Ten-Cycle Bench-Scale Study of Simplified Clay-Hydrogen Chloride Process for Alumina Production

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By D. E. Shanks

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mL	milliliter
g	gram	N	normal concentration
g/L	gram per liter	pct	percent
g/mL	gram per milliliter	ppm	part per million
h	hour	st/d	short ton per day
kg/(m²·h)	kilogram per square meter per hour	t/d	metric ton per day
L	liter	μg/mL	microgram per milliliter
L/min	liter per minute	°C	degree Celsius
min	minute		

TEN-CYCLE BENCH-SCALE STUDY OF SIMPLIFIED CLAY-HYDROGEN CHLORIDE PROCESS FOR ALUMINA PRODUCTION

By D. E. Shanks[1]

ABSTRACT

This U.S. Bureau of Mines (USBM) research simplified an earlier hydrogen chloride (HCl) leach-sparge process developed by the USBM to recover reduction-grade alumina from domestic kaolin clay. Improvements were made by decreasing the initial leaching acid concentration from 25 to 20 pct, decreasing the leaching time from 1 to 2 h to 15 to 30 min, eliminating the solvent extraction step for Fe removal, and eliminating the step to recover the Al content of the bleedstream circuit. A 10-cycle bench-scale experiment of the simplified process showed that the ferric chloride ($FeCl_3$) concentration built up to 9.3 g/L in the recycle stream. This did not interfere with any of the unit operations or final alumina product purity because Fe forms stable soluble chloride complexes when sparged with HCl and is easily washed from the large aluminum chloride hexahydrate (ACH) crystals. The reduced leaching time and acid concentration did not decrease Al extraction.

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[1]Supervisory research chemist, Reno Research Center, U.S. Bureau of Mines, Reno, NV (retired).

INTRODUCTION

The U.S. Bureau of Mines (USBM) has long been interested in alternative Al resources to bauxite and the technology for developing them as a viable alternative to the Bayer, Hall-Heroult process for Al production. The United States is almost totally dependent on foreign sources for bauxite. Most of these source nations have discovered that they can maximize their profits by processing bauxite and selling either alumina or Al. This increasing dependence on foreign sources for raw materials, and even finished products, is putting the United States at risk strategically and helping it to become more of a debtor nation. The shortage of Al raw materials is not the problem. Aluminum is the most plentiful metallic element in the Earth's crust. There are large deposits of Al-containing minerals in the United States, but with the exception of small deposits of high silica bauxite, all are lower grade than commercial bauxites and contain significant amounts of soluble silica. All of the free-world's Al production utilizes the Bayer process to extract pure alumina from bauxite for reduction to the metal. Large amounts of soluble silica cannot be tolerated in the Bayer process because the caustic soluble silica reacts with sodium aluminate to precipitate both Al and silica from solution, while some of the remaining silica finds its way to the Al metal product. The specification for silica in alumina calls for less than 0.015 pct.

A solution to this problem is to develop technology to economically utilize domestic resources. The USBM first started investigating Al recovery from clay in 1922 and made a major effort starting in 1973 to find a process to extract alumina from domestic nonbauxitic resources. The final method of choice was the hydrogen chloride (HCl) acidified aluminum chloride ($AlCl_3$) solution leach of calcined kaolin, HCl sparge crystallization route. Specific aspects of this process were investigated in several research centers, and the major unit operations were tested in a miniplant at the Boulder City (Nevada) Engineering Laboratory. Kaiser Engineers, Inc., under contract with the USBM, published plans for the design and operation of a 22.7-t/d (25-st/d) pilot plant based on this research.[2]

A flowsheet of the process investigated at Boulder City is illustrated in figure 1. The figure illustrates the major unit operations in the proposed pilot plant, which is hereinafter called the standard HCl process. Kaolin clay is

calcined at 750 to 800 °C to break the bonding between Al and Si. The calcined clay is leached for 1 to 2 h with recycled $AlCl_3$ liquor, initially acidified with 25 pct HCl at a boiling temperature of 104 °C. Ninety-five percent of the Al is extracted as $AlCl_3$, and the pregnant solution has a slight excess of HCl. The soluble $AlCl_3$ is separated from the siliceous residue, and Fe is removed by solvent extraction with a tertiary amine. The purified liquor is evaporated to 30 pct $AlCl_3$ and sparged with HCl gas to crystallize aluminum chloride hexahydrate (ACH). The impurity limits set for the process are stringent (table 1), and a bleedstream and second crystallization are required to meet specifications for reduction-grade alumina. Mother liquor and HCl are recycled through an acid-recovery unit to clay leaching and HCl sparging, respectively.

Table 1.—Suggested impurity limits for reduction-grade alumina determined by USBM-industry subcommittee, percent

Impurity	Limit
Na_2O	0.40
CaO	0.04
Fe_2O_3	0.015
SiO_2	0.015
K_2O	0.005
MgO	0.002
TiO_2	0.002
P_2O_5	0.001

The standard HCl process, as designed, cannot economically compete with the Bayer process in an open international market. Studies were carried out at a time when the cost of bauxite was starting to increase because of perceived shortages and there were fears of cartel action. The goal was to demonstrate that the United States could develop technology if forced and to avoid having to pay an artificially high price. Subsequently, exploration increased and large bauxite reserves were found in some tropical areas of the world. The price of bauxite stabilized, eliminating the need for pilot plant demonstration. However, before the technology was consigned to the archives, areas in the process that were amenable to simplification and that might make the standard HCl process more cost competitive with the Bayer process were investigated.

Variants to the standard HCl process that were explored were pressure leaching of raw clay (1),[3] a strong

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[2]OFR 122(1)-80. Alumina Process Feasibility Study and Preliminary Pilot Plant Design. Task 3 Report: Preliminary Design of a 25 Ton Per Day Pilot Plant. Volume I. Process Technology and Costs, by K. B. Bengston, P. Chuberka, R. F. Nunn, A. V. San Jose, G. M. Manarolis, and L. E. Malm.

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

Figure 1
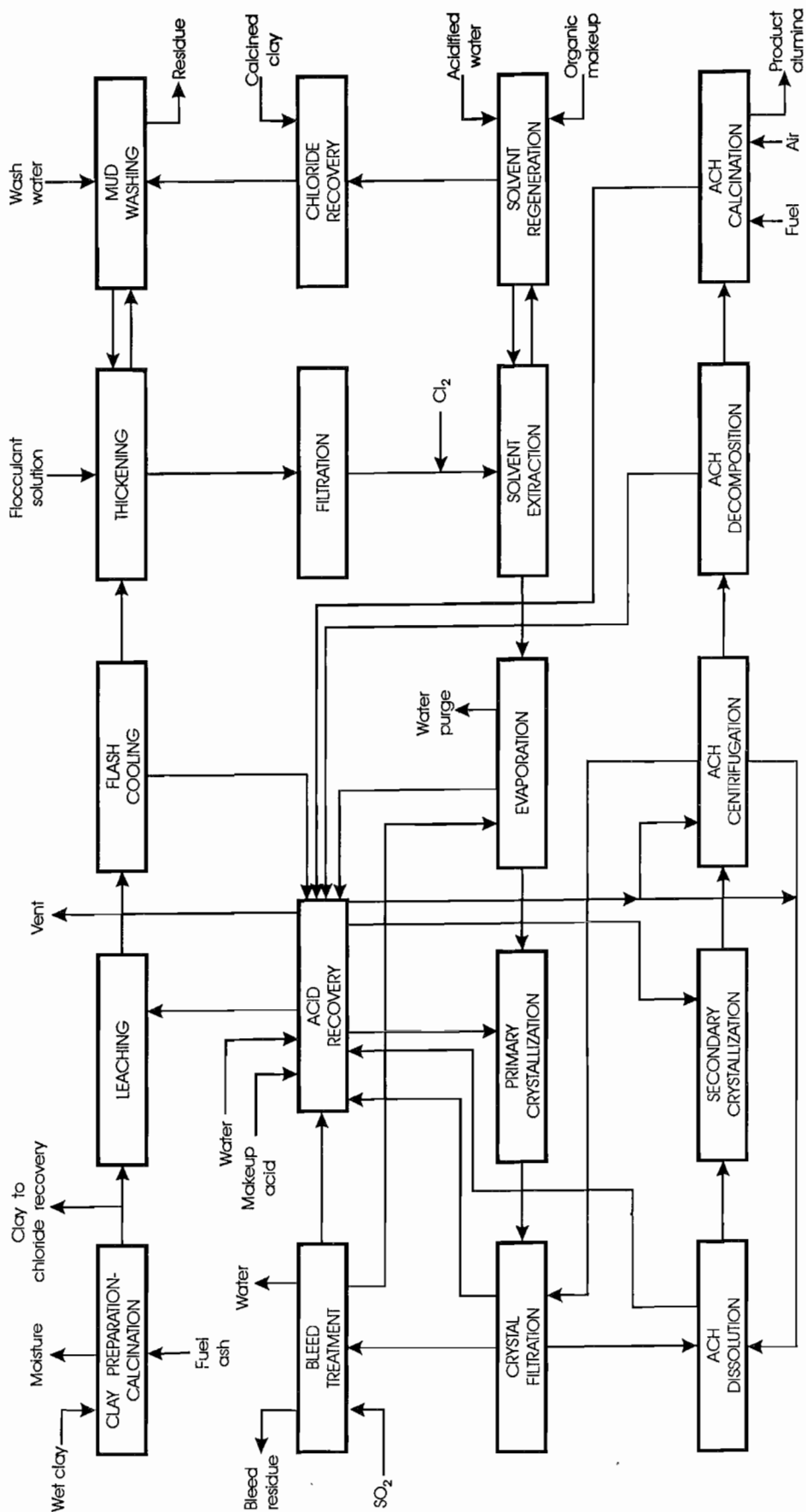
Flowsheet for proposed standard HCl process pilot plant (work cited in footnote 2).

acid-weak acid leach (2), AlCl₃ leaching (3), and the separation of Fe from Al in the sparging crystallization steps (4).

