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SUPPORTED LIQUID MEMBRANE SEPARATION OF ALUMINUM FROM COPPER LEACHING LIQUORS

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ABSTRACT

The Bureau of Mines, U.S. Department of the Interior, 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 concentrations, were measured using 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.

INTRODUCTION

An important application of separation technology in the metals industry is to recover metals from leaching solutions. One technique receiving increased attention is solvent extraction. The technique has evolved from an analytical procedure, through use under specialized conditions, to consideration as an industrial unit operation. One of the disadvantages of solvent extraction is the need to mix and separate two immiscible phases. This leads to losses of expensive extractants due to aqueous-phase entrainment and emulsion or crud formation. Crud formation is a major problem when treating turbid solutions (1). When the extractant phase becomes saturated with metal salts, mass transport also decreases.

A new separation method, which could alleviate some of the disadvantages of solvent extraction, is the use of supported liquid membranes (2-3). The method employs a microporous, hydrophobic membrane that can be impregnated with an extractant solution. Metal ions or salts are extracted at one membrane surface, transported through the membrane by the extractant solution, and released to a stripping solution. If the extractant is a cation exchanger, protons are transported in the reverse direction. No mixing of immiscible phases occurs and the extractant is continually regenerated, avoiding decreased mass transport.

The Bureau of Mines investigated the supported liquid membrane technique for recovering aluminum from copper leaching solutions, which contain up to 15 g aluminum per liter and represent more than 2,000 short tons of alumina per day (4). Previous research on recovering the aluminum used solvent extraction and ion exchange methods. Solvent extraction, using monododecyl phosphoric acid, successfully recovered an alumina product, but the need to maintain pH control necessitated additions of base to the circuit. To minimize reagent costs lime was added, resulting in formation of a gypsum precipitate. Traps were designed in the settling chambers to remove the gypsum, but crud formation was a major problem (4). The ion-exchange method also recovered aluminum, but yielded low loading of aluminum on the resin and poor selectivity. Stripping solutions contained aluminum, iron, and magnesium (5).

MATERIALS AND PROCEDURES

All research was performed with an extractant solution of di(2-ethylhexyl) phosphoric acid (DEHPA) in kerosene and a polypropylene support having a 0.02-µm pore size, 38-pct porosity, and 25-µm thickness. Metal transport rates were measured by suspending tubes of stripping acid contained by the supported liquid membrane in reservoirs of the test solution. A four-variable Box-Behnken experimental design (6) was made on simulated leaching solutions to model metal-ion transport rates. Verification tests were conducted on actual copper leaching solutions to test the validity of the

TABLE 1. - Variables used in four-variable tests

Variable		Levels		
		-1	0	+1
X_1	Vol pct DEHPA in Escaid 200[1]..	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]Reference to specific products does not imply endorsement by the Bureau of Mines.

models. The supported liquid membrane, experimental design, and the range of variables investigaated are discussed in detail in reference 7.

RESULTS AND DISCUSSION

The variables evaluated for their effects on metal-ion transport rates (table 1) were selected as a result of screening experiments (7). Results from the experimental design were subjected to regression analysis to develop models for metal-ion transport rates. A time factor was included by taking samples after 24, 72, and 96 h, and the three sets of data points incorporated in the regression analysis. Although the experiments were designed to measure aluminum transport rates, models were also derived for copper and iron. The models for metal-ion transport rate (table 2) demonstrate that all four of the variables influence the transport rate. Statistical evaluation of precision for the models (table 3) indicates good predictability for aluminum and slightly less accurate predictability for copper and iron.

Temperature had the greatest influence on aluminum-ion transport rate. A convenient method for evaluating its influence is to plot contours of aluminum-ion transport rate versus concentration of aluminum in the leaching solution at constant pH, DEHPA concentration, and time. Inspection of the plot for 65 pct DEHPA, pH 3.0, and 24 h (fig. 1) shows that 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. Temperature has a similar influence at all Al^{3+} concentrations between 2 and 16 g/L.

Figure 2 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 $\mu g/(cm^2 \cdot h)$ at pH 3 and 2 g/L Al^{3+}. At 16 g/L Al^{3+}, transport rate increases from 12 $\mu g/(cm^2 \cdot h)$ at pH 2 to 74 $\mu g/(cm^2 \cdot h)$ at pH 3.

TABLE 2. - Metal-ion transport models

Metal	Model[1]	Significance of coefficient[2]
Al....	$Y = 27$	.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....	$Y = 55$	.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....	$Y = 6$	.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

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[1] Y: Predicted transport rate in micrograms per square centimeter per hour.

