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Z. Sheng[a]; M. J. Murtha[a]; G. Burnet[a]
[a] AMES Laboratory, U.S.D.O.E. Department of Chemical Engineering, Iowa State University, Ames, Iowa

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Some Recent Results in the Separation of Metal Chlorides by Solvent Extraction

Z. SHENG, M. J. MURTHA, and G. BURNET

AMES LABORATORY, U.S.D.O.E.
DEPARTMENT OF CHEMICAL ENGINEERING
IOWA STATE UNIVERSITY
AMES, IOWA 50011

ABSTRACT

Solvent extraction is used to selectively separate an aqueous mixture of metal chlorides (Fe, Al and Ti) that is the product from the high-temperature chlorination of fly ash by the HiChlor process. Tertiary amines dissolved in xylene or kerosine are used to separate the Fe from the Al and Ti. Prior to extraction, the organic solution is contacted with HCl to convert the amine to the chloride salt. Data on the effects of organic-to-aqueous ratio, Fe, Al and Ti loadings, and HCl concentration in the aqueous phase are reported. Iron is stripped from the loaded organic phase using dilute HCl. The raffinate is subjected to sparge crystallization with HCl to recover $AlCl_3.6H_2O$.

The recovery of Ti from the aqueous phase after Fe removal requires the use of tributyl phosphate (TBP) in kerosine for the organic phase, and of higher acid concentrations. Decanol is used as a modifier to prevent formation of a third phase.

INTRODUCTION

Recovery of resource materials from coal solid wastes, principally fly ash from the combustion of pulverized coal, is receiving considerable attention today. Work is directed toward recovery of minerals from the ash and discovery of uses for the residues. Pro-

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cessing usually calls for some form of chemical attack to break down the vitreous, fused ash particles. Recovery of metal compounds from the product stream often involves solvent extraction and related separation methods.

The major constitutents in coal fly ashes from bituminous, subbituminous, and lignite coals (1) are shown in Figure 1. Of particular interest is the uniform alumina content of approximately 20 weight percent in the different ashes.

The processing of fly ash to recover minerals could provide an alternative to disposal, thus preventing additional environmental degradation. The ash would also be an indigenous source for some minerals now derived primarily from imported ores. The coal ash production projected for 1985 is 100 million tons, a figure that is expected to double by the year 2000 (2).

Acid digestion (3,4) and carbochlorination (5,6) are two processing methods that result in a product stream that consists primarily of metal chlorides. An example of the latter method is the Ames Laboratory HiChlor process. The product stream from a carbochlorination process will contain a higher concentration of Al(III) and will be less complex, being composed mainly of $AlCl_3$ and $FeCl_3$. The primary purpose of the present investigation is to examine the separation and recovery of metal chlorides from the HiChlor process product stream by solvent extraction coupled with sparge crystallization.

THE HICHLOR PROCESS

As shown in Figure 1, the bituminous coal fly ashes are high in Fe and low in Ca. Part of the Fe in the ash can be separated magnetically as an iron-rich fraction. The nonmagnetic fraction is amenable to chlorination for metal recovery. The low Ca content reduces the amount of Cl_2 consumed in the production of unwanted products.

In the HiChlor process (Figure 2) the nonmagnetic fraction is chlorinated in the presence of carbon or another reductant at high

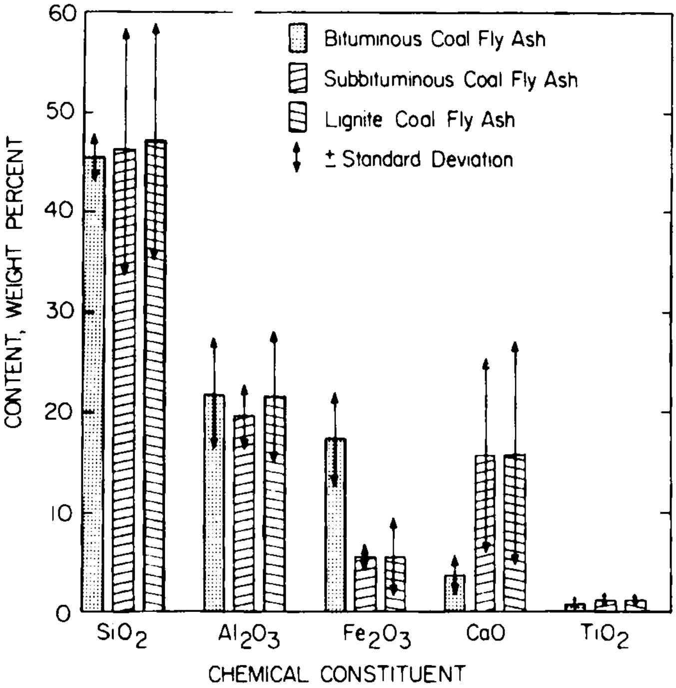

FIGURE 1. Chemical Compositions of U. S. Power Station Fly Ashes

temperature (800-900°C) to produce volatile metal chlorides. These chlorination products are then condensed and separated, while unreacted Cl_2 and $SiCl_4$ are recycled to the reactor. The recycle of $SiCl_4$ to the reactor suppresses the formation of additional $SiCl_4$.

