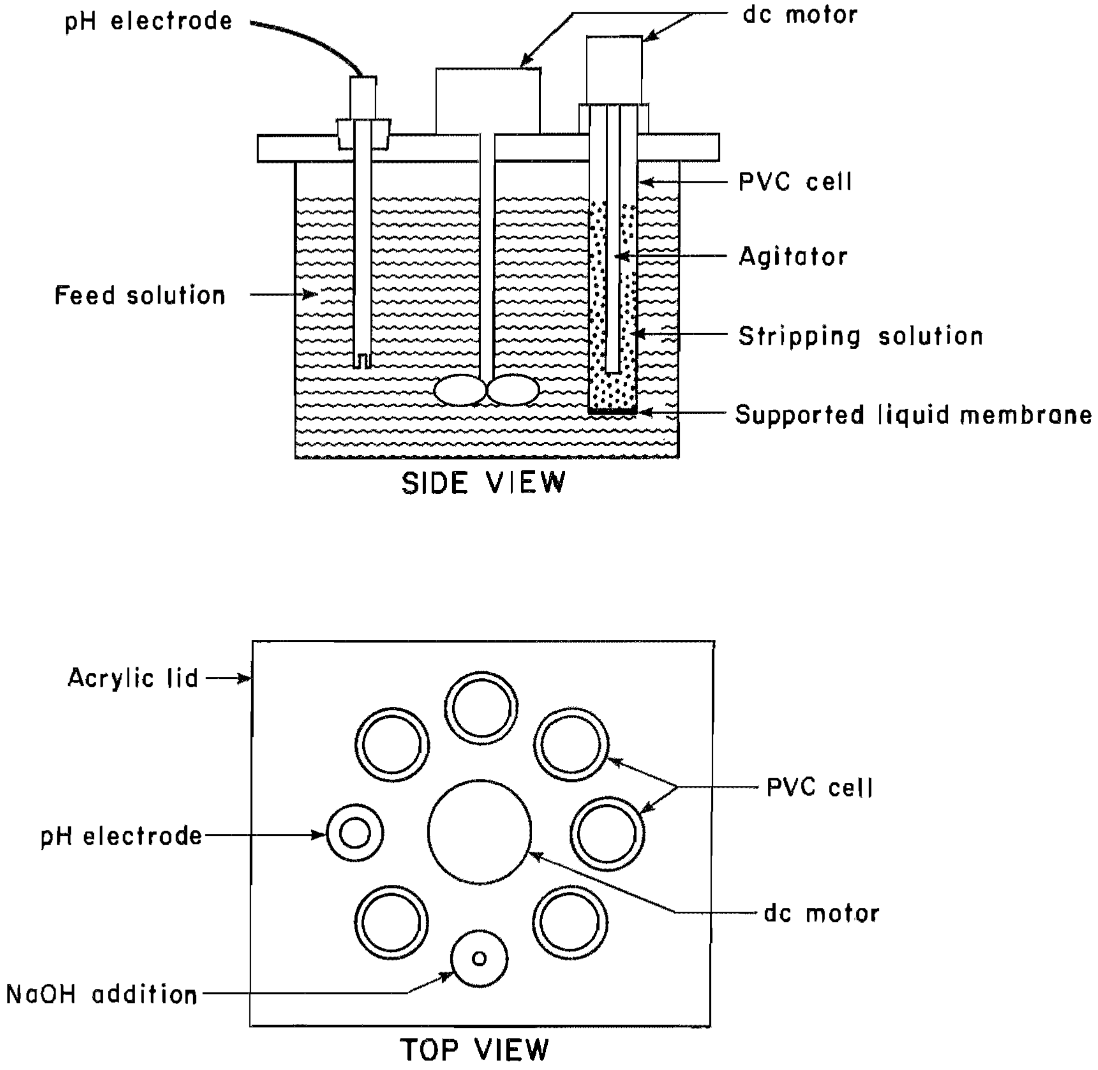

Figure 2.–Supported liquid membrane experimental apparatus.

placing the feed reservoir in a constant temperature bath. Feed pH was continuously monitored, and 10*N* NaOH was automatically added when the pH decreased below the set point. Control of pH was necessary because hydrogen ions (H^+) from the stripping solution were released into the feed solution as metal ions were extracted. Metal transport rates were calculated based on metal analyses of the stripping solution, stripping solution volume, membrane surface area, and elapsed time. Metal concentrations in the separatory funnel tests and the supported liquid membrane tests were determined by inductively coupled plasma-atomic emission spectroscopy.

One-variable supported liquid membrane tests were conducted to evaluate alternative diluents and membrane supports. Diluents tested included kerosene, decanol, xylene, and Escaid 200, an aliphatic diluent. Membrane supports tested were different types of Celgard microporous polypropylene films. Polypropylene was chosen because of its resistance to the high acid strengths required for stripping organophosphates. A description of the membrane supports tested is given in table 1. On the basis of these screening tests, Escaid 200 diluent and Celgard 2400 film were chosen for subsequent testing. The evaluation tests were conducted by measuring the transport of Al^{3+}, Cu^{2+}, and Fe^{2+} through supported liquid membranes as a function of time. The feed solution contained 2 g/L each of Al^{3+}, Cu^{2+}, and Fe^{2+}. The DEHPA concentration used was 25 pct. The stripping solution was 6*N* H_2SO_4. Experiments also were conducted to screen variables believed to influence aluminum transport through the supported liquid membrane. The variables included feed pH, DEHPA concentration, feed aluminum concentration, feed ferrous iron concentration, feed copper concentration, and feed stirring rate. The Celgard 2400 film membranes used in these tests were impregnated with DEHPA and Escaid 200 diluent.

Table 1.–Physical description of membrane supports

Support[1]	Thickness, µm	Pore size, µm	Porosity, pct
2400 . . .	25	0.02	38
2402 . . .	50	.02	38
2500 . . .	25	.04	45
2502 . . .	50	.04	45

[1] Celgard microporous polypropylene films.

A membrane stability test was conducted with a flow-through cell. The cell was a shell and tube configuration 14 in long. The tube inside diameter was 3/4 in. The shell inside diameter was 2-3/4 in. Sections of the tube were cut out, and pieces of Celgard 2400 film were cemented onto the tube to cover the sections removed. The Celgard 2400 film was impregnated with a 25-pct solution of DEHPA in Escaid 200 diluent by soaking the tube in the extractant solution. The effective membrane surface area was 103 cm^2 (16 in^2). Bellow pumps were employed to circulate 800 mL of 6*N* H_2SO_4 stripping solution through the tube and 800 mL of feed solution through the shell. The feed contained 6 g AL^{3+}, 1 g Cu^{2+}, and 2.5 g/L Fe^{2+}. Feed pH was controlled at 2.9 with a Mettler DC-11 titrator using 10*N* NaOH. The Celgard 2400 film was reloaded with fresh extractant solution after 188 h of operation.

