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CLAY LEACHING WITH ACIDS

Irundi S. Edelweiss
(Masters Thesis)

February 1968

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CLAY LEACHING WITH ACIDS

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ABSTRACT

Bauxite, the raw material for the production of aluminum, is found only in tropical and subtropical regions. The extraction of alumina in a sufficiently pure state from clay is therefore a problem of great economic importance.

Processes using sulfurous acid can be conducted in such a manner that the product satisfies the stringent specifications for iron. But no acid process produces alumina sufficiently low in silica ($SiO_2/Al_2O_3 < 0.0015$). The present study of clay extraction under various conditions shows that the silica-alumina of the extract can indeed be varied within a wide range. But the conditions do not offer much hope for technical improvements.

1. INTRODUCTION

1.1 Raw Materials for Aluminum Manufacture

Aluminum has numerous uses and demand has been increasing since World War II. It is largely utilized in the food and airplane industries and as construction material.

Aluminum is commercially obtained from bauxite. Bauxites are only found in the tropics and subtropics where the weathering of alumina silicates produces a high alumina ore with low silica content. A good bauxite ore has as much as 60 per cent of alumina and not more than 5 per cent of silica. Alumina is obtained from bauxite through Bayer's Process. It is based on the dissolution of the alumina in caustic soda, precipitation of iron oxide, silica and other impurities[3] (red mud) and final precipitation of alumina by cooling and dilution.

United States reserves of bauxite are located in the southeastern states mainly in Arkansas. Domestic contribution of bauxite is estimated to be one-fifth of consumption. The scarcity of a good alumina ore has drawn the attention to clay, a lower grade ore. Some clays may have up to 40 per cent alumina and the existence of such ore is practically unlimited. In the United States high alumina clays are found in the East and near the Pacific coast. Although many processes have been suggested for the production of alumina from clay, the development of an economically feasible process is still an open technological problem. The high silica content of clays (40 per cent) is the most harmful impurity. Table 1 shows approximate commercial compositions of clays and bauxites. In the Bayer Process silica is eliminated by precipitation of the insoluble

sodium alumina silicate. This elimination cannot be done with clays because of the inordinate alumina losses involved. It was initially sought to reduce the silica content of clays to a level tolerable in the Bayer Process. The present trend is toward the development of a process entirely dissociated from Bayer's. Many different processes have been suggested[7,8,9,10,16,20] but only the ones related to this work will be discussed.

Table 1. Compositions of Representative Clays and Bauxites

	Clay %	Bauxite %
alumina	38	58
ferric oxide	2	5
silica	42	5
titania	3	2
combined water	14	30

1.2 Processes for Recovery of Alumina from Clay

1.21 Modified Bayer Process

This process is essentially a Bayer Process with an additional step for the recovery of alumina from the red mud.

Clay is digested with caustic soda. The precipitate of sodium aluminum silicate is sintered in a kiln with a mixture of sodium and calcium carbonates. The residue is leached with water and the solution is added to the filtrate of the caustic digestion. Silica is retained in the precipitate as insoluble calcium silicate ($2CaO \cdot SiO_2$). The aluminate solution is hydrolyzed to aluminum hydroxide by cooling and dilution with water and crystallized by seeding. Aluminum hydroxide

is then filtered, washed, and calcined at 1200°C. A flow diagram is presented in Figure 1.

1.22 Sulfuric Acid Process

Calcined clay is treated with sulfuric acid. The mixture is filtered and the solution is crystallized by cooling. The crystals of aluminum sulfate $Al_2(SO_4)_3 \cdot H_2SO_4 \cdot 3H_2O$ are calcined producing alumina, sulfur dioxide and sulfur trioxide[5,11,15]. The gases are used to regenerate sulfuric acid. Alumina recovery by this process is very high. The flow diagram is presented in Figure 2.

1.23 Sulfurous Acid Process

The leaching of clay with aqueous sulfurous acid has been developed by investigators[13,24] of the Th. Goldschmidt A. G. in Essen, Germany[2].

