

OPTIONS IN THE HCL PROCESS FOR THE PRODUCTION  
OF ALUMINA FROM CLAY

D. E. Shanks, D. C. Thompson, R. M. Arington, G. L. Dan, and J. A. Eisele

Reno Research Center  
Bureau of Mines, U.S. Department of the Interior  
Reno, Nevada 89512, U.S.A

The Bureau of Mines has conducted in-depth studies on the recovery of aluminum chloride hexahydrate and alumina from domestic kaolinic clay. The original goal of the studies was to provide the technology for alumina production from domestic raw materials. Current research is focused on process modifications that would improve the economics of clay-HCl leaching and improve chances for transfer of the technology to commercial use. Options under investigation include direct leaching of raw clay, changes in leaching acid concentration and stoichiometry, decreased leaching duration, improved solid-liquid separations, elimination of solvent extraction for iron removal, and formation of basic aluminum chloride instead of aluminum chloride hexahydrate as an intermediate product. Implementation could decrease energy, equipment, and reagent costs by eliminating the calcination step, substituting filtration for thickening and washing circuits, and combining iron removal with aluminum chloride crystallization.

### Introduction

The Bureau of Mines has undertaken an extensive research program to provide technology to produce alumina economically from domestic resources and for use in a national emergency. A 25-ton-per-day pilot plant to produce alumina from kaolin clay by a HCl process was proposed (1), but not built because the world bauxite supply situation changed and eased the immediate need for this research. Unit operations of the process were piloted by the Bureau's Boulder City Engineering Laboratory (1-11) and problem areas were investigated at other Bureau of Mines Research Centers on a bench scale (12-26). This research demonstrated that the clay-HCl technology was feasible, but lack of commercial application indicated that industry was satisfied with the Bayer process if high-grade inexpensive bauxite was available. Current research is directed toward simplifying the HCl process and decreasing the energy consumption in the production of alumina from clay. In addition, several of the unit operations have not been thoroughly investigated and different stoichiometric ratios between HCl and alumina have not been investigated. This report describes the ongoing research program and presents preliminary results and conclusions.

A simplified flowsheet in Figure 1, hereinafter called the standard HCl process, shows the major unit operations in the proposed 25-ton-per-day pilot plant. Kaolin clay is calcined at 750° to 800° C to break the bonding between aluminum and silicon. The calcined clay is leached for 1 to 2 h with 25-pct acid at a

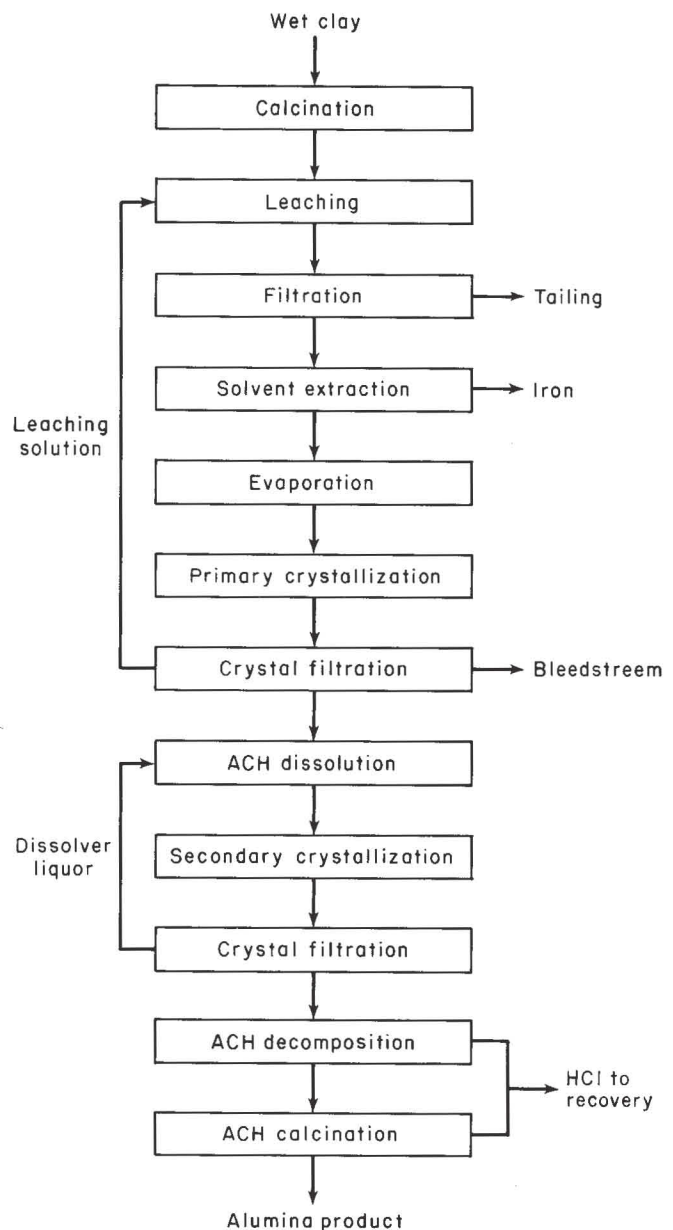


Figure 1. Simplified flowsheet for the proposed 25-ton-per-day clay-HCl pilot plant.

Table I. Maximum Limits for Selected Impurities in Reduction Grade Alumina Determined by USBM-Industry Subcommittee, percent

Impurity	Specification
Fe <sub>2</sub> O <sub>3</sub>	0.015
SiO <sub>2</sub>	.015
TiO <sub>2</sub>	.002
P <sub>2</sub> O <sub>5</sub>	.001
MgO	.002
Na <sub>2</sub> O	.40
CaO	.04
K <sub>2</sub> O	.005

boiling temperature of 104° C. Ninety-five percent of the aluminum is extracted as aluminum chloride and the pregnant solution has a slight excess of HCl. The soluble aluminum chloride is separated from the siliceous residue, and iron is removed by solvent extraction with Alamine 336.<sup>1</sup> The purified liquor is evaporated to 30 pct

AlCl<sub>3</sub> and sparged with HCl gas to crystallize aluminum chloride hexahydrate (ACH). The impurity limits are stringent (Table I) and a second crystallization and bleedstream are required to meet specifications for reduction-grade alumina. The purified ACH is calcined in two stages to alumina. Mother liquor and HCl are recycled through an acid recovery unit to clay leaching and HCl sparging.