Results from the screening experiments demonstrated difficulties in isolating the effects of the variables. To define aluminum transport, measurements at several aluminum concentrations, in combination with measurements at several levels of the other variables studied, were required. Since a statistical experimental design was a more efficient method for this type of study, a Box-Behnken design was used and is described in appendix A. The supported liquid membrane apparatus employed in the screening tests was used. Data obtained from the Box-Behnken design were used to derive predictive models for aluminum, copper, and iron transport rates. The models generated for copper and iron were less accurate than the aluminum model but are useful in estimating behavior.

A seven-variable Box-Behnken design was used to develop regression models relating metal transport rates to DEHPA concentration, feed pH, Al^{3+}, Fe^{2+}, and Fe^{3+} (ferric ion) concentrations, stripping acid normality, and temperature. The selection of these seven variables was based on the results of the screening experiments and on experience with similar solvent extraction systems. The levels of each variable were also chosen based on previous experience and are shown in table 2. The copper concentration was fixed at 2 g/L Cu^{2+} in this design because copper concentration did not affect Al^{3+} transport in the presence of Al^{3+} and Fe^{2+} in the screening tests. In each experimental run, two of the membrane cells were exposed to the feed solution for 24 h, two for 72 h, and two for 96 h in order to isolate the change in transport rates with time. The seven-variable design served as a screening design because variables that had a small influence on metal transport rates were eliminated from further testing and variable levels that were not achievable were redefined. Based on results of the seven-variable design, DEHPA concentration, feed pH, Al^{3+} concentration, and temperature were selected for evaluation in a four-variable design.

Table 2.-Limits set for seven-variable tests

Level[1]	-1	0	+1
X_1: DEHPA in Escaid 200 diluent . . vol pct . .	5	35	65
X_2: Feed pH	2.0	2.8	3.6
X_3: Feed Al^{3+} concentration . . . . g/L . .	2	7	12
X_4: Feed Fe^{2+} concentration . . . . g/L . .	0	3	6
X_5: Feed Fe^{3+} concentration . . . . g/L . .	0	3	6
X_6: Normality H_2SO_4 stripping solution	2	6	10
X_7: Temperature . . . . °C . .	25	40	55

[1] 3 equally spaced levels enclosing variable ranges of interest. Explanation in appendix A.

The predictive precision of the metal transport models generated from the four-variable design was determined by testing with a simulated leaching solution and three actual copper leaching liquors. The simulated leaching solution contained 16 g/L Al^{3+}, which was the maximum Al^{3+} level tested in the four-variable Box-Behnken design. The tests were run at 65 pct DEHPA in the supported liquid membrane, a feed solution pH of pH 3, and 55° C. These conditions gave the best aluminum transport rate in the four-variable Box-Behnken design.

Crystallization of ACH was accomplished in a 1-L, 4-port, jacketed sparging reactor (fig. 3), described in previous reports (*10*). Temperature was maintained at 40° C by circulating water from a constant temperature bath through the jacket. Solution samples were periodically withdrawn by inserting a fritted glass gas dispersion tube into the reactor, applying vacuum, and collecting the sample in a trap. Slurries were collected in the same manner using an open tube. Slurries were allowed to settle in a constant temperature bath; the supernate was decanted and returned to the reaction vessel. The H$^+$and Cl$^-$ (chloride ion) concentrations of the liquid phase were determined by titration using an automatic titrimeter. Solids were washed with 36 pct HCl prior to analysis.

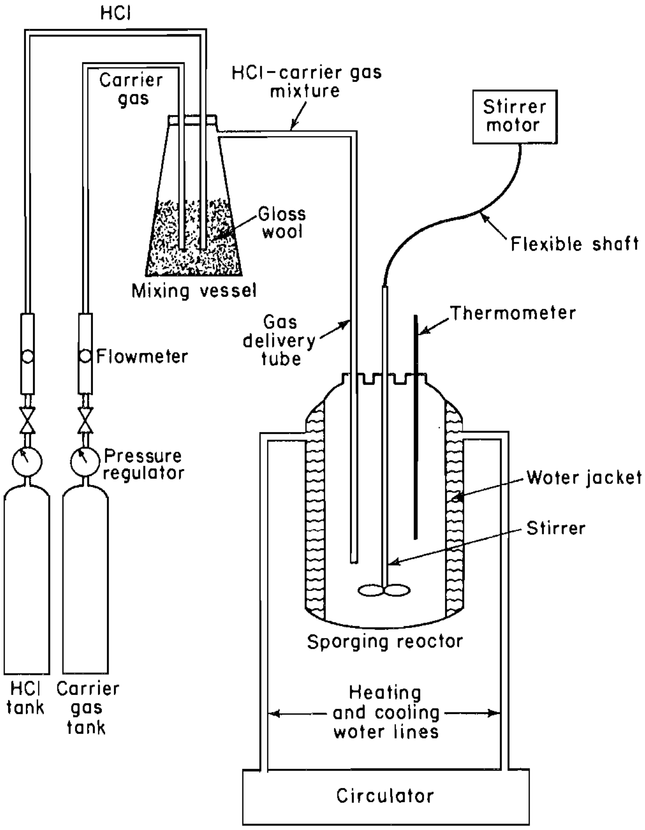

Figure 3.-Sparging apparatus.

RESULTS AND DISCUSSION

METAL EXTRACTION

Screening Tests

The results of the separatory funnel tests with DEHPA and Cyanex 272 extractant showed that DEHPA was a better extractant of Al^{3+} than Cyanex 272 extractant. At pH 2, the distribution coefficient of Al^{3+} in DEHPA was approximately 10, compared with approximately 0.1 in Cyanex 272 extractant. In both cases, the distribution coefficients improved with increasing pH. DEHPA extracted Fe^{2+} to the same extent as Al^{3+} but had less affinity for Cu^{2+}and Mg^{2+}. Cyanex 272 extractant had a greater affinity for Fe^{2+} than for Al^{3+}. Based on these results, DEHPA was used in this study.

Escaid 200 and kerosene diluents gave approximately the same Al^{3+} transport rates. Escaid 200 diluent was used for subsequent tests because it contained fewer unsaturated organic compounds than kerosene and minimized reaction of the diluent with the acidic stripping solution. Decanol and xylene were unsatisfactory diluents because the metals diffused through decanol with no extractant present and xylene rapidly evaporated from the membrane support.