The gaseous product consists of the chlorides of Si, Fe, Al, Ti, Na, K, Mg, and Ca, plus CO_2, CO, and unreacted Cl_2. The key recovery step is the separation of a purified aluminum chloride that can be converted to specification grade aluminum oxide for aluminum metal production. Iron and silicon chlorides are the principal impurities. The amount of $TiCl_4$ present is relatively small but must be separated; most fly ashes contain only about one weight percent TiO_2. The process shown in Figure 2 calls for a combination of anhydrous and aqueous recovery and separation steps.

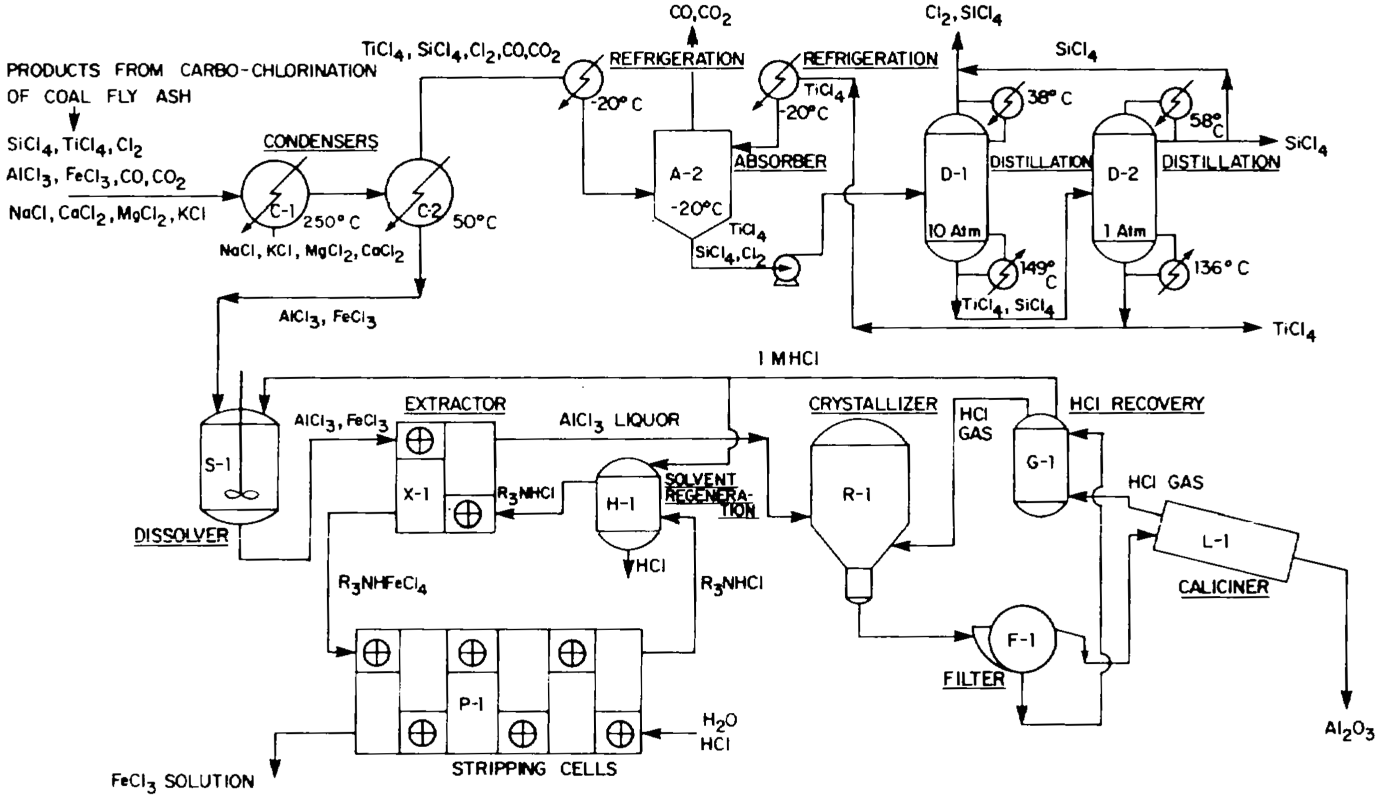

FIGURE 2. Schematic Flowsheet for the Recovery and Separation of HiChlor Products

