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Pressure Leaching Alumina From Raw Kaolinitic Clay Using Hydrochloric Acid

By Dwight L. Sawyer, Jr., and Theodore L. Turner



UNITED STATES DEPARTMENT OF THE INTERIOR



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	angstrom	mm	millimeter
atm	atmosphere	min	minute
°C	degree Celsius	mL	milliliter
ft	foot	m ² /g	square meter per gram
g	gram	oz	ounce
g/mL	gram per milliliter	pct	percent
h	hour	ppm	part per million
L	liter	psia	pound per square inch, absolute
µm	micrometer	wt pct	weight percent

PRESSURE LEACHING ALUMINA FROM RAW KAOLINITIC CLAY USING HYDROCHLORIC ACID

By Dwight L. Sawyer, Jr.,¹ and Theodore L. Turner²

ABSTRACT

The Bureau of Mines studied alumina extraction from uncalcined, kaolinitic clay at temperatures from 100° to 250° C using 20- or 27-wt-pct-HCl concentrations and with an acid-to-clay ratio of from 0.8 to 1.4 times stoichiometric. Autogenous digestion pressures ranged from atmospheric pressure to about 900 psia. Extraction of 96 pct of the alumina was obtained by HCl leaching at temperatures and leaching times that varied from 100° C for 120 h to 200° C for 15 min. Hydrochloric acid stoichiometry of the reaction $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 2\text{SiO}_2 + 5\text{H}_2\text{O}$ was studied at different temperatures and leaching times in a 750-mL tetrafluoroethylene-polymer-lined autoclave. A combination of high temperature and 20 wt pct excess HCl promoted rapid and almost quantitative extraction of alumina (99 pct in some tests).

Additional Bureau data obtained with 35-mL tantalum bombs and leaching tests with added fluoride are also provided. At high temperatures, the addition of fluoride did not result in a significant improvement over HCl alone and was deleterious to the filtering properties of the digest residue.

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INTRODUCTION

Investigations described were undertaken to establish conditions that would provide an evaluation of the effectiveness of HCl-pressure leaching of aluminum from uncalcined kaolin. Data in the literature strongly suggested that direct, HCl-pressure leaching was effective under controlled conditions. Experimental conditions were selected that represented a reasonable range of temperatures and associated autogenous pressures and HCl concentrations for bench-scale equipment constructed of corrosion-resistant materials. Information concerning the availability and quality of kaolin raw material and a review of pertinent literature are given in the following sections. This study did not include solid-liquid separation, which is covered in Reports of Investigations on the Bureau's alumina miniplant research.

RAW KAOLIN

Large reserves of clay suitable for the production of alumina (Al_2O_3) exist within the contiguous 48 States. Ward (1)³ states that the 3.5-billion-ton kaolin reserves in the Wrens District located in the northeastern section of the Georgia clay belt have the best potential for alumina production. Conditions are amenable for large-scale mining, reserves are adequate to support the operations of several companies, and the kaolin has a high alumina content. For potential alumina production, the deposit must have a minimum of 150 million tons of kaolin containing a minimum of 35 pct alumina in a single or contiguous body (1).

Kaolin is composed principally of the mineral kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; 39.49 pct Al_2O_3 , 46.60 pct SiO_2 , and 13.91 pct H_2O), in which the alumina content can be rendered almost completely acid-soluble by calcination in the temperature range of 600° to 850° C. Its high alumina content, the ease with

which the alumina may be dissolved and silica rejected (2-4), and the high ratio of acid-soluble alumina to impurities make kaolin a preferred source of alumina after bauxite. Kaiser Engineers determined that of six processes studied, the clay-HCl process using HCl gas-induced crystallization had the lowest capital and operating costs (5-7).

ATMOSPHERIC LEACHING

Short-time atmospheric leaching of kaolinite-containing aluminum ores with boiling dilute mineral acids results in low yields of alumina. Acceptable yields are obtained if the kaolinite is dehydrated and decomposed to amorphous alumina and silica by calcining prior to acid leaching. The amorphous alumina formed is soluble in most hot dilute mineral acids. The energy-intensive calcination step is indispensable for the acid leaching of ores containing kaolinite and constitutes an essential step in the clay-HCl process (2, 8).

Data from Gerber's investigation (9) of a German clay illustrated the enhanced aluminum solubility in acid that may be obtained by calcination (tables 1 and 2). Results of the HCl leaching experiments that used an excess of 7-wt-pct HCl at 91° C, show low aluminum solubility from the uncalcined clay (3-9 pct), compared with solubility of the calcined clay (59-74 pct).

In 1927, Tilley of the Bureau of Mines reported an extensive study of acid processes for extracting aluminum from plentiful nonbauxitic sources such as kaolin, alunite, leucite, and other aluminous minerals suitable for acid decomposition (10). At that time, H_2SO_4 systems were considered, because the combined waste production of SO_2 in Utah, Arizona, and Montana was several thousand tons daily. Because the HCl process offered easy removal of iron and the nitric acid process had been examined extensively in Norway, these processes were also investigated.

Tilley investigated the sulfuric acid leaching of air-dried raw clays.

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

TABLE 1. - Composition of Gerber's German clay and Aglietti's kaolin, percent

Component	Clay ¹	Kaolin ²
Al ₂ O ₃	33.88	37.11
Alkalies.....	2.61	NA
CaO.....	.70	NA
Fe ₂ O ₃	2.48	1.64
MgO.....	.31	.50
SiO ₂	46.08	45.94
TiO ₂	NA	.33
Water:		
Loss on ignition.....	13.44	NA
Loss on ignition 1,000° C..	NA	12.52
Total.....	99.50	98.04

NA Not available.

¹Reference 10. ²Reference 18.

TABLE 2. - Extraction of alumina from unroasted and roasted Gerber's German clay with 7-wt-pct HCl (10)

	<u>Wt pct</u>
Unroasted:	
1-h leach.....	3.4
	3.9
3-h leach.....	8.6
Roasted:	
700° C for 1 h, 1-h leach.....	58.9
	58.0
700° C for 2 h, 3-h leach.....	73.7

Variables included concentration of acid, ratio of acid to bases (stoichiometry), and temperature. Experimental results favored dilute acid, 15 wt pct, and indicated that concentrated acid, 80 wt pct, was less efficient in extracting aluminum. Stoichiometry tests at 170° C for 44 h demonstrated the effectiveness of excess 60-wt-pct H₂SO₄ as follows, in weight percent:

<u>Stoichiometric acid</u>	<u>Alumina extraction</u>
120.....	95
110.....	83
100.....	77
90.....	71

Leaching tests conducted for 96 h, in which the temperature was maintained at 105° C, provided conditions comparable

to atmospheric leaching with HCl. Extractions ranged from 95 to 98 pct. Tilley concluded that the efficiency of HCl and H₂SO₄ for dissolving aluminum from clays was about the same, except that HCl leaching did not dissolve titanium.

Petzold (11) investigated the extraction of aluminum from kaolin in an excess of boiling 3N HCl and as a function of pretreatment temperature and mechanical activation in a ball mill. Short-duration acid leaching did not attack kaolin dried at 110° C, but on prolonged heating up to 50 h, an 80-pct extraction was obtained. Kaolin that was heated to 400° C exhibited higher aluminum leachability, about 87 pct for a 50-h acid leach. The leachability of aluminum increased with increasing calcination temperatures up to about 850° C, and then decreased (8, pp. 23-24, 12).

