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By J. A. Eisele and D. J. Bauer



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8806

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CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Generalized flowsheet.....	2
Materials and experimental procedures.....	3
Results.....	4
Leaching.....	4
Sparging crystallization.....	4
Calcination and water washing.....	5
Alumina product purity.....	6
Bleedstream treatment.....	7
Flowsheet and material balance.....	8
Conclusions.....	10
References.....	10

ILLUSTRATIONS

1. Proposed processing of anorthosite by acid leaching.....	3
2. Equilibrium solubility curve of $AlCl_3$ in HCl.....	5
3. Conversion of mixtures of chloride salts to HCl versus temperature.....	7
4. Flowsheet for recovery of alumina from anorthosite by an HCl process.....	8

TABLES

1. Chemical analysis of anorthosite.....	3
2. Composition of simulated pregnant liquors to crystallization.....	4
3. Composition of $AlCl_3 \cdot 6H_2O$ crystallized from different feed liquors.....	5
4. Na_2O and CaO content of alumina after calcining and water washing.....	6
5. Analyses of alumina produced from liquors simulating different bleedstream compositions.....	7
6. Analyses of sparger feed (pregnant liquor) and alumina produced from anorthosite, 100-pct bleedstream.....	7
7. Material balance for alumina from anorthosite by an HCl process.....	9

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	L	liter
g	gram	lb	pound
h	hour	<u>N</u>	normal (1 g-equivalent/l)
kg	kilogram	pct	percent

RECOVERY OF ALUMINA FROM ANORTHOSITE BY AN HCl-F-GAS SPARGING CRYSTALLIZATION PROCESS

By J. A. Eisele¹ and D. J. Bauer¹

ABSTRACT

The Bureau of Mines is investigating the recovery of alumina from domestic nonbauxitic resources, including anorthosite. The United States has large reserves of anorthosite, but its aluminum content is less than 50 pct soluble in acid, unless a source of fluoride is added to the acid.

A flowsheet that includes leaching with HCl and fluoride followed by crystallization of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ from the pregnant liquor by HCl gas injection was designed. Approximately 90 pct of the aluminum values were recovered from the anorthosite when a ratio of 0.14 mole of fluorine per mole of aluminum was used. Sodium chloride is cocrystallized with the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ but is removed by water washing of the Al_2O_3 product. A material balance is given based on results of laboratory studies of the unit operations.

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INTRODUCTION

The Bureau of Mines is investigating methods to produce cell-grade alumina from domestic nonbauxitic materials as part of its goal to provide technology to help maintain an adequate supply of minerals to meet national economic and strategic needs. Anorthosite is widely available in the United States. In 1967 domestic anorthosite resources were estimated at 600 billion tons (10).² Anorthosite is a soda-lime feldspar rock composed of variable amounts of albite ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$) and anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$).

Alkaline sinter processes have been developed to recover alumina from anorthosite. In the lime-sinter process, anorthosite is sintered with CaO to form calcium silicate, and the alumina is leached with a sodium hydroxide solution. In the lime-soda sinter process, Na_2CO_3 and CaO are used in the sintering step; the sodium aluminate that is formed is leached with water. Both processes produce a sodium aluminate solution that can be processed similar to a Bayer liquor. The alumina recovered is similar in quality to Bayer alumina but contains more silica. Two disadvantages of the sintering processes are that energy consumption is high because a large quantity of material must be heated to $1,300^\circ\text{C}$, and, under certain uncontrollable conditions, the process slurries develop a cementlike consistency.

Direct acid leaching of anorthosite would avoid the high-temperature sintering step, but most U.S. anorthosites are

only partially acid soluble, unlike Norwegian anorthosite, which is soluble in dilute acid (6).

Although U.S. anorthosite is relatively insoluble in H_2SO_4 or HCl, if fluoride ion is added to the acid, solubility increases appreciably. The amount of fluoride required is much less than would be needed to form AlF_3 . The fluoride ion presumably functions as a catalyst, probably attacking the silicate structure and freeing the aluminum for reaction with the leaching acid. The silica-fluoride intermediate formed hydrolyzes and releases the fluoride for further reaction.