Approximate composition data for the chlorination product gases with melting point and boiling point data for the constiuents are given in Table 1. The melting and boiling points are such that it is possible to separate the low-boiling components of this mixture from the high-boiling components by fractional condensation. The alkali and alkaline earth chlorides (such as KCl, NaCl, $MgCl_2$, $CaCl_2$) can be separated from the product stream by cooling at atmospheric pressure to about 250°C (C-1, Figure 2). The remaining constituents undergo a second stage condensation (C-2) at about 50°C to remove more than 99.9% of the $AlCl_3$ and the $FeCl_3$ from the stream. Condensation of the $SiCl_4$ and $TiCl_4$ does not occur because the partial pressures are less than the vapor

TABLE 1

Composition and Properties of Predominant Fly Ash Chlorination Product Vapors (at 1 atmosphere)

Substance	Mole percent[a]	Melting point (Celsius)	Boiling point (Celsius)
CO	39.8	-205.06	-191.47
CO_2	19.9	- 56.6[b]	- 78.5[e]
Cl_2	16.1	-100.98	- 34.6
$SiCl_4$	12.2	- 70[c]	57.57
Al_2Cl_6	9.2	190[d]	180.2[e]
Fe_2Cl_6	2.3	306	315[f]
$TiCl_4$	0.6	- 25	136.4

[a] Computed from total oxide removed vs. time data, and from carbon oxides and Cl_2 monitoring at 1 hour, 850 degrees (6).

[b] At 5.2 atmospheres.

[c] Triple point.

[d] At 2.5 atmospheres.

[e] Sublimes.

[f] Decomposes to $FeCl_2$ and Cl_2.

pressures at 50°C due primarily to the large fraction of carbon oxides and chlorine in the vapor.

The principal difficulty in separating $AlCl_4$ and $FeCl_3$ mixtures by anhydrous means is the formation of a volatile mixed-metal complex. Both $AlCl_3$ and $FeCl_3$ are monomeric in the solid state but, when vaporized, form a dimer analog:

$$Al_2Cl_{6(g)} + Fe_2Cl_{6(g)} \rightleftarrows 2FeAlCl_{6(g)} \qquad (1)$$

The introduction of $FeAlCl_6$ into the $AlCl_3$-$FeCl_3$ system causes the appearance of an apparent minimum subliming azeotrope (7). Therefore, to recover a metallurgical grade Al_2O_3 product, efforts have been directed toward development of an aqueous separation and recovery scheme.

In the aqueous method, the metal chlorides (mainly $AlCl_3$ and $FeCl_3$) recovered from the second condenser (C-2) are dissolved in dilute aqueous HCl. The solution may be filtered to remove any undissolved solid such as SiO_2 that may form during the dissolution. Alamine 336 in kerosine is then used to extract Fe(III) ion from the solution. Aluminum is precipitated from the raffinate as $AlCl_3.6H_2O$ and the Ti present is then extracted using TBP solvent.

AQUEOUS SEPARATION OF Fe(III) FROM Al(III)

Feed Solution

A typical mixed chloride solution after dissolution contains about 2M $AlCl_3$, 0.45M $FeCl_3$, 1M HCl, 8.3-8.5M total Cl^- and a trace of Ti(IV). A HCl concentration of at least 1M is required for extraction of the Fe(III) and to prevent any Ti(IV) present from hydrolyzing.

The Choice of Extractant and Diluent

Trivalent Fe in the chloride system is very easily extracted. Extraction of Fe(III) from HCl can be accomplished with various solvents with negligible $AlCl_3$ removal. The solvents which are widely used in practice are HDEHP, TBP, and high molecular weight amines.

Although Fe(III) was efficiently extracted from an HCl solution with virtually no Al(III) extraction by HDEHP, the distribution coefficient of Fe(III) was strongly dependent on the solution acidity. The E_a^o of Fe(III) was more than 10^2 when the HCl concentration in the aqueous phase was 0.01M to 0.1M. On the other hand, it was difficult to strip the Fe(III) from the loaded organic HDEHP with either water or dilute acid.