X_i: Normalized level of variable.

T: Normalized time factor.

[2] Significance: A statistical measure of importance. The smaller the significance, the less likely the variation was due to random error.

TABLE 3. - Statistical measurements of precision of metal transport models

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

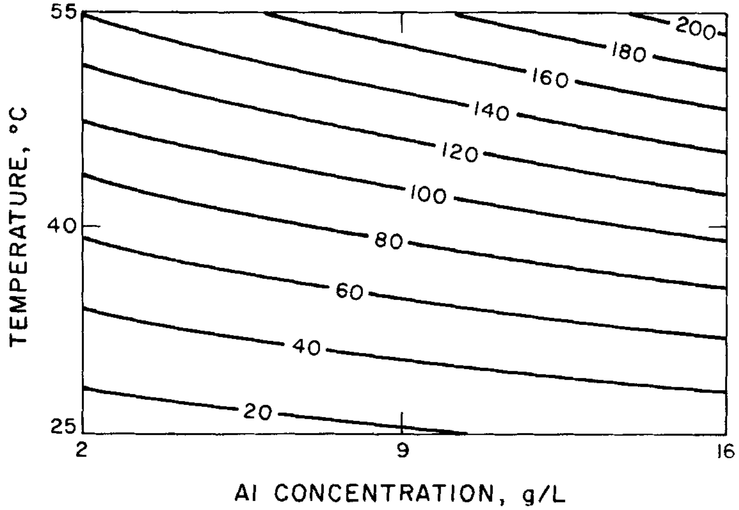

Fig. 1. Effect of temperature and aluminum concentration on aluminum transport rate using 65-pct DEHPA, pH 3.0, and 24 h. Contour lines are transport rate in micrograms per square centimeter per hour.

Figure 2 demonstrates the importance of pH control in Al^{3+} transport rate. When metal ions are extracted by the membrane, H^+ ions are released into the feed solution. Unless the H^+ ions are neutralized, the pH of the feed solution will decrease to unacceptable levels for Al^{3+} transport.

The effect of DEHPA concentration and Al^{3+} concentration at pH 2.5, 40° C, and 24 h is illustrated in figure 3. At 9 g/L Al^{3+}, transport rate increases from 10 µg/(cm²•h) at 5 pct DEHPA to 30 µg/(cm²•h) at 35 pct DEHPA. When DEHPA concentration is increased from 35 to 65 pct, transport rate increases from 30 to 38 µg/(cm²•h). The smaller net increase in transport rate,

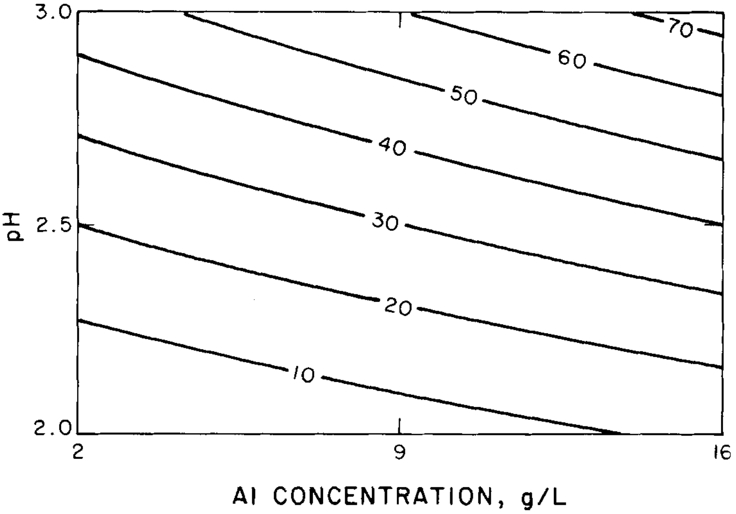

Fig. 2. Effect of pH and aluminum concentration on aluminum transport rate at 35-pct DEHPA, 40° C, and 24 h. Contour lines are transport rate in micrograms per square centimeter per hour.