The objective of the pressure leaching work was to bypass the calcination of raw clay, eliminating a significant cost in the process. The report showed that raw clay can be satisfactorily leached to recover the Al, but did not address the liquid-solid separation of pregnant solution from the silica residue. The strong acid-weak acid leaching research demonstrated that alumina purity was enhanced by leaching the clay in strong HCl; the impurities were dissolved and the Al remained insoluble as ACH until leached with dilute acid or water. But questions remained about handling problems under such corrosive conditions. An AlCl₃ method for leaching clay was successful in obtaining higher Al loadings in solution with lower energy expenditure. However, this initial study did not address product purity or handling problems. A study on the sparging crystallization of halide salts indicated that ferric chloride ($FeCl_3$) might not interfere with the purity of the final alumina product. The Fe remains in solution as a soluble chloride complex, $FeCl_4^-$, in concentrated chloride solution. This had possible significance in simplifying the standard HCl process because it meant that Fe could be separated from Al in the HCl sparging crystallization step and thereby eliminate the need for a separate solvent extraction step.

Subsequently, more thorough studies (5-7) showed that pressure leaching of raw clay was not feasible because the finely divided silica residue was difficult to separate from the pregnant liquor and also difficult to wash. Evaluation of more extensive data showed that the gains in purity with the strong acid-weak acid scheme were not significant enough to justify the handling problems associated with 36 pct HCl at over 100 °C. The AlCl₃ leaching method was not feasible because handling problems were severe and large amounts of silica dissolved in the AlCl₃ solution. However, the above studies (5-7) and earlier leaching research at the USBM's Albany (Oregon) Research Center (8-10) demonstrated that HCl concentration was not critical and even stoichiometric deficiencies of HCl up to 5 pct gave 95-pct Al recovery. Leach times over 15 to 30 min did not increase Al extraction and had a detrimental effect on the leach residue handling operations. Figures 2 through 5 illustrate these points. Figure 2 (5, 9) was plotted from data gathered under the standard HCl process conditions of leaching with 25 pct HCl.[4] It shows that 95-pct Al extraction was achieved in 15 min. Figure 3

(5) was plotted from data gathered to show the effect of temperature on the rate of Al extraction with 36 pct HCl. Extraction at 104 °C, the same leaching temperature as in figure 2, demonstrates that the leach times for 25 and 36 pct HCl are approximately the same. Figure 4 (7) shows the effects of time and HCl stoichiometry on Al

Figure 2
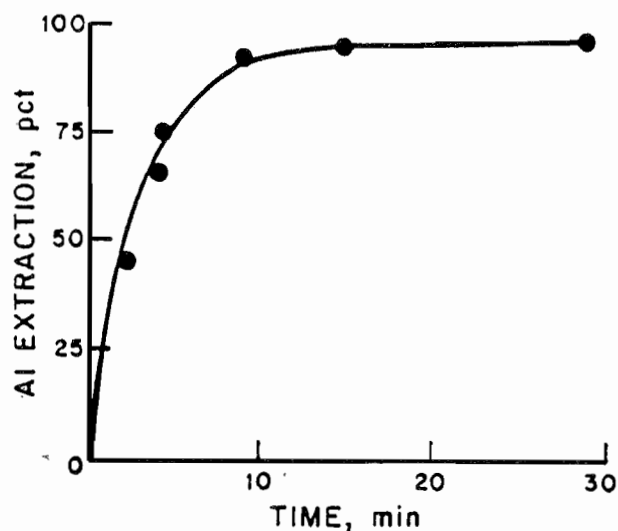
Aluminum extraction as function of leaching time for misted clay in batch, stirred-tank reactor (5, 9). Conditions: clay calcined at 750 °C, 5 pct excess of 25 pct HCl, 104 °C at atmospheric pressure.

Figure 3

Temperature dependence of 36 pct HCl leaching rate of calcined kaolin (5).

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[4]For simplicity, the convention of stating the starting acid concentration has been used in this and most other alumina project research. In a batch process, the HCl concentration will decrease as the reaction proceeds and the AlCl₃ will increase. Both AlCl₃ and HCl are leachants and contribute to the dissolution of alumina and impurities from the clay.
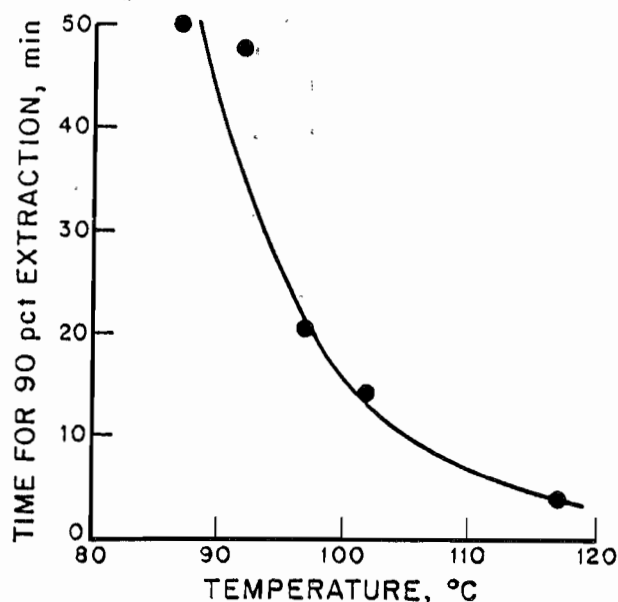
extraction with 20 pct HCl. The extraction rate using 20 pct HCl was comparable with the extraction rates with 25 and 36 pct HCl. Figure 5 (6) is a plot of dry cake form rate as a function of cake thickness. It compares the effect of leaching time on the filterability of two misted, calcined clay leaching residues. The data in the upper curve were collected from a 15-min leach, while the data in the lower curve were collected from a 1-h leach. The dry cake form rates were about two orders of magnitude faster for the clay leached for the shorter time.

These data and the preliminary results on Fe separation from Al during HCl sparging crystallization of $AlCl_3$ were the basis for the changes incorporated in this work. These changes have the potential to significantly decrease the cost of alumina made by the standard HCl process. If the Fe can be removed in the HCl sparging crystallization step, the solvent extraction step, which consists of unit operations for Fe oxidation, solvent extraction, stripping, and $FeCl_3$ recovery, could be eliminated. The Fe could be removed with the other impurities in the bleedstream. The decreased leaching time would result in less breakup of the silica residue and allow for filtration as a means of liquid-solid separation instead of extensive thickening and mud washing. The decreased acid concentration should lead to less corrosion and reduced HCl losses.

The feasibility of these goals was realized by conducting research to gather additional data on the solubility of HCl, $AlCl_3$, and $FeCl_3$ in the system HCl-$AlCl_3$-$FeCl_3$-H_2O and by conducting 10 cycles of a bench-scale experiment to verify that the modifications and deletions of unit operations to the standard HCl process significantly simplified

the process without compromising yield and purity of the alumina product. The modifications included elimination of the solvent extraction circuit to remove Fe, elimination of the circuit to recover ACH from the bleedstream, decrease of the leaching time to 15 to 30 min, decrease of the recycled leaching acid concentration to 20 pct HCl, and a decrease in final HCl concentration in the mother liquor of the second crystallization to 20 pct. Modeling of the proposed circuit showed that Fe, as $FeCl_3$, should achieve a steady-state concentration of 0.82 pct (9.3 g/L) in the recycle stream to leaching and the yield of alumina from the process could be expected to be approximately the same as the 93 pct originally planned by Kaiser. The increased load of Fe in the circuit would have to be handled by the bleedstream, which would make it harder to recover ACH from the bleedstream circuit before disposal. However, the Al content of the bleedstream is projected to be only 3.5 pct of the total, so the loss will not be great. Although HCl concentration in the recycle liquor

Figure 5
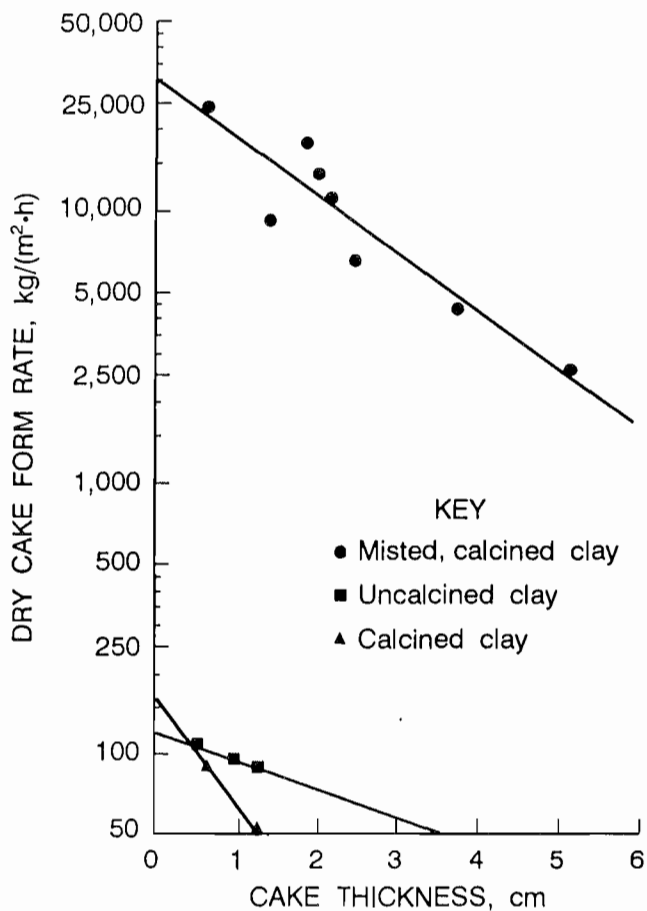
Dry cake form rate as function of cake thickness (6).