The use of amines for the extraction of Fe(III) has been widely investigated. Fe(III) can be extracted from H_2SO_4 by primary amines (8) but, for the extraction from HNO_3 or HCl solutions, secondary or tertiary amines give improved distribution coefficients (9, 10, 11, 12). It has been reported that the distribution coefficient is more than 10^4 for Fe(III) from chloride solution with Alamine 336 (12).

Tributyl phosphate (TBP) is also an excellent extractant for Fe(III) from HCl solutions of about 2M. For both TBP and Alamine 336, $AlCl_3$ is not extracted and will enhance the extraction of Fe(III) through its action as a salting-out agent (12).

Because tertiary amines such as Alamine 336 have the advantage of higher Fe(III) distribution coefficients and less dependency on acid concentration, Alamine 336 (General Mills Chemicals, Inc.) was used for this research. The organic solvent was contacted with 1M HCl to convert the amine to the chloride salt form prior to the extraction tests.

Both xylene and kerosine were tested as a diluent for Alamine 336. It is convenient to use xylene in the chloride system because xylene does not cause a third phase. Kerosine is often used, however, because of lower cost and flammability but, in the extraction of Fe(III), the organic phase will separate into two phases if the Fe(III) concentration is very high. This phase transition can be prevented by adding a modifier such as decanol to the kerosine. Tests to determine the amount of modifier required revealed that the addition of 9 percent (v/v) of 1-decanol can eleminate the third phase for a mixture of 20 percent Alamine 336 in kerosine and that 10 percent (v/v) 1-decanol is satisfactory for 30 percent (v/v) Almine 336 in kerosine. The extraction isotherms (Figure 3) indicate that there is almost no difference in performance when xylene or kerosine plus decanol is used as the diluent. However, the stripping data for Fe(III) (Figure 4) show that the use of kerosine plus decanol gives significantly improved Fe(III) stripping from the loaded Alamine 336 with 0.01M-0.03M HCl. Improved stripping efficiency is important because more contact stages are needed for stripping than for extraction.

Effect of Acidity and Cl^- Concentration on Fe(III) Extraction

Fe(III) extraction by Alamine 336 as a function of total Cl^-, acidity and predominant cation are shown in Figure 5. The added

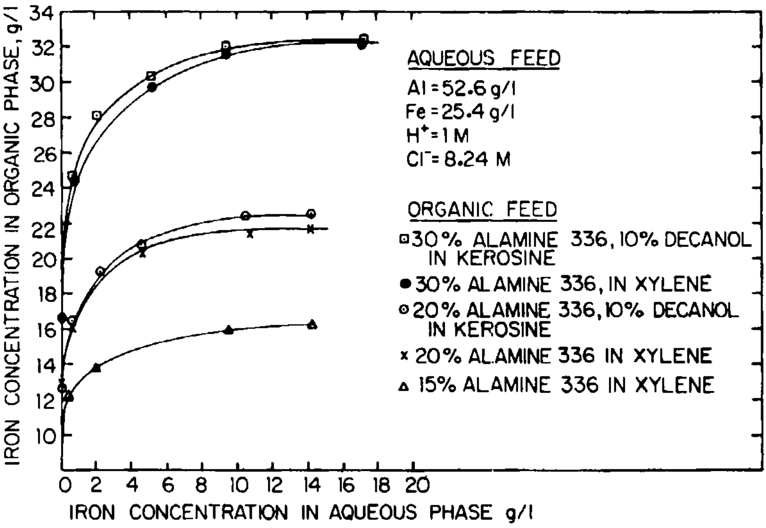

FIGURE 3. Isotherms for the Extraction of Fe(III)