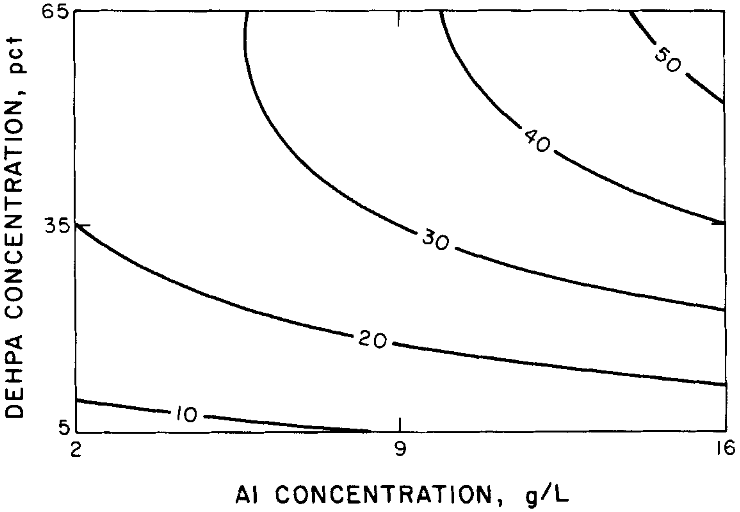

Fig. 3. Effect of DEHPA concentration and aluminum concentration on aluminum transport rate at pH 2.5, 40° C, and 24 h. Contour lines are transport rate in micrograms per square centimeter per hour.

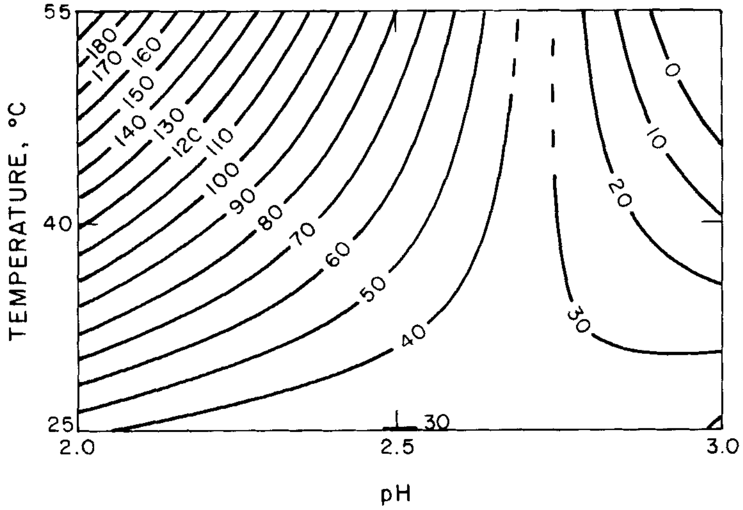

Fig. 4. Effect of temperature and pH on iron transport rate at 9 g/L Al^{3+}, 35-pct DEHPA, 25° C, and 24 h. Contour lines are transport rate in micrograms per square centimeter per hour.

8 $\mu g/(cm^2 \cdot h)$, compared to 20 $\mu g/(cm^2 \cdot h)$ 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 importance of pH and temperature on minimizing iron transport is demonstrated in figure 4. At 9 g/L Al^{3+}, 35 pct DEHPA, 24 h, and 25° C, iron transport rate is 30 to 40 $\mu g/(cm^2 \cdot h)$ over the pH range 2.0 to 3.0. At pH 2.0, however, iron transport rate increases from 40 to 200 $\mu g/(cm^2 \cdot h)$ as temperature increases from 25° to 55° C. At pH 3.0, iron transport decreases with increasing temperature from 40 $\mu g/(cm^2 \cdot h)$ at 25° C to 0 at 45° C. The change in behavior of iron is due to hydrolysis precipitation at higher temperature and pH. Iron precipitates did not adhere to the supported liquid membrane, and there was no evidence of inhibition of metal-ion transport rates.

Copper-ion transport rate as a function of temperature and Al^{3+} concentration at 35 pct DEHPA, pH 2.5, and 24 h (fig. 5) shows that transport rate 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

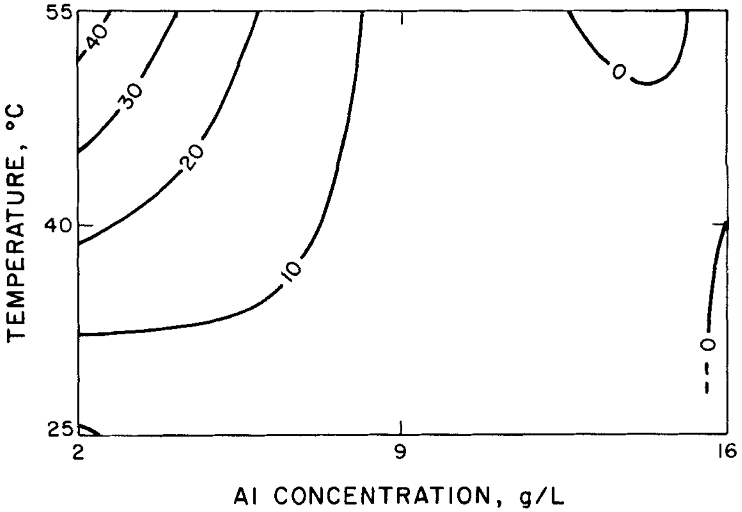

Fig. 5. Effect of temperature and aluminum concentration on copper transport rate at 35-pct DEHPA, pH 2.5, and 24 h. Contour lines are transport rate in micrograms per square centimeter per hour.