Figure 4

Aluminum extraction during leaching of calcined kaolin with 20 pct HCl at 104 °C (7).

would be reduced to 20 pct without any anticipated loss in Al recovery, the HCl concentration in first sparge-crystallization had to remain at 26 pct to minimize Al loss in the bleedstream. The same was not true of the second crystallizer circuit, so the HCl was sparged to a final solution concentration of 20 pct to see if this had any serious effect on final ACH purity. Aluminum recovery from the second crystallization will be decreased, but this should pose no problem because the Al recycles in the circuit and will eventually be recovered.

MATERIALS AND EQUIPMENT

The calcined clay was supplied by the USBM's Albany Research Center, from stocks produced in its misted clay feed preparation research (8-10). The raw clay for the misting process was obtained from the Thiele Kaolin Co., Sandersville, GA. The clay was reduced to minus 0.64 cm in a jaw crusher and further reduced to minus 35 mesh in a roller mill (44.3 pct minus 150 mesh). This material was moistened with a fine spray of water while tumbling on a rotating disk, dried at 130 to 325 °C, and calcined at 750 °C. The screen analysis and composition of the raw and calcined, misted kaolin clays are shown in tables 2 and 3, respectively. The constituent elements are shown as oxides to conform to alumina industry practice, although the actual compounds may be more complex, especially in the raw clay.

appropriate sized resin kettles, equipped with four-port lids, variable speed plastic propeller stirrers, water-jacketed condenser, thermometers, and external heaters. Insoluble residues were separated from slurries with glass fiber filter paper, while ACH crystals were separated from solution by vacuum filtration through coarse porosity glass frits.

Hydrogen chloride gas sparging crystallization of ACH was conducted in 1- to 5-L water-jacketed glass resin kettles (figure 6), depending on the size of the experiment. The kettles were capped with four-port lids through which were inserted a stirring shaft and bushing, a condenser, a thermocouple or thermometer, a sample tube, and a gas

Table 2.—Screen analysis of kaolin clay, Tyler screen scale equivalent

Mesh size	Raw, pct finer	Misted, calcined, pct finer
35	100	14
65	95	3
100	66	1
150	44	0.2

Table 3.—Composition of kaolin clay, percent

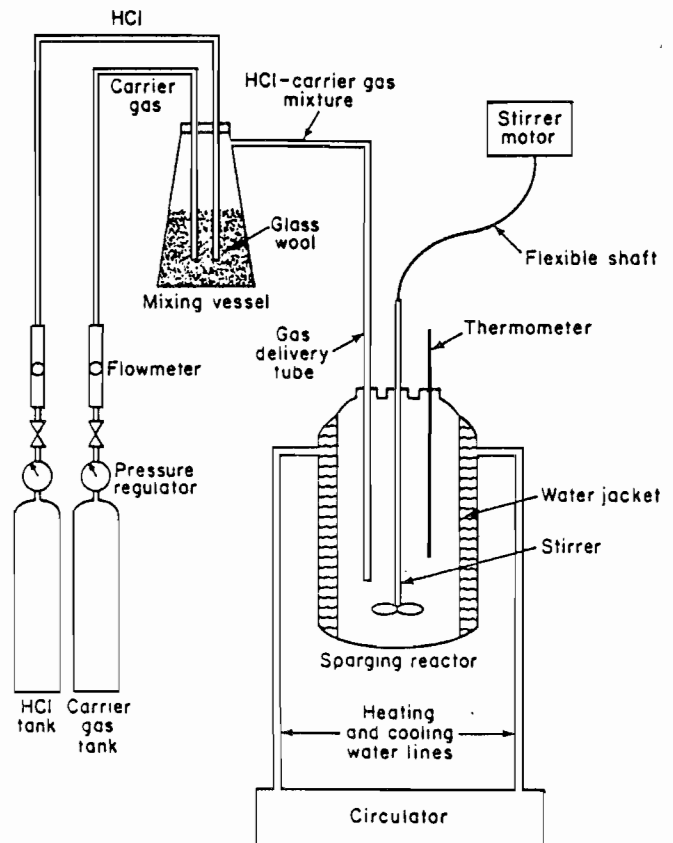| Compound:	Raw		Misted, calcined	
SiO_2	47.0	± 0.7	53	± 2
Al_2O_3	36.0	± 0.6	43	± 2
TiO_2	2.2	± 0.1	2.5	± 0.1
Fe_2O_3	0.98	± 0.09	1.14	± 0.10
K_2O	0.12	± 0.04	0.14	± 0.05
MgO	0.06	± 0.02	0.07	± 0.02
P_2O_5	0.060	± 0.007	0.070	± 0.008
Na_2O	0.033	± 0.007	0.038	± 0.008
CaO	0.030	± 0.009	0.035	± 0.010
Other	0.16		0.19	
LOI at 750 °C	13.70		NAp	

LOI   Loss on ignition.
NAp   Not applicable.

Bench-scale experiments were conducted in standard borosilicate glassware. Leaching tests were conducted in

Figure 6

Sparging apparatus (4).

delivery tube. Temperature was controlled by a heating-refrigerating circulator containing a circulating fluid of ethylene glycol for experiments above 60 °C and water for tests below 60 °C. Sparging and carrier gases were delivered through pressure regulators and flowmeters to a mixing chamber and through a gas sparging tube located just above the propeller blades in the sparger vessel. For details of the gas sparging technique, see previous USBM study (4).

Solution densities were measured with a Mettler/Parr DMA 35 density meter, which withdrew and returned 1 mL aliquats from solutions to be tested.

ANALYSES

The constituents Al, Ca, Cl, Fe, H, K, Mg, Na, P, Si, and Ti in the process streams for the 10 cycles were analyzed by a combination of inductively coupled plasma-atomic emission spectrometry (ICP-AES), atomic adsorption (AA), flame emission, and wet chemistry. The metal oxides accounted for 99.8 pct of the content of the calcined kaolin clay. Previous research showed that P and Mg were the limiting impurities in circuits where Fe was removed in advance (11). A problem in obtaining a material balance for the process was the difficulty in determining the exact composition of the clay. The composition of the clay is shown in table 3, along with the precision. The 1 sigma standard deviations relative to the average of all analyses ranged from 4.0 pct for titanium dioxide (TiO_2) to 36 pct for potassium monoxide (K_2O). Both these extremes occurred with calcined clay. The primary reason for this poor precision was the lack of reproducibility and interferences produced by the sodium metaborate fusion needed to solubilize the clay. The precision of solution analyses was better and is shown in table 4. These data were accumulated over a period of 8 years for the 151-g/L Al_2O_3 (alumina) standard solution and 1 year for the 3.7- and 73.4-g/L Al_2O_3 standard solutions by submitting the standards with the experimental samples. As expected, the precisions were concentration dependent and never better than 3.2 pct, except for direct titrations of hydrogen ion H^+ and chloride ion (Cl^-). ICP-AES analysis was used for Al, Fe, Si, and Ti. Both liquid and solid samples from the clay-HCl process were analyzed using a simultaneous ICP-AES. Liquid samples were diluted in 2 pct HCl and compared with standards prepared in 2 pct HCl. Solid samples (0.1000 g) were fused with 1.4 g of lithium meta borate ($LiBO_2$) in a Pt-Au crucible at 900 °C. The resulting bead was dissolved in 2 pct HCl and compared with standards containing an equivalent amount of $LiBO_2$ in 2 pct HCl. AA analysis was used for Ca, K, Mg, and Na. All samples were made up in 2 pct HCl-0.4 pct Cs as the chloride. Calcium and magnesium were analyzed by AA with an acetylene-nitrous oxide flame. Burner height and fuel flow adjustments are critical; the point of maximum signal is not the point of maximum accuracy. To adjust these parameters, two solutions were used: One contains 10 μg/mL Ca, 0.4 pct Cs, and 2 pct HCl; the other contains the above plus 100 ppm Fe, 20 ppm Si, and 200 ppm Al. These two standards were then compared while adjusting gases and burner height until equal absorbencies were obtained. Magnesium should also be analyzed at these settings. The Jarrell-Ash 850 AA spectrometer used requires a 15-min warmup for Mg and a 45-min warmup for Ca. The Ca-Mg lamp should be run at close to its maximum setting. Other makes of instruments will have similar requirements. Potassium and sodium are analyzed with the conventional lean acetylene-air flame. Either absorbance or emission mode gives equally good results. The factory recommended wavelengths and slit settings are used. Wet chemistry was used for P, H^+ and Cl^-.

PROCEDURES

HCl SPARGING OF AlCl₃-FeCl₃ SOLUTIONS

Three chloride-salt-saturated solutions were made by adding different amounts of aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) to H_2O in order to test the effect of Fe on the sparging crystallization of ACH. The compositions were (1) 32 pct $AlCl_3$ and 1.3 pct $FeCl_3$; (2) 26.4 pct $AlCl_3$ and 11.8 pct $FeCl_3$; and (3) 22 pct $AlCl_3$ and 18.2 pct $FeCl_3$.

Each solution was sparged with HCl gas at 25 °C, as previously described, and 1 mL samples were periodically withdrawn to determine specific gravity and concentrations of $AlCl_3$, $FeCl_3$, and HCl. Volumes were greater than 2 L so that material losses due to sampling did not significantly affect the results. Solution weights were recorded at the

start and finish of the experiments. The experiments were terminated when HCl was no longer absorbed. (HCl concentration remained constant for two consecutive measurements.) The final crystals were filtered, washed with 36 pct HCl, dissolved in H_2O, and analyzed for $AlCl_3$, $FeCl_3$, and HCl.

