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Iron Extraction From Simulated Aluminum Nitrate Leach Liquor

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UNITED STATES DEPARTMENT OF THE INTERIOR

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IRON EXTRACTION FROM SIMULATED ALUMINUM NITRATE LEACH LIQUOR

by

J. A. Eisele,[1] F. R. Smith,[2] and D. J. Bauer[1]

ABSTRACT

As part of its goal of maintaining an adequate supply of minerals to meet national economic and strategic needs, the Bureau of Mines has studied the removal of iron from simulated aluminum nitrate leach liquors by solvent extraction. Iron must be removed from aluminum nitrate liquor produced by leaching calcined kaolinitic clay with HNO_3 to reduce the iron level in alumina to less than 0.02 wt-pct Fe_2O_3 for use in reduction cells. The parameters reported are for (1) extracting iron from a feed containing 1.5 g/l Fe with di(2-ethylhexyl) phosphoric acid (EHPA), (2) stripping loaded organic phase with 20-pct HCl, and (3) water washing of loaded and stripped organic phase. Recommended operating conditions are two extraction stages using 15 vol-pct EHPA in kerosene and three stripping stages using 20-pct HCl. Results are also given for tests using other extractants and stripping agents.

INTRODUCTION

Alumina intended for feed to electrolytic cells to produce aluminum metal is made in the United States from bauxite by the Bayer process. The United States is currently dependent on bauxite imports. The need for a domestic source of alumina as feedstock to aluminum smelting and rising bauxite prices made it desirable to develop technology for production of alumina from domestic source materials. In 1973, the Bureau of Mines initiated research to study the recovery of alumina from domestic resources.

The United States has large reserves of kaolinitic clay that cannot be treated by the Bayer process because of its high silica content. Much work has been done to develop processes to produce high-purity alumina from these domestic clay resources. The alumina content can be leached from calcined kaolin with any of the strong mineral acids. However, a problem associated with any acid process is that iron present in the clay is also extracted by the acid, and unless the iron is separated from the aluminum, the product alumina will not be of an acceptable purity. To meet specifications for cell-grade alumina, the iron content must be less than 0.02 wt-pct ferric oxide (Fe_2O_3).

In a proposed clay-nitric acid (HNO_3) process, calcined kaolin is leached with HNO_3 to dissolve the alumina. Two approaches have been taken to control the level of iron in leach liquor. In one approach, less than a stoichiometric amount of HNO_3 is used for

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leaching (6).[3] Under these conditions iron is less soluble than aluminum and is rejected with the tailings; however, some aluminum is also rejected. The second approach is to leach calcined clay with a slight excess of HNO_3 and remove dissolved iron from the leach liquor by solvent extraction (1, 5). In either case, the purified aluminum nitrate ($Al(NO_3)_3$ liquor is evaporated to crystallize out the hydrated aluminum nitrate. Aluminum oxide (Al_3O_3) and HNO_3 are recovered by thermal decomposition.

This report describes investigations by the Bureau of Mines on the removal of iron from aluminum nitrate solution by solvent extraction. Previous Bureau reports described removal of iron from aluminum chloride and aluminum sulfate liquors (4, 8).

MATERIALS, EQUIPMENT, AND PROCEDURES

Solvent-extraction experiments were conducted on a solution whose composition simulated leach liquor obtained when low-iron (1.0 wt-pct Fe_2O_3) calcined kaolin is leached with HNO_3. Using distilled water 849 g $Al(NO_3)_3 \cdot 9H_2O$, 10.9 g $Fe(NO_3)_3 \cdot 9H_2O$, and 15 ml of 15.4M HNO_3 were diluted to 1 liter. This gave a solution containing 61 g/l Al, 1.5 g/l Fe, and 15 g/l HNO_3; the density of the solution was 1.35 g/ml.

The extractants examined in this study are commercially available and representatives of common extractant classes are included, as shown in table 1. The extractants were used without further purification and diluted with kerosene to the desired volume-percent.