As early as 1905, a British patent was issued that reported the leaching of aluminum from refractory silicates by adding H_2SiF_6 to an acid lixiviant (5). Since that time, numerous patents and articles have described the use of an acid containing a fluoride compound to leach aluminum from aluminosilicates (1-2, 7-8, 11). The Bureau of Mines studied the leaching of anorthosite with HCl and fluoride and showed that a counter-current leaching mode gave the best utilization of reagents (3). The research summarized in this report is an extension of the study reported in reference 3 and focuses on processing the pregnant liquor to produce alumina for use in reduction cells. A flowsheet was designed in conjunction with laboratory studies of the different steps involved, and a material balance was made.

GENERALIZED FLOWSHEET

Figure 1 is a simplified flowsheet for recovering alumina from anorthosite by acid leaching. Aluminum is dissolved

in the HCl-F-leaching liquor and forms AlCl_3 . Many of the other constituents of anorthosite also dissolve and form metal chlorides. Aluminum is crystallized from the solution and, at the same time, separated from most of the other chloride salts by sparging HCl gas into the liquor. Sodium chloride cocrystallizes

²Underlined numbers in parentheses refer to items in the list of references at the end of this report.

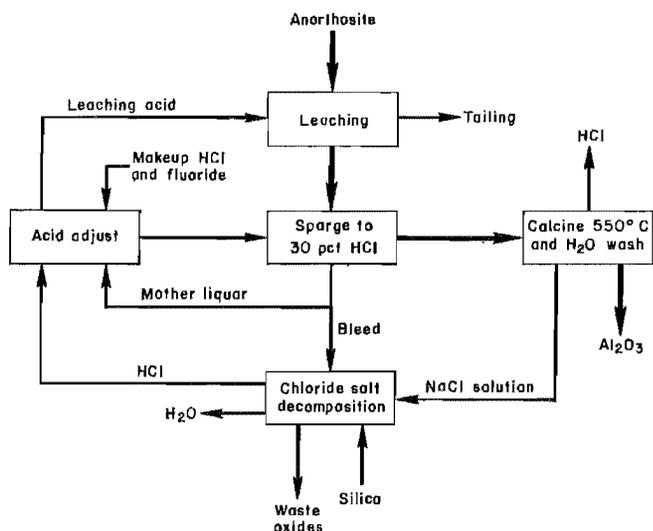


FIGURE 1. - Proposed processing of anorthosite by acid leaching.

with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and is separated after calcining at 550°C . The $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is converted to water-insoluble Al_2O_3 , while NaCl does not decompose and is removed by washing with water. Since large quantities of Ca , Na , and Fe are dissolved in leaching, a large bleedstream must be taken or the liquor will become saturated with chloride salts. The remaining mother liquor is recycled. The bleedstream and the NaCl solution from alumina washing are combined and evaporated to recover free HCl and to crystallize the chloride salts. The salts are decomposed by calcining at 800°C , and more HCl is recovered. An acid-adjustment step combines the HCl recovered from the different sources and returns the proper quantities to leaching and sparging.

MATERIALS AND EXPERIMENTAL PROCEDURES

The anorthosite used came from Wyoming. A 17-kg sample was ground to minus 100-mesh and blended. The chemical analysis is given in table 1. Fifty-gram samples were used. The leaching procedure is described in detail in reference 3. Leaches were conducted for 6 h at 104°C , the boiling point of the ore-acid slurry. Sparging crystallization tests were conducted in a 2-L bench-scale crystallizer (9). Hydrogen chloride gas was slowly injected into the solution. A draft tube and impeller provided mixing.

TABLE 1. - Chemical analysis of anorthosite

Compound	pct
SiO_2	51.6
Al_2O_3	29.0
CaO	11.5
Na_2O	5.1
Fe_2O_3	2.0
K_2O30
MgO26
P_2O_504
Other.....	.20

Thermal decomposition tests were conducted to recover HCl from chloride salts that would be crystallized from the bleedstream. The appropriate salt mixture was placed in a ceramic boat and held for 2 h at $1,000^\circ\text{C}$ in a tube furnace. Nitrogen and steam were passed through the furnace to remove the liberated HCl gas. Hydrochloric acid evolved was collected in a caustic solution and measured by titration.

Aluminum analyses were carried out by a wet-chemical method for solutions and by activation analysis for residues. Analyses of Ca , Na , Fe , and Mg in solution were made by atomic absorption. Fluoride content was determined with a specific ion electrode for solutions and by activation analysis for solids. Analyses for Fe_2O_3 , CaO , K_2O , and Na_2O in the alumina were made by X-ray fluorescence, SiO_2 was determined by spectrographic analysis, P_2O_5 by wet chemical analysis, and MgO by dissolution and atomic absorption analysis. All chemicals were reagent grade.