Clay is calcined at 800°C to form acid soluble compounds[4,21,22] and leached with sulfurous acid. Best leaching temperatures are between 50 and 60°C[13,24]. The extraction rate is very low below 50°C. At atmospheric pressure and temperatures above 60°C the concentration of sulfur dioxide in solution is lower and therefore the reaction rate decreases. Recent studies agree with earlier suggestions from Fulda, Wiedbrauck and Büche for use of pressure for better leaching rates[13,17]. The merit of using pressure, however, is questionable in view of the increase in equipment and operating cost.

The leach liquor is separated from the silica residue by filtration. The operation is difficult because the precipitate is slimy. Boiling of the liquor is sufficient to expel most of the SO_2 and precipitate basic aluminum sulfite[12,25]. The precipitate, after being filtered, is

Figure 1. Flow Diagram of the Modified Bayer Process.

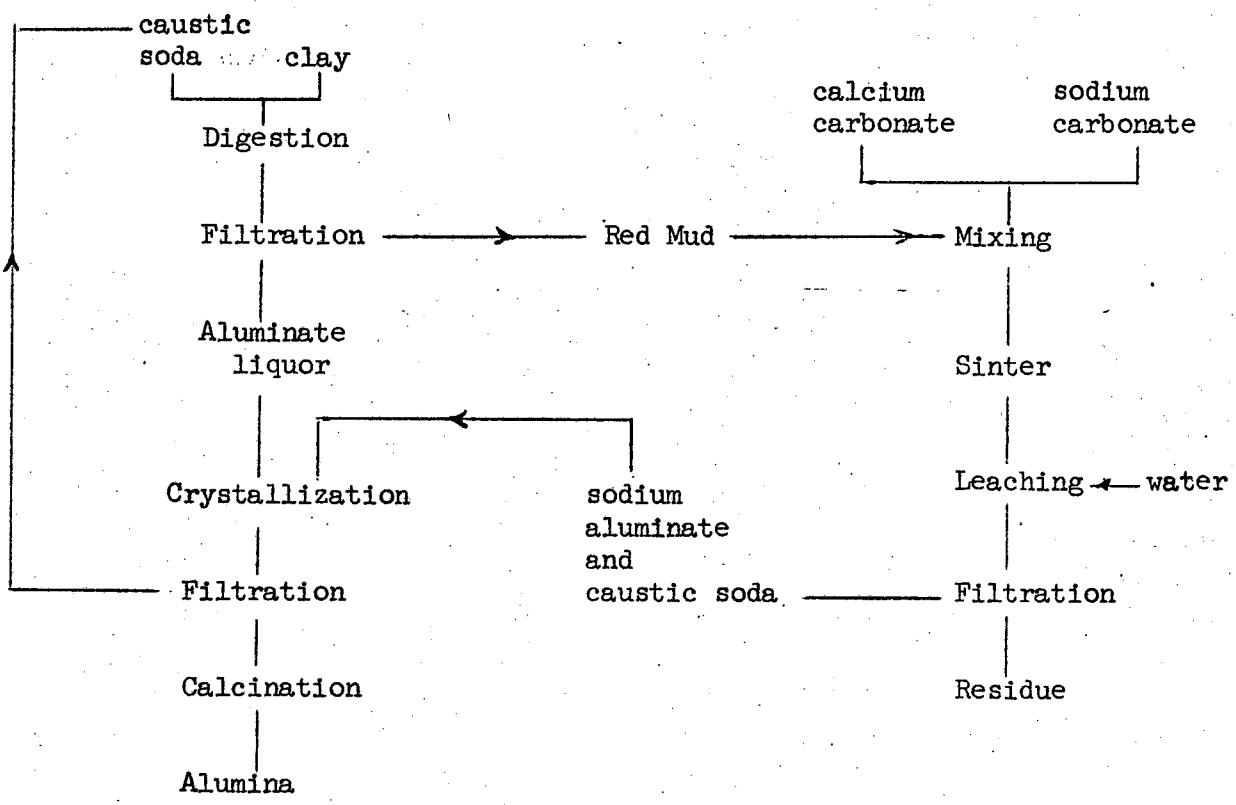
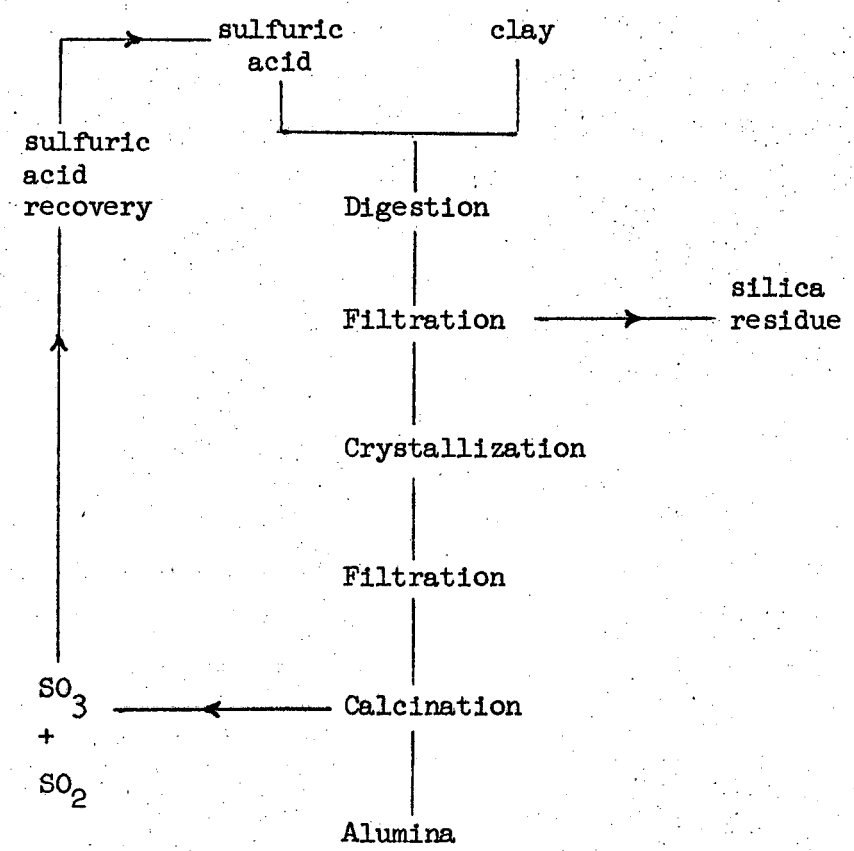