TABLE 1. - Extractants tested for iron removal

Extractant[1]	Class
Di(2-ethylhexyl)phosphoric acid (EHPA)	Acid organophosphate.
Tributyl phosphate (TBP).............	Neutral organophosphate.
Primene JMT..........................	Primary amine.
Amberlite LA-2.......................	Secondary amine.
Alamine 336..........................	Tertiary amine.
Aliquat 336..........................	Quaternary amine.
Kelex 120............................	Chelating extractant.
LIX 64N..............................	Do.

[1] Reference to specific brands or companies is for identification only and does not imply endorsement by the Bureau of Mines.

Table 2 lists the chemicals tested as possible stripping agents. All chemicals used were reagent grade.

TABLE 2. - Stripping agents tested

Stripping agent	Solution, pct	Stripping agent	Solution, pct	Stripping agent	Solution, pct
HNO_3..........	(1)	NH_4NO_3........	20	$NH_4H_2PO_4$......	20
HCl...........	20	$(NH_4)_2CO_3 \cdot H_2O$.	20	Na_3PO_4........	20
H_3PO_4.........	(1)	NH_4HCO_3.......	20	$(NH_2OH)_2 \cdot H_2SO_4$	[2]NAp
H_2SiF_6........	30	NH_4Cl.........	20	HCOOH.........	[2]NAp
H_2O...........	NAp	$(NH_4)_2HPO_4$....	20	HCHO..........	[2]NAp
$NaNO_3$.........	20				

NAp Not applicable. [1] Various. [2] In HNO_3.

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

Separatory funnels were used to contact portions of organic and aqueous feeds by shaking. Contact time was 60 sec. Experiments were conducted at room temperature. The extract and raffinate were analyzed for iron by counting ^{59}Fe radioactive tracer that had been added to the aqueous feed. Some samples were also analyzed for iron by titration.

When the organic phase was to be analyzed for aluminum content, it was first put through phase-separating paper to remove entrained aqueous feed. Aluminum analyses were performed by atomic absorption spectroscopy. The organic phase was put through phase-separating paper before equilibrium-curve data were generated for water washing of loaded and stripped organic phase. After contact and separation from the organic phase, the water washes were analyzed for nitrate or chloride by specification electrodes.

RESULTS AND DISCUSSION

Iron Extraction

EHPA was the only extractant to significantly extract iron; all others extracted less than 5 pct of the iron in a single contact. For example, TBP, which is known to be a good extractant from nitrate media, was ineffective (9). Even after the aluminum nitrate solution was strongly acidified with HNO_3, a condition where TBP was expected to extract iron, it did not. All further studies were conducted with EHPA.

Data for equilibrium curves were obtained by contacting organic and aqueous feed at various phase ratios. Curves obtained for 30 and 15 vol-pct EHPA in kerosene are shown in figure 1. The data show that 30 and 15 vol-pct EHPA have loading capacities of 22 and 11 g/l iron, respectively. Extraction conducted at a phase ratio of 1:6 (organic-to-aqueous) and using two stages produced an organic phase containing 9 g/l iron and an aqueous phase containing less than 0.2 g/l iron. Use of 30 vol-pct EHPA to extract iron from a 1.5-g/l-iron solution is inefficient since less than half its capacity is utilized at phase ratios lower than 1:7. When using mixer-settler equipment, it is difficult to run at phase ratios much above 1:6 since good phase separation of the minor phase is hard to achieve. Therefore, operation at high phase ratios is undesirable. If clay with a higher iron content were to be leached to produce leach liquors with higher iron concentrations, 30 vol-pct EHPA would be useful. The 15 vol-pct EHPA was adequate for removing iron from an aluminum nitrate solution containing 1.5 g/l iron.