Celgard 2400 and 2402 films demonstrated a greater rejection of Cu^{2+} than Celgard 2500 and 2502 films. Results with Celgard 2500 film suggested that leakage occurred because of higher porosity and larger pore size. Celgard 2502 film is thicker than Celgard 2500 film and may have retained the organic within its pores to a greater extent than Celgard 2500 film. Better Al^{3+} transport was achieved with Celgard 2400 film compared with Celgard 2402 film because the greater thickness of Celgard 2402 film increased the diffusion time of the extractant complexes across the membrane. Based on these results, Celgard 2400 film was chosen for the membrane support.

The effects of DEHPA concentration and feed solution composition on metal transport rates through the supported liquid membrane were compared with the results of separatory funnel tests. As expected, aluminum transport rate increased with increasing pH between 2 and 3.5. Iron transport rate decreased through this pH range and was contrary to its behavior in separatory funnel tests. A reddish-brown precipitate indicated slow oxidation and hydrolysis of the iron in the feed solution. Copper transport rate was negligible throughout the range of pH because of its inability to compete with Al^{3+} and Fe^{2+} for extraction sites. However, copper transport rates similar to those obtained for aluminum could be achieved if copper is the only metal ion in the feed solution. Transport rates for all three metals increased when DEHPA concentration was increased from 10 to 35 pct in the extractant solution.

The screening tests also provided information on the effect of metal ion diffusion. Tests were made in which the stirrer motor in the feed solution was operated at 30 and 150 rpm. No change in transport rates for Al^{3+}, Cu^{2+}, or Fe^{2+} was detected. Thus, even gentle mixing of the feed solution will minimize diffusional boundary layer effects on metal transport rates.

The tests also demonstrated that HCl was an inappropriate stripping solution. Chloride ion was detected in feed solutions at the conclusion of tests using HCl as the stripping acid. The detection of chloride ion was attributed to back extraction of undissociated HCl by adduct formation with the oxygen of the DEHPA. Since the loss of stripping acid and buildup of chloride in the copper leaching liquor would be undesirable in a continuous operation, all subsequent tests used H_2SO_4.

Evidence of membrane degradation was observed in the test conducted with a flowthrough cell. The aluminum transport rate decreased with time (fig. 4). The decrease in aluminum transport rate was due to loss of extractant solution from the membrane support. Regenerating the membrane by soaking it in fresh extractant solution recovered the aluminum transport rate.

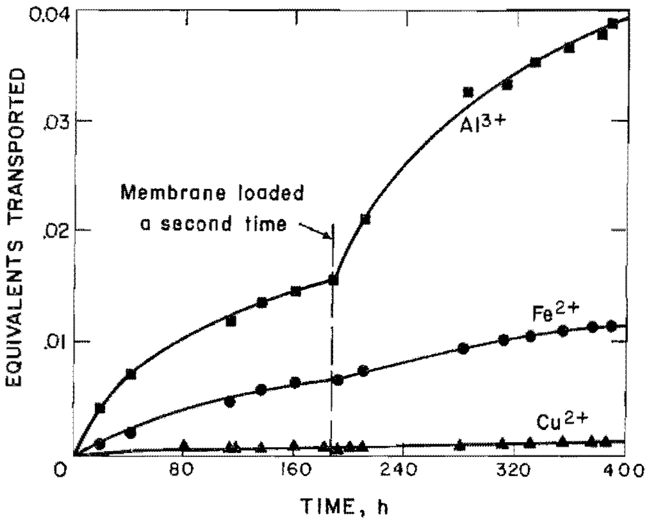

Figure 4.–Effect of extractant loss from membrane support on metal transport rates.

Seven-Variable Box-Behnken Experiments

In conducting the experiments of the seven-variable design, several problems arose. Aluminum began to precipitate from solution at pH 3.6 and 40° C. Iron also precipitated above pH 2.8. Since Al^{3+}, Fe^{2+}, and Fe^{3+} concentrations were not adequately controlled at the designated levels, the seven-variable experimental design was utilized to screen variables of small influence and to focus on the significant variables. In a screening design, only the linear effects and their statistical significance are determined. The experimental variables that are not statistically significant[5] typically do not have significant interaction or curvature effects. Linear effects of the experimental variables from the seven-variable design were determined by regression analysis and are shown in table 3. The table shows the linear effects of the variables on Al^{3+}, Fe^{2+}, Fe^{3+}, and Cu^{2+} transport in micrograms per square centimeter per hour in 24, 72, and 96 h. An increase in the experimental variable level from -1 to 0 or 0 to +1 will produce an average change in metal transport rate equal to its linear effect. The linear effects with a significance of 0.05 or less were considered statistically significant, or

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[5] A significance of 0.05 or less supports the conclusion that the regression coefficient is not due to random variation.

important. In the case of Al^{3+} transport, the important variables are DEHPA concentration, feed pH, feed Al^{3+} concentration, and temperature, each of which increases Al^{3+} transport. In the case of Fe^{2+} and Fe^{3+}, feed pH decreases transport, while temperature increases transport rate. Feed pH masks the effects of ferrous and ferric iron concentrations by creating conditions for iron hydrolysis. Copper transport was decreased by increased Al^{3+} concentration, whereas an increase in temperature increased Cu^{2+} transport rate. The general decrease in linear effects with time indicates the degradation of the supported liquid membrane.

Table. 3.–Linear regression analysis of seven-variable Box-Behnken data

Variable	24 h		72 h		96 h	
	Effect on transport rate,[1] $\mu g/(cm^2 \cdot h)$	Significance of coefficient[2]	Effect on transport rate,[1] $\mu g/(cm^2 \cdot h)$	Significance of coefficient[2]	Effect on transport rate,[1] $\mu g/(cm^2 \cdot h)$	Significance of coefficient[2]
			Al^{3+} TRANSPORT RATE			
X_1	15	0.04	14	0.01	16	0.00
X_2	33	.00	27	.00	24	.00
X_3	15	.04	14	.01	14	.01
X_4	-5	.50	-4	.45	-3	.50
X_5	-10	.19	-6	.23	-5	.27
X_6	7	.32	5	.35	4	.46
X_7	52	.00	38	.00	35	.00
			Fe^{2+} AND Fe^{3+} TRANSPORT RATE			
X_1	1	0.95	1	0.93	2	0.78
X_2	-48	.00	-42	.00	-38	.00
X_3	-17	.10	-13	.11	-12	.07
X_4	7	.48	5	.51	6	.37
X_5	14	.17	10	.21	7	.28
X_6	11	.27	9	.26	7	.26
X_7	26	.01	20	.01	17	.02
			Cu^{2+} TRANSPORT RATE			
X_1	2	0.71	1	0.66	2	0.56
X_2	3	.53	2	.49	2	.57
X_3	-8	.06	-6	.05	-5	.04
X_4	-5	.21	-4	.21	-3	.20
X_5	2	.70	2	.45	2	.41
X_6	2	.68	1	.80	1	.06
X_7	10	.02	8	.01	7	.01

[1] Magnitude of coefficient from linear regression analysis. Average change in transport rate caused by increasing the variable by 1 normalized unit.