Options under investigation for changing the flowsheet include direct leaching of raw clay to eliminate calcination and pelletizing operations, decreased leaching duration and better reactor design to improve solid-liquid separations, changes in leaching acid concentration and stoichiometry to decrease corrosion and form basic aluminum chloride instead of ACH as an intermediate product, and elimination of solvent extraction for iron removal by combining iron removal with ACH crystallization.

Direct Leaching of Raw Clay

Clay calcination uses about 12 pct of the processing energy to produce alumina, but for atmospheric pressure leaching it is needed to break the bonding between aluminum and silicon. The best alternative is pressure leaching, which allows leaching temperatures greater than the 104° C atmospheric boiling point of the acid-clay-AlCl<sub>3</sub> slurry. A 1-gal glass-lined Pfaudler reactor was used. Figure 2 shows aluminum extraction as a function of leaching temperature for 2-h leaches. Stoichiometry was 105 pct of the HCl needed to convert contained aluminum to AlCl<sub>3</sub>. Leaching acid concentration ranged from 17 to 37 pct and was not a significant factor. Pressure was varied from 15 to 130 psig and also was not a significant factor. Aluminum extraction in 2-h leaches was not significant at temperatures below 125° C, and was not acceptable for temperatures less than 145° C. Kinetic data by Sawyer and Turner (27) showed that 15- to 30-min leaching times are adequate if the temperature is 175° to 200° C. The research at temperatures 175° and 200° C was done in a fluorocarbon polymer-lined autoclave. Standard glass-lined pressure vessels that can tolerate HCl service cannot be used at temperatures greater than 160° C. Direct leaching of raw clay is feasible, but preliminary research showed that slurry filterability was impaired. Cost comparisons for standard and pressure HCl leaching must be made when better filtration data are available.

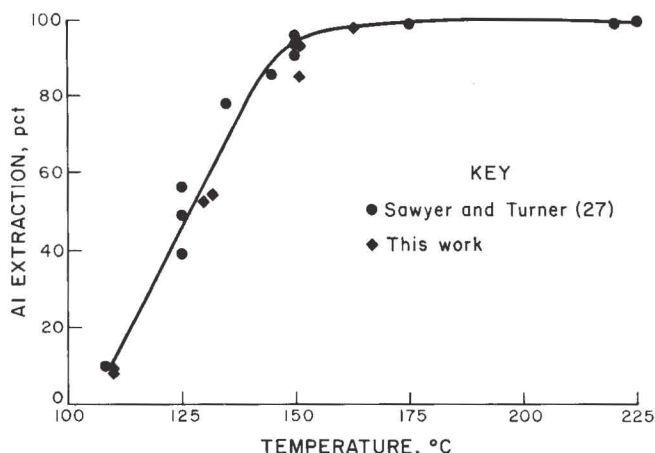


Figure 2. Aluminum extraction as a function of direct leaching of raw clay for 2 h with a 5 pct excess of 17- to 35-pct HCl.

The Effect of Leaching Parameters on Solid-Liquid Separation

The 25-ton-per-day pilot plant operating plan and design included 1- to 2-h residence times for the slurries in the leaching reactors. This insured greater than 95 pct aluminum extraction but led to extreme degradation of the siliceous residue. Extensive thickening, mud washing, and filtration circuits were planned to cope with large fines generation. Research at Boulder City Engineering Laboratory (4-5, 7,9-11), and at Reno and Albany Research Centers (20, 24-25) demonstrated that filtration problems can be decreased by a misting technique prior to clay<sup>2</sup> calcination, but this only partially solves the problem. A recent process evaluation study at the Avondale Research Center also indicated a cost of \$25/ton for producing calcined misted clay. This is much higher than the cost of methods not involving the misting technique used by the clay industry. Typical form times, cake thicknesses, and filter rates for calcined misted clay leached for 1.5 h at 104° C in an unbaffled, well-agitated reactor were 20 min, 0.5 in, and 7 lb/(ft<sup>2</sup>·h), respectively. Properly designed reactors with the minimum possible agitation decreased form time to 1 to 4 sec at cake thicknesses of 0.6 to 1.1 in, and increased filtration rates to 3,000 lb/(ft<sup>2</sup>·h). Decreasing the leaching time from 2 h to 15 min in a well-agitated unbaffled reactor also decreased form time to less than 4 sec at cake thicknesses of 0.6 to 1.1 in, and increased filtration rates to 3,000 lb/(ft<sup>2</sup>·h).

Published data and ongoing research show that, regardless of test conditions, leaching is very rapid if enough heat is added to start the exothermic reaction that reaches equilibrium at 104° C under atmospheric conditions. Figure 3 is typical of the kinetics for leaching kaolin clay calcined at 750° C and leached with a slight excess of HCl. Eighty percent

<sup>1</sup>Reference to trade names or specific manufacturers does not imply endorsement by the Bureau of Mines.

<sup>2</sup>Misted clay is produced by moistening crushed clay with a fine mist of water while tumbling on a rotating disc, followed by drying and calcining the dried clay in a fluidized bed at 750° C.

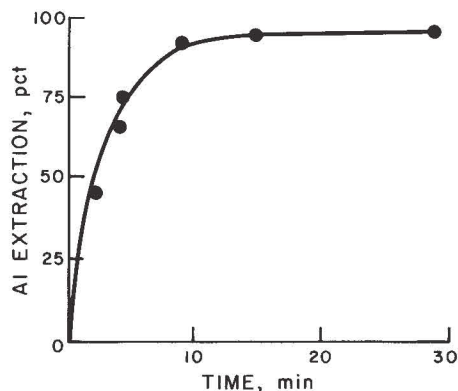


Figure 3. Aluminum extraction as a function of leaching time for misted clay in a stirred-tank reactor. Conditions: clay calcined at 750° C, 5 pct excess of 25-pct HCl, temperature 104° C at atmospheric pressure.

of the aluminum is leached in 5 min. After 15 min, 95 pct of the aluminum has been leached. Additional leaching time extracts only 1 to 2 pct. A considerable savings in settling, filtration, and washing circuitry should be realized by better leaching reactor design and shorter leaching times because of decreased attrition of the residue. There is no reason to compromise filterability and washability to gain a few percent aluminum recovery from low-value clay.