Figure 2. Flow Diagram of the Sulfuric Acid Process



is decomposed by calcination at 1000°F[14] or by rapidly heating the slurry to a temperature between 110°C to 160°C under 4 to 6 atm of pressure[17]. Alumina and sulfur dioxide are obtained. Sulfur dioxide is recycled. The yield of alumina is about 80 per cent. The flow diagram is shown in Figure 3.

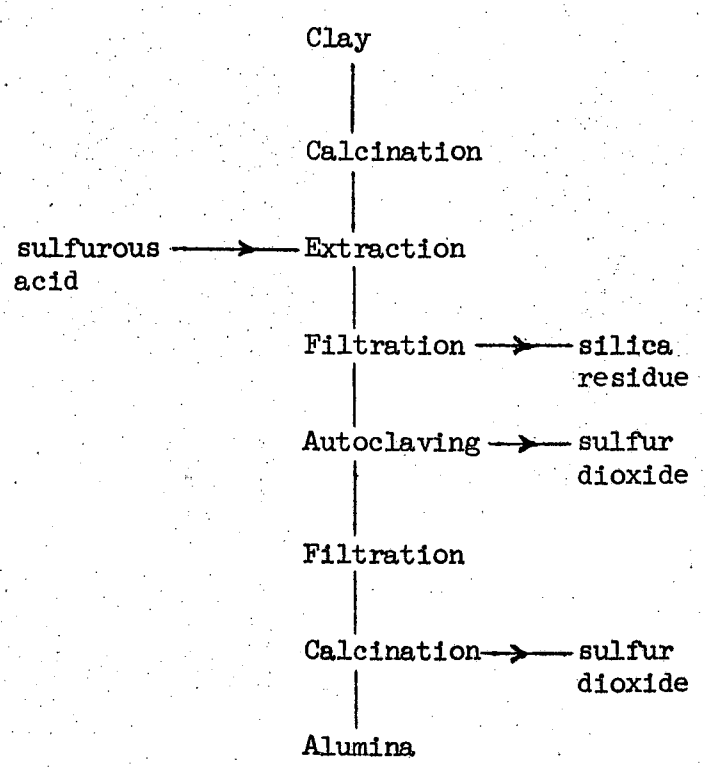
1.24 The Combined Sulfurous-Sulfuric Acid Process

The disadvantages of the modified Bayer Process are high consumption of calcium carbonate and sodium carbonate and a complicated operation. The process is suitable at best for low silica clays.

The sulfuric process has the advantages of high yield of alumina and high rate of extraction. On the other hand it requires high calcination temperatures and a troublesome recovery of sulfuric acid from the gaseous mixture leaving the furnace. Alumina obtained by this method requires a further treatment for elimination of silica and iron impurities.

Some of those disadvantages are eliminated in the sulfurous acid method. The leaching acid can be easily recovered by absorption of sulfur dioxide in water. Basic aluminum sulfite is precipitated free of iron if air is excluded from the operation. But silica impurities amount to 1 or 2 per cent of the precipitate. The process has other disadvantages, namely, low leaching rates and the relatively low alumina recovery. The difficult filtration of the basic aluminum sulfite is a serious problem, though it can be solved to some extent if precipitation is carried out either by dropping fresh liquor over another portion of aluminum sulfite free preheated liquor or heating the liquor with a countercurrent flow of steam. The sulfurous acid is cheaper than any other acid and requires lower decomposition temperatures of its salts. For all the acid

Figure 3. Flow Diagram of Sulfurous Acid Process



processes dehydration of the clay and acid proof tanks are necessary.