[2] A significance of 0.05 or less supports the conclusion that the regression coefficient is not due to random variation.

Four-Variable Box-Behnken Experiments

The variables that were statistically significant in the seven-variable design–DEHPA concentration, feed pH, Al^{3+} concentration, and temperature–were incorporated into a four-variable Box-Behnken design (table 4). The upper level of feed pH was adjusted to pH 3.0 to avoid Al^{3+} precipitation. The Al^{3+} upper concentration level was adjusted to 16 g/L to encompass the Al^{3+} concentrations in actual leaching liquors. The normality of the stripping solution was fixed at 6*N*. The concentration of ferric iron was fixed at 2 g/L. The copper concentration remained fixed at 2 g/L Cu^{2+}. Ferrous iron was not added to the feed solutions of the four-variable design.

The regression results calculated from the four-variable experiment are presented in tables 5 and 6. Rather than calculate a model for each time period, a time factor was introduced into the Box-Behnken model to account for changes in transport rate due to membrane degradation. A stepwise regression procedure was utilized so that only the coefficients with a significance of 0.33 or less were included in the equations. In following this procedure, those coefficients that are close to being significant can be observed while those that are not are excluded. Also, adjusted R^2 is maximized.[6]

Table 4.–Variables used in four-variable tests

Level[1]	-1	0	+1
X_1: DEHPA in Escaid 200 diluent .. vol pct ..	5	35	65
X_2: Feed pH	2.0	2.5	3.0
X_3: Feed Al^{3+} concentration .... g/L ..	2	9	16
X_4: Temperature .... °C ..	25	40	55

[1] 3 equally spaced levels enclosing variable ranges of interest. Explanation in appendix A.

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[6] Adjusted R^2 is a measure of the ability of the regression equation to predict the response. Perfect fit yields R^2 = 1.

Table 5.–Metal ion transport models

Metal	Model	Significance of coefficient[1]
Al^{3+} . . .	$\hat{Y} = 27$	0.00
	$+14X_1$	.00
	$+27X_2$	.00
	$+10X_3$	.00
	$+36X_4$	.00
	$+18X_1X_2$	.00
	$+7X_1X_3$	.01
	$+19X_1X_4$	.00
	$+4X_2X_3$	.18
	$+24X_2X_4$	.00
	$+13X_3X_4$	.00
	$-6X_1^2$	.01
	$+3X_2^2$	.19
	$+11X_4^2$	.00
	$-3T$	.01
Fe^{3+} . .	$\hat{Y} = 55$	.00
	$-44X_1$	.26
	$-56X_2$	.00
	$-18X_3$	.00
	$-25X_4$	.00
	$+14X_1X_2$	.04
	$+7X_1X_4$	.31
	$+7X_2X_3$	.32
	$-55X_2X_4$	.00
	$-16X_3X_4$	.02
	$-17X_1^2$	.00
	$+12X_2^2$	.03
	$-73X_3^2$	.18
Cu^{2+} . .	$\hat{Y} = 6$	.00
	$+2X_2$	.05
	$-11X_3$	.00
	$-10X_2X_3$	.00
	$-11X_3X_4$	.28
	$-7X_1^2$	.00
	$+4X_3^2$	.00
	$+10X_2X_3^2$	.00
	$+11X_3X_1^2$	.00
	$+12X_4X_3^2$	.00
	$-1T$	.06

$\hat{Y}$ Predicted transport rate in micrograms per square centimeter per hour.

X_i Normalized level of variable.

T Normalized time factor.

[1] A significance of 0.05 or less supports the conclusion that the regression coefficient is not due to random variation.

Table 6.–Statistical measurements[1] of precision of metal transport models

Model	Al	Fe	Cu
R^2	0.95	0.85	0.90
Adjusted R^2	.94	.82	.88
Significance of regression	.00	.00	.00

[1] Definitions: R^2–A measure of how well the regression equation fits the data. Perfect fit yields $R^2 = 1$.

Adjusted R^2–A measure of the ability of the regression equation to predict the response. Perfect prediction yields adjusted $R^2 = 1$.

Significance of regression–A significance of 0.05 or less supports the conclusion that one or more of the regression coefficients are not due to random variation.

The regression equations explain the relationship between metal transport rate in micrograms per square centimeter per hour and the four experimental variables, in terms of linear, interaction, and nonlinear effects. The adjusted R^2 value of 0.94 for the Al^{3+} model indicates excellent prediction of aluminum transport rates. The Fe^{3+} and Cu^{2+} models are not good predictive tools. Iron hydrolysis at pH 2.5 and 3.0 made the iron model less reliable. Analysis of test data indicated that higher order terms were needed in the Cu^{2+} model. The complex interactions ($X_iX_j^2$) (table 5) that were significant in the copper model indicate that Al^{3+} plays a very important role in predicting Cu^{2+} transport rate. The membrane degradation occurred linearly with time with respect to Al^{3+} and Cu^{2+} transport. A significant time effect was not observed in the Fe^{3+} transport rate data.

The regression models yield a quantitative understanding of the dependence of metal transport rate on the four experimental variables. The dependence on the variable level combinations can be viewed graphically by plotting the equations in contour plots, which reveal the response surface. Response surface diagrams of Al^{3+}, Fe^{3+}, and Cu^{2+} transport rates are shown in figures 5 through 12. Each contour represents the predicted average metal transport rate in micrograms per square centimeter per hour for the time period shown.