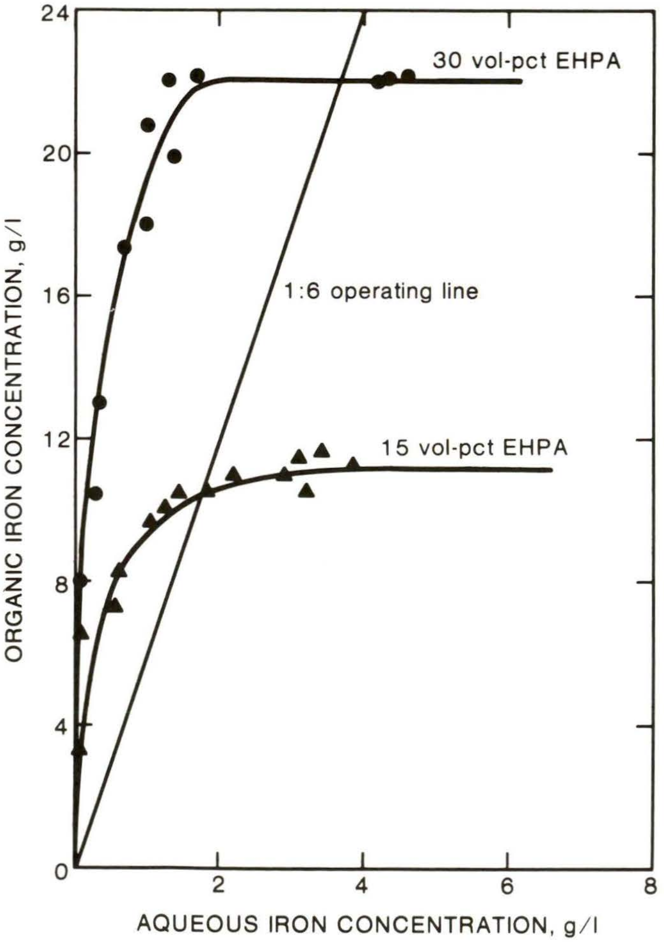

FIGURE 1. - Equilibrium extraction curves for iron extraction from aluminum nitrate liquor using 30 and 15 vol-pct EHPA.

Stripping Iron From Loaded Organic Phase

The ideal stripping agent for iron-loaded organic phase would be HNO_3 since small amounts of entrainment would not result in cross contamination between feed and strip solutions. Unfortunately, HNO_3 did not strip iron from the loaded organic phase.

HCl, H_3PO_4, $(NH_4)_2HPO_4$, NH_4HCO_3, and $(NH_4)_2CO_3$ stripped significant amounts of iron from the organic phase in a single contact; however, when $(NH_4)_2HPO_4$, NH_4HCO_3 and $(NH_4)_2CO_3$ were used, a precipitate formed in the aqueous phase, rendering them unsuitable as stripping agents.

The ability of HCl to strip iron from the iron-loaded organic phase was examined further. Figure 2 shows the equilibrium curves for stripping iron from 30 and 15 vol-pct EHPA with 20-pct HCl. Since HCl is an efficient stripping agent, it was possible to remove most of the iron from the organic phase at high phase ratios of organic to aqueous. Using 15 vol-pct EHPA a phase ratio as high as 6:1 can be used and most of the iron was stripped in three stages. Thirty volume-percent EHPA is not likely to be used unless it were to be loaded with more than 9 g/l iron. Based on figure 2, a phase ratio of 3:1 or lower is needed to strip a 30 vol-pct EHPA organic phase that contains more than 9 g/l iron. The resulting strip liquor will be less concentrated in iron than the strip liquor from 15 vol-pct EHPA, which will contain 54 g/l iron. Since the iron concentration should be as high as possible in the strip liquor to facilitate further processing, it is desirable to operate at high phase ratios.