RESULTS

LEACHING

When Wyoming anorthosite is leached with HCl, about 50 pct of the aluminum dissolves. If a source of fluoride, such as H_2SiF_6 , Na_2SiF_6 , or CaF_2 , is added to the HCl, more than 90 pct of the aluminum is dissolved. Simulated countercurrent leaching tests with fluoride using 0.78 lb of HCl per pound of anorthosite (90 pct of the HCl required to react stoichiometrically with all acid-soluble constituents) extracted 90 pct of the Al_2O_3 , CaO, Na_2O , and K_2O . The fluoride added to the leach was 0.15 lb per pound of anorthosite, or 0.14 mole of fluorine for each mole of aluminum in the anorthosite. Sixty percent of the fluorine added to the leach remained in the pregnant liquor; 40 pct was converted to an insoluble form and exited in the tailing.

SPARGING CRYSTALLIZATION

The composition of a pregnant liquor in a continuous process will differ from the composition of a one-pass leaching liquor. Based on the known composition of pregnant liquor from countercurrent leaching, test solutions were made by dissolving salts to simulate projected 100-, 50-, and 25-pct bleedstream liquors under steady-state conditions (table 2).³ Crystallization tests were performed on

the liquors to determine the effect of feed liquor composition on the $AlCl_3 \cdot 6H_2O$ crystallized.

When crystallizing $AlCl_3 \cdot 6H_2O$, the $AlCl_3$ concentration in the feed liquor should be as high as possible, that is, close to saturation (10). In the case of recirculating anorthosite leaching liquor, the concentration of $AlCl_3$ is considerably less than saturation. The $AlCl_3$ content cannot be increased by evaporation or evaporative crystallization because the concentrations of the other metal chloride salts are high and they will cocrystallize. Since a large amount of calcium is leached, the steady-state liquor builds up a calcium content equal to or exceeding the aluminum content.

Aluminum chloride hexahydrate was crystallized by injecting HCl gas into the pregnant liquor until HCl concentration in the mother liquor was 9N (30 pct HCl). The crystals were washed with 36-pct HCl to remove entrained mother liquor, dried, and analyzed. The results are shown in

³A 100-pct bleedstream liquor is the same as a one-pass leaching liquor, since all of the liquor is rejected after each use and fresh solution is used each time for leaching.

TABLE 2. - Composition of simulated pregnant liquors to crystallization, percent¹

	Al_2O_3	CaO	Na_2O	Fe_2O_3	K_2O	P_2O_5	F
100-pct bleedstream:							
Composition simulated	4.7	2.2	0.57	0.30	0.046	0.006	0.25
Actual analysis.....	4.9	2.0	.58	.30	.048	.008	.30
50-pct bleedstream:							
Composition simulated	4.7	4.4	1.13	.60	.09	.012	.50
Actual analysis.....	4.8	4.8	1.24	.66	.11	.013	.56
25-pct bleedstream:							
Composition simulated	4.7	8.8	2.3	1.2	.18	.024	1.0
Actual analysis.....	4.7	8.6	2.24	1.2	.21	.025	1.1

¹Present in liquor as chlorides, but reported as percent oxides, except for fluorine.

table 3. Large amounts of sodium crystallized with the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ because the solubility of NaCl also decreases when HCl concentration increases. Potassium chloride should behave in a similar manner but has a concentration that is too low for such behavior to be observed. The calcium content of the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was low even though the concentration of CaCl_2 in the sparger feed was high. The amount of fluoride in the crystals was independent of the fluoride concentration in the sparger feed and remained fairly constant. In an actual process liquor, the amount of fluoride would not increase as shown in table 2, because only enough makeup fluoride would be added to maintain a constant level in the leaching step.

TABLE 3. - Composition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ crystallized from different feed liquors, percent¹

	Bleedstream		
	100 pct	50 pct	25 pct
CaO.....	0.0021	0.0084	0.014
NaO.....	2.16	4.8	4.9
Fe_2O_30021	.0014	.0059
K_2O0009	.0022	.0028
P_2O_500067	.00070	.0015
F.....	.06	.05	.04

¹Reported as percent oxides, except for fluorine, although their chemical form in the crystals was not determined.