Figures 5 and 6 illustrate the importance of temperature in predicting Al^{3+} transport rate. In figure 5, the influences of temperature and Al^{3+} concentration at 65 pct DEHPA, pH 3.0, and 24 h are shown. At 9 g/L Al^{3+}, an increase in temperature from 25° to 30° C doubles Al^{3+} transport rate from 20 to 40 $\mu g/(cm^2 \cdot h)$. Transport rate is doubled again by increasing temperature from 30° to 40° C. Of the four experimental variables, Al^{3+} transport rate was most sensitive to temperature. In figure 6, the effects of temperature and Al^{3+} concentration at 35 pct DEHPA, pH 2.5, and 24 h are shown. At low

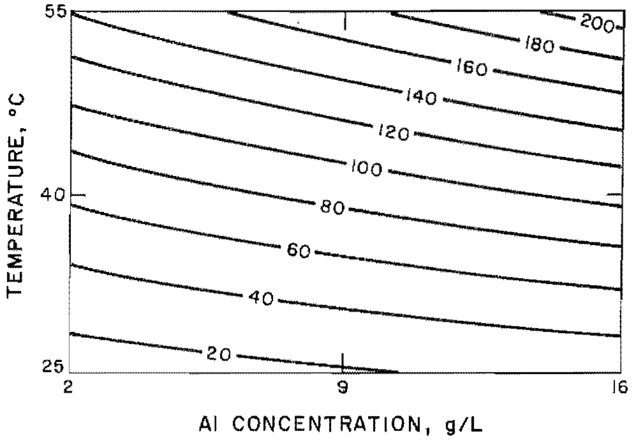

Figure 5.–Effects of temperature and aluminum concentration on aluminum transport rate using 65 pct DEHPA. Aluminum transport, micrograms per square centimeter per hour; DEHPA, 65 pct; pH, 3.0; time, 24 h.

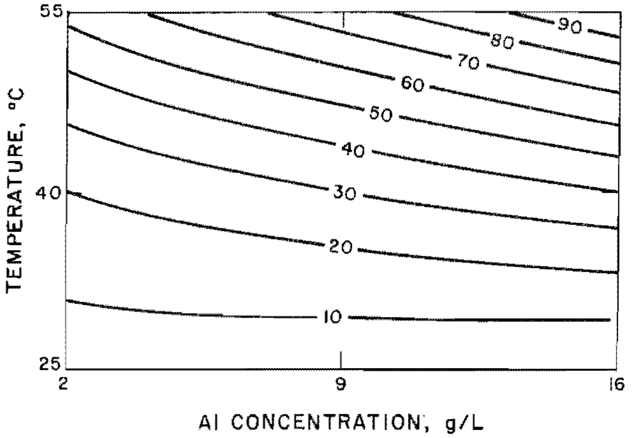

Figure 6.–Effects of temperature and aluminum concentration on aluminum transport rate using 35 pct DEHPA. Aluminum transport, micrograms per square centimeter per hour; DEHPA, 35 pct; pH, 2.5; time, 24 h.

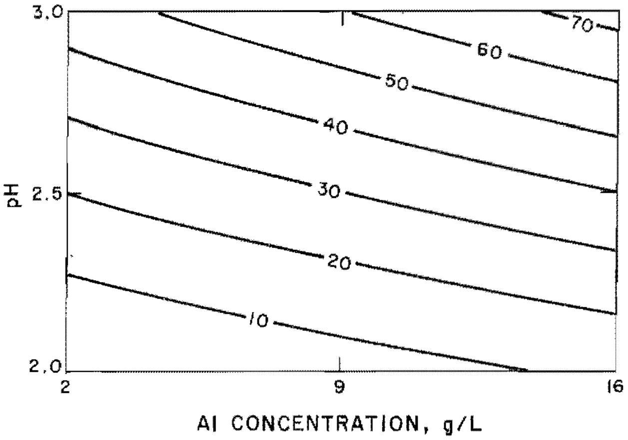

Figure 7.–Effects of feed solution pH and aluminum concentration on aluminum transport rate. Aluminum transport, micrograms per square centimeter per hour; DEHPA, 35 pct; temperature, 40° C; time, 24 h.

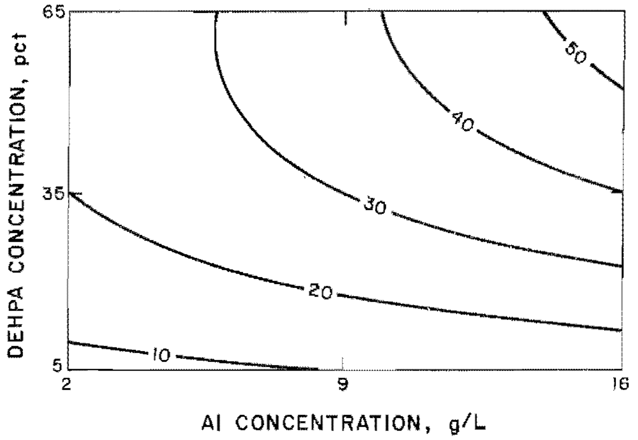

Figure 8.–Effects of DEHPA concentration and aluminum concentration on aluminum transport rate. Aluminum transport, micrograms per square centimeter per hour; pH, 2.5; temperature, 40° C; time, 24 h.

temperatures, the effect of Al^{3+} concentration are less than at higher temperatures. At 25° C, there is negligible change in transport rate when Al^{3+} concentration is increased from 2 to 16 g/L. At 55° C, the same increase in Al^{3+} concentration produces a 50-μg/(cm^2•h) increase in transport rate.

Figure 7 shows the influence of feed pH on Al^{3+} transport rate at 35 pct DEHPA, 40° C, and 24 h. A zero transport rate is predicted at pH 2 and 2 g/L Al^{3+}. Transport rate increases to 46 μg/(cm^2•h) at pH 3 and 2 g/L Al^{3+}. At 16 g/L Al^{3+}, transport rate increases from 12 μg/(cm^2•h) at pH 2 to 74 μg/(cm^2•h) at pH 3. Figure 7 demonstrates the importance of pH control in Al^{3+} transport rate. When metal ions are extracted by the membrane, H$^+$ is released into the feed solution. Unless the H$^+$ is neutralized, the pH of the feed solution will decrease to unacceptable levels for Al^{3+} transport.

The effects of DEHPA concentration and Al^{3+} concentration at pH 2.5, 40° C, and 24 h are illustrated in figure 8. At 9 g/L Al^{3+}, transport rate increases from 10 μg/(cm^2•h) at 5 pct DEHPA to 30 μg/(cm^2•h) at 35 pct DEHPA. When DEHPA concentration is increased from 35 to 65 pct, transport rate increases from 30 to 38 μg/(cm^2•h). The smaller net increase in transport rate, 8 μg/(cm^2•h), compared with 20 μg/(cm^2•h) from 5 to 35 pct DEHPA, is caused by increased viscosity of the organic phase. Increased DEHPA concentration results in more carriers for metal transport, but the movement of the carriers is slowed by increased viscosity. The interaction between DEHPA and Al^{3+} concentrations is also evident in figure 8. At 5 pct DEHPA, the increase in transport rate with increasing Al^{3+} concentration is less than at 65 pct DEHPA.