In an investigation of the attack of dilute HCl on two typical kaolinitic clays, Gastuche (13) established that leaching of the kaolinite structure proceeded uniformly on all surfaces as a first-order reaction directly proportional to acid concentration from 0.1N to 2.0N.

PRESSURE LEACHING

Acid digestion at high temperatures and pressures has been used by analytical chemists to dissolve refractory aluminous materials. Wichers (14) describes an analytical method in which refractory oxides, ceramic materials, and minerals may be prepared for analysis by decomposition with HCl or HI at temperatures up to 300° C. The techniques and equipment used for treating refractory samples with aqueous HCl in sealed, heavy-walled, borosilicate glass tubes have also been described (15).

While no specific mention of kaolin was made, a number of porcelains⁴ containing 36 to 97 pct alumina and up to 57 pct

⁴A translucent ceramic ware, usually glazed, existing in many varieties according to composition and method of manufacture, but characterized by a glassy fracture and a high chemical resistance to mineral acids except hydrofluoric.

silica were successfully decomposed at 300° C. The attack on borosilicate glass under these conditions was negligible.

Gewecke (16) discusses the digestion of partially calcined clay (450° C) in nitric acid of different concentrations. He states that greater quantities of Al_2O_3 are dissolved under conditions of higher temperature and pressure.

Sutyryn (17) studied the decomposition of montmorillonite under conditions equivalent to those used for the autoclave treatment of boehmite-kaolinite materials with 40-wt-pct HNO_3 in 200 wt pct excess. After 2-h digestions at 180° C, 78 pct of the aluminum was dissolved from the natural mineral and 81 pct after a 2-h heat treatment at 700° C.

Extraction of aluminum from raw kaolin by H_2SO_4 solutions at 150° to 170° C was reported by Aglietti (18), who worked with Teflon⁵ tetrafluoroethylene (TFE)-polymer-coated 25-mL steel autoclaves. Trends were established that parallel Bureau findings using HCl. In contradiction to Tilley's study, greater extraction was reported with higher concentrations of H_2SO_4 (to 60 wt pct), 100 wt pct excess at temperatures of 150° to 170° C, and with digestion times exceeding 2 h. A maximum Al_2O_3 extraction of 90 pct was obtained in 4 h at 150° C and with a H_2SO_4 - Al_2O_3 molar ratio of 3 (100 wt pct excess acid). Increasing the temperature to 170° C increased extractions by 5 to 8 pct.

Leaching of uncalcined kaolin with H_2SO_4 was reported by Oh (19). The best concentrations of the acid for calcined and uncalcined samples were 40 and 50 wt pct, respectively. The extraction rate increased with an increase in leaching temperature, and the extraction of alumina from uncalcined kaolin was 90 pct at 120° C, whereas extraction from

calcined kaolin was 90 pct at 100° C. Aluminum extraction increased with increasing leaching time up to 1 h.

Simplification of the clay-HCl process flowsheet (2) by eliminating most of the kaolin preparation steps and the energy-intensive calcination operation may be obtained by adoption of HCl pressure leaching of aluminum from uncalcined kaolin. These changes probably would require the use of thickeners in the solid-liquid separation circuit because of the increase in fines produced in HCl pressure leaching of raw kaolin (3-4).

FLUORIDE-ENHANCED LEACHING

The use of fluoride ion in the mineral acid leaching of aluminosilicates to promote the extraction of aluminum by disruption of the crystal structure was recognized by a number of investigators. Hamer (20) and Ripley (21), in their respective papers on fluoride-assisted leaching of anorthosite and fly ash, cite Korean research (22) that used HCl leaching with the addition of HF or CaF_2 . Bremner (23) investigated CaF_2 , Na_2SiF_6 , and H_2SiF_6 as fluoride sources in the HCl leaching of Wyoming anorthosite. Belsky's patent (24) claimed that the addition of a small amount of H_2SiF_6 to the aqueous solution of HCl used for leaching resulted in the destruction of the kaolinite structure and high solubilization of the aluminum. The exact mechanism was complex, but it was claimed that 97 pct of the aluminum in the ore may be extracted by means of HF enhancement. Farrell's method (25) for preparing solutions from a range of mineral samples for chemical analysis is not considered commercially applicable, but the technique demonstrates the dissolving power of a HF-enhanced acid-leaching system.

EXPERIMENTAL

MATERIALS

With the exception of the air-floated kaolin product,⁶ the kaolinitic clays

used were typical eastern Georgia kaolins. The Kaiser kaolin and the Bureau's 100-ton bulk sample were the same as

⁵Reference to specific products does not imply endorsement by the Bureau of Mines.

⁶Supplied by the Thiele Kaolin Co. from deposits and process facilities east of the Ogeechee River, Jefferson County, GA.

those processed in the Bureau's alumina miniplant (2, 26). The 100-ton sample was a representative cross section of a 39-ft-thick kaolin bed. Industrial cooperators in the Bureau's alumina miniplant program considered the material to be typical of abundant reserves of eastern Georgia kaolin clays and suitable for aluminum extraction processes. Analyses of the three different batches of kaolin used in experiments reported here are given in table 3. The materials used by the authors are referred to as standard kaolin and air-floated kaolin. The material used in King's work is referred to as Kaiser kaolin. Although the analyses differ slightly, the Kaiser and the standard kaolin are equivalent.

Kaolin contains small amounts of mineral impurities and diluents. Most of the iron oxide minerals⁷ are soluble in hot HCl and are the primary source of iron in HCl pregnant liquors (2, 27, p.

12). Other trace impurities are leached from the kaolinite, other clay minerals, and the micas, which are slightly soluble in HCl during prolonged atmospheric digestion or pressure leaching at elevated temperatures.

Air classification is used to upgrade filler-grade kaolin by separation of the finer kaolinite particles from the larger-grained gangue minerals, which are usually quartz and mica. Air-floated kaolin was selected as a commercially

⁷The standard kaolin was examined with optical techniques and X-ray microprobe. The iron-stained kaolinite particles ranged in color from slightly off white through pink to almost brick red. The only apparent difference was the iron oxide content. There were a few iron-stained quartz grains, but most grains were clear.

TABLE 3. - Chemical analysis of kaolinitic clay, percent¹

Component	Kaolinite, Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	Kaolin ²		
		Air-floated ³	Standard	Kaiser
Al ₂ O ₃ :				
Total.....	39.49	35.87	35.22	34.96
Acid-soluble fraction.....	NAp	(2.07)	(1.08)	ND
Fe ₂ O ₃ :				
Total.....	NAp	1.35	1.17	.84
Acid-soluble fraction.....	NAp	(.17)	(.12)	ND
CaO.....	NAp	.011	.116	.03
CO ₂	NAp	<.01	<.01	ND
K ₂ O.....	NAp	.064	.081	.13
Li ₂ O.....	NAp	.027	.030	ND
MgO.....	NAp	ND	.108	.43
MnO ₂	NAp	.0047	.004	ND
Na ₂ O.....	NAp	.033	.033	.03
P ₂ O ₅	NAp	.059	.059	.051
SiO ₂	46.60	44.15	46.66	47.55
TiO ₂	NAp	3.37	2.41	2.31
Water loss on ignition:				
At 750° C.....	NAp	13.82	⁴ 12.81	⁴ 12.82
Theoretical.....	13.91	NAp	NAp	NAp
Total.....	100.00	98.77	98.71	99.15
pH of 20-wt-pct slurry.....	ND	3.87	4.0	ND

NAp Not applicable. ND Not determined.

¹ Values in parentheses not included in totals.

² Bone-dry basis.

³ Thiele Kaolin Co. air-floated kaolin, grade EG-21 (NA TS 715).