When $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is crystallized from relatively pure AlCl_3 solutions, the amount crystallized can be predicted from the equilibrium curve of AlCl_3 - H_2O - HCl given in reference 4, shown in circular points in figure 2. Although large quantities of other chloride salts were present in simulated anorthosite liquors, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ crystallization closely followed the solubility curve for a pure AlCl_3 solution. Figure 2 shows the square points from four crystallizations with differing amounts of HCl in the mother liquor falling on the AlCl_3 solubility curve. The feed liquors for the four square points had the range of compositions shown in table 2, and composition did not affect AlCl_3 crystallization.

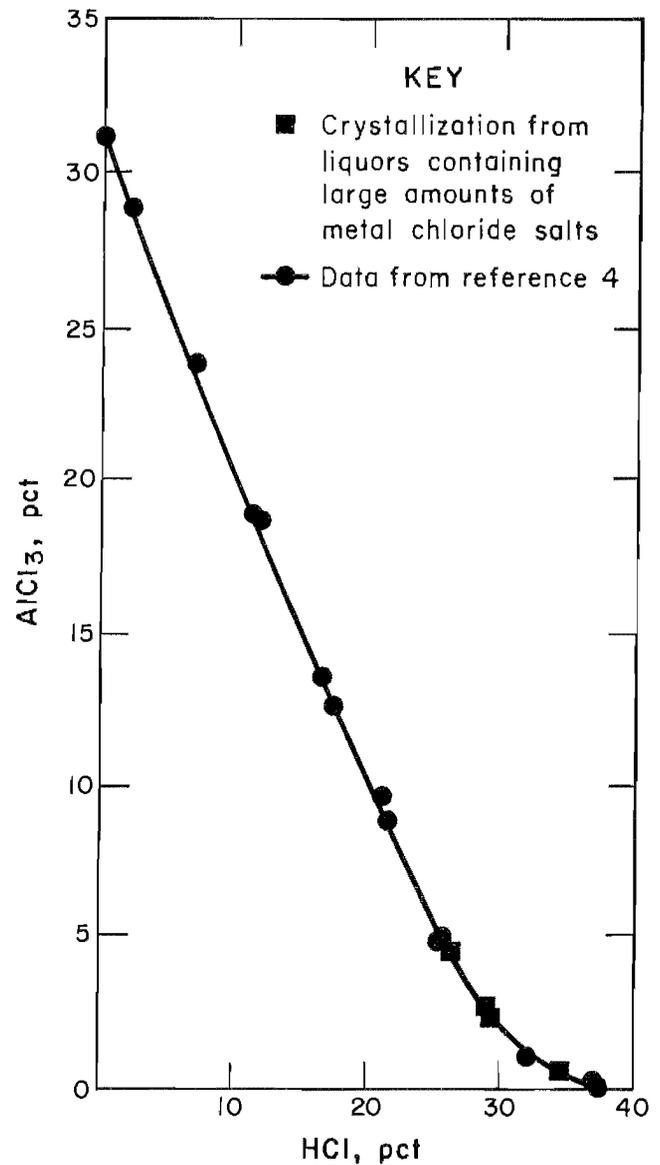


FIGURE 2. - Equilibrium solubility curve of AlCl_3 in HCl .

CALCINATION AND WATER WASHING

The amount of NaCl cocrystallized with the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is more than can be tolerated in alumina for Hall reduction cells (usually 0.35 to 0.45 pct). Since $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ decomposes at a relatively low temperature and forms an insoluble oxide, while NaCl does not, calcining was investigated as a means for separating the sodium from the aluminum.

Aluminum chloride hexahydrate was crystallized from a liquor containing 2 pct Na_2O and produced crystals containing an unacceptable amount of NaCl . After washing and drying, portions of the crystals were calcined between 450° and 850° C. The cooled calcine was washed with water to dissolve the NaCl and then analyzed. Preliminary tests showed that calcining at a temperature of less than 450° C produced a material that formed a gelatinous mass on contact with water and could not be washed. Table 4 shows the amount of sodium and calcium remaining in the alumina after calcining and washing. Although sodium removal was very good at 450° C, the calcine produced at this temperature did not wash satisfactorily and filtered very slowly. Above 550° C the amount of Na_2O and CaO retained in the washed alumina increased considerably. The best temperature for this step is from 500° to 550° C.