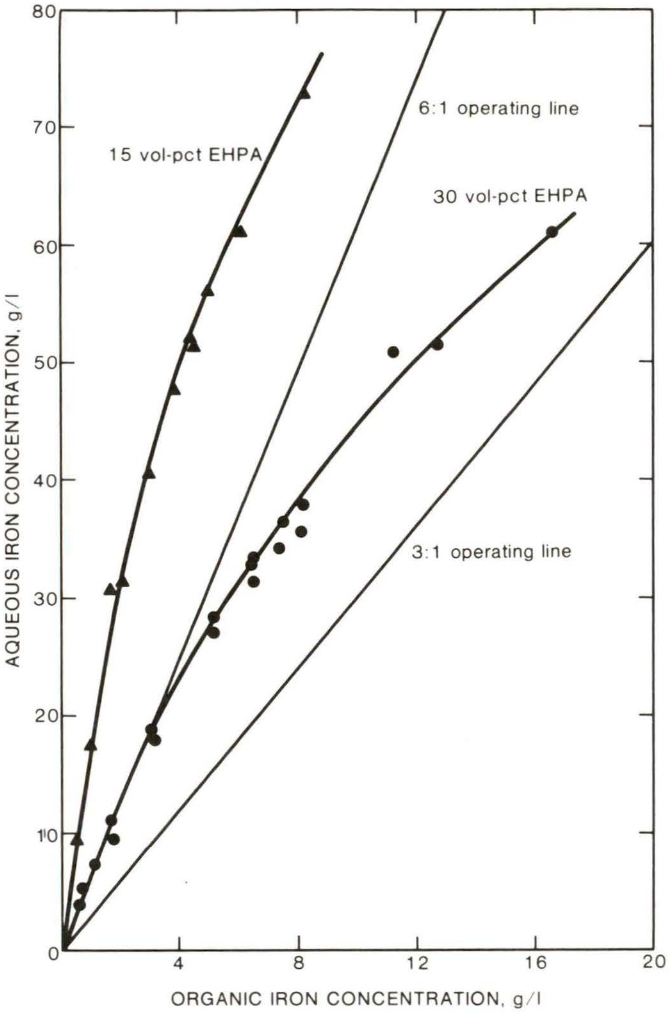

FIGURE 2. - Equilibrium stripping curves for stripping iron-loading EHPA with 20-pct HCl.

Figure 3 shows the equilibrium curves for stripping iron-loaded 30 vol-pct EHPA with various concentrations of H_3PO_4 as stripping agents, 5- and 10-pct H_3PO_4 are not effective. At a phase ratio of 6:1, 25-pct H_3PO_4 can be used for stripping, but 2 to 3 g/l iron will remain in the organic phase. At the same phase ratio, 50-pct H_3PO_4 can be used to strip an organic phase containing more than 9 g/l iron. The iron will be removed in three stages. Therefore, if 30 vol-pct EHPA is used to extract iron from aluminum nitrate liquor, 50-pct H_3PO_4 will be a better stripping agent than 20-pct HCl.

Water Washing

The use of aqueous HCl for stripping requires two water-washing steps to prevent carryover of anions by the organic phase. The iron-loaded organic phase contains 6 g/l nitrate ions, which will enter the HCl strip solution unless first washed out. Figure 4 is the equilibrium curve for nitrate removal from the loaded organic phase. A phase ratio of 3:1 is