Leaching Acid Concentration and Stoichiometry

The process proposed in the 25-ton-per-day pilot plant utilizes a 24.8-pct HCl and 4.1-pct AlCl<sub>3</sub> solution for leaching kaolin at 105 pct stoichiometry. There are many possible leaching conditions ranging from dilute to concentrated HCl and from 50 to 400 pct stoichiometry. Acid concentration had very little effect on leaching efficiency. Acid concentrations of 20 to 37 pct gave rapid leaching and greater than 95 pct extraction of aluminum in atmospheric and pressure reactors for stoichiometries of 95 pct or greater. Pressure, per se, had no effect on leaching, but prevented vaporization of HCl, which is a problem for all but dilute concentrations of HCl, particularly those above the azeotropic concentration of 20-pct HCl.

A strong acid leaching method (28) was investigated to determine if aluminum would be converted directly to insoluble ACH while the leachable impurities would be separated from the ACH-siliceous residue by the strong acid. Ninety-nine percent of the alumina content of the clay was converted to ACH in less than 5 min. The ACH was not solubilized until leached with dilute acid and most of the impurities reported in the strong acid. The ACH purity was not substantially different from that produced in the standard HCl process, as shown by the data in Tables II to IV. Strong acid leaching solubilizes up to 10 pct of the titanium content in kaolin. The titanium is found in concentrations that exceed specifications in the first stage crystals, but does not report to the purified crystals in second stage crystallization. The slight gain in purity probably does not justify the use of pressure reactors and makeup HCl to keep the acid concentration above 36 pct. An interesting sidelight of strong acid leaching that may

warrant more attention was that the ACH generated within the silica grains ruptured the grains and gave a porous, uniform-sized filter cake that was easily separated from the pregnant liquor and washed.

Table II. Concentration of Impurities (on a calcined solids basis) in Pregnant Liquors for Standard and Strong Acid Processes, percent<sup>1</sup>

Compound	Bleedstream, pct					
	100		33		17	
	SP <sup>2</sup>	SAP <sup>3</sup>	SP	SAP	SP	SAP
Al <sub>2</sub> O <sub>3</sub>	96.6	96.1	94.9	90.9	85.3	68.6
Fe <sub>2</sub> O <sub>3</sub> <sup>4</sup>	2.7	2.7	4.0	6.4	11.9	24.4
MgO	.16	.19	.20	.42	.58	1.4
P <sub>2</sub> O <sub>5</sub>	.18	.18	.26	.53	.60	1.3
TiO <sub>2</sub>	.01	.37	.01	.27	.02	.31
CaO	.16	.18	.10	.30	.41	1.0
K <sub>2</sub> O	.17	.25	.38	.94	1.01	2.6
Na <sub>2</sub> O	.05	.07	.09	.19	.23	.28
SiO <sub>2</sub>	.01	.03	.04	.03	.01	.02

<sup>1</sup>The chemical compositions of the impurities were not determined, but in most cases they should be chlorides. They are reported as percent oxides in Al<sub>2</sub>O<sub>3</sub> to conform to industry practice.

<sup>2</sup>Standard process.

<sup>3</sup>Strong acid process.

<sup>4</sup>Iron not removed by solvent extraction.

Table III. Concentration of Impurities in Aluminum Chloride Hexahydrate after One Crystallization (reported as percent oxide in Al<sub>2</sub>O<sub>3</sub>)

Compound	Bleedstream, pct					
	100		33		17	
	SP <sup>1</sup>	SAP <sup>2</sup>	SP	SAP	SP	SAP
Fe <sub>2</sub> O <sub>3</sub>	0.0003	0.0003	0.028	0.0051	0.030	0.0010
MgO	.0020	.0023	.011	.0028	.013	.011
P <sub>2</sub> O <sub>5</sub>	.0094	.0072	.020	.013	.024	.035
TiO <sub>2</sub>	.0003	.021	.0002	.013	.0010	.014
CaO	.021	.014	.0088	.014	.0087	.014
K <sub>2</sub> O	.0008	.0037	.0044	.0044	.035	.012
Na <sub>2</sub> O	.0040	.0047	.0030	.0044	.0043	.0071
SiO <sub>2</sub>	.003	.003	.02	.01	.01	.01

<sup>1</sup>Standard process.

<sup>2</sup>Strong acid process.

Table IV. Concentration of Impurities in Aluminum Chloride Hexahydrate after Two Crystallizations (reported as percent oxide in Al<sub>2</sub>O<sub>3</sub>)

Compound	Bleedstream, pct					
	100		33		17	
	SP <sup>1</sup>	SAP <sup>2</sup>	SP	SAP	SP	SAP
Fe <sub>2</sub> O <sub>3</sub>	0.0003	0.0003	0.0044	0.008	0.0010	
MgO	.0003	.0013	NA	.0011	.0030	
P <sub>2</sub> O <sub>5</sub>	.0008	.0007	NA	.0014	.0019	
TiO <sub>2</sub>	.00005	.0013	NA	.0013	.014	
CaO	.004	.0040	NA	.011	.0039	
K <sub>2</sub> O	.0009	.0067	NA	.0035	.0052	
Na <sub>2</sub> O	.0014	.0040	NA	.0040	.0052	
SiO <sub>2</sub>	.01	.01	NA	.01	.01	

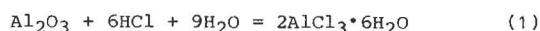
NA Not available.

<sup>1</sup>Standard process.

<sup>2</sup>Strong acid process.