In figure 9, the degradation of the membrane with time is represented. The time effect is negative and linear. The difference between average Al^{3+} transport rate for 24 h compared with 96 h is 6 μg/(cm^2•h). At 9 g/L Al^{3+}, transport decreases from 30 μg/(cm^2•h) at 24 h to 24 μg/(cm^2•h) at 96 h. Another way of looking at it is that with the passage of time, more driving force, i.e., increased Al^{3+} concentration, is required to maintain a given transport rate. For 96 h, an Al^{3+} concentration of 13 g/L is required to achieve a transport rate of 30 μg/(cm^2•h), whereas the same transport rate can be achieved with 9 g/L Al^{3+} over 24 h.

Contour plots of Fe^{3+} transport rate are shown in figures 10 and 11. The effects of temperature and Al^{3+} concentration on Fe^{3+} transport rate at 35 pct DEHPA, pH 2.5, and 24 h are presented in figure 10. Temperature increases Fe^{3+} transport rate, while Al^{3+} concentration has the opposite effect. At 2 g/L Al^{3+}, Fe^{3+} transport rate increases from 25 μg/(cm^2•h) at 25° C to 107 μg/(cm^2•h) at 55° C. At 16 g/L Al^{3+}, transport rate increases from 21 μg/(cm^2•h) at 25° C to 39 μg/(cm^2•h) at 55° C. The membrane selectivity for Fe^{3+} is dependent on the Al^{3+} concentration in the feed solution and is also dependent on feed pH, as shown in figure 11. Of the four experimental variables, Fe^{3+} transport rate was most sensitive to pH, because of hydrolysis of the iron as pH increased. The decrease in the Fe^{3+} transport with an increase in temperature can be reversed by changing the pH from 3 to 2. The iron precipitate did not inhibit metal transport through the supported liquid membrane.

Copper ion transport rate as a function of temperature and Al^{3+} concentration at 35 pct DEHPA, pH 2.5, and 24 h (fig. 12) increases with decreasing Al^{3+} concentration and increasing temperature. Of the four experimental variables, Cu^{2+} transport rate was most sensitive to Al^{3+} concentration. A zero transport rate can be expected at Al^{3+} concentrations greater than 9 g/L Al. Figures 10 and 12 indicate that Al^{3+} concentration in the feed solution can be manipulated to achieve a desired selectivity level of Al^{3+} compared with Cu^{2+} and Fe^{3+}.

To check the metal transport rate models, tests were made on a simulated copper leaching liquor and three copper leaching solutions. Compositions of the feed solutions are listed in table 7. Measured and predicted metal transport rates are compared in table 8.

Table 7.–Composition of solutions used to test transport models, grams per liter

Solution	Al	Ca	Cu	Fe^{2+}	Fe^{3+}	Mg	Mn	Na	Zn
Simulated leaching solution	16	0	2	0	2	0	0	1	0
Cu plant solvent extraction feed	13	.5	.9	0	.6	12	3	.1	2
Cu plant solvent extraction raffinate	13	.5	.1	0	.7	12	3	.1	2
Cu cementation plant effluent	3.4	.4	.1	.8	.9	8	.3	.1	.3

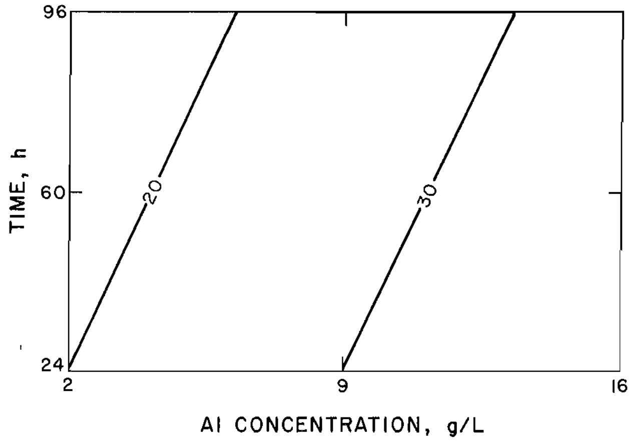

Figure 9.–Effects of time and aluminum concentration on aluminum transport rate. Aluminum transport, micrograms per square centimeter per hour; DEHPA, 35 pct; pH, 2.5; temperature, 40° C.

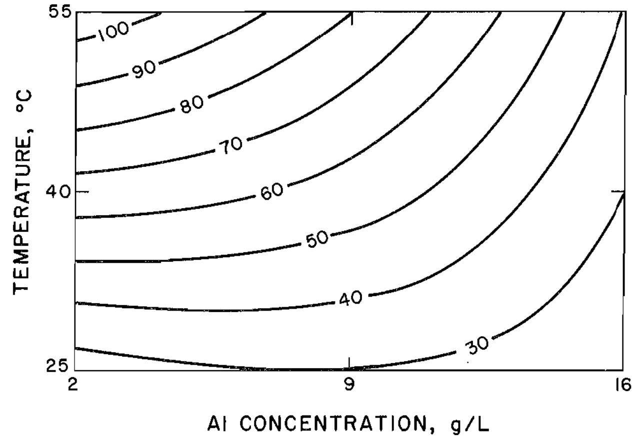

Figure 10.–Effects of temperature and aluminum concentration on iron transport rate. Iron transport, micrograms per square centimeter per hour; DEHPA, 35 pct; pH, 2.5; time, 24 h.

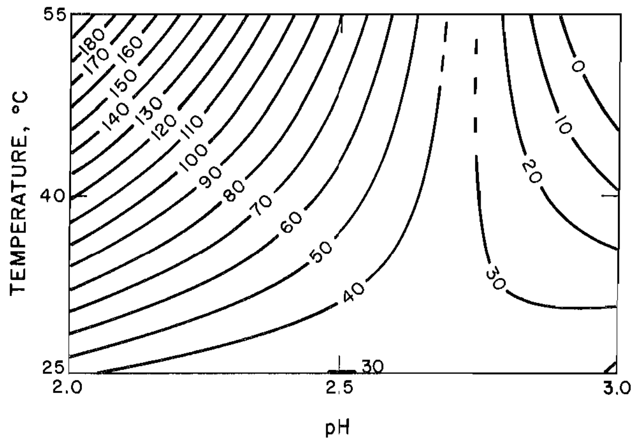

Figure 11.–Effects of temperature and feed solution pH on iron transport rate. Iron transport, micrograms per square centimeter per hour; DEHPA, 35 pct; aluminum concentration, 9 g/L; time, 24 h.