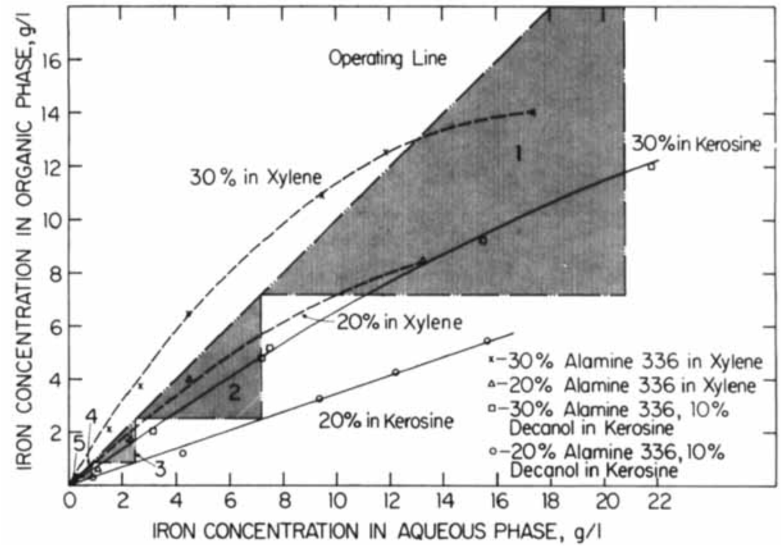

FIGURE 4. Isotherms (23°C) for the Stripping of Fe(III) by 0.01-0.03M HCl

total Cl^- was defined as the sum of the concentrations of Cl^-, not including that of the $FeCl_3$. It is obvious from this plot that Fe(III) extraction improves markedly as the Cl^- concentration increases. These data show that the distribution coefficient of Fe(III) is highly dependent on the added Cl^- concentration in the aqueous phase, and less dependent on whether H^+ or Al^{3+} is the predominant cation. The presence of $AlCl_3$ in solution is beneficial for the Fe(III) extraction.

Fe(III) Extraction Isotherms

Isotherms for the extraction of Fe(III) from chloride solution by different concentrations of Alamine 336 in kerosine-decanol and xylene diluents are shown in Figure 3. The extraction equilibrium of $FeCl_3$ with Alamine 336 is attained rapidly. One minute of shaking brings the system near equilibrium and 3 minutes is sufficient to reach equilibrium.

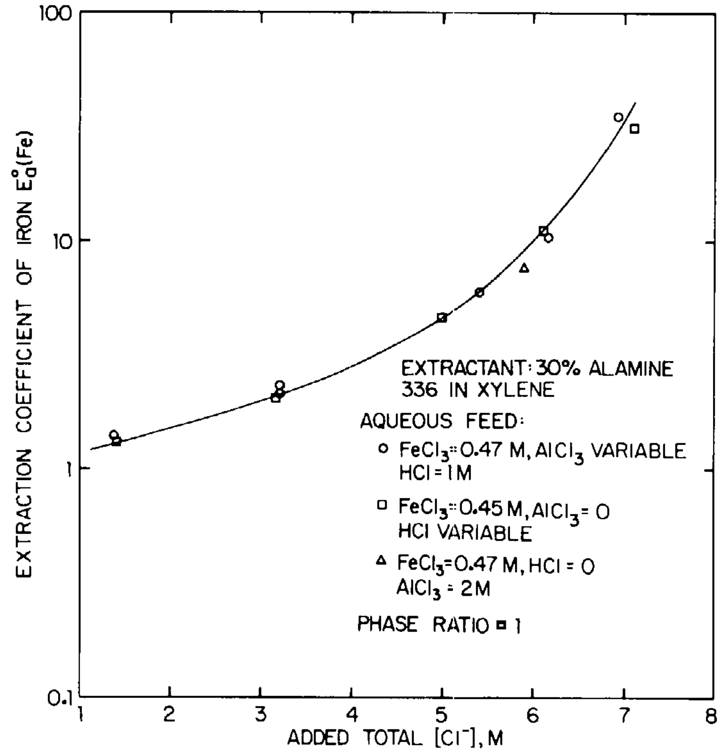

FIGURE 5. Effect of Chloride Ion Concentration on the E_a^o of Fe(III)

It is generally agreed that the mechanism of $FeCl_3$ extraction using an amine is one of anion exchange (13);

$$Fe^{+++}_{(aq)} + 4Cl^{-}_{(aq)} \rightleftarrows FeCl^{-}_{4(aq)} \qquad (2)$$

$$R_3N_{(org)} + H^{+}_{(aq)} + Cl^{-}_{(aq)} \rightleftarrows R_3NHCL_{(org)} \qquad (3)$$

$$R_3NHCl_{(org)} + FeCl^{-}_{4(aq)} \rightleftarrows R_3NHFeCl_{4(org)} + Cl^{-}_{(aq)} \qquad (4)$$

When amine solutions are saturated with Fe(III), the molar ratio

(R_3N):(Fe) = 1:1 (Equation 4). The data in Figure 3 substantiated this. At the saturated Fe(III) concentration for the organic phase, the molar ratio of amine to Fe(III) ranged from 1:1 to 1:1.05 for an amine average mol. wt. of 392 and sp. g. of 0.81.