⁴ At 1,000° C.

available and purer product than the standard kaolin. Concentrations of non-kaolinitic minerals found in standard and air-floated kaolin are given in table 4. Typical distribution of the minerals in the plus and minus 200-mesh fractions of standard kaolin is shown in table 5. The ultimate particle size analyses of deliberately dispersed,⁸ air-floated, and

⁸Usually by means of a polyphosphate dispersant in an aqueous slurry.

standard kaolin are listed in table 6. Screen analysis of the ground standard kaolin is shown in table 7.

EQUIPMENT

Atmospheric Leaching

King's research at or below the boiling point (~115° C) was performed in borosilicate glass flasks fitted with stirrers and reflux condensers (28).

TABLE 4. - Typical nonkaolinitic mineral content in standard and air-floated kaolin

Mineral	Level and comments	
	Standard kaolin	Air-floated kaolin ¹
Quartz, SiO ₂	Generally 2 to 5 wt pct and plus 200-mesh particles.	Trace.
Rutile, TiO ₂	Mostly in the range of 0.1 to 0.5 wt pct as coarse particles.	Trace.
Anatase, TiO ₂	Predominant TiO ₂ mineral, especially below 325 mesh, usually 1.6 to 2.4 wt pct. Most anatase contains 10 wt pct iron.	1.6 to 2.4 wt pct.
Zircon, ZrSiO ₄	0.2 to 0.5 wt pct in the 40-μm range.	Trace.
Smectite (montmorillonite), (Mg,Ca)O·Al ₂ O ₃ ·5SiO ₂ ·nH ₂ O.	Highly variable, usually 0 to 0.2 wt pct, mostly as fine particles.	Highly variable, usually 0 to 0.2 wt pct, mostly as fine particles.
Muscovite, KAl ₂ (OH) ₂ (AlSi ₃ O ₁₀).	Variable, from 0 to 1 wt pct, usually as plus 325-mesh particles.	Trace.
Iron, Fe ₂ O ₃	0.9 to 1.1 wt pct in the kaolinite, as a mineral rim, and associated with anatase. In rare cases a small amount of pyrite is observed as coarse particles and aggregates.	0.9 to 1.1 wt pct in the kaolinite, as a mineral rim, and associated with anatase. In rare cases a small amount of pyrite is observed as coarse particles and aggregates.
Organic carbon, C.....	Trace amounts in clays with a grey tint, finely dispersed, rarely concentrated in zones.	Trace amounts in clays with a grey tint.
Graphite, C.....	Trace, usually associated with plus 2-μm-size fraction.	Trace.

¹Air-floated kaolin, grade EG-21, Thiele Kaolin Co., Sandersville, GA.

TABLE 5. - Mineral grain count of standard kaolin, particles per 100 particles¹

Mineral	200-mesh fraction	
	Plus	Minus
Clays.....	95	96
Quartz.....	4-5	3-4
Feldspar.....	ND	ND
Epidote.....	<1	Trace
Opaque minerals:		
Pyrite.....	<1	Trace
Ilmenite.....	ND	ND
Magnetite.....	<1	Trace
Hornblende.....	Trace	ND
Pyroxene.....	Trace	ND
Rutile.....	ND	ND
Staurolite ²	<1	ND
Urident-silicates.....	<1	Trace

ND Not detected.

¹Results are specific for 1 sample, but indicate general mineralogy.

²Identification uncertain.

TABLE 6. - Particle size analysis of dispersed air-floated and standard kaolin¹

ESD..... $\mu\text{m}.$	Cumulative percent finer ¹				
	10	3	1	0.6	0.25
Air floated, ² av					
ESD of 40 $\mu\text{m}.$	97	91	82	69	32
Standard, ³ av ESD					
of 38 $\mu\text{m}.$	93	84	76	69	35

ESD Equivalent spherical particle diameter.

¹Determined by SediGraph particle size analyzer.

²Typical EG-21: screen residue plus 75 μm , 0.05 to 0.1 pct; plus 45 μm , 0.17 to 0.3 pct; finer than 2 μm , 86 to 92 pct.

³See table 7.

The Bureau's atmospheric pressure leaching was performed in a 4-L resin kettle with baffles. A Chesapeake-style stirrer and seal bearing was fitted with a glass stirring rod and a TFE polymer blade. Stirring was powered by a high-torque, feedback-type, constant-speed motor. The other ports in the cover contained a condenser, a thermometer well, and an access port for charging and

TABLE 7. - Screen analysis of ground, standard kaolin used in HCl leaching tests

Screen size, ¹ mesh	Cumulative percent finer
28.....	99.9
35.....	99.8
48.....	93.1
65.....	71.2
100.....	52.1
150.....	37.7

¹Tyler standard sieve.

sampling. A fiberglass-insulated heating mantle with a silicon-controlled rectifier heated the lower section of the flask.

Pressure Leaching

King's hydrothermal extractions were conducted in 35-mL tantalum bombs that were heated by insertion into an aluminum block maintained at the desired temperature. About 10 min was required to heat the bombs to temperatures of 175° to 250° C.

A Berghof 750-mL-capacity TFE-polymer-lined autoclave was used in experiments performed by the Bureau. The practical working volume of the autoclave was 400 mL. The autoclave, figure 1, had a type 316 stainless steel shell that contained a molded TFE polymer liner and was rated at 200 atm and 250° C. All internal parts were made from or were covered with TFE polymer. Agitation was provided by a hollow impeller shaft that mounted up to three impellers machined from TFE polymer. Only the two lower impellers were used. A thermocouple entered through the hollow central fitting in the lid. Two other access ports were provided for gas addition or release, pressure gauges, and rupture disks. A pressure gauge was used with a TFE-polymer-covered gauge isolator.

Agitation was produced by a rotating magnetic field operating on the rotor through the nonmagnetic stainless steel shell of the autoclave. The temperature measured by the thermocouple inside the impeller, which was in the center of the

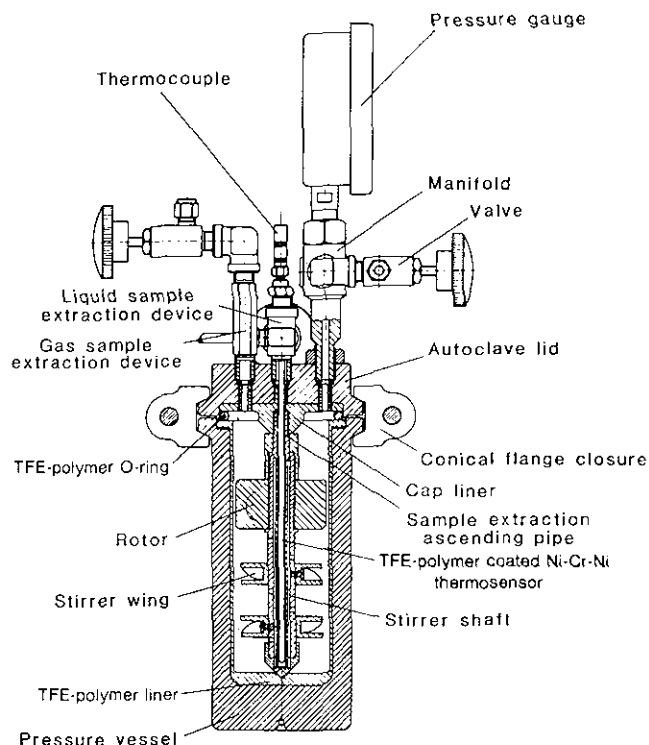


FIGURE 1. - Berghof TFE-polymer-lined autoclave.
(Courtesy of Berghof America, Inc.)

plastic-lined autoclave, responded very slowly to changes in the temperature of the heating mantle. Controlling the temperature with this thermocouple was difficult. Improved operation was obtained by exchanging the heating mantle for a fluidized-bed heating bath with a separate temperature control. The stirrer motor and autoclave were suspended from the ceiling. Cooling could be done slowly by raising the reactor out of the fluidized bed, faster by spraying the walls of the reactor with a water mist, or rapidly by lowering the reactor into a tank of cold water.