Although a strong acid pressure leaching and sparging circuit is probably not cost effective, a pressure reactor may be useful for leaching with lesser concentrations of HCl because HCl cannot evaporate and leaching temperatures above the boiling point of the acid-clay slurry improve leaching kinetics. Figure 4 shows the temperature dependence of the 36-pct-HCl leaching rate of calcined clay. Leaching times for 90 pct extraction range from almost 2 h for the threshold temperature of 77° C to 4 min at 117° C.

Stoichiometry above 95 pct has little effect on leaching. Greater than 95 pct extraction is achieved when the HCl-to-alumina stoichiometries for the reaction



are between 95 and 400 pct. Substoichiometric amounts of HCl leach more aluminum than expected because aluminum chloride will dissolve alumina and produce a basic aluminum chloride (27,29). The reaction is much slower than the HCl-Al<sub>2</sub>O<sub>3</sub> reaction. Figure 5 shows the kinetics for leaching with substoichiometric amounts of 20-pct HCl with Cl-Al ranging from 1.5 to 3.0. The initial HCl leaching is very rapid and takes 10 min or less. When the HCl is consumed, the aluminum chloride continues to leach the clay, but at a much slower rate. The aluminum chloride leaching component increases in importance when the Cl-Al ratio decreases.

Aluminum chloride can also be used to leach calcined clay. Figure 6 shows the kinetics for leaching calcined clay with 24-pct aluminum chloride solution. The rate and amount of extraction decrease with decreasing Cl-Al ratio and are less than if the same Cl-Al ratio were provided by HCl. Although

maximum extractions were less than 90 pct, substoichiometric leaching may have promise because corrosion is greatly decreased and basic aluminum chlorides [3AlCl<sub>3</sub>·26Al(OH)<sub>3</sub> and 2AlCl<sub>3</sub>·11Al<sub>2</sub>O(OH)<sub>4</sub>], which take much less energy than ACH to decompose to oxide, can be recovered from solution by hydrolysis at 200° C. Figures 7 and 8 show hydrolytic recovery of aluminum from solution as functions of Cl-Al ratio, time, and seeding. Yields of up to 50 pct have been obtained by hydrolysis at 200° C for 6 h from a seeded solution. Problems being investigated include difficult filtration and washing of the fine crystalline product from the viscous mother liquor and purification of the liquor prior to crystallization.

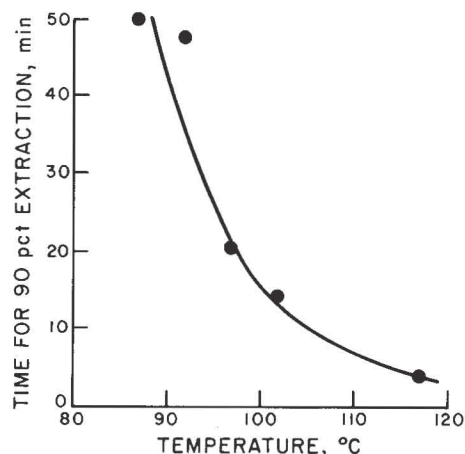


Figure 4. Temperature dependence of 36-pct HCl leaching rate of calcined kaolin.

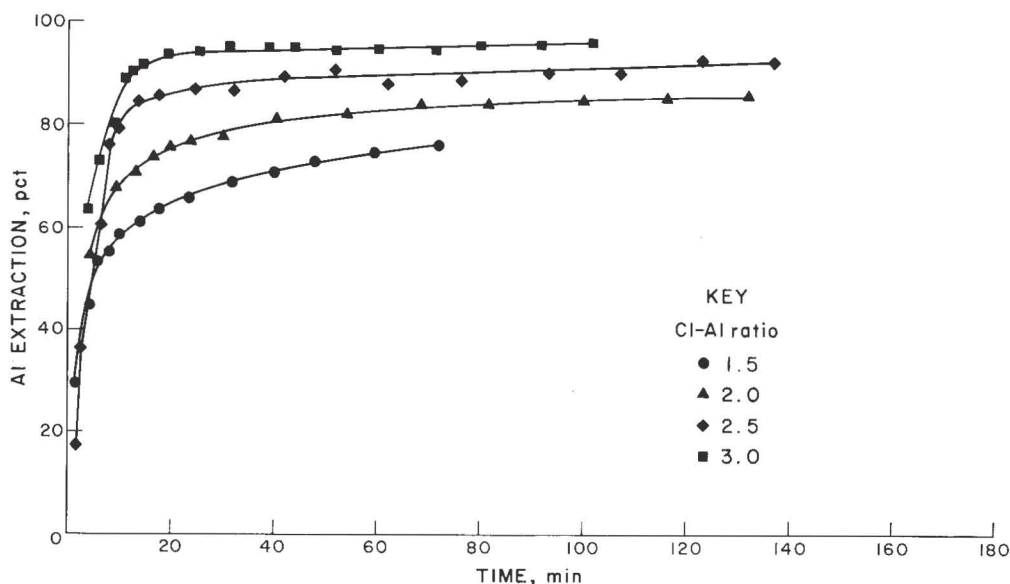


Figure 5. Aluminum extraction rate for leaching of calcined kaolin with 20-pct HCl at 104° C.