TEN-CYCLE STUDY OF SIMPLIFIED PROCESS

A block diagram of the simplified flowsheet is shown in figure 7. The procedure for the 10-cycle study is described by unit operation. The sought-after conditions were often hard to achieve in batch, bench-scale experiments where the parts were interdependent, tedious, and complex.

Leaching

Eight-hundred grams of calcined, misted kaolin clay were leached with 3,848 g (3,373 mL) of solution

Figure 7

Leaching wet clay process flow diagram with streams numbered.
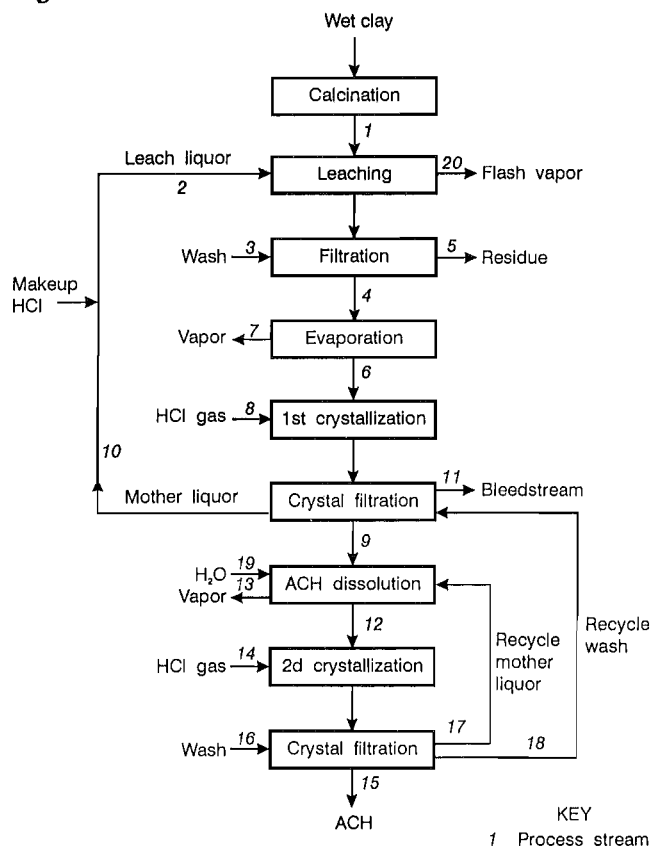
Bench-scale multicycle experiment flowsheet of modified clay-HCl process (20 pct HCl, 15 min leach, no solvent extraction for Fe).

containing 20 pct free HCl.[5] To approach an approximate steady-state composition as rapidly as possible, the first cycle leaching solution was made to simulate calculated steady-state composition (tables 5 through 13, cycle 1).

For subsequent cycles, filtrate from the first crystallization (minus the bleedstream) was combined with the acid wash and adjusted to an average of 3,848 g of 20 pct HCl with makeup concentrated HCl and with makeup water (figure 7, stream 2). The recycle leaching solution was heated to 96 °C (boiling point of the solution in Reno) in a boiling flask that had a reflux condenser to decrease HCl loss and a fresh charge of 800 g of calcined, misted kaolin clay was added. The stirring speed needed to be temporarily increased to reduce frothing. External heating combined with heat of reaction quickly brought the slurry to the boiling temperature of 105 °C. As the leaching continued, the temperature reached a final value of 109 °C. Leaching times ranged from 15 to 30 min. HCl loss from the reflux condensers was minor.

Filtration and Washing

The silica residue was separated from the pregnant liquor by vacuum filtration through Whatman GF/A glass filter paper in an 18.5-cm Buchner funnel. The residue was washed with two 750-mL portions of deionized water by displacement. The temperature was maintained between 90 and 95 °C during filtration and washing. The wash water was combined with the pregnant liquor. The silica residue was weighed after the washing step, dried for 24 h at 215 °C, reweighed, and analyzed.

Evaporation

Sparging crystallization research (4) showed that cleaner crystals were produced when the crystallizer feed solution was nearly saturated with $AlCl_3$. The loss of water with the leaching residue and bleedstream was not great enough to balance the water entering the circuit, especially in a bench-scale experiment of this nature in which excessive amounts of water must be used to ensure adequate washing. For these reasons, an evaporation step was needed prior to crystallization. The combined pregnant and wash liquors were heated to boiling and maintained at the boiling point until the temperature reached 113 °C, which equated to a density of 1.315 g/mL and a final $AlCl_3$ concentration of 30 pct (395 g/L). This is a highly energy-intensive step that should be eliminated, or at least not required to remove as much water, in a scaled-up process.

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[5]The acid requirement was based on 105 pct of the stoichiometric need for recovering all of the Al contained in the kaolin clay.

Table 4.—Reproducibility of analyses of three standard solutions

Compound[1]	Inductively coupled plasma		Atomic absorption		Wet chemistry	
	1 σ SD, g/L	RSD, pct	1 σ SD, g/L	RSD, pct	1 σ SD, g/L	RSD, pct
3.7 g/L Al$_2$O$_3$ STANDARD SOLUTION, 45 DETERMINATIONS OVER 1-YEAR PERIOD						
Al$_2$O$_3$	3.7 ± 0.28	7.6	NA	NA	NA	NA
CaO	0.086 ± 0.015	17	0.095 ± 0.0032	3.4	NA	NA
Fe$_2$O$_3$	2.16 ± 0.12	5.6	NA	NA	NA	NA
HCl	NA	NA	NA	NA	369 ± 4.46	1.2
K$_2$O	0.36 ± 0.062	17	0.34 ± 0.032	9.4	NA	NA
MgO	0.15 ± 0.028	19	0.14 ± 0.0079	5.6	NA	NA
Na$_2$O	0.071 ± 0.020	28	0.072 ± 0.0039	5.4	NA	NA
P$_2$O$_5$	0.20 ± 0.055	28	NA	NA	0.20 ± 0.012	6.0
SiO$_2$	<0.05	NAp	NA	NA	NA	NA
TiO$_2$	0.028 ± 0.0053	19	NA	NA	NA	NA
73.4 g/L Al$_2$O$_3$ STANDARD SOLUTION, 45 DETERMINATIONS OVER 1-YEAR PERIOD						
Al$_2$O$_3$	73.4 ± 3.7	5.0	NA	NA	NA	NA
CaO	<0.03	NAp	<0.01	NAp	NA	NA
Fe$_2$O$_3$	0.027 ± 0.0054	20	NA	NA	NA	NA
HCl	NA	NA	NA	NA	74.7 ± 1.28	1.7
K$_2$O	<0.05	NAp	0.0050 ± 0.00099	20	NA	NA
MgO	0.027 ± 0.021	78	0.017 ± 0.0011	6.5	NA	NA
Na$_2$O	<0.02	NAp	0.0058 ± 0.0014	24	NA	NA
P$_2$O$_5$	<0.05	NAp	NA	NA	0.018 ± 0.0029	16
SiO$_2$	<0.05	NAp	NA	NA	NA	NA
TiO$_2$	0.0066 ± 0.0044	67	NA	NA	NA	NA
151 g/L Al$_2$O$_3$ STANDARD SOLUTION, 56 DETERMINATIONS OVER 8-YEAR PERIOD						
Al$_2$O$_3$	151 ± 4.8	3.2	NA	NA	NA	NA
CaO	NA	NA	NA	NA	NA	NA
Fe$_2$O$_3$	NA	NA	NA	NA	NA	NA
HCl	NA	NA	NA	NA	NA	NA
K$_2$O	2.12 ± 0.14	6.6	NA	NA	NA	NA
MgO	2.77 ± 0.20	7.2	NA	NA	NA	NA
Na$_2$O	1.14 ± 0.088	7.7	NA	NA	NA	NA
P$_2$O$_5$	1.54 ± 0.10	6.5	NA	NA	NA	NA
SiO$_2$	NA	NA	NA	NA	NA	NA
TiO$_2$	NA	NA	NA	NA	NA	NA

NA   Not analyzed.
NAp   Not applicable.
RSD   Relative standard deviation.
SD   Standard deviation.
[1]Present as chlorides, but reported as oxides.

Table 5.—Total mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle										Average	SD
	1	2	3	4	5	6	7	8	9	10		
2—Leach liquor	3,848	3,848	3,848	3,848	3,848	3,850	3,848	3,848	3,848	3,849	3,848	±0.7
4—Pregnant liquor	4,983	4,576	4,553	4,565	4,543	5,087	5,053	5,141	5,089	5,110	4,870	±271
5—Leach residue	[2]502	[2]503	859	894	903	881	929	884	881	885	890	±20
6—1st CX feed	3,415	3,317	3,351	3,679	3,764	3,573	3,613	3,567	3,515	3,481	3,528	±142
10—1st CX mother liquor ..	2,489	2,683	2,817	2,854	2,917	2,932	2,931	2,883	2,768	2,745	2,802	±139
11—Bleedstream	802	728	774	905	892	859	858	862	842	815	834	±54
12—2d CX feed	3,415	3,820	3,723	3,766	4,386	4,086	3,997	3,774	3,690	3,834	3,849	±260
15—ACH product	1,638	1,589	1,637	1,631	1,805	1,880	1,852	1,907	1,751	1,644	1,733	±120
17—Dissolver liquor	1,739	2,008	2,046	2,088	2,579	2,300	2,207	2,024	2,031	2,251	2,127	±223
18—Recycle wash	1,391	1,392	1,307	1,394	1,470	1,413	1,411	1,325	1,315	1,362	1,378	±51
Sampling loss	215	217	223	177	144	133	138	137	134	125	164	±40

CX   Crystallizer.
SD   Standard deviation.
[1]See figure 7.
[2]Not used in average.