PROCEDURES

Atmospheric Leaching

King conducted his experiments at or below the boiling point in borosilicate glass flasks fitted with stirrers and reflux condensers. The acid was heated to temperature before the kaolin was added. The reaction mixtures were filtered hot through sintered glass filters.

The residue was washed thoroughly and the washings were combined with the main filtrate.

Extended atmospheric pressure leaching tests conducted by the Bureau with boiling 20-wt-pct HCl were started by heating 2,880 g of 20-wt-pct HCl to boiling in the resin kettle and adding 625 to 748 g of kaolin. Reaction time was counted from the beginning of the kaolin addition and stirring was continuous. At specific intervals, usually multiples of 24 h, slurry samples were aspirated from the reaction vessel into 8-oz centrifuge bottles and cooled. The slurry was weighed, then centrifuged to separate the solids. The solids were repulped, washed three times, centrifuged to remove wash water, dried, and weighed. Chemical analyses were made of the pregnant liquor and washed residue.

Pressure Leaching

A typical charge in the 35-mL tantalum bombs used in King's investigations consisted of 6.6 g of kaolin and 22 g of 27-wt-pct HCl (~20 mL). About 10 min was required to heat the charged bombs to temperatures of 175° to 250° C. The bombs were cooled rapidly by immersion in cold water at the completion of the experiments. The contents were washed into weighed sintered-glass filtering crucibles with hot distilled water. The total wash volume was about five times the reaction mixture volume. Washed residues were dried overnight at 100° C and weighed.

For a Berghof autoclave run, about half the required quantity of 20-wt-pct HCl was poured into the removable reactor liner and the measured quantity of raw kaolin, which was dried at 125° C, was added. These were mixed by manually swirling the liner until the solids were slurried, and the walls were washed with the remaining acid. The agitator was inserted and blunged a few times to mix the wall washings and the main slurry. After installation of the liner in the autoclave body, the agitator was tested with the open autoclave mounted in the stirrer motor stator. The autoclave was sealed

and suspended in the fluidized sand bed and agitation was started.

Temperature changes were monitored with a digital meter and were recorded with an analog recorder. A typical recorder trace is illustrated in figure 2. At the end of the prescribed time, the reactor was removed from the fluidized bed and cooled in a small tank of cold water. Cooling was most rapid when the stirrer was left operating. After it was cooled to room temperature, the reactor was opened and the liner removed.

Equal portions of slurry from the reactor were placed in bottles, centrifuged for 30 min, and the liquor decanted for measuring the weight and density and for chemical analysis. The solids were repulp-washed three times with acidified distilled water and finally with distilled water. Acidification of the wash water prevented peptization of undigested kaolin or finely divided residues and hydrolysis of the AlCl_3 . After each repulping, the bottles were centrifuged. The washed residues were dried overnight at 125°C , weighed, and sampled.

Analytical Methods

With the exception of solution densities and loss on ignition determinations, analytical data were obtained by inductively coupled plasma emission spectroscopy (ICP). Solid samples, either kaolin or leach residues, were solubilized for ICP by the following method:

Solids were dried at 125°C and pulverized; a 0.2-g sample was mixed with 1.4 g of LiBO_2 and fused for 15 min at 900°C in a 5-pct-gold,

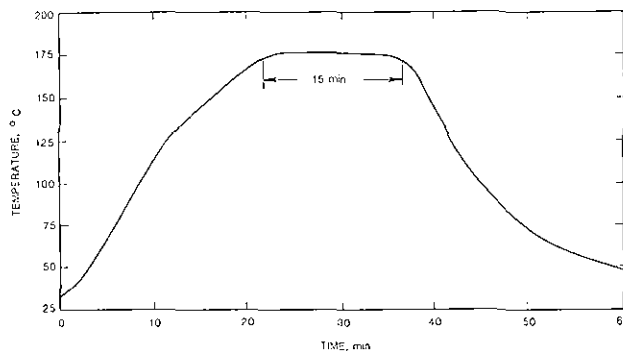


FIGURE 2. - Heating curve for TFE-polymer-lined autoclave with fluidized-bed heater.

95-pct-platinum crucible. The re-resulting glass bead was dissolved with stirring in 250 mL of 4-wt-pct HNO_3 at about 40°C . A National Bureau of Standards clay sample, standard reference material SRM 97a, was included in each series of solid samples as a control.

Acid-soluble alumina and iron contents were determined by a 2-h bench-scale leaching procedure under reflux conditions and with excess 20-wt-pct HCl .

King's (28) pregnant liquors, which contained AlCl_3 , HCl , FeCl_3 , and other chlorides, were analyzed for aluminum by the Watts-Utley method (29) using sodium gluconate to complex iron and aluminum. Iron was determined separately (the total iron content was assumed to be present as chloride) and subtracted from the combined aluminum and iron analysis to obtain the aluminum analysis. If CaCl_2 and MgCl_2 were high, this method gave superior results to methods in which iron was removed by precipitation as a hydrous oxide.

RESULTS AND DISCUSSION

ATMOSPHERIC LEACHING

Leaching uncalcined kaolin with HCl at the atmospheric boiling point for short periods of time gave poor results. The Bureau obtained 9.7-pct alumina extraction from air-floated kaolin with 20-wt-pct HCl in 2 h at Boulder City, NV (2,500-ft elevation). King reported 40.9 pct extraction with 27-wt-pct HCl in

2.5 h.⁹ The Bureau investigated longer leaching times and used both standard and air-floated kaolins with 20-wt-pct HCl and acid stoichiometry ratios that ranged from 0.83 to 1.24. Alumina extractions increased to more than 92 pct in 48 h and in one test to 98.6 pct in

⁹Kaiser Aluminum & Chemical Corp., Pleasanton, CA (about 200-ft elevation).

142 h. Figure 3 and tables 8 and 9 show that excess acid improved the extraction of alumina. The use of HCl equivalent to the acid-consuming compounds present showed a consistently lower extraction than the 1.20 stoichiometric test. King reported one test (table 10) run below the boiling temperature at 100° C in which 96.2 pct of the alumina was extracted in 120 h using 27-wt-pct HCl.

King established the utility of using fluoride ions when leaching with 27-wt-pct HCl at lower temperatures (115° C). The addition of 0.07 wt pct F⁻ to 20-wt-pct excess HCl extracted 74 pct of the alumina in 6 h and 95 pct in 24 h (table 10). Increasing the fluoride content in the leaching solution to 0.27 wt pct increased the extraction to 87.6 pct in 6 h and 97.4 pct in 17 h. This confirms the vulnerability of the kaolinite structure to longer digestion time with stronger acid and enhanced attack on the silica-alumina bond by fluoride ion.