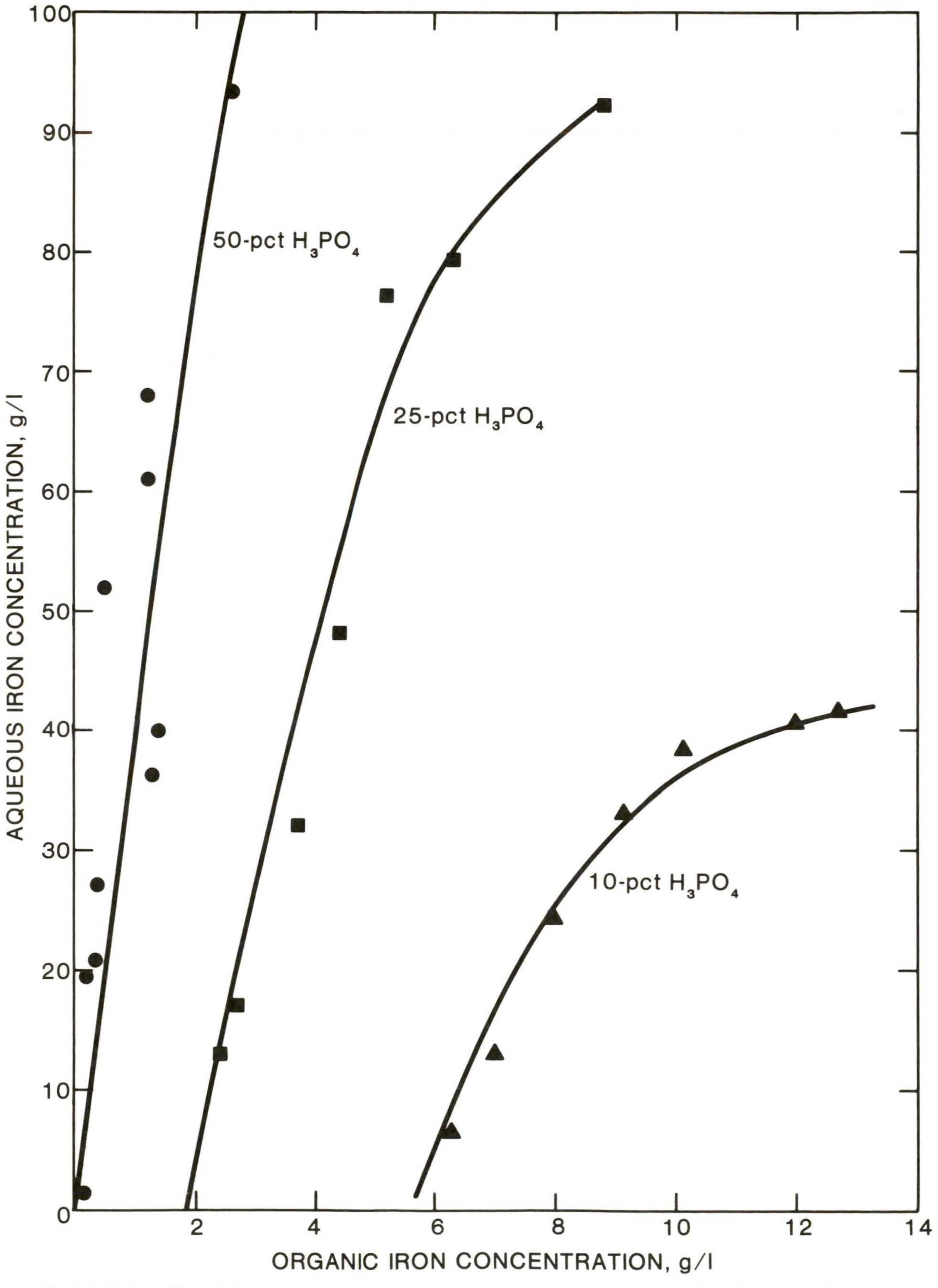

FIGURE 3. - Equilibrium stripping curves for stripping iron-loaded 30 vol-pct EHPA with various concentrations of H_3PO_4.