TABLE 4. - Na_2O and CaO content of alumina after calcining and water washing, percent

Calcination temperature, $^\circ\text{C}$	Na_2O	CaO
450.....	<0.015	<0.005
500.....	ND	<.005
550.....	<.015	<.005
600.....	.030	.016
650.....	.41	.053
700.....	.53	.065
850.....	.64	.063

ND Not determined.

ALUMINA PRODUCT PURITY

Aluminum chloride hexahydrate crystals sparged from three simulated anorthosite liquors having the compositions shown in table 3 were calcined at 550° C. The calcines were water-washed and calcined at $1,000^\circ$ C.

Table 5 gives the analyses of alumina produced from the three simulated bleedstream liquors and the impurity values

calculated from the analysis of unwashed $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Table 5 shows that large quantities of sodium and smaller amounts of calcium were washed out. For the impurities listed in table 5, the analyzed impurity levels in the Al_2O_3 product are consistent, regardless of the bleedstream size.

Seven-hundred-gram batches of anorthosite were leached countercurrently to provide pregnant liquor for sparging crystallization and to produce alumina for analysis. This was done to compare countercurrent with batch leaching and the impurity level of alumina produced from anorthosite with that of Bayer alumina. Leaching conditions were simulated three-stage countercurrent leaching with 90 pct of the HCl stoichiometrically required to react with leachable components and a molar ratio of 0.27 of F to Al (0.78 lb of HCl and 0.029 lb of F per pound of anorthosite). The pregnant liquors from the leaching tests represented 100-pct bleedstream conditions. The acid-washed $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was calcined at 550° C, washed with water, and recalcined at $1,000^\circ$ C. Table 6 gives sparger feed composition and alumina analysis based on the average of four replicate tests. An analysis of a Bayer alumina, which was conducted by the same techniques, is also shown. The alumina produced from anorthosite is less contaminated than the Bayer alumina except for MgO and SiO_2 . There is twice as much MgO and approximately an order of magnitude more SiO_2 in anorthosite alumina than in Bayer alumina.

Although the values shown in table 6 are for a 100-pct bleedstream liquor, comparison with table 5 shows that the alumina impurity levels should not change much when crystallizing from a 50-pct bleedstream liquor. Except for the higher Na_2O level in table 6, the countercurrent impurity levels are comparable to the impurity levels of the simulated leach liquors of table 5.

TABLE 5. - Analyses of alumina produced from liquors simulating different bleedstream compositions, percent¹

	Na ₂ O	CaO	Fe ₂ O ₃	K ₂ O	P ₂ O ₅
100-pct bleedstream:					
Analyzed.....	0.11	<0.005	<0.02	<0.015	0.002
Calculated from AlCl ₃ ·6H ₂ O composition..	10.2	.010	.010	.004	.003
50-pct bleedstream:					
Analyzed.....	.08	.007	<.02	<.015	.003
Calculated from AlCl ₃ ·6H ₂ O composition..	22.6	.040	.007	.103	.003
25-pct bleedstream:					
Analyzed.....	<.1	.006	.02	<.015	.005
Calculated from AlCl ₃ ·6H ₂ O composition..	23.0	.066	.028	.013	.007

¹Averaged F⁻ concentration, 0.2 pct.

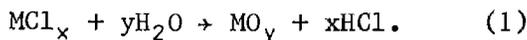
TABLE 6. - Analyses¹ of sparger feed (pregnant liquor) and alumina produced from anorthosite, 100-pct bleedstream, weight-percent

	Sparger feed	Product alumina	Bayer alumina
Na ₂ O.....	1.03	0.22	0.5
CaO.....	2.30	.010	.03
Fe ₂ O ₃47	.006	.02
K ₂ O.....	.075	.0025	.004
MgO.....	.049	.011	.005
P ₂ O ₅007	.002	.004
SiO ₂002	.15	.02

¹Average of 4 tests.