PRESSURE LEACHING

Effect of Temperature

Air-floated kaolin was leached for 2 h at 125° to 225° C with 20-wt-pct HCl. The authors selected 20-wt-pct HCl solutions, rather than the 27-wt-pct concentration used by King, because of kaolin suspension dilution requirements imposed

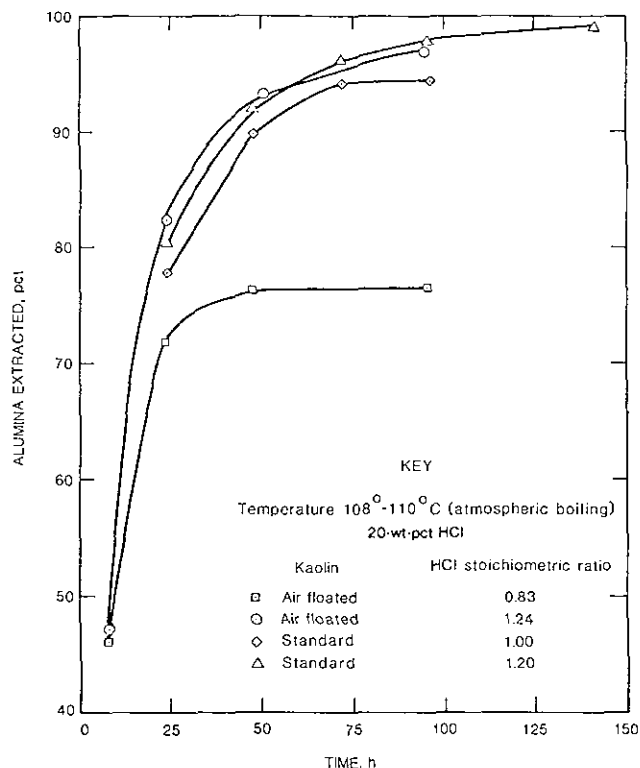


FIGURE 3. - Alumina extraction versus time for atmospheric pressure leaching of kaolin.

by the Berghof autoclave stirring mechanism rather than by process chemistry. The results of the tests are given in table 11 and are plotted in figure 4, and show that aluminum extraction increases with temperature and with the acid stoichiometry. More than 90 pct of the

TABLE 8. - Effect of stoichiometry and time on atmospheric leaching of alumina from air-floated kaolin with 20-wt-pct HCl, and analysis of pregnant liquors and residues

Stoichiometry ¹	Time, h	Al ₂ O ₃ extracted, pct	Pregnant liquor				Residue, pct			
			Al ₂ O ₃ , pct	Fe ₂ O ₃ , pct	Free HCl, pct	Density, 20° C, g/mL	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂
0.83....	8	47.2	5.9	0.13	6.98	1.177	25.6	0.64	59.8	3.2
	24	72.5	8.7	.19	1.09	ND	15.7	.48	70.1	3.9
	48	76.8	9.6	.21	.12	1.236	13.8	.45	72.9	4.1
	96	77.0	10.3	.23	.00	1.264	13.5	.48	82.2	4.1
1.24....	8	48.2	3.9	.078	ND	1.155	24.9	.65	59.2	3.3
	24	82.7	6.7	.14	ND	1.202	10.6	.36	75.7	4.3
	48	93.4	8.3	.18	ND	1.239	4.46	.22	82.6	4.7
	96	97.4	10.2	.23	2.03	1.282	1.82	.17	81.3	4.8

ND Not determined.

¹Ratio of quantity of HCl used to quantity of HCl required to react with total Al₂O₃ and other acid-soluble components in the kaolin.

TABLE 9. - Effect of stoichiometry and time on atmospheric leaching of alumina from standard kaolin with 20-wt-pct HCl, and analysis of pregnant liquors and residues

Stoichiometry ¹	Time, h	Al ₂ O ₃ extracted, pct	Pregnant liquor ²				Residue, pct			
			pct		ppm		Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂
			Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂				
1.00.....	24	76.6	7.3	0.21	<30	74	13.3	0.48	75.6	4.1
	48	89.2	8.7	.25	730	31	6.76	.31	83.2	ND
	72	92.6	9.0	.27	98	<4	4.76	.27	85.4	ND
	96	93.2	11.5	.36	59	<5	4.41	.28	85.1	ND
1.20.....	24	79.6	8.0	.23	950	190	11.8	.43	76.5	4.2
	48	91.6	8.2	.23	540	120	5.31	.27	84.0	4.6
	72	95.9	8.1	.23	500	82	2.76	.20	87.9	4.9
	96	97.6	8.1	.24	520	64	1.55	.17	86.1	5.0
	142	98.6	8.8	.26	<30	56	.94	.15	90.5	5.0

ND Not determined.

¹Ratio of quantity of HCl used to quantity of HCl required to react with total Al₂O₃ and other acid-soluble components in the kaolin.

²Values for liquor densities were very similar to values obtained in experiments with atmospheric leaching of air-floated kaolin (table 8).

TABLE 10. - Extraction of alumina from Kaiser kaolin (table 3) with 20- and 27-wt-pct HCl at temperatures from 100° to 150° C, with and without NaF additions, using 20 wt pct excess acid (28)

Experimental conditions				
Temperature, °C	Time, h	Liquor composition, wt pct		Al ₂ O ₃ extraction, wt pct
		HCl	NaF as F ⁻	
100....	120	27	0.0	96.2
115 ¹ ...	6	27	.07	74.0
	24	27	.07	95.2
	6	27	.27	87.6
	17	27	.27	97.4
	2.5	27	.0	40.9
150 ² ...	6	27	.0	73.9
	1	27	.0	89.1
	1	20	.0	89.0
	2.25	20	.0	95.7

¹Boiling.

²Pressure leaching.

alumina was extracted in 2 h at >150° C if sufficient HCl was present. A stoichiometric ratio of 0.80 gave approximately 80 to 84 pct alumina extraction at 175° to 225° C. Increasing the leaching acid to 100 pct of the theoretical acid required for the acid-consuming elements in the kaolin extracted only 90 pct of

the alumina at 150° C. Increasing the acid available to 105 and 120 pct of the theoretical amount increased the alumina

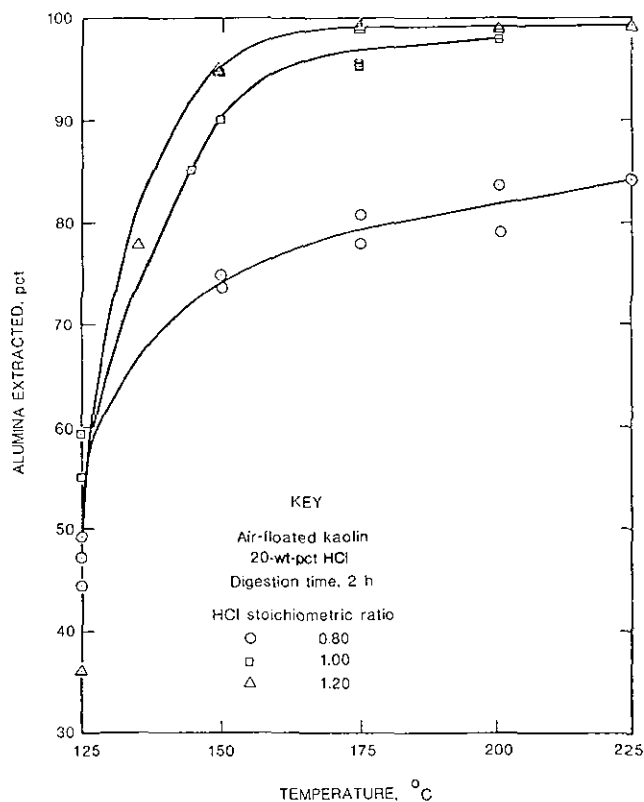


FIGURE 4. - Effect of temperature on pressure leaching of alumina from air-floated kaolin.