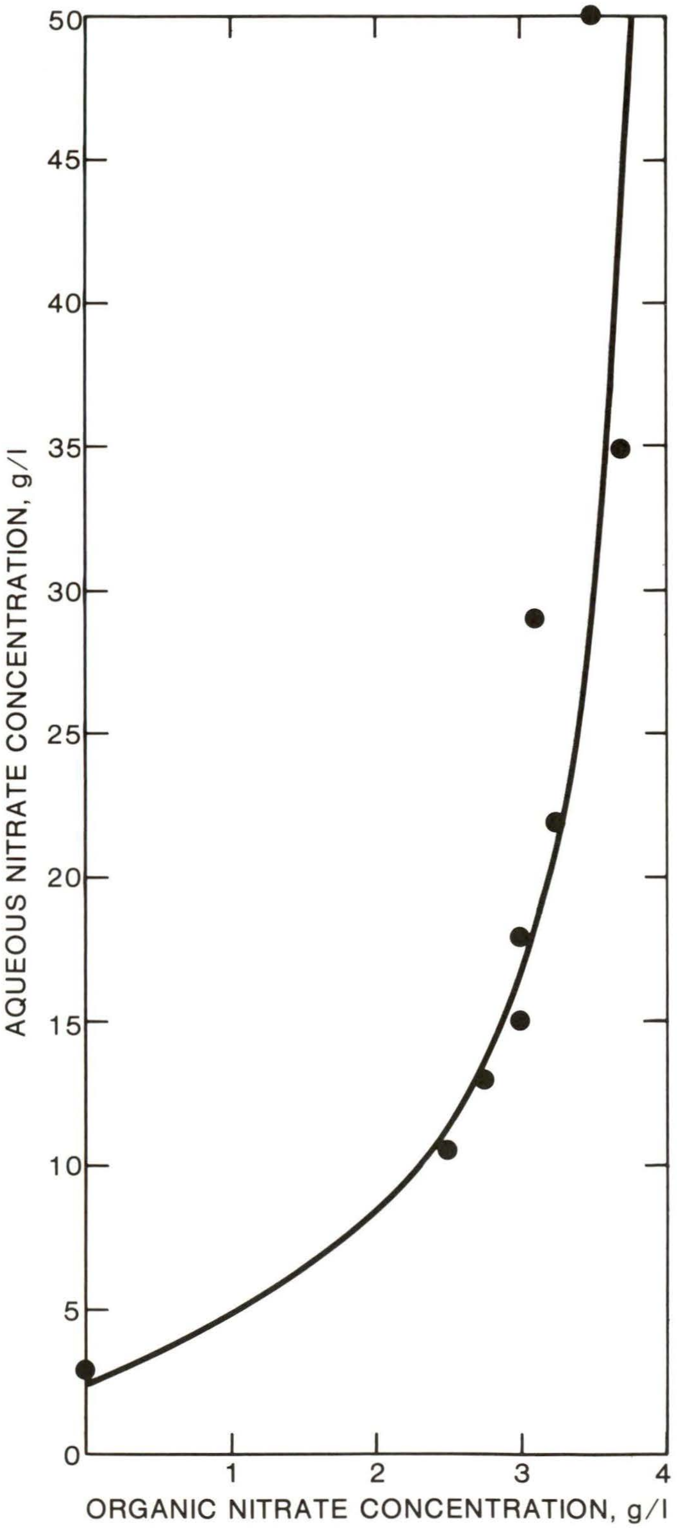

FIGURE 4. - Equilibrium washing curve for water washing iron-loaded 15 vol-pct EHPA to remove nitrate.