Effect of Feed Composition on Fe(III) Extraction

A mole ratio of Al to Fe of about 4.5:1 results from the chlorination of a low-iron content fly ash. The isotherms (23°C) for the extraction of Fe(III) by 20 percent Alamine 336 in kerosine plus decanol shown in Figure 6 are for the range of $AlCl_3$ concentration expected in the aqueous feed. An increase in the concentration of $AlCl_3$ improves the Fe(III) extraction. It is, therefore, desirable to have the feed solution near the solubility limit of $AlCl_3$, not only to minimize the volume of treated solution but also to improve the extraction of Fe(III).

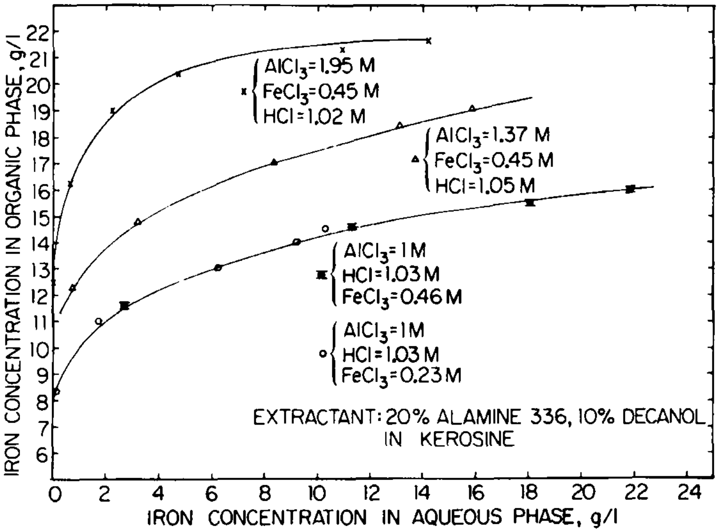

FIGURE 6. Effect of the Feed Composition on the Extraction of Fe(III). Compositions shown are for the aqueous feeds investigated.

Stripping of Fe(III) from the Organic Solution

Fe(III) can be stripped from Alamine 336 using dilute acid, the use of which also ensures that the Fe(III) will not hydrolyze in the aqueous phase. Figure 4 is the equilibrium diagram for stripping iron-loaded Alamine 336 with 0.01-0.03M HCl. These data show the effect of both Alamine 336 concentration and the type of diluent on Fe(III) distribution. Although Fe(III) extraction is proportional to the amine concentration (Figure 3), Fe(III) stripping becomes more difficult as the amine concentration increases and the driving force for the transfer of Fe(III) decreases. The choice of 20 percent Alamine 336 in kerosine plus 10 percent decanol proved to be a good compromise. For an organic-aqueous phase ratio of 1:1 (Figure 4), six theoretical stages are required to remove the Fe(III) from the organic phase. Even more stages would be require for higher Alamine 336 concentrations.

Simulated Countercurrent Extraction

Because solvent extraction processes are usually countercurrent operations, a series of batch extractions were made to simulate a continuous countercurrent two-stage process. A 1M aqueous HCl feed stream containing 25.26 g/l Fe(III) and 53.56 g/l Al(III), and an organic phase consisting of 20 percent (v/v) Alamine 336 in kerosine plust 10 percent decanol were used. To meet Fe specifications (14) for the recovered Al_2O_3 product, the Fe concentration of the raffinate had to be reduced to 10 mg/l of Fe(III). On the assumption that 90-95 percent of the Alamine 336 would complex with Fe(III), an organic-aqueous ratio of 1.2:1 was required.

Equilibrium calculations indicated that only two theoretical stages would be required for this separation. The data collected to verify this are shown in Figure 7. With two stages of extraction, the concentration of Fe(III) was reduced to 1.05 mg/l, with no detectable loss of Al. The reported change

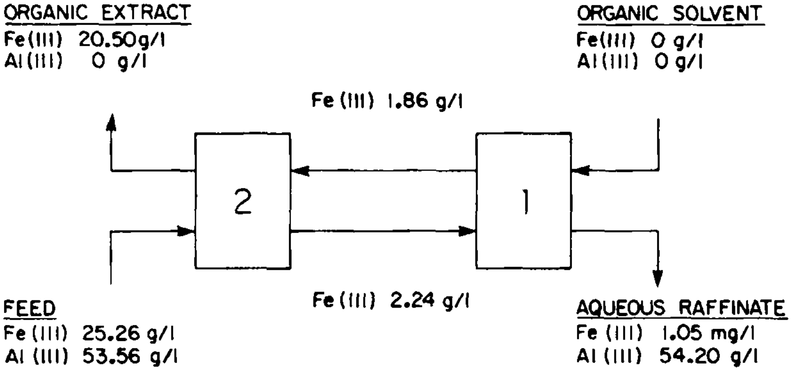

FIGURE 7. Schematic Flowsheet for $FeCl_3$ Extraction by Alamine 336

in Al(III) concentration in the aqueous phases was due primarily to a reduction in volume.