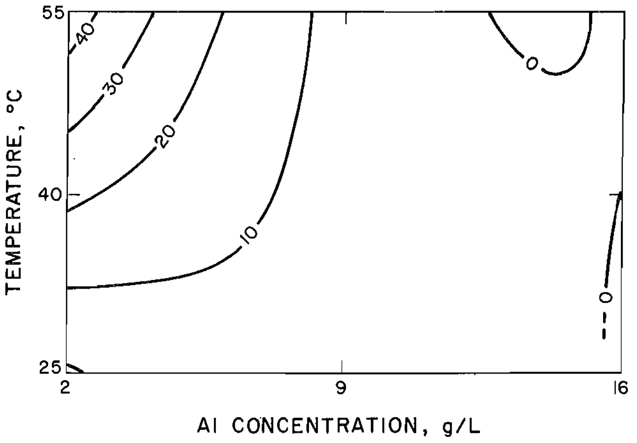

Figure 12.–Effects of temperature and aluminum concentration on copper transport rate. Copper transport, micrograms per square centimeter per hour; DEHPA, 35 pct; pH, 2.5; time, 24 h.

Table 8.–Comparison of measured versus predicted metal transport, micrograms per square centimeter per hour

	Measured			Predicted		
	24 h	72 h	96 h	24 h	72 h	96 h
Al:						
Simulated leaching solution	224	199	199	210±18	206±18	204±18
Cu plant solvent extraction feed	159	127	156	195±18	191±18	189±18
Cu plant solvent extraction raffinate	154	160	143	195±18	191±18	189±18
Cu cementation plant effluent	172	146	156	149±18	145±18	143±18
Fe:						
Simulated leaching solution	4	4	4	0	0	0
Cu plant solvent extraction feed	11	8	9	0	0	0
Cu plant solvent extraction raffinate	13	12	10	0	0	0
Cu cementation plant effluent	4	4	4	0	0	0
Cu:						
Simulated leaching solution	3	2	2	6	5	4
Cu plant solvent extraction feed	1	1	2	0	0	0
Cu plant solvent extraction raffinate	1	0	0	0	0	0
Cu cementation plant effluent	1	1	1	34±22	33±22	32±22

NOTE.–Ranges of predicted values are based on the 95-pct-confidence interval. Ranges yielding predictions of negative metal transport rates were set to zero because negative transport rates have no physical meaning.

Observed Al^{3+} transport rates from the simulated leaching solution and cementation solution were not statistically different from the predicted rates. In both cases, the observed transport rates were within the 95-pct-confidence intervals[7] associated with the predictions. The observed Al^{3+} transport rates from the copper plant feed and raffinate solutions were outside their respective 95-pct-confidence intervals and were statistically different from the predicted rates. Zinc transported from these solutions at rates of 80 to 195 $\mu g/(cm^2 \cdot h)$. The competition of Zn^{2+} with Al^{3+} for membrane sites explains the lower than expected Al^{3+} transport rates. Although zinc also transported from the cementation effluent, there was a smaller amount of Zn^{2+} in this solution than in the copper solvent extraction solutions.

Observed Fe^{3+} and Cu^{2+} transport rates for most of the tests were very low as predicted by the models. In the case of Cu^{2+} transport from the cementation effluent, high copper transport rates of 34, 33, and 32 $\mu g/(cm^2 \cdot h)$ were predicted for 24, 72, and 96 h, respectively. The predictions were based on the presence of 2 g/L Cu^{2+}. The cementation effluent contained 0.1 g/L Cu^{2+}, which explains the lower than predicted copper transport rates. Magnesium transport in the four tests ranged from 1 to 8 $\mu g/(cm^2 \cdot h)$.

SPARGING CRYSTALLIZATION AND CALCINATION

Having demonstrated that aluminum can be transferred from a copper leaching solution to an H_2SO_4 solution, tests were done to confirm that reduction-grade Al_2O_3 could be obtained. Crystallization tests were done on a simulated stripping solution containing 22 g/L Al^{3+} as aluminum sulfate in 6*N* H_2SO_4. Pure HCl gas was sparged into the solution to simulate known technology (*7*). The solution was sparged to HCl saturation of ~26 pct HCl and aluminum solubility decreased to 1.8 g/L. Analysis of the acid-washed solids averaged 3 pct sulfate.

To determine the source of sulfate contamination, additional tests were made with nitrogen to dilute the HCl. The dilution would slow crystal growth and minimize entrainment of mother liquor. Analysis of acid-washed crystals from these tests showed that the sulfate content had increased to more than 6 pct. Since entrainment of H_2SO_4 did not appear to be the source of sulfate contamination, crystallization of aluminum sulfate was considered. Tests were made on duplicate crystal slurry samples taken after 35 and 60 min. One of the samples taken at each time increment was allowed to equilibrate overnight in a constant temperature bath at 40° C. The other sample was filtered and washed immediately. Analysis of washed crystals showed sulfate contents of 2.8 pct after 35 min of sparging and 3.0 pct after 60 min for samples filtered immediately after collection. Sulfate content increased to 3.1 pct after 35 min and 3.4 pct after 60 min for samples equilibrated at 40° C prior to filtration and washing. The results indicated that aluminum sulfate was crystallizing, but at a slower rate than ACH, and that no practical method for avoiding sulfate contamination was possible.

Since the ACH product from crystallization must be calcined to Al_2O_3, tests were made to determine if sulfate could be removed during the calcination step. Calcination of ACH containing 0.74, 1.5, and 2.2 pct SO_3 as $Al_2(SO_4)_3 \cdot 18H_2O$ at 850° C lowered sulfate contamination to 0.33, 0.23, and 0.29 pct SO_3, respectively. Grinding and recalcination of samples did not lower the sulfate content. Calcination tests on ACH containing 2.4 pct SO_3 at 900°, 950°, and 1,000° C lowered SO_3 content in the product Al_2O_3 to 0.097, 0.090, and 0.097 pct, respectively. The target of less than 0.25 pct SO_3 in Al_2O_3 (*8*) was achieved by calcining ACH to Al_2O_3 at 900° C.