Table 6.—Al_2O_3 mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle										Average	SD
	1	2	3	4	5	6	7	8	9	10		
2—Leach liquor	44.1	40.8	37.6	57.2	66.9	60.7	76.6	60.5	57.6	50.4	55.2	±12.1
4—Pregnant liquor	359	363	364	404	386	395	386	400	382	393	383	±16
5—Leach residue	27.6	29.2	23.3	27.3	23.8	9.3	29.1	14.2	15.9	14.4	21.4	±7.3
6—1st CX feed	375	362	408	403	413	400	400	408	393	402	396	±16
10—1st CX mother liquor ..	44.3	33.7	56.7	65.7	58.0	75.9	56.5	53.4	50.8	53.0	54.8	±11.3
11—Bleedstream	9.8	7.4	8.5	16.8	9.8	17.3	10.9	13.1	12.8	14.4	12.1	±3.4
12—2d CX feed	427	436	449	428	474	462	447	455	422	437	444	±16.7
15—ACH product	312	305	308	293	325	346	334	363	317	316	322	±20.8
17—Dissolver liquor	78.4	85.1	80.1	85.4	101	80.8	79.4	63.0	69.7	86.0	80.9	±10.1
18—Recycle wash	30.8	33.4	32.9	35.6	41.1	33.6	30.8	25.8	25.2	28.6	31.8	±4.7
Sampling loss	8.6	10.8	12.4	10.4	8.2	7.9	7.7	7.6	7.3	7.0	8.8	±1.8

CX   Crystallizer.
SD   Standard deviation.
[1]See figure 7.

Table 7.—Fe_2O_3 mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle										Average	SD
	1	2	3	4	5	6	7	8	9	10		
2—Leach liquor	17.7	15.6	15.7	15.8	14.4	14.8	15.7	15.5	14.9	15.1	15.5	±0.9
4—Pregnant liquor	24.2	23.8	23.4	24.9	21.5	23.1	23.0	24.0	22.3	24.1	23.4	±1.0
5—Leach residue	1.80	1.53	1.17	1.17	1.46	0.61	1.39	0.73	0.99	0.81	1.17	±0.38
6—1st CX feed	25.2	23.7	25.7	22.7	22.2	23.4	23.5	24.2	22.7	24.6	23.8	±1.1
10—1st CX mother liquor ..	16.3	16.1	18.4	14.9	14.9	14.6	14.3	15.1	15.5	15.9	15.6	±1.2
11—Bleedstream	7.99	6.79	7.85	7.34	7.01	7.22	7.02	7.28	7.82	7.54	7.39	±0.40
12—2d CX feed	0.69	0.56	0.69	0.78	0.78	0.75	0.89	0.83	0.79	0.83	0.76	±0.09
15—ACH product	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NAp	NAp
17—Dissolver liquor	0.42	0.39	0.48	0.57	0.58	0.54	0.61	0.58	0.53	0.56	0.53	±0.07
18—Recycle wash	0.19	0.15	0.10	0.22	0.20	0.17	0.21	0.20	0.19	0.18	0.18	±0.03
Sampling loss	0.83	0.72	0.69	0.54	0.47	0.43	0.45	0.46	0.45	0.44	0.55	±0.14

CX   Crystallizer.
NAp   Not applicable.
ND   Not detected (<0.002 g).
SD   Standard deviation.
[1]See figure 7.

Table 8.—HCl mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle 1	2	3	4	5	6	7	8	9	10	Average	SD
2—Leach liquor	767	778	778	785	788	789	796	808	760	810	786	±16
4—Pregnant liquor	39	38	36	21	12	15	11	27	13	26	24	±11
5—Leach residue	3	2	6	5	6	0	2	2	2	2	3	±2
6—1st CX feed	11	10	5	6	8	3	0	3	0	3	5	±4
10—1st CX mother liquor	656	727	709	689	705	692	745	723	762	740	715	±31
11—Bleedstream	204	218	214	228	246	216	233	223	237	222	224	±12
12—2d CX feed	68	58	89	35	38	53	85	32	41	26	53	±22
15—ACH product	75	70	76	77	92	140	166	100	77	70	94	±33
17—Dissolver liquor	353	390	416	425	520	520	484	500	463	486	456	±57
18—Recycle wash	328	333	318	350	347	352	360	376	361	365	349	±18
Sampling loss	23.4	30.8	33.2	19.2	18.9	16.0	18.4	18.1	18.3	14.2	21.1	±6.3

CX   Crystallizer.
SD   Standard deviation.
[1]See figure 7.

Table 9.—K₂O mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle 1	2	3	4	5	6	7	8	9	10	Average	SD
2—Leach liquor	1.09	1.19	1.09	1.19	1.16	1.23	1.45	1.57	1.61	1.27	1.29	±0.19
4—Pregnant liquor	1.88	1.88	1.92	1.82	1.85	2.03	2.15	2.53	2.50	2.37	2.09	±0.28
5—Leach residue	0.31	0.32	0.55	0.32	0.26	0.11	0.23	0.94	0.52	0.31	0.39	±0.23
6—1st CX feed	1.85	1.80	1.94	1.86	1.89	2.05	2.01	2.44	2.44	2.35	2.06	±0.25
10—1st CX mother liquor	1.21	1.23	1.13	1.19	1.24	1.31	1.33	1.51	1.72	1.50	1.34	±0.18
11—Bleedstream	0.57	0.52	0.53	0.60	0.58	0.65	0.65	0.70	0.83	0.72	0.64	±0.10
12—2d CX feed	0.017	0.016	0.031	0.043	0.046	0.046	0.051	0.054	0.063	0.056	[2]0.075	NAp
15—ACH product	<0.008	<0.008	<0.008	<0.009	<0.01	<0.01	<0.01	<0.009	<0.008	<0.008	<0.008	NAp
17—Dissolver liquor	0.008	0.011	0.022	0.032	0.036	0.035	0.039	0.041	0.046	0.041	[2]0.061	NAp
18—Recycle wash	0.004	0.006	0.009	0.012	0.013	0.011	0.013	0.014	0.016	0.013	[2]0.020	NAp
Sampling loss	0.12	0.056	0.050	0.042	0.040	0.038	0.041	0.047	0.050	0.042	0.053	±0.024

CX   Crystallizer.
NAp   Not applicable.
SD   Standard deviation.
[1]See figure 7.
[2]Calculated equilibrium value.

Table 10.—MgO mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle 1	2	3	4	5	6	7	8	9	10	Average	SD
2—Leach liquor	1.03	0.84	0.79	0.81	0.71	0.75	0.81	0.84	0.81	0.78	0.82	±0.08
4—Pregnant liquor	1.40	1.23	1.24	1.30	1.15	1.22	1.27	1.31	1.32	1.25	1.27	±0.07
5—Leach residue	0.13	0.25	0.15	0.094	0.15	0.13	0.12	0.24	0.21	0.15	0.16	±0.05
6—1st CX feed	1.45	1.32	1.34	1.19	1.15	1.23	1.38	1.32	1.31	1.29	1.30	±0.09
10—1st CX mother liquor	0.93	0.83	0.80	0.77	0.77	0.74	0.84	0.87	0.89	0.83	0.83	±0.06
11—Bleedstream	0.44	0.36	0.37	0.38	0.36	0.36	0.41	0.42	0.44	0.40	0.39	±0.03
12—2d CX feed	0.027	0.051	0.061	0.057	0.089	0.082	0.11	0.085	0.12	0.099	[2]0.14	NAp
15—ACH product	<0.002	<0.002	<0.002	<0.003	<0.003	<0.003	0.006	0.008	<0.003	<0.003	<0.003	NAp
17—Dissolver liquor	0.020	0.033	0.040	0.035	0.056	0.055	0.074	0.065	0.074	0.054	[2]0.087	NAp
18—Recycle wash	0.010	0.013	0.014	0.015	0.020	0.018	0.024	0.024	0.023	0.015	[2]0.031	NAp
Sampling loss	0.045	0.042	0.034	0.027	0.022	0.021	0.024	0.024	0.027	0.021	0.029	±0.009

CX   Crystallizer.
NAp   Not applicable.
SD   Standard deviation.
[1]See figure 7.
[2]Calculated equilibrium value.

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Table 11.—P$_2$O$_5$ mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle										Average	SD
	1	2	3	4	5	6	7	8	9	10		
2—Leach liquor	1.10	0.97	0.97	0.94	0.90	0.91	0.74	0.93	0.88	0.96	0.93	±0.09
4—Pregnant liquor	1.56	1.25	1.38	1.28	1.30	1.33	1.34	1.34	1.43	1.49	1.37	±0.10
5—Leach residue	0.12	0.14	0.12	0.11	0.10	0.14	0.11	0.14	0.13	0.12	0.12	±0.01
6—1st CX feed	1.70	1.30	1.46	1.40	1.35	1.44	1.04	1.39	1.34	1.45	1.39	±0.16
10—1st CX mother liquor	1.02	0.60	0.94	0.86	0.83	0.93	0.88	0.94	0.87	0.90	0.88	±0.11
11—Bleedstream	0.50	0.29	0.44	0.41	0.40	0.44	0.44	0.45	0.41	0.41	0.42	±0.05
12—2d CX feed	0.041	0.071	0.089	0.12	0.11	0.17	0.14	0.16	0.17	0.17	[2]0.18	NAp
15—ACH product	<0.003	<0.003	0.003	0.006	0.006	0.009	0.009	0.006	0.013	0.010	[2]0.013	NAp
17—Dissolver liquor . . .	0.029	0.048	0.070	0.091	0.12	0.12	0.10	0.11	0.12	0.12	[2]0.13	NAp
18—Recycle wash	0.010	0.017	0.028	0.034	0.041	0.039	0.029	0.037	0.044	0.039	[2]0.042	NAp
Sampling loss	SL	0.039	0.037	0.029	0.027	0.027	0.025	0.027	0.027	0.026	0.029	±0.005

CX   Crystallizer.
NAp   Not applicable.
SD   Standard deviation.
SL   Sample lost.
[1]See figure 7.
[2]Calculated equilibrium value.