BLEEDSTREAM TREATMENT

The chloride values contained in the bleedstream must be recovered for recycle. Tests were run to determine the feasibility of recovering the chloride content by thermal decomposition of the chloride salts. On heating, a chloride salt decomposes according to the following reaction:



A mixture of salts representing the major components in the anorthosite bleedstream (55 pct CaCl₂·2H₂O, 20 pct NaCl, 13 pct AlCl₃·6H₂O, 12 pct FeCl₃·6H₂O) was heated at different temperatures, and the HCl liberation was measured. The salts were heated in a ceramic boat in a tube furnace. In preliminary tests, on heating, the salt mixture melted and, without agitation, very little HCl was evolved. When silica was mixed with the

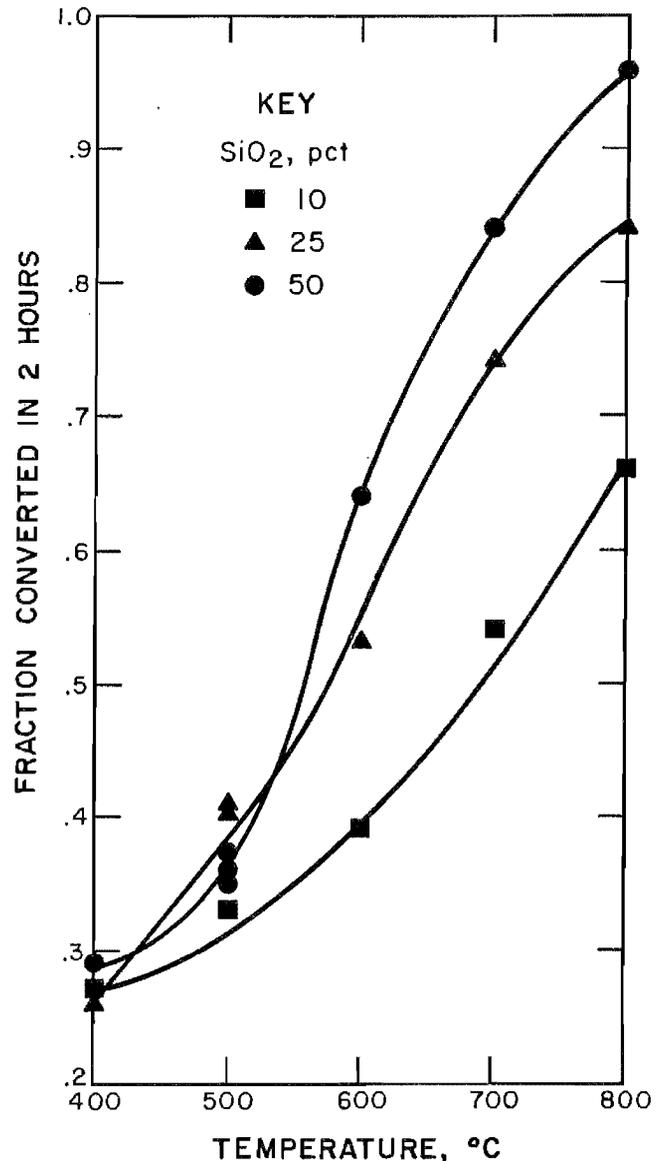


FIGURE 3. - Conversion of mixtures of chloride salts to HCl versus temperature.

salt mixture before heating, the mass did not liquefy and HCl evolution was increased. Silica was added to the salt mixtures in this series of tests. Operating in a fluidized bed may eliminate the need for silica.

and 800° C. Since the quantity of silica mixed with the salts had an appreciable effect on the amount of HCl recovered, the silica may enter into the reaction. These tests show that at 800° C, 96 pct of the chloride can be recovered as HCl.

Figure 3 shows the results obtained at decomposition temperatures between 400°

FLWSHEET AND MATERIAL BALANCE

Based on the test results, a flowsheet and material balance were developed and are shown in figure 4 and table 7. The material balance is based on 1,000 units

of alumina. Several features of the flowsheet and material balance should be noted.