TABLE 11. - Effect of stoichiometry and temperature of 20-wt-pct HCl on 2-h pressure leaching of alumina from air-floated kaolin, and analysis of pregnant liquors and residues

Test	Stoichiometry ¹	Temp, °C	Al ₂ O ₃ extraction, pct	Analysis, ² pct							
				Pregnant liquor ³				Residue			
				Al ₂ O ₃	Fe ₂ O ₃	Free HCl	Density, g/mL	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂
1...	0.8	⁴ 108	9.8	1.9	0.074	ND	1.128	34.1	0.83	46.5	2.6
2...	.8	125	49.2	5.0	.11	4.88	1.139	24.4	.63	59.0	3.3
3...	.8	150	75.0	7.3	.15	ND	1.164	13.5	.45	66.6	3.9
4...	.8	175	80.4	7.5	.16	ND	1.167	11.2	.35	70.8	4.2
5...	.8	200	82.3	7.1	.15	ND	1.170	10.9	.62	75.2	4.3
6...	.8	225	83.9	5.8	.15	.09	1.154	9.91	.57	76.4	4.3
7...	1.0	125	56.2	5.5	.12	7.83	1.172	22.8	.60	64.1	3.6
8...	1.0	145	84.9	7.5	.16	ND	1.195	8.55	.31	69.5	4.2
9...	1.0	150	89.8	8.2	.17	ND	1.212	6.80	.28	81.8	4.8
10..	1.0	175	95.1	8.5	.19	.46	1.217	3.28	.19	83.5	4.9
11..	1.0	200	97.6	8.6	.19	ND	1.217	1.65	.15	85.5	5.2
12..	1.05	150	92.9	7.9	.17	ND	1.209	4.62	.22	79.8	4.8
13..	1.2	125	39.0	3.4	.077	ND	ND	27.2	.68	55.0	3.0
14..	1.2	135	77.4	6.1	.13	ND	1.177	13.5	.39	73.4	4.1
15..	1.2	150	95.3	6.5	.14	3.93	1.193	2.92	.17	77.8	4.5
16..	1.2	175	98.8	7.3	.16	ND	1.196	.86	.14	85.3	5.1
17..	1.2	200	98.8	7.3	.16	3.38	1.197	.81	.12	85.3	5.0
18..	1.2	225	99.1	6.5	.14	ND	1.190	.61	.12	87.4	5.0

ND Not determined.

¹Ratio of quantity of HCl used to quantity of HCl required to react with total Al₂O₃ and other acid-soluble components in the kaolin.

²Averages of several tests conducted under the conditions given.

³SiO₂ content of liquors from tests 1, 2, and 13 was less than 30 ppm.

⁴Atmospheric pressure.

extraction to 93 and 95 pct, respectively. Ninety-nine percent extractions for the 175° and 200° C tests with 1.20 HCl stoichiometric ratios indicate that excess acid is necessary. King obtained similar data. Tests performed at 150° C with 20-wt-pct HCl at 1.20 stoichiometric ratio required about 2.3 h to extract 96 pct of the alumina (table 10).

A scale formed on the walls of the TFE-polymer liner when low stoichiometric ratio leaches were carried out at 200° to 225° C. Test 6 (table 11) was run for 2 h at 225° C and 0.8 HCl stoichiometry and produced scale that was 1 to 2 mm thick. Analysis of the scale, which was ground but not washed, was 52.4 pct Al₂O₃, 29

pct Fe₂O₃, 0.91 pct TiO₂, and 15.2 pct SiO₂, compared with 11.0, 0.32, 4.4, and 71.9 pct, respectively, for the residue. The material contained some chloride because it was not washed. X-ray analysis indicated the existence of unknown crystalline materials, which had lines at d spacings of 2.18, 11.8, 5.9, 3.40, 3.98, and 2.93 Å. Dilution of the slurry with water decreased the quantity of scale formed. The scale is the decomposition product of AlCl₃. Krishnan and Bartlett (30) produced boehmite from AlCl₃ solutions by heating to 200° C or more, but found that the presence of free HCl in the feed solution decreased the conversion.

Effect of Time

Digestion time was investigated to define the minimum retention time for maximum extraction of aluminum at a minimum effective temperature and pressure. Air-floated kaolin was leached with 20-wt-pct HCl at 175° and 200° C for periods of 15 min to 2 h. Test data are plotted in figure 5 and are given in table 12 (as averages where more than one test was run at a given condition). More than 90 pct of the alumina was extracted in most tests that had leaching times of 30 min, and all curves showed an increase in extraction with time. Significant differences in the slopes of curves are related to the HCl stoichiometric ratio. In tests with a stoichiometric ratio equal to or greater than 1.20, 98 to 99 pct of the alumina was extracted in 60 min. Little alumina was extracted after 60 min for tests conducted with a stoichiometric ratio of 1.20. Analysis of the data in table 12 indicates that increasing HCl stoichiometry from 1.00 to 1.20 is more effective in improving extraction than increasing leaching temperature from 175° to 200° C, or digestion time from 30 to 60 min, or both.

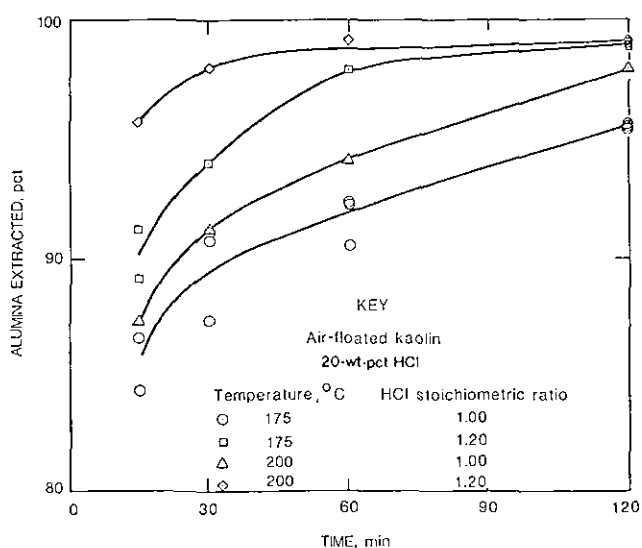


FIGURE 5. - Effect of time and HCl stoichiometry on pressure leaching of alumina from air-floated kaolin at 175° and 200° C.

For standard kaolin, data from a similar series of tests are given in table 13 and are plotted in figure 6. Although the curves have different shapes, the features are similar. High extractions occurred in 1 h with a 1.20 HCl stoichiometric ratio at both 175° and 200° C. With a stoichiometry of 1.00, a 92-pct extraction was obtained in 60 min at 175° C and in 15 min at 200° C, and Al_2O_3 extraction continued after 2 h at either temperature.