RECOVERY OF ALUMINA

The solubility of $AlCl_3$ in aqueous solution decreases with increasing concentration of HCl. This behavior has been the subject of numerous investigations and patents (15, 16). Thus, when HCl is added, Al can be precipitated in the form of $AlCl_3 \cdot 6H_2O$ which can be subsequently calcined to Al_2O_3. The precipitation reaction is very selective and the impurities in the precipitate come only from the entrainment of mother liquor. The precipitate is highly crystalline and can be readily washed with concentrated HCl to yield a pure product. As part of this work, the solubility of $AlCl_3 \cdot 6H_2O$ in the mother liquor was determined (Figure 8) and found to agree with previously reported results (15).

The raffinate from the $FeCl_3$ solvent extraction step contained 54.20 g/l of Al and 1.05 mg/l of Fe, and was brought in contact with anhydrous HCl in a sparge crystallizer. Sparging was continued with stirring until a desired HCl concentration (9-11M) was reached and the crystal crop of $AlCl_3 \cdot 6H_2O$ had formed.

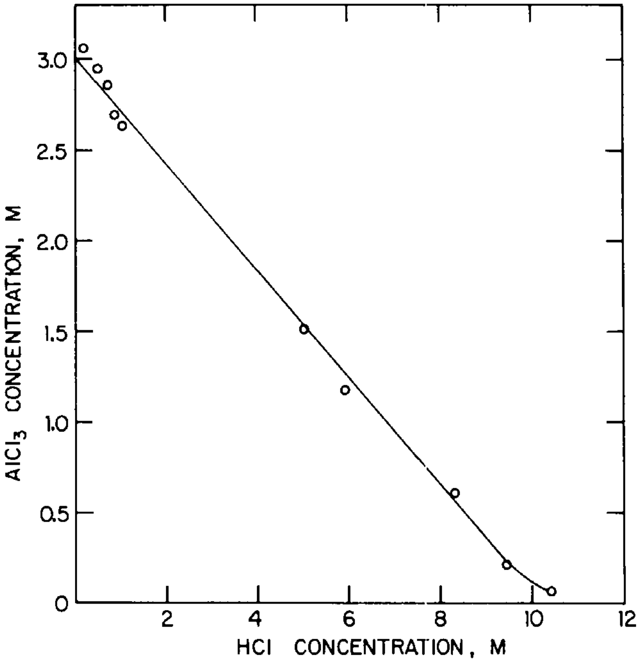

FIGURE 8. Solubility of Al in HCl Solution

After letting the crystals age, the precipitate was filtered and twice washed with 12M HCl. The crystals were then dried and calcined at 700°C for 2 hours to produce Al_2O_3. The yield of alumina, a function of the HCl concentration in the mother liquor, was 90-96%. The residual $AlCl_3$ was returned to the dissolution step. The HCl evolved during calcination would be quantitatively recovered using available technology (17, 18).

RECOVERY OF Ti(IV)

Depending upon the product recovery scheme used, $TiCl_4$ could occur in the aqueous mixed chloride feed, being condensed with the $FeCl_3$ and $AlCl_3$. In this work, Ti(IV) remained in the aqueous phase after Fe extraction and $AlCl_3.6H_2O$ crystallization. The combined filtrate and washings from the $AlCl_3.6H_2O$ crystallization contained Ti(IV), residual Al(III), and traces of Fe in about 10M HCl.

It was found that TBP (Eastman Chemical Company) was suitable to extract Ti(IV) from the above solution when the HCl concentration was kept high. A TBP concentration of 30 percent was used and both xylene and kerosine were tested as diluents. Because of the large volume change that occurs on equilibration of TBP with HCl in solution, the extractions were carried out using TBP which had been pre-equilibrated with HCl.