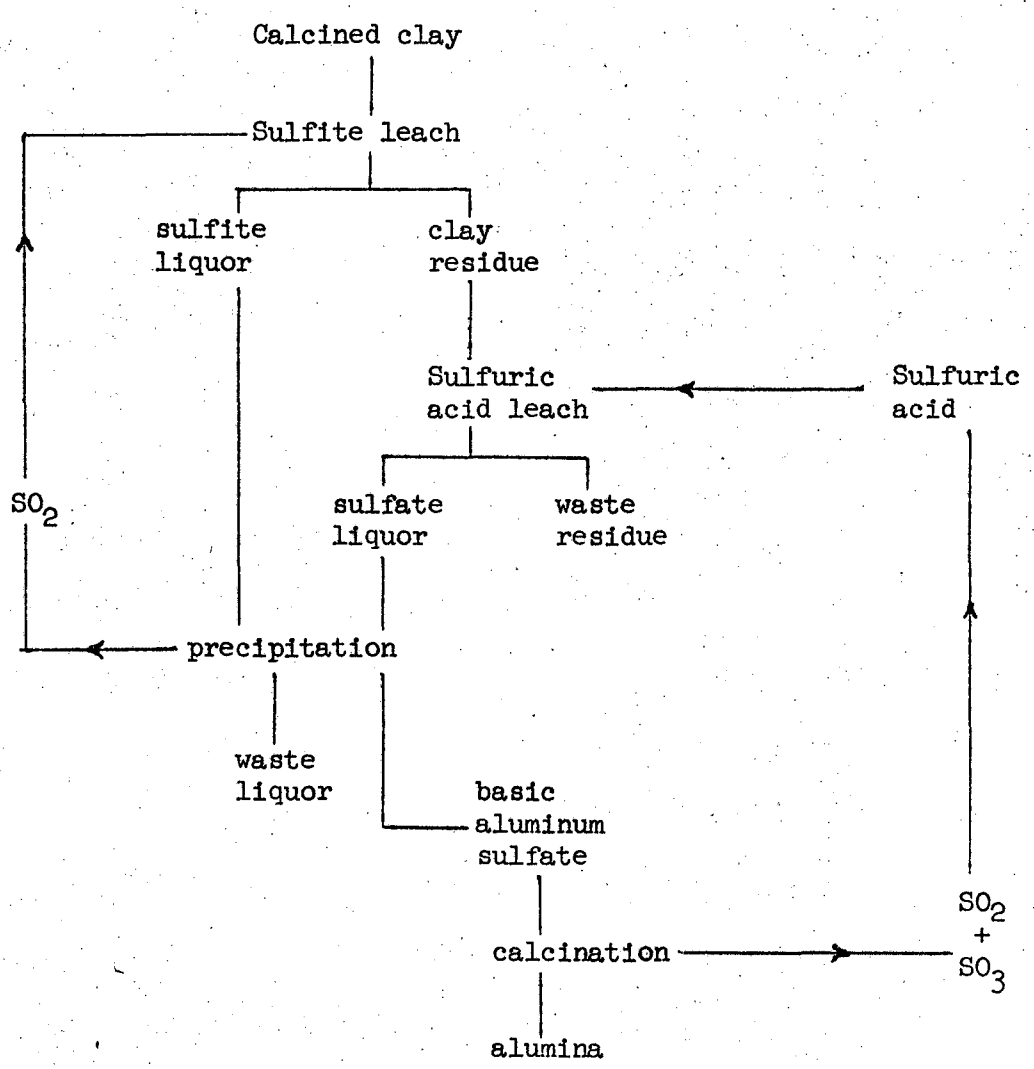
In 1946 a combination of sulfate and sulfite processes was proposed[18]. From the combination resulted a new process without most of the disadvantages of either one. According to this process clay is calcined as in previous methods and leached with sulfurous acid until most of the alumina is extracted. The residue with the remaining alumina is leached with sulfuric acid. This operation allows a decrease in leaching time and a better alumina recovery. The two leach liquors are mixed, providing three equivalents of alumina for each one of sulfate. Sulfur dioxide is completely expelled by boiling the solution, while a very easily filterable basic aluminum sulfate precipitates. In the present process sulfur dioxide is recovered in a single operation, unlike the sulfurous acid process. Iron is entirely kept in solution if air is excluded. The basic aluminum sulfate can be calcined to alumina and sulfur dioxide and trioxide. The process flow diagram is presented in Figure 4.

1.25 Impurities

The alumina obtained in all acid processes is not pure. Silica impurities are present at a level of 1 to 2 per cent of the final product[18]. So far the only efficient method to eliminate silica impurities is an autoclave treatment with caustic soda, essentially a simplified Bayer process[17,19]

It is this addition of an expensive purification step that destroys any chance of economic competition of clay leaching with the traditional manufacture from bauxite. Iron is very efficiently eliminated in the combined sulfite-sulfate process. Only silica remains as a serious

Figure 4. Flow Diagram of the Sulfurous-Sulfuric Acid Process



obstacle for the cheap production of alumina from clay.

In this situation a closer study of the problem is indicated. Any lead to a method of obtaining sufficiently pure alumina should be followed up.

It had been observed that different leaching conditions applied to various kinds of clay resulted always in silica contents of about the same level of 1 to 2 per cent (referred to alumina). The possibility was considered that this much silica is present in clays in a specific, easily soluble form. If this is true, one might hope to find a pre-leaching method to remove the easily soluble silica so that in the principal leach pure alumina would be extracted.