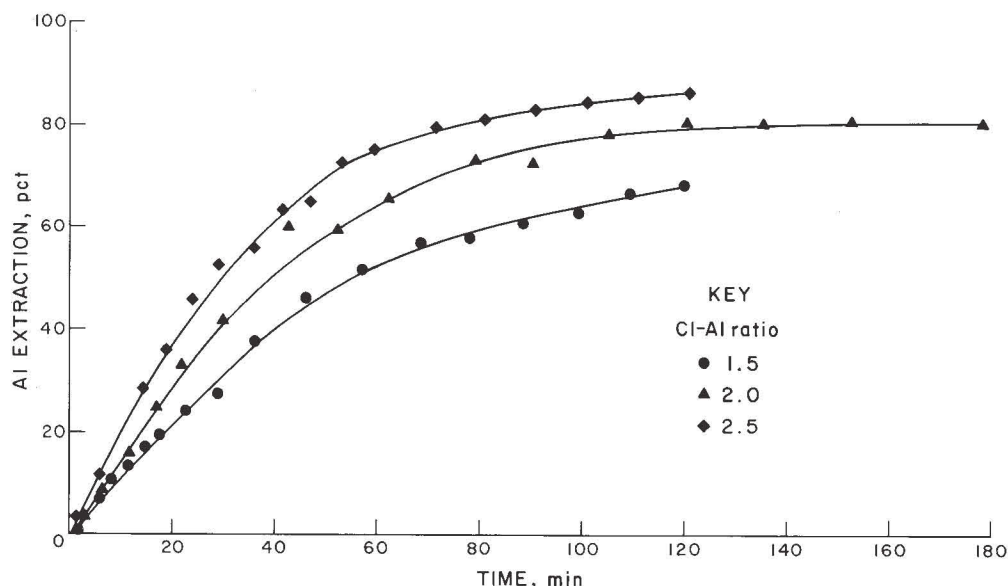


Figure 6. Aluminum extraction rate for leaching of calcined kaolin with 24-pct  $AlCl_3$  at  $104^\circ C$ .

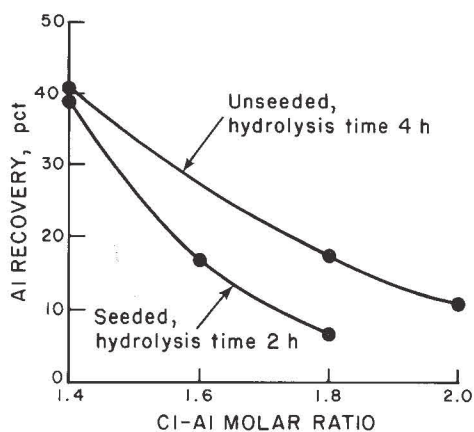


Figure 7. Hydrolytic recovery of aluminum as a function of chloride-to-aluminum ratio and seeding. Temperature  $200^\circ C$ .

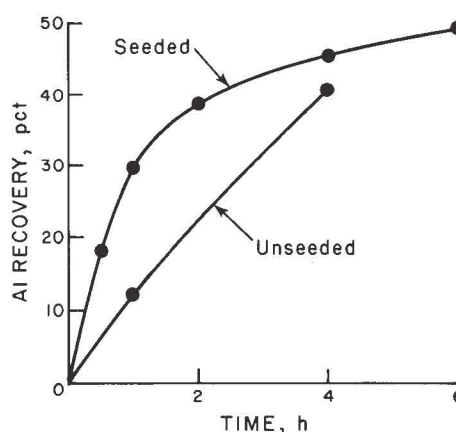


Figure 8. Hydrolytic recovery of aluminum as a function of hydrolysis time and seeding. Cl-Al molar ratio 1.4, temperature  $200^\circ C$ .

Iron Removal

Proposed HCl leaching schemes include a solvent extraction circuit to remove iron from the pregnant liquor. Calcined clay contains about 1.2 pct  $Fe_2O_3$ , which leaches in the same proportion as the aluminum. If 95 pct of the aluminum is recovered as  $AlCl_3$ , 95 pct of the iron will be leached into the pregnant solution as  $FeCl_3$ . Hydrochloric acid sparging crystallization of ACH gives good purification of aluminum with respect to iron. Ferric iron forms strong chloride complexes and remains in solution when the ACH salts out. The Bayer alumina specification of a maximum of 0.015 pct  $Fe_2O_3$  in  $Al_2O_3$  is easily attained with two crystallizations and can be met with a single crystallization and efficient washing. The ferric chloride will build up in the circuit until it is balanced by the bleedstream removal. Investigations are in progress to determine if the 1.5 pct ferric chloride that will be in the circuit at steady state has any effect on process unit operations other than crystallization. Sparging crystallization experiments

on solutions saturated with equal weights of ferric and aluminum chlorides showed that HCl saturation was reached at a lower concentration and that ACH salted out more completely than from a solution containing only aluminum chloride. Saturated ferric chloride solution may enhance aluminum leaching. If so, and if the iron causes no problems in the system, solvent extraction of iron can be eliminated. One possible problem is that iron will interfere with ACH and HCl recovery from the bleedstream circuit.

In order to study these possibilities and to optimize the clay-HCl process, a multicycle campaign is in progress. The block flow diagram is shown in Figure 9 and the material balance in Table V. Major differences from the proposed 25-ton-per-day pilot plant process are that HCl concentration is 20 pct instead of 25 pct, leaching time is 15 min instead of 1 to 2 h, and iron is not removed by solvent extraction. For the initial run, 795 g of calcined kaolin clay was leached for 15 min with 3,845 g of solution whose composition approximated a steady state recycle