Ti(IV) extraction from HCl solution with TBP is strongly dependent upon the HCl concentration in the aqueous phase (19, 20, 21). This is confirmed by the data shown in Figure 9. When kerosine was used as the diluent, three phases again formed at HCl concentrations greater than 7M, while with xylene this was not a problem. However, for the reasons discussed previously, it is desirable to use kerosine as the diluent. As was the case for the Fe(III) extraction, 8 percent (v/v) of decanol modifier was used for the 30 percent (v/v) TBP in kerosine to prevent the

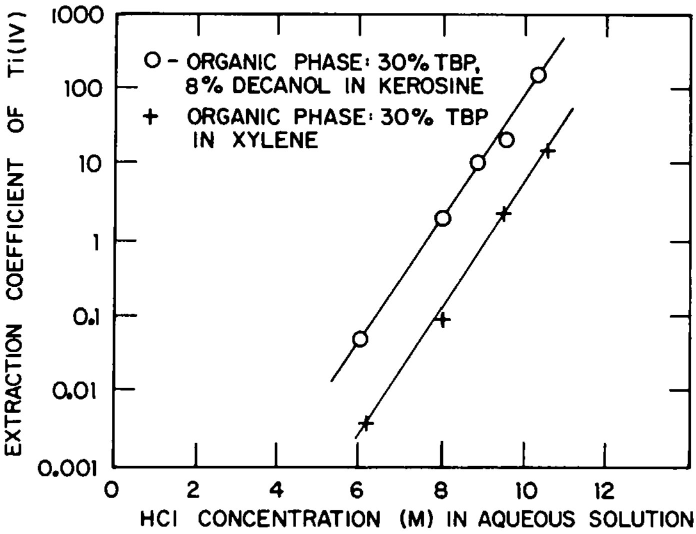

FIGURE 9. The Effect of HCl Concentration on Ti(IV) Extraction

formation of the third phase. The modifier also resulted in improved Ti(IV) extraction as is shown in Figure 9. For HCl concentrations in the feed lower than 6M there was virtually no extraction of Ti(IV) but when the HCl concentration was 9M or greater, the distribution coefficients for Ti(IV) were satisfactory. Ti(IV) is easily stripped from the loaded organic phase with 1M HCl solution, the 1M acidity being required to prevent the $TiCl_4$ from hydrolyzing.

The extraction of Ti(IV) from HCl has not been well studied according to the literature. The formation of a complex, as shown in the following reaction, has been suggested (19, 20, 22):

$$Ti^{4+}_{(aq)} + 4Cl^-_{(aq)} + 2TBP_{(org)} \rightleftarrows TiCl_4 \cdot 2TBP_{(org)} \qquad (5)$$

It thus appeared that Cl^- would play an important role in the extraction of Ti(IV) so an effort was made to determine the salting-out effect of $AlCl_3$.

The effect of total Cl^- concentration on Ti(IV) extraction by TBP is shown by the data in Table 2. The addition of $AlCl_3$ to the aqueous phase increases the distribution coefficient of Ti(IV). However, the distribution coefficient is not sufficiently high for extraction of Ti(IV) from the aqueous solution until the total Cl^- concentration is at least 8.5M. The decrease in solubility of $AlCl_3 \cdot 6H_2O$ with increasing HCl concentration (Figure 8) limits the use of $AlCl_3$ as a salting-out agent. Therefore, to obtain a high distribution coefficient for Ti(IV) extraction, it is best to increase the HCl concentration in the initial solution. The introduction of other chloride-bearing agents could contaminate the final products. The TBP solvent gave suitable extractions in the presence of the HCl already in the liquor from the sparge crystallization.

CONCLUSIONS

A process of anhydrous condensation followed by aqueous separation can be used to recover and separate Al, Fe, and Ti from

TABLE 2

Effect of Total Chloride Ion Concentration on Ti(IV) Extraction[a]

Initial HCl (M)	Added $AlCl_3$ (M)	Total Cl^- (M)	$E(Ti^{+4})$
3.88	0	4.26	-
	0.64	6.06	0.02
	1.10	7.56	0.4
	1.40	8.27	1
6.23	0	6.60	0.05
	0.98	9.54	6.5
8.05	0	8.45	1.5
	0.49	9.92	10.6
9.27	0	9.65	9.5
	0.12	10.02	16
9.76	0	10.14	21

[a] Aqueous: 0.09M $TiCl_4$ + $AlCl_3$ + HCl. Organic: 30% (v/v) TBP, 8% decanol in kerosine. Temperature: 23°C.

the product stream that results from the high-temperature chlorination of fly ash by the HiChlor process. The Fe can be separated effectively from the Al and Ti by Alamine 336 extraction in a chloride system. Aluminum can be recovered from the raffinate by sparge crystallization as $AlCl_3.6H_2O$, which can then be calcined to obtain metallurgical grade Al_2O_3. Titanium can be recovered from the aqueous phase after Fe removal using TBP extraction at the high HCl concentration already present in the liquor from the sparge-crystallization. The process has been demonstrated on a laboratory scale.

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