Table 12.—CaO mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle										Average	SD
	1	2	3	4	5	6	7	8	9	10		
2—Leach liquor	1.07	0.77	0.66	0.56	0.43	0.50	0.53	0.47	0.49	0.42	[2]0.47	NAp
4—Pregnant liquor	1.28	0.84	0.72	0.65	0.54	0.69	0.68	0.61	0.63	0.61	[2]0.64	NAp
5—Leach residue	0.27	0.20	0.48	0.21	0.48	0.59	0.61	0.75	0.52	0.25	0.44	±0.19
6—1st CX feed	1.20	0.78	0.73	0.62	0.58	0.71	0.61	0.63	0.63	0.61	[2]0.64	NAp
10—1st CX mother liquor	0.92	0.79	0.62	0.46	0.45	0.45	0.47	0.45	0.48	0.46	[2]0.46	NAp
11—Bleedstream	0.39	0.35	0.29	0.23	0.21	0.22	0.23	0.22	0.25	0.21	[2]0.22	NAp
12—2d CX feed	0.048	0.039	0.042	0.033	0.038	0.037	0.033	0.034	0.031	<0.03	[2]0.032	NAp
15—ACH product	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	NAp
17—Dissolver liquor	0.033	0.029	0.031	0.027	0.028	0.027	0.033	0.025	0.026	<0.02	0.028	±0.004
18—Recycle wash	0.007	0.006	0.006	0.005	0.006	0.006	0.007	0.005	0.005	0.005	[2]0.006	NAp
Sampling loss	0.038	0.023	0.023	0.014	0.012	0.014	0.013	0.013	0.014	0.012	0.018	±0.008

CX   Crystallizer.
NAp   Not applicable.
SD   Standard deviation.
[1]See figure 7.
[2]Calculated equilibrium value.

Table 13.—Na$_2$O mass distribution during 10-cycle test, grams

Process stream[1] number and description	Cycle										Average	SD
	1	2	3	4	5	6	7	8	9	10		
2—Leach liquor	0.32	0.29	0.30	0.31	0.25	0.30	0.42	0.38	0.41	0.32	0.33	±0.06
4—Pregnant liquor	0.49	0.42	0.45	0.45	0.48	0.48	0.51	0.49	0.55	0.51	0.48	±0.04
5—Leach residue	0.08	0.19	0.10	0.07	0.30	0.25	0.08	0.12	0.31	0.07	0.16	±0.10
6—1st CX feed	0.49	0.41	0.47	0.44	0.48	0.52	0.50	0.49	0.55	0.56	0.49	±0.05
10—1st CX mother liquor	0.30	0.28	0.27	0.30	0.33	0.32	0.37	0.41	0.48	0.39	0.35	±0.07
11—Bleedstream	0.14	0.11	0.13	0.14	0.15	0.15	0.17	0.19	0.23	0.19	0.16	±0.04
12—2d CX feed	0.021	0.014	0.022	0.028	0.046	0.059	0.080	0.062	0.065	0.057	[2]0.081	NAp
15—ACH product	0.01	0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	NAp
17—Dissolver liquor	0.015	0.012	0.020	0.032	0.052	0.055	0.080	0.052	0.055	0.046	[2]0.056	NAp
18—Recycle wash	0.005	0.007	0.009	0.014	0.021	0.017	0.027	0.019	0.019	0.014	[2]0.025	NAp
Sampling loss	0.016	0.015	0.013	0.009	0.011	0.010	0.011	0.010	0.012	0.010	0.012	±0.002

CX   Crystallizer.
NAp   Not applicable.
SD   Standard deviation.
[1]See figure 7.
[2]Calculated equilibrium value.

First Sparging Crystallization With HCl Gas

To obtain optimum crystal purity and size, the saturated AlCl₃ solution was sparged at 60 °C with a slow gas addition rate using an inert carrier gas to evenly distribute the HCl and prevent fouling of the delivery tube tip. HCl and nitrogen (N_2) gases were introduced at rates of 1.75 and 0.27 L/min, respectively, until the solution density reached 1.196 g/mL, which equated to a final HCl concentration of 26 pct (8.5N). The stirring rate was adjusted to the slowest speed that would keep the crystals suspended.

First Crystallizer Filtration and Wash

ACH crystals were easily separated from the depleted liquor by filtration through a coarse porosity fritted disk Buchner funnel. After filtration and before washing, the crystals were weighed in the funnel. The assumption was made, based on previous research results (4), that 9.1 pct of the crystal weight was due to entrained mother liquor. From the calculated weight of entrained mother liquor and the weight of recovered mother liquor, the weight of the bleedstream was calculated by multiplying the adjusted filtrate weight by 0.345. This relatively large bleedstream is needed in both this and the standard HCl process to meet purity requirements and eliminate excess water from the circuit. It is critical that the bleedstream be taken at this point because soluble Al is at its lowest concentration in the circuit. The mother liquor bleedstream was set aside and the remaining mother liquor plus the wash solution were combined, adjusted to a weight of 3,848 g and an HCl content of 20 pct with concentrated HCl and H₂O, and used as the leaching solution for the next cycle (figure 7, stream 2). The wash solution for the crystals in the first cycle, first crystallization was 1,065 g (909 mL) and contained 24 pct HCl, 2.0 pct Al₂O₃, and 0.04 pct Fe₂O₃ (ferric oxide). In subsequent cycles, the wash solution consisted of 16.8 pct of the mother liquor plus all of the wash from the second crystallization of the previous cycle (figure 7, stream 18).

Dissolution of Crystals From First Crystallization

Previous research showed that two crystallizations of ACH were necessary to achieve adequate purity of the product alumina (4). The ACH crystals from the first crystallization were weighed, dissolved, and the solution was concentrated to 30 pct AlCl₃ by evaporation prior to

the second crystallization. The Kaiser flowsheet[6] calls for a dissolver circuit consisting of a countercurrent flow of mother liquor from the second crystallization and the ACH crystals from the first crystallization. Upon heating, HCl is driven off and recovered for future use and ACH is dissolved. Countercurrent dissolution was difficult to simulate in a bench-scale study, so the ACH was dissolved by adding an excess of water to the mother liquor from the second crystallization, boiling the solution to reduce the volume, obtain a nearly saturated AlCl₃ solution, and drive off the HCl. For the first cycle dissolution, a simulated second crystallization mother liquor was used that was composed of 435 g ACH, 1.66 g FeCl₃·6H₂O, 100 g of 37 pct HCl, and 1,602 g H₂O. For subsequent cycles, the dissolver solution consisted of 83.2 pct of the mother liquor from the second crystallization of the previous cycle (figure 7, stream 17) and the excess water.

Second Sparging Crystallization With HCl Gas

The redissolved crystals, constituting a 30-pct AlCl₃ solution (determined by density measurements), were sparged with HCl gas and N₂ carrier gas in the same manner as in the first crystallization, except the sparging was stopped when the HCl concentration reached 20 pct. This lower HCl concentration was an experiment to see if lower acid concentrations caused any problems in the sparging circuit. Twenty percent HCl concentration was achieved by sparging to a solution density of 1.205 g/mL (6.6N).

Second Crystallizer Filtration and Wash

The same techniques were used as in the first filtration. After filtration, the crystals were weighed and 9.1 pct of that weight was assumed to be due to trapped mother liquor. Eighty-three and two-tenths (83.2) percent of the adjusted weight of mother liquor was recycled as dissolver liquor for the next cycle (figure 7, stream 17). The remaining mother liquor and the wash acid were recycled as the first crystallizer wash for the next cycle (figure 7, stream 18). The wash acid consisted of 823 g of 32 pct HCl. The purified ACH crystals were weighed to obtain a material balance, then dissolved for analysis. In an industrial process, the purified ACH crystals would have been calcined to alumina and HCl gas recovered for recycle, but these stages were not carried out for this study.

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[6]Work cited in footnote 2.

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RESULTS

The data and results are presented in the following two sections in reflection of the fact that the solubility data were gathered as basic research to determine how the Fe influenced a simple controlled system during HCl sparging. The solubility data are complementary to the data gathered in the 10-cycle run and help strengthen the case for not removing Fe in advance of crystallization.

$AlCl_3$, $FeCl_3$, AND HCl SOLUBILITIES IN SYSTEM HCl-$AlCl_3$-$FeCl_3$-H_2O

Data on the effect of $FeCl_3$ concentration on the solubility of $AlCl_3$ when sparged with HCl gas are presented in table 14 for three different compositions of saturated solutions. They are plotted in figure 8 as a family of curves representing $AlCl_3$ concentration in aqueous solution as a function of HCl concentration. For comparison (12), the solubility of $AlCl_3$ when sparged with HCl is included in this figure.