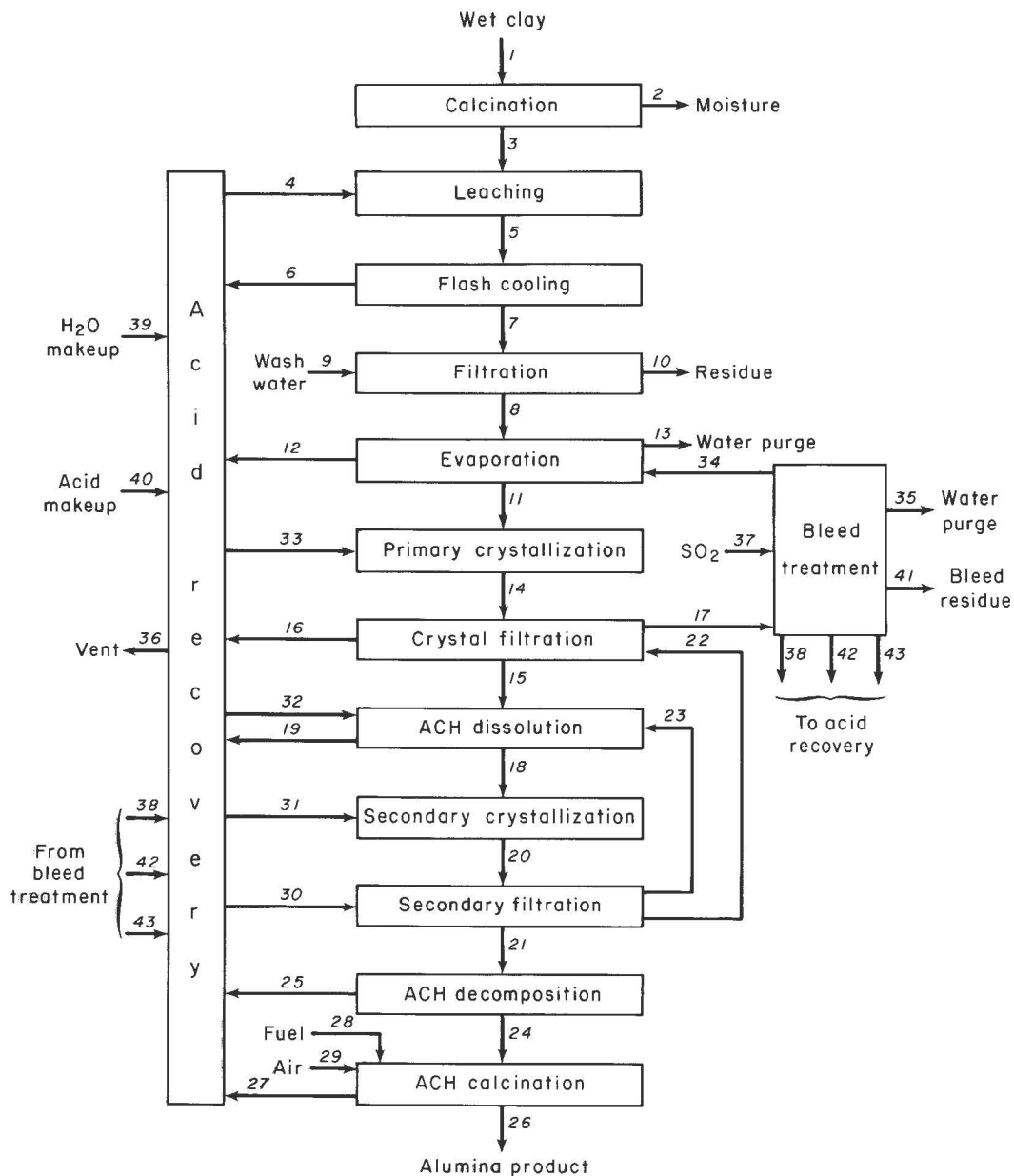


Figure 9. Flowsheet for a modified process for a 25-ton-per-day pilot plant.

Table V. Material Balance for a Process Based on a Modified Flowsheet of the Kaiser Engineers' 25-ton-per-day Pilot Plant, grams

Process stream	Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub> ·6H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub> and SiO <sub>2</sub>	HCl	H <sub>2</sub> O (free)	Total <sup>1</sup>
1: Wet clay.....	342	-	-	10	440	-	340	1,135
2: Stack moisture.....	-	-	-	-	-	-	340	340
3: Calcined clay feed.....	342	-	-	10	440	-	-	795
4: Leach acid.....	-	213	60	-	-	767	2,801	3,845
5: Hot slurry.....	21	1,733	86	2	440	68	2,282	4,640
6: Flash vapor.....	-	-	-	-	-	33	452	485
7: Cooled slurry.....	21	1,733	86	2	440	35	1,830	4,155
8: ACH solution.....	-	1,733	86	-	-	35	2,386	4,247
9: Wash water.....	-	-	-	-	-	-	1,020	1,020
10: Residue.....	21	-	-	2	440	-	464	928
11: Crystal feed.....	-	1,761	86	-	-	11	1,542	3,407
12: HCl solution.....	-	-	-	-	-	24	722	746
13: Water purge.....	-	-	-	-	-	-	125	125
14: ACH slurry.....	-	1,761	86	-	-	573	1,542	3,969
15: ACH cake.....	-	1,614	1	-	-	1	127	1,743

Table 5 (continued)

Process stream	Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub> ·6H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub> and SiO <sub>2</sub>	HCl	H <sub>2</sub> O (free)	Total <sup>1</sup>
16: Filtrate.....	-	213	60	-	-	639	1,573	2,489
17: Bleed.....	-	38	26	-	-	221	514	802
18: Refined ACH solution.....	-	2,050	2	-	-	39	1,212	3,303
19: Dissolver HCl.....	-	-	-	-	-	299	6	305
20: Refined ACH slurry.....	-	2,050	2	-	-	441	1,212	3,705
21: Refined ACH cake.....	-	1,510	-	-	-	75	144	1,729
22: Primary crystal wash.....	-	104	1	-	-	288	672	1,065
23: Filtrate.....	-	436	1	-	-	337	960	1,734
24: Calcine feed.....	287	151	-	-	-	-	-	438
25: Decomposer gas.....	-	-	-	-	-	691	601	1,292
26: Product alumina.....	319	-	-	-	-	-	-	319
27: Calcine gas.....	-	-	-	-	-	68	51	119
28: Fuel.....	-	-	-	-	-	-	-	-
29: Air.....	-	-	-	-	-	-	-	-
30: Wash acid.....	-	-	-	-	-	259	564	823
31: HCl sparge.....	-	-	-	-	-	402	-	402
32: Dissolver makeup.....	-	-	-	-	-	-	131	131
33: HCl sparge.....	-	-	-	-	-	562	-	562
34: ACH recycle.....	-	28	-	-	-	-	3	31
35: Water purge.....	-	-	-	-	-	-	432	432
36: Gas vent <sup>2</sup> .....	-	-	-	-	-	-	-	-
37: SO <sub>2</sub> <sup>2</sup> .....	-	-	-	-	-	-	-	-
38: HCl from bleed calcine.....	-	-	-	-	-	74	25	99
39: Makeup H <sub>2</sub> O <sup>2</sup> .....	-	-	-	-	-	-	-	-
40: Makeup acid <sup>2</sup> .....	-	-	-	-	-	-	-	-
41: Bleed residue.....	2	-	-	8	-	-	-	12
42: Dilute HCl.....	-	-	-	-	-	74	32	106
43: HCl evaporate.....	-	-	-	-	-	88	34	122

- Less than 0.5 g.