Other contaminants placed in the 6*N* H_2SO_4 stripping solution based on extraction tests using copper leaching

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[7] An interval that contains the population value of an estimate with 95-pct probability.

liquors were Cu^{2+}, Fe^{2+}, and Zn^{2+}. A crystallization test was made in which 0.1 g Cu^{2+}, 0.7 g Fe^{2+}, and 5.0 g/L Zn^{2+} as sulfates were added to simulate stripping acid compositions obtained during the model verification tests. Analysis of ACH crystals showed iron and zinc contamination, but copper was below reduction-grade specification [0.01 pct CuO (copper oxide) in Al_2O_3]. Iron contamination could be lowered to reduction-grade specifications [0.015 pct Fe_2O_3 (ferric oxide) in Al_2O_3] by washing with 36 pct HCl (*6*). Zinc contamination ranged from 0.021 to 0.062 pct ZnO (zinc oxide) in Al_2O_3 and was not affected by HCl washing. Reduction-grade specification is 0.02 pct ZnO. Since the presence of zinc in copper leaching liquors is a problem, carefully controlled sparging is required to meet zinc specifications.

PROPOSED RECOVERY PROCESS

Having demonstrated the individual unit operations for recovering Al_2O_3, consideration was given to their combination into a possible process flowsheet. The flowsheet was based on the use of calcium hydroxide [$Ca(OH)_2$] as a neutralizing agent even though bench-scale tests employed NaOH. $Ca(OH)_2$ would be more economical but is very difficult to use in small-scale tests. However, $Ca(OH)_2$ was used successfully in the earlier mixer-settler work (*1*). Sparging of H_2SO_4 stripping solutions converts $Al_2(SO_4)_3$ to $AlCl_3 \cdot 6H_2O$ (aluminum chloride hydrate) and H_2SO_4, which can be recycled to the stripping step. Recycle of the stripping acid would result in buildup of impurities, such as copper, iron, and zinc, which are not removed during sparging crystallization, and would necessitate a bleedstream. Since the system was not operated as a continuous process, no information was generated to determine the size of the bleedstream. Residual HCl would be removed from the recycled stripping acid by distillation (*7*). HCl consumed during crystallization of ACH would be recovered during calcination. Calculated mass balances based on a proposed flowsheet showed that the major reagent cost was lime consumed in maintaining the pH during aluminum transport. The consumption was 2.17 lb of $Ca(OH)_2$ for each pound of recovered Al_2O_3, representing a significant operating cost.

Treatment of 20,000 gal of copper leaching solutions per day was estimated to require 565,000 ft^2 of membrane support. The only available cost estimate, obtained by discussions with a representative of the manufacturers of Celgard membrane supports, was $300 per 25 ft^2 module. The capital investment required for 565,000 ft^2 of membrane support would therefore be $6,780,000.

CONCLUSIONS

Supported liquid membrane was successfully used to recover aluminum from copper leaching liquors, and conditions for minimizing coextraction of iron and copper were defined. However, the aluminum transport rate was slow. Transport rate could be improved by operation at higher temperatures, which probably would not be practical on a commercial scale. Under the best conditions evaluated for aluminum transport, a large amount of membrane surface area would be required. The cost of the membrane support would be a significant factor in the capital cost of a commercial operation. Magnesium coextraction and hydrolysis precipitation of iron were not important factors in liquid membrane separation. Zinc was identified as a potential Al_2O_3 contaminant.

The three unit operations–aluminum transport, sparging crystallization, and calcination–should enable most of the acid and chloride to be recovered. The major operating cost is lime consumed in maintaining the pH. Even though the production of Al_2O_3 from copper leaching solutions is possible, the high capital and operating costs for a supported liquid membrane system severely limit its potential for commercial application.

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APPENDIX.-BOX-BEHNKEN EXPERIMENTAL DESIGN

Statistical experimental designs are a useful tool for defining the effects of several independent variables on a dependent variable. These designs are particularly useful when the dependent variable is affected by interactions among the independent variables. Independent variables and their ranges define the factor space of the experimental design. By measuring the response of the dependent variable at predetermined locations of the factor space, the response surface of the dependent variable within the factor space can be estimated if no discontinuities occur. The Box-Behnken experimental design was selected for the purposes of this study *(11)*.[1]

A three-variable Box-Behnken design is shown in figure A-1 in matrix and geometric form. Three equally spaced levels of each variable are chosen so that the variable ranges of interest are enclosed. The variable levels are normalized to -1, 0, and +1 using the equation

$$\text{normalized level} = \frac{(\text{variable level - middle level})}{(\text{high level - low level})/2}.$$

Normalization is used for convenience and to simplify calculations in regression analysis. In matrix form, each row corresponds to an experimental run. Geometrically, the experimental runs of the design are the center points of the edges of a cube whose dimensions are defined by the variable ranges and a replicate point at the center of the cube. Three replicates at center point experimental conditions are used to estimate experimental error. Least squares regression analysis of the experimental results yields polynomial models of the form

$$\hat{Y} = (\text{constant}) + \begin{pmatrix}\text{linear}\\ \text{effects}\end{pmatrix} + \begin{pmatrix}\text{interaction}\\ \text{effects}\end{pmatrix} + \begin{pmatrix}\text{nonlinear}\\ \text{effects}\end{pmatrix}$$

$$= b_o + \sum^{p} b_i X_i + \sum^{p} b_{ij} X_i X_j + \sum^{p} b_{ii} X_i^2,$$

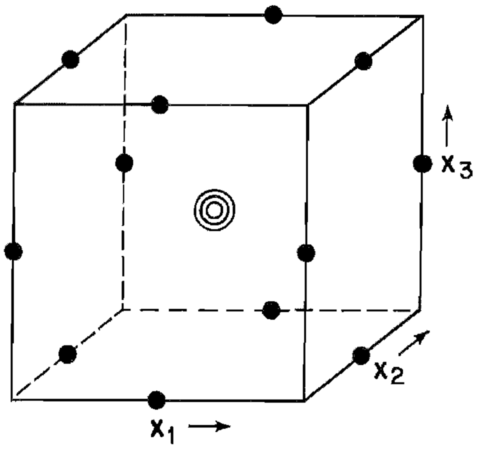
where $\hat{Y}$ = predicted response,

X_i or X_j = normalized level of variable,

p = number of experimental variables,

and b = coefficients of model.

The coefficients represent the effects that the experimental variables have on the response. When the polynomial models are plotted, the effects of the independent variables on the dependent variable are more easily viewed. Box-Behnken designs having more than three experimental variables have the same geometry as the three-variable design but encompass multidimensional space.



Experimental sets of normalized variables

X_1	X_2	X_3	
+1	+1	0	
+1	-1	0	
-1	+1	0	
-1	-1	0	
+1	0	+1	
+1	0	-1	
-1	0	+1	
-1	0	-1	
0	+1	+1	
0	+1	-1	
0	-1	+1	
0	-1	-1	
0	0	0	Center point
0	0	0	
0	0	0	

Figure A-1.-Box-Behnken experimental design.

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[1] Italic number in parentheses refer to items in the list of references preceding the appendix.

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