Analysis of the ACH crystals produced by HCl sparging of a solution containing 16.6 pct $AlCl_3$ and 18.2 pct $FeCl_3$ showed that 0.37 pct of the Fe cocrystallized and the ACH after one crystallization contained 0.08 pct Fe. This would equate to 0.52 pct Fe_2O_3 in the product alumina from one crystallization. Since two crystallizations are required to meet the purity requirements for P and Mg, a second crystallization would reduce the Fe_2O_3 concentration in the product alumina to about 0.0019 pct (well below the specification of 0.015 pct) if the purification factor for the second crystallization was anywhere close to that for the first crystallization. Analysis of the ACH crystals produced from one cycle of crystallization from a solution saturated

Figure 8
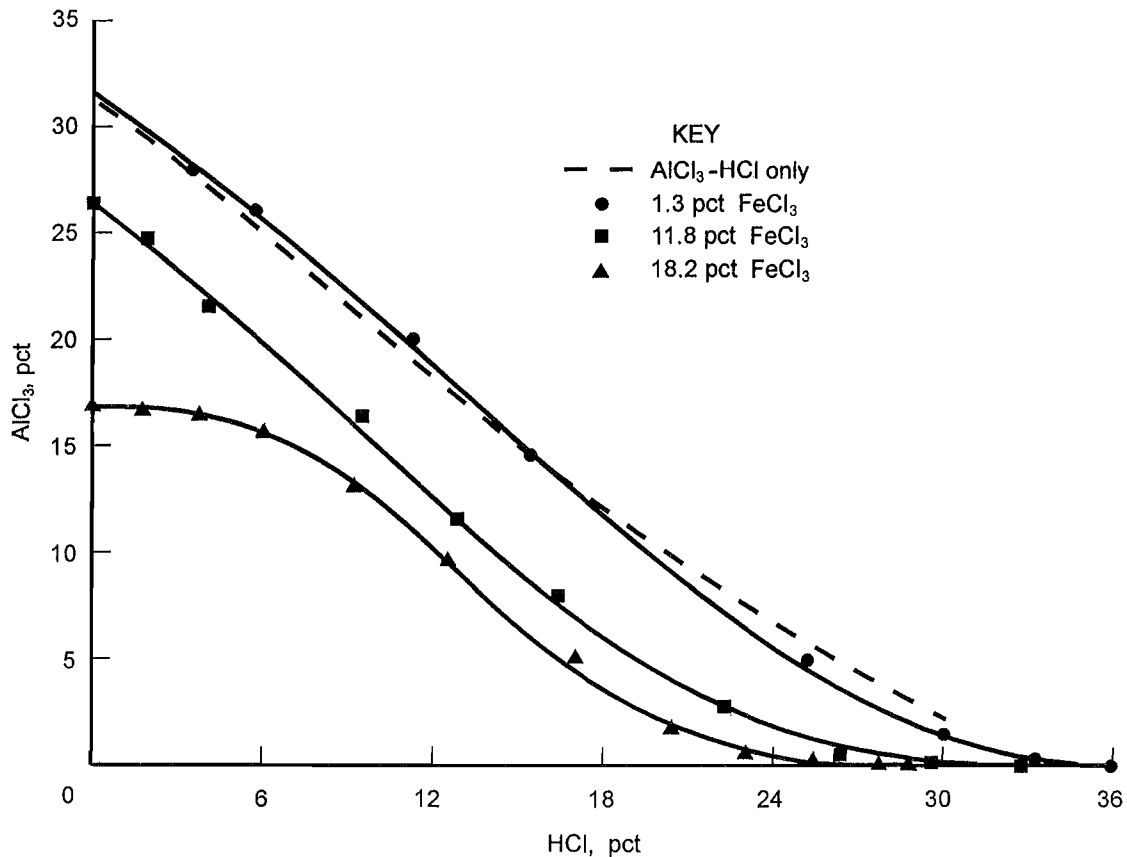
Solubility of $AlCl_3$ as function of HCl concentration in system $AlCl_3$-HCl-$FeCl_3$-H_2O at 25 °C. Dashed curve, from the work of Brown (12), included for comparison.

with 26.4 pct $AlCl_3$ and 11.8 pct $FeCl_3$ showed the Fe content to be 1.1 g $FeCl_3$ in 1,160 g $AlCl_3$. This equates to 0.12 pct Fe_2O_3 in the Al_2O_3 from the first crystallization and represents a purification factor of 480. Extrapolating these ratios to a second crystallization would give a final alumina product purity of 0.00025 pct Fe_2O_3, which is well below the maximum allowable Fe content. There is no reason to believe the second crystallization purification factor will be as large as the first, but it certainly ought to be sufficient to meet the Fe specification. Since the purification factors are so large and $FeCl_3$ concentrations are much greater than would be experienced in a clay-HCl process circuit, this research strongly suggests that adequate alumina purity with respect to Fe ought to be obtained by two HCl sparging crystallizations.

Solution analyses showed a decrease in Al concentration and an increase in Fe concentration with increasing HCl concentration as the sparging crystallization progressed. When the solutions were nearly saturated with HCl and depleted of $AlCl_3$, the Fe concentration showed a slight decrease. The changes were due to a decrease in density as the $AlCl_3$ crystallized out of solution and a slight increase in density when the $AlCl_3$ was essentially gone, but HCl concentration was still increasing.

The family of curves in figure 8 shows that $FeCl_3$ up to 1.3 pct had little effect on the decrease in solubility of $AlCl_3$ during HCl sparging. Greater amounts of $FeCl_3$ decreased $AlCl_3$ solubility and the amount of HCl needed to crystallize $AlCl_3$ out of solution.

Table 14.—Solubility of $AlCl_3$ in saturated aqueous solution at 25 °C as functions of HCl and $FeCl_3$ concentrations

Specific gravity	Volume, L	$AlCl_3$		$FeCl_3$		HCl	
		g/L	pct	g/L	pct	g/L	pct
STARTING COMPOSITION, 32 pct $AlCl_3$, 1.25 pct $FeCl_3$							
1.285	1.00	411	32.0	16.0	1.25	0	0
1.296	1.20	361	27.9	13.4	1.03	46.7	3.6
1.287	1.16	335	26.0	13.8	1.07	70.8	5.5
1.255	1.04	251	20.0	15.4	1.23	138	11.0
1.227	1.03	178	14.5	15.6	1.27	189	15.4
1.185	0.95	58	4.9	16.9	1.43	297	25.1
1.175	0.94	16	1.4	17.1	1.46	351	29.9
1.185	0.87	2.1	0.2	18.5	1.56	392	33.1
STARTING COMPOSITION, 26.4 pct $AlCl_3$, 11.8 pct $FeCl_3$							
1.378	3.26	364	26.4	162	11.8	0	0
1.368	3.22	337	24.7	165	12.0	23.4	1.7
1.355	3.11	293	21.6	171	12.6	56.0	4.1
1.329	2.96	217	16.3	179	13.4	124	9.3
1.310	2.84	152	11.6	187	14.3	166	12.6
1.291	2.75	102	7.9	193	14.9	211	16.4
1.265	2.66	34	2.7	199	15.7	279	22.1
1.257	2.63	6.5	0.5	201	16.0	331	26.3
1.259	2.80	1.1	0.09	189	15.0	373	29.6
1.266	2.96	<0.1	<0.01	179	14.1	414	32.7
STARTING COMPOSITION, 22.0 pct $AlCl_3$, 18.2 pct $FeCl_3$							
1.374	1.00	302	22.0	250	18.2	0	0
1.375	0.99	210	15.2	248	18.0	22.6	1.6
1.380	0.98	207	15.0	244	17.7	50.5	3.7
1.382	0.96	200	14.5	240	17.3	82.1	5.9
1.371	0.97	164	11.9	242	17.6	126	9.2
1.352	0.99	116	8.6	248	18.3	167 ·	12.4
1.328	1.01	60	4.5	252	19.0	225	17.0
1.313	1.01	22	1.7	252	19.2	266	20.3
1.302	1.00	7.6	0.6	250	19.2	298	22.9
1.303	0.97	1.4	0.1	242	18.5	330	25.3
1.305	0.94	<0.05	<0.01	236	18.1	360	27.6
1.310	0.93	<0.05	<0.01	232	17.7	377	28.8

NOTE.—Filter cakes weighing 1,160 and 816 g, containing 1.1 and 3.3 g $FeCl_3$, were recovered at the completion of the tests that started with 26.4 and 16.6 pct $AlCl_3$, respectively.

TEN-CYCLE STUDY OF SIMPLIFIED PROCESS

The bench-scale multicycle flowsheet of the modified clay-HCl process shown in figure 7 can be conveniently broken into two parts based on the first and second crystallizer circuits. The first circuit was easy to balance because the calculated compositions of the starting solutions for the first cycle were a good approximation of steady-state conditions for a circuit from which a 34.5-pct bleedstream was removed (tables 5 through 13, cycle 1). The goal for the first circuit research was to see if the solution compositions changed significantly during or after 10 cycles of operation. There were minor variations in the compositions of the process streams for each cycle, but the values remained close to the originally calculated values (tables 5 through 13), with no trends toward increasing or decreasing concentration. Therefore, to increase precision, the masses of the constituent elements were averaged rather than taking the final values in the series as the steady-state values. The averaged values for 10 cycles were iterated by computer to produce a balanced circuit for the first six-unit operations and process streams 1 through 11 and 20 in figure 7. All of the calculated values were within ±5 pct of the averaged experimental data and are shown in table 15. For simplicity, most of the mass values are

reported as oxides. To make the individual constituents add up to the total mass column, it will be necessary to convert all of the solution constituents to chlorides.

The second crystallizer circuit was more difficult to balance because compositions of the recycle streams, which had to be synthesized to start the first cycle, could not be calculated except for $AlCl_3$, $FeCl_3$, and HCl. The behavior of $AlCl_3$ and HCl were known from existing data, and $FeCl_3$ concentration was estimated by knowing the amount entering the second crystallizer circuit and assuming that no Fe would cocrystallize with the $AlCl_3$. Sufficient information was not available to estimate the steady-state concentrations of the other impurities, so none were added and the other impurities built up in the circuit with each cycle of operation (tables 5 through 13, streams 12, 17, and 18). Ten cycles of operation were not enough to establish steady state for a circuit in which only about 5.8 pct of the second crystallizer circuit impurities were removed from the overall process. (About 16.8 pct of the impurities were removed from the second crystallization circuit with each cycle, but since the process bleedstream only removed 34.5 pct of the above amount, the remainder of the impurities eventually recycled back to the second crystallization circuit.)