King's Hydrothermal Digestion of Kaolin

Experimental conditions and results for hydrothermal digestion of Kaiser kaolin using a simulated recycle HCl solution containing $AlCl_3$ and other salts, such as NaCl, $CaCl_2$, and $MgCl_2$, H_3PO_4 , and H_2SO_4 , are shown in table 14. The composition of the recycle acid solution was similar to that expected in a clay-HCl alumina plant (7). The effect of digestion time on the extraction efficiency was also determined. Leaching with 27-wt-pct HCl in a simulated plant recycle leaching solution showed a leveling off of the alumina extraction at 94 to 96 pct after 30 min (fig. 7). King (28) reported that the

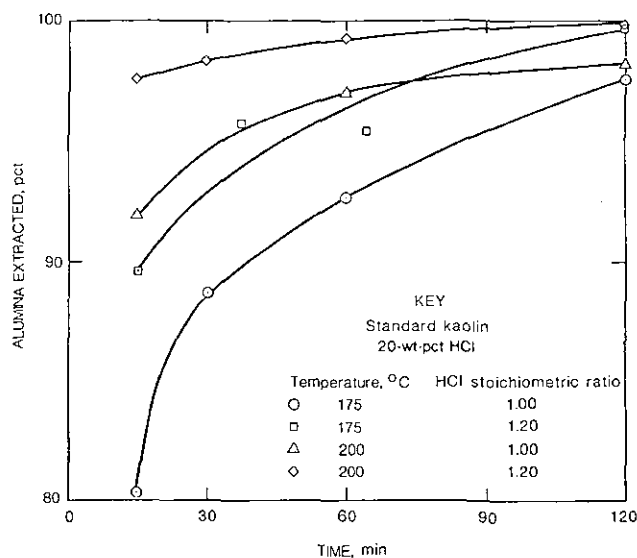


FIGURE 6. - Effect of time and HCl stoichiometry on pressure leaching of alumina from standard kaolin at 175° and 200° C.

TABLE 12. - Effect of stoichiometry, temperature, and time on 20-wt-pct HCl pressure leaching of alumina from air-floated kaolin, and analysis of pregnant liquors and residues

Test	Stoichiometry ¹	Temp, °C	Time, min	Al ₂ O ₃ extraction, pct	Analysis, ² pct							
					Pregnant liquor				Residue			
					Al ₂ O ₃	Fe ₂ O ₃	Free HCl	Density, g/mL	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂
23...	1.00	175	15	85.3	7.9	0.18	2.42	1.206	9.42	0.33	78.8	4.6
	1.00	175	30	89.6	8.2	.18	1.30	1.210	6.86	.27	81.7	4.7
25...	1.00	175	60	91.3	8.4	.20	.94	1.213	5.84	.25	83.1	4.8
26...	1.00	175	120	95.1	8.5	.19	.46	1.217	3.28	.19	83.5	4.9
27...	1.00	200	15	87.3	8.0	.17	ND	ND	8.31	.29	80.6	4.7
28...	1.00	200	30	91.2	8.3	.18	ND	1.215	5.77	.24	80.7	4.8
29...	1.00	200	60	94.0	8.6	.19	ND	1.217	4.18	.23	85.1	5.0
30...	1.00	200	120	97.6	8.6	.19	ND	1.217	1.65	.19	85.3	5.2
31...	1.20	175	15	90.2	7.4	.16	ND	1.189	7.05	.26	82.1	4.7
32...	1.20	175	30	94.1	7.3	.16	ND	1.193	4.05	.20	83.7	4.8
33...	1.20	175	60	97.8	7.5	.17	ND	1.196	1.58	.16	88.1	5.1
34...	1.24	175	120	98.8	7.3	.16	ND	1.196	.86	.14	85.3	5.1
35...	1.20	200	15	95.7	7.5	.16	ND	1.197	3.03	.15	87.5	5.0
36...	1.20	200	30	97.9	7.3	.16	ND	1.197	1.49	.14	88.0	5.1
37...	1.20	200	60	99.1	7.5	.17	ND	ND	.64	.12	90.3	5.3
38...	1.24	200	120	98.8	7.3	.16	3.38	1.197	.81	.12	85.3	5.0
39...	1.24	225	120	99.1	6.5	.14	ND	1.190	.61	.12	87.4	5.0

ND Not determined.

¹Ratio of quantity of HCl used to quantity HCl required to react with total Al₂O₃ and other acid-soluble components in the kaolin.

²Leach liquors from tests 35 through 37 analyzed 45, 28, and 28 ppm TiO₂, and 130, 30, and 30 ppm SiO₂.

TABLE 13. - Effect of stoichiometry, temperature, and time on 20-wt-pct HCl pressure leaching of alumina from standard kaolin, and analysis of pregnant liquors and residues

Test	Stoichiometry ¹	Temp, °C	Time, min	Al ₂ O ₃ extraction, pct	Analysis									
					Pregnant liquor					Residue, ² pct				
					pct		ppm		Density, ³ g/mL	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	
					Al ₂ O ₃	Fe ₂ O ₃	Free HCl	SiO ₂						TiO ₂
1....	1.00	175	15	79.8	7.0	0.20	ND	<30	64	1.192	11.9	0.44	78.2	4.3
2....	1.00	175	30	88.4	7.6	.22	ND	47	22	1.206	7.31	.33	83.4	4.6
3....	1.00	175	60	92.4	8.1	.23	ND	190	16	1.210	4.93	.27	85.8	4.8
4....	1.00	175	120	97.4	8.3	.23	0.88	100	8.1	1.216	1.71	.17	86.3	4.7
5....	1.00	200	15	91.7	7.9	.23	ND	30	12	1.183	5.36	.28	85.6	4.7
6....	1.00	200	60	96.9	8.2	.23	ND	47	<4	1.189	2.11	.20	88.6	4.9
7....	1.00	200	120	98.0	8.4	.25	.64	92	13	1.218	1.31	.18	85.7	4.9
8....	1.20	175	15	89.3	6.7	.19	ND	880	170	1.190	6.77	.31	83.5	4.5
9....	1.20	175	37	95.5	6.8	.19	ND	250	72	1.191	2.98	.27	88.3	4.8
10...	1.20	175	64	95.3	7.1	.20	ND	200	50	1.192	3.18	.21	89.8	5.0
11...	1.24	175	120	99.8	7.0	.20	3.98	140	48	1.193	.13	.12	91.9	5.0
12...	1.20	200	15	97.7	7.1	.20	ND	<30	47	1.195	1.59	.17	89.6	4.9
13...	1.20	200	30	98.4	7.5	.21	ND	330	51	1.197	1.09	.15	89.9	4.9
14...	1.20	200	60	99.3	7.2	.20	ND	<30	37	1.198	.49	.13	90.7	5.0
15...	1.24	200	120	99.8	7.2	.21	3.79	<30	44	1.194	.14	.11	91.2	4.9

ND Not determined.

¹Ratio of quantity of HCl used to quantity of HCl required to react with total Al₂O₃ and other acid-soluble components in the kaolin.

²Dried at 125° C.

³20° C.

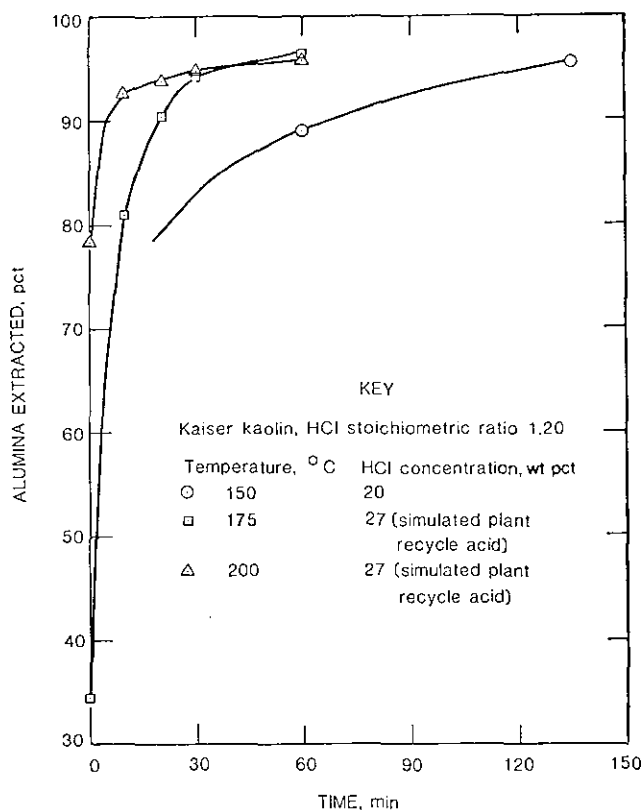


FIGURE 7. - Effect of time and temperature on pressure leaching of alumina from Kaiser kaolin.

presence of impurities in the 27-wt-pct HCl did not, within the estimated experimental error (± 0.5 pct), have an effect of extraction efficiency at 200° C. For hydrothermal digestions equal to or exceeding 30 min, there was no advantage of 200° over 175° C.