<sup>1</sup>Minor impurities followed only in the total column, but most have approximately the same distribution as iron. Weights rounded to nearest gram.

<sup>2</sup>Variable depending on requirements.

solution with a 34.5-pct bleedstream from which iron is not removed by solvent extraction. The solution contained 20 pct HCl, 3.0 pct AlCl<sub>3</sub>, 0.9 pct FeCl<sub>3</sub>, and minor amounts of impurities. The slurry was filtered and the solids washed with 1,020 g of water. Six percent of the alumina and 19 pct of the iron oxide in the feed clay, all the silica and titania and 464 g of water reported to the residue. The filtrate was evaporated to 30 pct AlCl<sub>3</sub> or 54.3 pct ACH and sparged at 60° C to a final HCl concentration in the mother liquor of 26 pct. The crystal slurry was filtered and the mother liquor split in two fractions: (1) 34.5 pct was taken as a bleed stream and (2) the remainder plus 1,124 g of wash liquor was returned to acid leaching. Makeup HCl and H<sub>2</sub>O were added as necessary. The crystals were slurried in simulated mother liquor from the second crystallization and heated to drive off HCl and allow the ACH crystals to dissolve. The purified solution was sparged at 60° C to a mother liquor HCl concentration of 20 pct and the slurry filtered. The high-purity ACH crystals were calcined to alumina. The mother liquor from second crystallization was split into a recycled stream to the ACH dissolver (83.2 pct) and a 16.8-pct stream for combination with 1,015 g of 31-pct HCl wash solution for washing the first crystallization filter product. At steady state, the mother liquor from the first crystallization, which was split to a 34.5-pct bleedstream, contained 27.6 pct HCl, 1.9 pct FeCl<sub>3</sub>, and 2.6 pct AlCl<sub>3</sub>. The HCl process designed for the pilot plant recovered HCl and aluminum from the bleedstream by evaporative crystallization. Evaporative crystallization experiments are in progress to determine the

suitability of this circuit when large amounts of iron are present. Ninety-three percent of the alumina contained in the clay feed was recovered per cycle as a purified product that was equivalent to Bayer-grade alumina.

#### Summary and Conclusions

Research to gather data for economic evaluations of the best options for producing alumina by HCl leaching of kaolin clay is continuing. The following experimental results should weigh heavily in a final process selection:

- Aluminum extractions of greater than 95 pct can be obtained from raw clay by increasing the leaching temperature to at least 160° C, but separation of the pregnant liquor from leach residue is a major problem.
- Acid concentrations of 20- to 37-pct HCl gave rapid leaching and greater than 95 pct extraction of aluminum in atmospheric and pressure reactors if the stoichiometry exceeded 95 pct and leaching time exceeded 15 to 30 min. High concentrations of HCl will flash at boiling temperature unless contained under pressure.
- Clay particle degradation must be kept to a minimum to prevent filtration difficulties. Duration of leaching has a large effect on particle degradation and must be kept to a minimum.

- Substoichiometric concentrations of HCl give a combined HCl-AlCl<sub>3</sub> leaching mechanism, more concentrated aluminum solutions, and decreased corrosion. Leaching rates and filterability of the solids are decreased.
- Leaching and crystallization in the pulps maintained at 37 pct HCl by sparging HCl gas in a pressure reactor give greater than 99 pct aluminum recovery in less than 5 min and produce an easily filtered siliceous residue. Titanium is dissolved from the clay and alumina purity is not increased.
- Ferric chloride is easily separated from aluminum chloride by HCl crystallization and acid washing, and decreases the amount of HCl required to crystallize ACH from pregnant liquor.
- None of the leaching systems will produce Bayer-grade alumina without double crystallization and a bleedstream greater than 20 pct.

The best clay-HCl process will be a tradeoff between maximum aluminum recovery and minimum process cost. Clay is an inexpensive raw material and aluminum extractions less than 90 pct may provide the lowest process cost. The cost comparisons between clay-HCl and Bayer processes are difficult because Bayer technology is well refined and HCl is not.