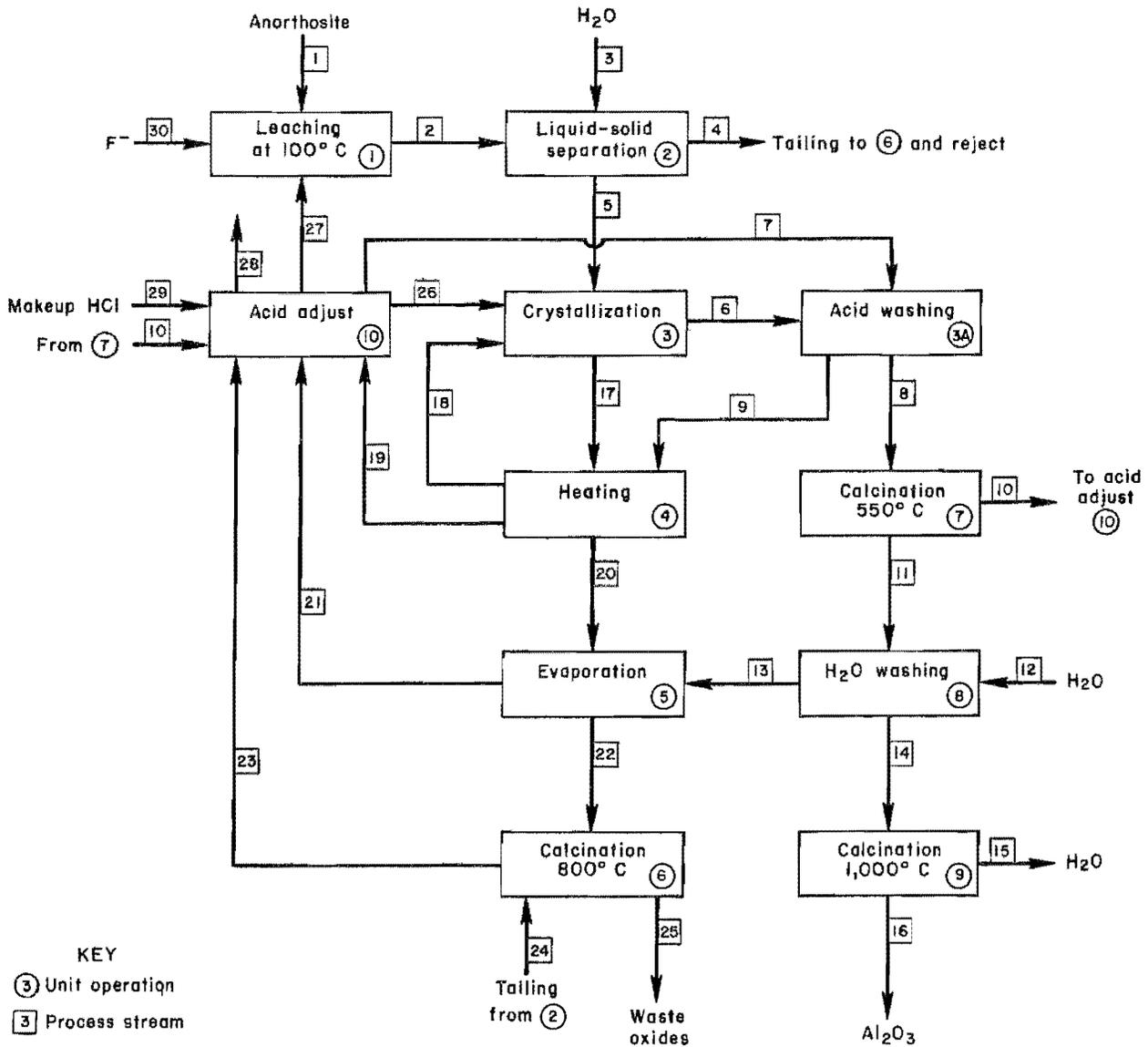


FIGURE 4. - Flowsheet for recovery of alumina from anorthosite by an HCl process.

TABLE 7. - Material balance for alumina from anorthosite by an HCl process

(Based on 1,000 units of recovered alumina)