Table 15.—Calculated steady-state distribution of Al_2O_3, HCl, H_2O, and impurities in process streams of modified clay-HCl process, grams

	Al_2O_3	HCl	H_2O	Fe_2O_3	SiO_2	TiO_2	CaO	K_2O	MgO	Na_2O	P_2O_5	Total[2]
Process stream:[1]												
1	344	NDt	NDt	9.12	424	20.0	0.28	1.12	0.56	0.30	0.56	800
2	56	769	2,887	15.5	NDt	NDt	0.45	1.34	0.81	0.33	0.92	3,849
3	NDt	NDt	1,500	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	1,500
4	387	25	4,085	23.7	NDt	NDt	0.67	2.09	1.21	0.49	1.36	5,179
5	13	3	430	0.96	424	20.0	0.06	0.37	0.16	0.14	0.12	892
6	387	5	2,609	23.7	NDt	NDt	0.67	2.09	1.21	0.49	1.36	3,683
7	NDt	20	1,476	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	1,496
8	NDt	650	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	650
9	351	67	556	0.21	NDt	NDt	0.006	0.020	0.031	0.025	0.05	1,914
10	56	705	2,063	15.5	NDt	NDt	0.45	1.34	0.81	0.33	0.92	2,949
11	12	221	540	8.16	NDt	NDt	0.22	0.75	0.40	0.16	0.43	812
12	432	50	2,541	0.76	NDt	NDt	0.032	0.075	0.14	0.081	0.18	3,723
13	NDt	460	2	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	462
14	NDt	513	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	513
15	320	43	83	<0.0002	<0.05	<0.01	<0.03	<0.008	<0.003	<0.01	0.01	1,642
16	NDt	261	608	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	869
17	81	443	1,465	0.55	NDt	NDt	0.026	0.055	0.11	0.056	0.13	2,121
18	31	338	922	0.21	NDt	NDt	0.006	0.020	0.031	0.025	0.04	1,342
19	NDt	NDt	150	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	150
20	NDt	29	49	NDt	NDt	NDt	NDt	NDt	NDt	NDt	NDt	78
Samples[3]	7	18	99	0.53	0	0	0.01	0.040	0.03	0.010	0.03	125

NDt   Not determined.

[1]See figure 7.

[2]Data do not add to totals shown because all analytical results reported as oxides for simplicity and many of the process streams were chlorides.

[3]Material removed for analysis.

A mathematical model was constructed to predict the steady-state concentration of each impurity. This was done by plotting the weight of each impurity in the feed to the second crystallizer (process stream 12) for all 10 cycles and fitting a curve through these points. Then, ideal curves were plotted from calculated data points, based on a series of different recycle amounts, until the ideal curves matched the data curves from the first 10 cycles. The point at which the best fit ideal curve for each impurity reached a plateau was considered the steady-state value. The steady-state concentrations for the second crystallization circuit process streams 13 through 19 in figure 7 were calculated from the ratios between the cycle 10 values and the calculated steady-state values for process stream 12. These calculated steady-state values were then iterated in the same manner as for the first crystallization circuit to balance the circuit. The final balance is tabulated in table 15.

An example is illustrated in figure 9 for phosphorus pentoxide (P_2O_5). The curve for 78 pct recycle, which best fits the data, is shown. The curve was calculated by assuming 0.041 g of new P_2O_5 (first cycle concentration)

Figure 9
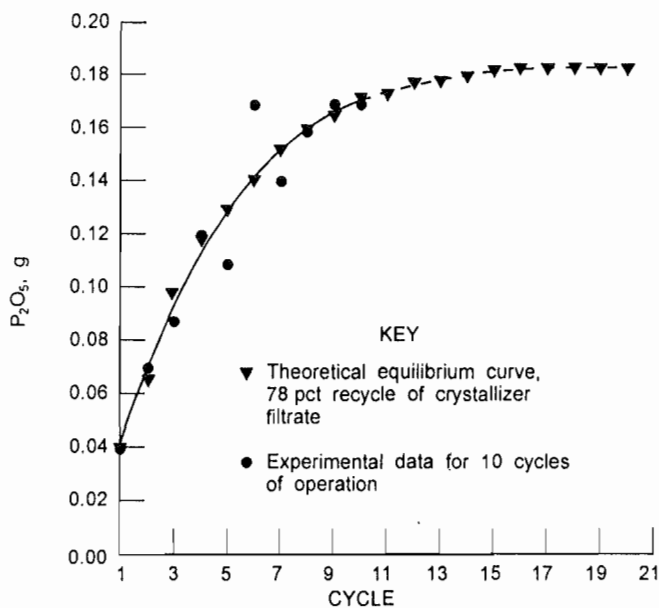
P_2O_5 buildup in second crystallizer feed with each cycle.

came into the circuit with each cycle plus 78 pct of the P_2O_5 from the previous cycle. Steady state (greater than 99 pct of equilibrium value) was attained after 19 cycles with a weight of 0.18 g P_2O_5 (109 pct of the cycle 10 value). Three other impurities, sodium oxide (Na_2O), K_2O, and magnesium oxide (MgO), when evaluated the same way, were best described by 84 pct recycle curves, and their steady-state concentrations were approximately 120 pct of the cycle 10 concentrations. When the P_2O_5 value was corrected for the 0.01 g lost with the final alumina product, the value coincided with 83 pct recycle. Recycling of 83 to 84 pct of the impurities in the second crystallizer circuit is about 10 pct lower than expected if the true bleed from the total process is 5.8 pct; however, the samples taken increased the bleed of impurities by an average of 6.2 pct, and minor losses in handling probably accounted for the remainder of the difference. Iron content started at 0.69 g and, after three cycles, built up to a steady-state value of 0.81 ±0.05 g. Iteration changed this value to 0.76 g for a final circuit steady-state calculation. Calcium was peculiar in that it started high in all process streams, then came to a lower steady-state value. Apparently, the original estimate of calcium dissolution was high.

The final product purity met specifications for all constituents except P_2O_5, which was 0.003 pct (table 15, stream 15). The purity requirement for P is 0.001 pct P_2O_5 in Al_2O_3, which is difficult to meet and probably unrealistic since a commercial Bayer alumina contains 0.004 pct (13). In an earlier crystallization study (4), decreased ACH purity was noted when sparging wasn't carried to at least 26 pct HCl concentration. It is probable that the P value of 0.003 pct P_2O_5 in Al_2O_3 is a result of the 20 pct HCl sparging step. However, since Bayer alumina used in reduction cells contains up to 0.004 pct P_2O_5, this should not cause problems. If it is necessary to meet the 0.001 pct P_2O_5 level, sparging to 26 pct HCl in the second crystallizer should improve the purity of the ACH.

The calculated material balance in table 15 shows that 93 pct of the alumina present in the clay was recovered by the modified process. This is comparable with the recovery from the standard HCl process. Losses include 3.8 pct in leaching (tails) and 3.5 pct to the bleedstream. The standard HCl process called for recovering the alumina from the bleedstream since it contained a significant amount. However, it is doubtful if it is worth recovering a 3.5 pct loss.

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CONCLUSIONS

The 10-cycle batch, bench-scale study of the modified clay-HCl process demonstrated that the shortened leaching time of 15 to 30 min, decreased leaching acid concentration of 20 pct, and removal of the solvent extraction circuit had no serious effects on alumina product yield and purity when compared with the standard HCl process. Alumina recovery was 93 pct of the total alumina contained in the clay feed in both this study and the standard HCl process. The product met reduction-grade purity requirements, except for P. The increased P_2O_5 level may be attributed to the fact that the second crystallizer sparged to an HCl concentration of 20 pct instead of 26 pct.

The reduced acid concentration and leaching time should improve the leaching and filtration circuits because of reduced HCl vapor pressure and corrosion and less attrition of the leach residue.

The buildup of $FeCl_3$ in the leach circuit to 9.3 g/L does not decrease alumina product purity with respect to Fe because of efficient Fe rejection in the sparging crystallization circuits and subsequent elimination in the bleedstream. This makes it possible to eliminate the Fe oxidation, solvent extraction, solvent recovery, and $FeCl_3$ recovery steps from the process.

The presence of 2 pct $FeCl_3$ in the bleedstream complicates the recovery of alumina from the bleedstream, but the loss of alumina is only 3.5 pct of the total alumina present in the original clay feed. The proposed circuit for the recovery of bleedstream alumina in the standard HCl process is complicated and possibly more costly than the value of the recovered alumina. In light of the small alumina loss and the simplifications introduced by only having to recover HCl from the bleedstream, the decision to eliminate the reprocessing step for alumina appears to be justified.

Cost analyses contained in the Kaiser report[7] showed the standard HCl process to be most economical of the acid leach systems under study, but still not competitive with the Bayer process. Incorporation of the modifications to the standard HCl process described in this study should help to lower costs. A revised cost estimate should be made based on these data, and if encouraging, a more thorough study of the waste processing circuits should be carried out. It should be emphasized that this study was a far cry from a continuous equilibrium process. True steady-state operation would give different results. But previous alumina project experience has demonstrated that there is a built-in safety margin with bench-scale tests. Scale up and continuous operation usually give better results, especially in terms of product purity. Two areas where bench-scale experiments can lead to better than real-world results are in bleedstream and washing efficiency. This is because bench-scale tests always take more wash water then scaled-up tests and sampling can lead to a significant additional bleedstream and thereby artificially increase the purity. Therefore, it is very important that these tests be repeated with continuous scaled-up operation. This research was only intended to show that the next development stage is warranted when future market conditions favor an alternative process.

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[7]Work cited in footnote 2.

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