Most of the HCl leaching research reported by King (tables 10, 14-16) was made with a 20-wt-pct excess of 27-wt-pct HCl solution. This choice was based on calculations to provide the maximum concentration of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in the pregnant liquor while remaining below the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ saturation point (31-32). Higher HCl concentrations would cause the precipitation of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in the leaching slurry, which would lead to scaling and blinding of the filters. Lower

TABLE 14. - Effect of residence time on hydrothermal extraction of alumina from Kaiser kaolin with simulated recycle acid from the clay-HCl process at 175° and 200° C (28)

Experiment	Conditions ¹		Al ₂ O ₃ extraction, pct
	Temp, °C	Time, min	
9.....	175	20	34.5
10.....	175	10	81.1
11.....	175	20	90.7
12.....	175	30	94.3
13.....	175	60	96.4
14.....	200	20	78.6
15.....	200	10	92.7
16.....	200	21	93.8
17.....	200	30	94.9
18.....	200	60	95.8

¹All reaction mixtures consisted of 6.60 g Kaiser kaolin (table 3) and 22.0 g of simulated recycle from the clay-HCl process containing, in percent, AlCl_3 , 2.67; CaCl_2 , 0.04; HCl, 27.0; H_3PO_4 , 0.099; H_2SO_4 , 0.105; KCl, 0.110; MgCl_2 , 0.158; NaCl, 0.052. Specific gravity was 1.161 at 20° C.

²Heated to digestion temperature during 10-min period and immediately cooled.

concentrations would require evaporation. Using a double extraction did not improve the filtration characteristics of the residue. There was only a slight increase in particle densification measured by a decrease in the specific surface of the residues reported in table 15.

King extended the leaching temperature to 250° C and used 27-wt-pct-HCl leaching acid in 10 wt pct excess with and without added HF (table 16). Digestion under these extreme conditions for 30 and 60 min did not exceed the amount of alumina extracted at 175° and 200° C for the same times without the fluoride ion (table 14). In two experiments, F^- was deleterious to the filtering properties of the leached residue (table 16).

SUMMARY AND CONCLUSIONS

Alumina was leached from uncalcined kaolinitic clay by 20-wt-pct-HCl solutions at digestion temperatures that

ranged from 108° to 225° C. In the presence of excess acid, atmospheric leaching with boiling HCl extracted more than

TABLE 15. - Effect of stoichiometry, temperature, and time on hydrothermal extraction of alumina from Kaiser kaolin with 27-wt-pct HCl (28)

Ex-periment	Conditions ¹			Residue surface area, m ² /g	Al ₂ O ₃ extraction, wt pct	Ex-periment	Conditions ¹			Residue surface area, m ² /g	Al ₂ O ₃ extraction, wt pct
	Stoi-chiom-etry ²	Temp, °C	Time, min				Stoi-chiom-etry ²	Temp, °C	Time, min		
1....	1.1	200	35	73	93.8	5....	1.4	200	60	63	96.8
2....	1.2	200	30	77	94.3	6....	1.1	³ 250	30	57	94.1
3....	1.2	200	60	67	96.4	7....	1.1	³ 250	60	56	96.2
4....	1.4	200	30	63	95.1	8....	³ NR	200	30	52	⁴ 22.9

NR Not reported.

¹All extractions made in 35-mL tantalum bombs. Residues averaged 53 pct of raw kaolin feed weight.

²Ratio of quantity of HCl used to quantity of HCl required to react with total Al₂O₃ and other acid-soluble components in the kaolin.

³Pressure equaled approximately 900 psia (33).

⁴Dried residue from experiment 6 releached to investigate possible improvement in filtration characteristics. Values calculated by authors; 19 times as much acid present as required. Overall alumina extraction was 95.5 pct.

TABLE 16. - Effect of F⁻ ion addition on the hydrothermal extraction of alumina from Kaiser kaolin with 27-wt-pct HCl at 250° C (28)

Experiment	Reactants, ¹ g			Conditions		Residue ² surface area, m ² /g	Al ₂ O ₃ extraction, pct
	Kaolin	HCl	HF	Time, min	Bomb wall material		
6.....	6.55	20.0	0.0	30	Tantalum.....	57	94.1
7.....	6.55	20.0	.0	60	...do.....	56	96.2
19.....	6.55	20.0	.116	30	Teflon ³	76	91.8
20.....	6.55	20.0	.116	60	...do ³	62	93.9
21.....	2.62	8.0	.232	30	Pyrex.....	61	94.6
22.....	2.62	8.0	.232	40	...do.....	59	95.4

¹Kaiser kaolin (table 3), 27-wt-pct HCl in 10 wt pct excess of that required to react with available alumina, and 49.2-wt-pct HF. Bomb heat-up time assumed to be 10 min to reach 250° C.

²Residues from experiments 21 and 22 were gellike and filtered slowly. Releaching of residue from experiment 6 did not significantly improve filtration characteristics (see experiment 8, table 15). The weight of dried, acid-leached residues ranged from 52.9 to 53.7 pct of the weight of kaolin.

³TFE-polymer liners were slightly permeable to HCl at 250° C.

92 pct of the alumina in 48 h and 97 pct in 96 h. An excess of acid was necessary to achieve satisfactory leaching efficiencies and to accelerate leaching rates.

King (28) reported comparable results on a similar Georgia kaolin at 100° to 250° C. Since his autoclaves were small, he was able to employ 27-wt-pct HCl, which produced almost saturated AlCl₃ solutions. King evaluated a leaching solution containing NaCl, KCl, MgCl₂, CaCl₂, H₂SO₄, and H₃PO₄ impurities in

27-wt-pct HCl to simulate a plant recycle leaching solution and found no change in aluminum extraction. King's data also indicated that 175° C is a satisfactory design temperature for a raw kaolin pressure leaching process. The addition of 0.27 wt pct fluoride ion to the 27-wt-pct HCl leaching solution increased the leaching rate at 115° C, but at 250° C, the effect on leaching was inconclusive and the siliceous residues were gellike and filtered slowly.

Pressure leaching uncalcined kaolin with excess 20-wt-pct HCl at temperatures that ranged from 150° to 225° C resulted in alumina extractions greater than 90 pct, and digestion periods were 2 h or less. By using a HCl stoichiometry ratio of 1.20, a retention time of 15 min was required at 175° C to leach more than 90 pct of the alumina. At 200° C, 95 pct of the alumina was extracted in the same

time. These data indicate a choice between a faster reaction at 200° C or a slower reaction at a lower pressure at 175° C (33). Two samples of typical eastern Georgia kaolins, a representative bulk sample from a 39-ft-thick kaolin bed, and an air-floated filter-grade kaolin, gave similar alumina leaching characteristics.

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