Process stream ¹	HCl, free	HCl, combined	H ₂ O	Al ₂ O ₃	AlCl ₃ ·6H ₂ O	CaO	Na ₂ O	NaCl	Fe ₂ O ₃	K ₂ O	MgO	P ₂ O ₅	H ₂ SiF ₆	SiO ₂	Other	Total
1.....	0	0	0	1,218	0	483	214	0	84.0	12.6	10.9	1.68	0	2,167	8.40	4,200
2.....	0	4,254	10,241	1,313	0	918	278	0	160	23.9	20.7	3.19	80.6	2,167	8.40	19,468
3.....	0	0	2,712	0	0	0	0	0	0	0	0	0	0	0	0	2,712
4.....	0	0	202	121.8	0	48.3	21.4	0	8.40	1.26	1.09	.17	32.2	2,167	8.40	2,612
5.....	0	4,254	12,751	1,191	0	870	257	0	151.6	22.7	19.6	3.02	48.4	0	0	19,568
6.....	374	97.9	704	9.53	4,736	43.5	6.38	242	7.56	1.13	.97	.17	2.44	0	0	6,226
7.....	1,512	0	2,688	0	0	0	0	0	0	0	0	0	0	0	0	4,200
8.....	151	0	269	0	4,736	0	0	242	0	0	0	0	0	0	0	5,398
9.....	1,735	97.9	3,123	9.53	0	43.5	6.38	0	7.56	1.13	.97	.17	2.44	0	0	5,027
10.....	2,298	0	1,857	0	0	0	0	0	0	0	0	0	0	0	0	4,155
11.....	0	0	0	1,000	0	0	0	242	0	0	0	0	0	0	0	1,242
12.....	0	0	1,050	0	0	0	0	0	0	0	0	0	0	0	0	1,050
13.....	0	0	958	0	0	0	0	242	0	0	0	0	0	0	0	1,200
14.....	0	0	92.4	1,000	0	0	0	0	0	0	0	0	0	0	0	1,092
15.....	0	0	92.4	0	0	0	0	0	0	0	0	0	0	0	0	92.4
16.....	0	0	0	1,000	0	0	0	0	0	0	0	0	0	0	0	1,000
17.....	6,090	1,856	10,844	181	0	826	121.8	0	144	21.5	18.7	2.86	45.8	0	0	20,152
18.....	4,763	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4,763
19.....	1,531	977	6,985	95.3	0	435	64.3	0	75.6	11.3	9.83	1.51	24.2	0	0	10,210
20.....	1,531	977	6,985	95.3	0	435	64.3	0	75.6	11.3	9.83	1.51	24.2	0	0	10,210
21.....	1,531	0	7,573	0	0	0	0	0	0	0	0	0	24.2	0	0	9,127
22.....	0	0	0	0	452	0	0	363	0	0	0	1.51	0	0	0	22,280
23.....	1,071	0	346	0	0	0	0	0	0	0	0	0	28.0	0	0	1,445
24.....	0	0	176	106.1	0	42.0	18.6	0	7.31	1.10	.95	.15	28.0	1,888	7.31	2,275.5
25.....	0	0	176	201	0	477	163	90.3	82.9	12.4	10.8	1.66	0	1,888	7.31	3,110
26.....	1,701	0	349	0	0	0	0	0	0	0	0	0	0	0	0	2,050
27.....	3,277	977	10,231	95.3	0	435	64.3	0	75.6	11.3	9.83	1.51	76.4	0	0	15,254
28.....	0	0	3,491	0	0	0	0	0	0	0	0	0	0	0	0	3,491
29.....	60.1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	60.1
30.....	0	0	9.6	0	0	0	0	0	0	0	0	0	4.12	0	0	13.7

¹Process streams in figure 4.

²Includes CaCl₂·2H₂O (1,140), FeCl₃·6H₂O (256), KCl (18.1), and MgCl₂·6H₂O (49.6).

1. Ninety percent of the aluminum and other soluble components is extracted in the leaching step.

2. The soluble components are present as chlorides but are reported in the material balance as oxides until they exit as chloride salts.

3. A weight ratio of approximately 1 between wash solution and cake is used for all washing steps.

4. The mother liquor from the sparging step contains 30 pct HCl and 2 pct AlCl_3 .

5. Eighty-five percent of the contained AlCl_3 is crystallized in the sparging step.

6. A 50-pct bleedstream is taken to control impurities.

7. When the mother liquor from sparging is heated, HCl gas is expelled until

the concentration in the liquor is 15 pct HCl, which is less than the azeotropic concentration (20 pct) because a concentrated solution of chloride salts functions as an azeotrope breaker.

8. The source of silica for the waste chloride thermal decomposition step is the dried tailing. Eighty-seven percent of the tailing is used in this step.

9. Ninety-five percent of the contained HCl is recovered in thermal decomposition of the waste chloride salt mixture. The 5 pct chloride not recovered is assumed to exit as NaCl, which is the most difficult salt of the mixture to decompose.

10. The fluoride in the tailing should be volatilized during thermal decomposition and recovered with the HCl, so that the makeup fluoride requirement is very small.

CONCLUSIONS

The major steps of a proposed flowsheet for producing alumina from anorthosite by an HCl-fluoride process were shown to be feasible on a bench scale. The alumina produced was purer than a reference Bayer alumina except for MgO and SiO_2 content.

Acid processing avoids the high-energy calcination step of the basic sintering process; however, the thermal decomposition steps to recover Al_2O_3 from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and to recover HCl from waste chloride salts will be energy intensive.

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