#### References

1. K. B. Bengtson, P. Chuberka, R. F. Nunn, A. U. San Jose, G. M. Manarolis, and L. E. Malm, Alumina Process Feasibility Study and Preliminary Pilot Plant Design, Task 3 Report: Preliminary Design of a 25 TPD Pilot Plant, Volume I. Process Technology and Costs, U.S. Bur. Mines Open File Rep. 122-80(1), 1980, 231 pp.; NTIS PB 81-125031.
2. R. T. Sorenson, E. B. Amey III, and D. L. Sawyer, The Removal of Iron From Aluminum Chloride Leach Liquor by Solvent Extraction, U.S. Bur. Mines Rep. Invest. 8560, 1981, 28 pp.
3. J. H. Maysilles, D. E. Traut, and D. L. Sawyer, Jr., Aluminum Chloride Hexahydrate Crystallization by HCl Gas Sparging, U.S. Bur. Mines. Rep. Invest. 8590, 1982, 38 pp.
4. R. L. Rickel, P. J. Barrett, and D. M. Starrett, Sand Bed Dewatering of Alumina Miniplant Tailings, U.S. Bur. Mines. Rep. Invest. 8677, 1982, 10 pp.
5. John L. Schaller, Don B. Hunter, and Dwight L. Sawyer, Jr., Alumina Miniplant Operations--Production of Misted Raw Kaolin Feed, U.S. Bur. Mines. Rep. Invest. 8712, 1982, 20 pp.
6. Theodore L. Turner, Dwight L. Sawyer, Jr., Don B. Hunter, and Earle B. Amey III, Alumina Miniplant Operations--Calcination of Kaolin in a Direct-Fired Rotary Kiln, U.S. Bur. Mines. Rep. Invest. 8736, 1982, 24 pp.
7. Daniel T. Rogers and Roy T. Sorenson, Jr., Computer Simulation Applied to the Separation of Porous Leach Residue Solids From Liquor by Horizontal Belt Filtration, U.S. Bur. Mines Inf. Circ. 8873, 1982, 27 pp.
8. Dwight L. Sawyer, Jr., Theodore L. Turner, and Don B. Hunter, Alumina Miniplant Operations--Overall Mass Balance for Clay-HCl Acid Leaching, U.S. Bur. Mines Rep. Invest. 8759, 1983, 29 pp.
9. Roy T. Sorenson, Dwight L. Sawyer, Jr., and Theodore L. Turner, Alumina Miniplant Operations--Separation of Aluminum Chloride Liquor From Leach Residue Solids by Classification and Thickening, U.S. Bur. Mines Rep. Invest. 8805, 1983, 23 pp.
10. Roy T. Sorenson and Dwight L. Sawyer, Jr., Alumina Miniplant Operations--Separation of Aluminum Chloride Liquor From Leach Residue by Horizontal Belt Filtration, U.S. Bur. Mines Rep. Invest. 8831, 1984, 44 pp.
11. Don B. Hunter, Dwight L. Sawyer, Jr., and Theodore L. Turner, Alumina Miniplant Operations--Influence of Reactor Design on the Attrition of Calcined Kaolin During HCl Leaching, U.S. Bur. Mines Rep. Invest. 8877, 1984, 21 pp.
12. J. A. Eisele, L. E. Schultze, D. J. Berinati, and D. J. Bauer, Amine Extraction of Iron From Aluminum Chloride Leach Liquors, U.S. Bur. Mines Rep. Invest. 8188, 1976, 10 pp.
13. R. R. Brown, G. E. Daut, R. V. Mrazek, and N. A. Gokcen, Solubility and Activity of Aluminum Chloride in Aqueous Hydrochloric Acid Solutions, U.S. Bur. Mines. Rep. Invest. 8379, 1979, 17 pp.
14. L. Keith Hudson and Jamie K. Carnevale, Direct Calcination of AlCl<sub>3</sub>·6H<sub>2</sub>O With Off-Gas Use for Crystallization, U.S. Bur. Mines Open File Rep. 62-81, 1979, 28 pp.; NTIS PB 81-214827.
15. N. A. Gokcen, Partial Pressures of Gaseous HCl and H<sub>2</sub>O Over Aqueous Solutions of HCl, AlCl<sub>3</sub>, and FeCl<sub>3</sub>, U.S. Bur. Mines Rep. Invest. 8456, 1980, 18 pp.
16. J. A. Eisele, Producing Alumina From Clay by the Hydrochloric Acid Process, A Bench-Scale Study, U.S. Bur. Mines Rep. Invest. 8476, 1980, 20 pp.
17. B. S. Covino, Jr., M. Rosen, and W. D. Riley, Corrosion Resistance of Materials in the Aqueous Hydrochloric Acid Environments Associated With the Recovery of Aluminum From Kaolinitic Clays, U.S. Bur. Mines. Rep. Invest. 8565, 1981, 28 pp.
18. D. E. Shanks, J. A. Eisele, and D. J. Bauer, Hydrogen Chloride Sparging Crystallization of Aluminum Chloride Hexahydrate, U.S. Bur. Mines Rep. Invest. 8593, 1981, 15 pp.
19. William D. Riley and Bernard S. Covino, Jr., Effect of Ferric Ion on Corrosion Resistance of Zirconium in HCl-AlCl<sub>3</sub> Environment, U.S. Bur. Mines. Rep. Invest. 8610, 1982, 18 pp.
20. R. S. Olsen, W. G. Gruzensky, S. J. Bullard, and J. L. Henry, Effects of Feed Preparation on HCl Leaching of Calcined Kaolinitic Clay to Recover Alumina, U.S. Bur. Mines Rep. Invest. 8618, 1982, 24 pp.
21. Jack C. White, Jack L. Henry, and Charles J. Krogh, Removal of Organic Contaminants From Aluminum Chloride Solutions, U.S. Bur. Mines Rep. Invest. 8619, 1982, 17 pp.



22. James P. Bennett, Corrosion Resistance of Ceramic Materials to Hydrochloric Acid (20 Wt-Pct at 50° C), U.S. Bur. Mines Rep. Invest. 8650, 1982, 11 pp.

23. Robert M. Doerr, Laboratory Studies on the Treatment of Ferric Chloride Stripping Liquor From a Clay-Hydrochloric Acid Leaching Process, U.S. Bur. Mines Rep. Invest. 8725, 1982, 7 pp.

24. R. S. Olsen, S. J. Bullard, W. G. Gruzensky, R. V. Mrazek, and J. L. Henry, Leaching Rates for the HCl Extraction of Aluminum From Calcined Kaolinitic Clay, U.S. Bur. Mines Rep. Invest. 8744, 1983, 11 pp.

25. R. S. Olsen, W. G. Gruzensky, S. J. Bullard, and Jack L. Henry, Factors Affecting the Preparation of Misted Clay Feed and Solids-Liquid Separation After HCl Leaching, U.S. Bur. Mines Rep. Invest. 8772, 1983, 2 pp.

26. James P. Bennett, Corrosion Resistance of Ceramic Materials to Hydrochloric Acid, U.S. Bur. Mines Rep. Invest. 8807, 1983, 14 pp.

27. D. L. Sawyer, Jr., and T. L. Turner, Pressure Leaching Alumina From Raw Kaolinitic Clay Using Hydrochloric Acid, U.S. Bur. Mines Rep. Invest. 8978, 1985, 18 pp.

28. D. J. Bauer, D. E. Shanks, and J. A. Eisele, A Strong Acid-Weak Acid Method for Producing Aluminum Chloride Hexahydrate From Kaolinitic Clay, U.S. Bur. Mines Rep. Invest. 8908, 1984, 7 pp.

29. P. R. Bremner, L. J. Nicks, and D. J. Bauer, A Basic Chloride Method for Extracting Aluminum From Clay, U.S. Bur. Mines Rep. Invest. 8866, 1984, 8 pp.