than 9 g/L Al^{3+}. A minimal Al^{3+} concentration in the feed solution must be maintained to achieve a desired selectivity level of Al^{3+} compared to Cu^{2+}.

Al^{3+} and Cu^{2+} transport rates were influenced by time. The effect was linear, caused decreasing transport and indicated degradation of the supported liquid membrane. A test was made in a tube and shell flow-through cell. The supported liquid membrane contained 25 vol-pct DEHPA in kerosene. The simulated leaching solution contained 16 g/L Al^{3+}, 1 g/L Cu^{2+}, and 2.5 g/L Fe^{2+} at pH 2.9 and ambient temperature. The stripping solution was $6\underline{N}$ H_2SO_4. Transport rate for Al^{3+} decreased with time. The influence on Cu^{2+} transport rate was not apparent owing to its low transport rate under test conditions. There was no influence on Fe^{2+} transport rate as predicted by the model (table 2). After 188 h the supported liquid membrane was removed and reimpregnated with extractant solution. The treatment rejuvenated Al^{3+} transport rate, indicating that membrane degradation was due to loss of extractant solution rather than deterioration of the membrane support or plugging of the pores.

To check the rate models for metal transport, tests were made on a simulated copper leaching liquor and three copper leaching

TABLE 4. - 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	0	2.0	0	0	1.0	0
Copper plant solvent extraction feed............	13	.5	.9	0	.6	12	3	.1	2
Copper plant solvent extraction raffinate........	13	.5	.1	0	.7	12	3	.1	2
Cementation plant effluent...	3.4	.4	.1	.8	.9	8	.3	.1	.3

TABLE 5. - 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
Aluminum:						
Simulated leaching solution.............	224	199	199	210±18	206±18	204±18
Copper plant solvent extraction feed.......	159	127	156	195±18	191±18	189±18
Copper plant solvent extraction raffinate..	154	160	143	195±18	191±18	189±18
Copper cementation plant effluent........	172	146	156	149±18	145±18	143±18
Iron:						
Simulated leaching solution.............	4	4	4	0	0	0
Copper plant solvent extraction feed.......	11	8	9	0	0	0
Copper plant solvent extraction raffinate..	13	12	10	0	0	0
Copper cementation plant effluent........	4	4	4	0	0	0
Copper:						
Simulated leaching solution.............	3	2	2	6	5	4
Copper plant solvent extraction feed.......	1	1	2	0	0	0
Copper plant solvent extraction raffinate..	1	0	0	0	0	0
Copper 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.

solutions. Composition of the feed solution is listed in table 4. Measured and predicted metal transport rates are compared in table 5. 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 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^{2+} and Cu^{2+} transport rates for most of the tests, as predicted by the models, were very low. In the case of Cu^{2+} transport from the cementation effluent, Cu 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 Cu transport rates. Magnesium transport in the four tests ranged from 1 to 8 $\mu g/(cm^2 \cdot h)$.

SUMMARY AND CONCLUSIONS

Aluminum can be recovered from copper leaching solutions by using a supported liquid membrane. Operating conditions that yielded the highest Al^{3+} transport rates provided the best selectivity. Formation of fine precipitates in feed solutions due to hydrolysis of Fe^{3+} did not interfere with the extraction system. Models for metal-ion transport rates gave good predictions of measured transport rates when test conditions were within the range of the experimental design. Since deviations from the range of the experimental design, such as the presence of competing extractable species or exceeding the designed limits of test variables, led to inaccurate predictions, care must be taken in choosing the conditions for the experimental design.

Although use of a supported liquid membrane was successful, certain weaknesses were apparent when viewed as a potential commercial unit operation. The best Al^{3+} transport rate of 210 $\mu g/(cm^2 \cdot h)$ would require large areas of membrane support that represent a large capital investment. Loss of extractant solution from the supported liquid membrane necessitates periodic regeneration and contingent labor costs. Improved retention of the extractant solution by the membane support and decreased cost of the membrane support would enhance the potential of the separation technique as a commercial unit operation.

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