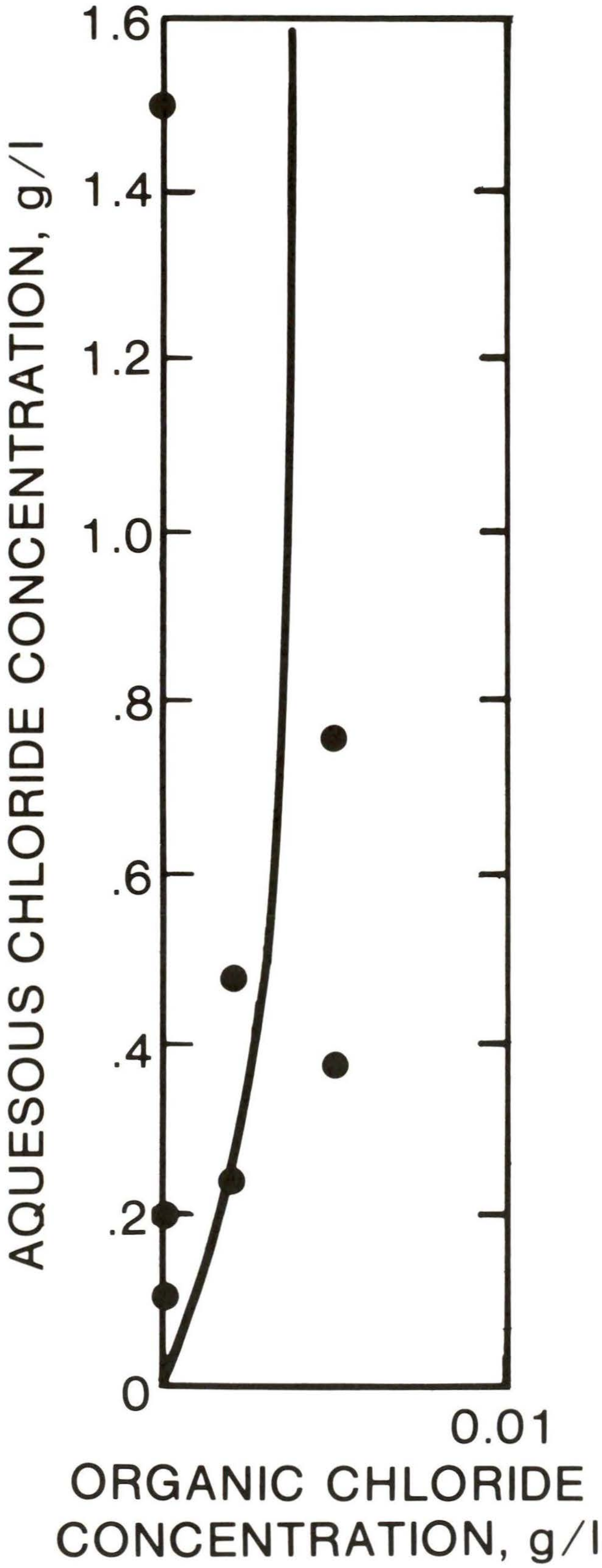

FIGURE 5. - Equilibrium washing curve for water washing stripped 15 vol-pct EHPA to remove chloride.

the highest that can be used. Operations at this phase ratio will require five to six stages to wash all nitrate out of the organic phase; concentration of the wash solution will be 18 g/l nitrate. The volume of the nitrate wash solution will be one-eighteenth of the volume of the incoming leach liquor for solvent extraction.

Chloride must be removed from the stripped organic phase before it contacts fresh aluminum nitrate feed or chloride will enter the nitrate solution. Figure 5 presents the equilibrium curve for washing chloride out of 15 vol-pct EHPA that has been stripped of its iron content with HCl. The steep slope of the curve means that a very high phase ratio can be used for washing. In a mixer-settler, the phase-ratio limit is physically about 6:1; however, this limitation can be overcome by recycling the strip solution until the desired concentration is built up. Even though the concentration of chloride in the stripped organic phase is only 0.05 g/l chloride, it should be possible to build up the concentration to 1 to 2 g/l chloride in the final wash solution.

Coextraction of Aluminum

The first water wash to remove nitrate from the loaded organic phase and the HCl strip solution were analyzed to determine if aluminum was being extracted and washed and/or stripped.

Only the HCl strip represents a potential loss of aluminum since the nitrate wash would be returned to the circuit. Analyses showed that 0.1 pct of the aluminum in the aluminum nitrate feed reported to the water wash and less than 0.01 pct reported to the HCl strip solution, indicating that aluminum loss from the circuit should be virtually nil.

DISPOSITION OF EFFLUENT STREAMS

The aqueous effluent from the extraction circuit is the purified aluminum nitrate solution that is crystallized for aluminum recovery.

The first water wash containing around 20 g/l NO_3 can be utilized as part of the wash solution for the leached clay residue, and thus can be returned to the circuit.

The HCl-ferric chloride ($FeCl_3$) strip liquor, which will contain around 50 g/l iron, could be handled in two ways. One way would be to evaporate the solution to concentrate its $FeCl_3$ content and expel free HCl for recycle. Thirty-percent-$FeCl_3$ solution can be marketed as a flocculant for water treatment plants (2). The other way would be to spray-roast the solution to recovery Fe_2O_3 and HCl for recycle. Technology already exists to handle spent pickle liquors containing $FeCl_2$ and HCl (7).

If H_3PO_4 is used to strip iron from 30 vol-pct EHPA, the resulting strip solution could be neutralized with lime. The calcium phosphate recovered should be marketable as fertilizer.

The chloride wash solution from the second washing step is the most troublesome stream to treat since it is so dilute. Since the volume of this stream will be only one-fifth the volume of the HCl strip, it may find application as a scrubbing solution to absorb HCl gas from the spray-roasting operation. If spray-roasting is not used for disposal of the $FeCl_3$-HCl strip, the solution might be made suitable for either discharge or recycle by contacting it with activated carbon, which absorbs HCl from dilute solution (3).

CONCLUSIONS

The following operating conditions are recommended to remove iron from aluminum nitrate liquor containing 1 to 2 g/l iron:

1. Extraction: 15 vol-pct EHPA in kerosene at a 1:6 organic-to-aqueous phase ratio, two extraction stages.

2. First water wash: Water at a 3:1 organic-to-aqueous phase ratio, six washing stages.

3. Stripping: 20-pct HCl at a 6:1 organic-to-aqueous phase ratio, three stripping stages.

4. Second water wash: Water at a 5:1 organic-to-aqueous phase ratio, two washing stages. Recycle wash solution until 1.5 g/l chloride is reached.

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