The object of the present work has been to study acid leaching of clay under varied conditions and to concentrate the attention on the ratio of silica to alumina extracted and to the amounts of silica removed.

2. ANALYSIS

Frequent analytical determinations of the dissolved silica and alumina were required.

Silica was determined by a colorimetric method developed by Adams[1]. The method is reliable for evaluation of small quantities of silica in the presence of alumina, ferric oxide, titanium oxide and phosphorus, substances present in clays. Besides, Adams, presented variants for cases not satisfactorily handled by the standard method.

Procedure

A filtered sample of the leach liquor containing not more than 10 milliequivalents of cations per milligram of silica is evaporated

almost to dryness in a small platinum dish. Perchloric acid, about twice the amount equivalent to the basic constituents is added. The solution is then evaporated until copious fumes of perchloric acid are evolved. The residue is extracted with hot water and filtered through a filter paper (no. 40 Whatman). The paper should contain all the insoluble residue; it is ignited in the same dish. The ignited residue is fused in a sufficient amount of sodium carbonate, then dissolved in hot water and transferred to a 250 ml volumetric flask. The solution is titrated with sulfuric acid (10 N), with phenolphthalein as indicator. About the same volume of sulfuric acid is added once more to expel the carbon dioxide completely. After filling up the 250 ml flask, one transfers 10 ml to a 100 ml volumetric flask. Sulfuric acid (1 ml of 10 N acid) is added to bring up the acid concentration to 0.1 N, and 4 ml of 10 per cent ammonium molybdate solution is added. The molybdate forms a yellow complex with the silica in solution. Readings are made five minutes after the addition of the molybdate and dilution to 100 ml with water. A small portion of this solution is transferred to a cell of a spectrophotometer and the readings are made with a blank in another cell. The blank solutions contain all the reagents in the same amounts as used in the original solution.

The method and the spectrophotometer were checked and calibrated by comparison with a colorimetric standard for silica. According to Swank and Mellon[23] a water solution containing 0.63 g of potassium chromate per liter is equivalent to a solution containing 100 mg per liter of silica in a solution of 0.4 N acid. For a 0.01 N acid one has to take 0.58 g of potassium chromate. Adams established 0.602 g of potassium chromate as the amount required for a 0.1 acid.

The absorbancies read from a spectrophotometer for silica solutions of known concentrations were plotted against the concentration. The results agreed within 10 per cent with the standard of Adams. This was considered sufficient for the present purpose. Silica standard solutions were prepared gravimetrically from pure silica gel of known moisture content.

Alumina was determined gravimetrically by precipitation with ammonia at pH 8. The error due to the precipitation of impurities such as iron oxide and silica is of minor importance for the present objective. The precipitates were filtered and calcined in a weighed platinum crucible at 1200°C.

3. CLAY SAMPLES

Clay samples were moistened and then calcined in the form of sheets, 2 cm thick, at 800°C. After calcination the sheets were broken up to 1 cm lumps, which were used in the leaching operation. The smaller lumps were discarded.

A clay from Ione, California, very high in kaolin, was investigated first. The study was then extended to a clay from Troy, Idaho, representative of large deposits. Table 2 shows alumina and silica composition of the clays. The usual method of sampling was observed in the selection of samples from the clays.

Table 2. Compositions of the Clays.

	Ione	Troy
Alumina %	42	37
Silica %	~40	~40

4. EXPERIMENTAL RESULTS

The 58 tests carried out to explore the effect of the various leaching conditions on silica and alumina may be divided in seven groups, devised to answer various questions. The results are shown in Tables 3-5. The tables contain the leaching time, the volume of leaching acid, its concentration in moles per liter, the amount of alumina extracted per 100 g clay, the amount of silica extracted per 100 g clay, and the ratio SiO_2/Al_2O_3 in per cent. A zero for silica means that the amount of silica extracted from 100 g clay is lower than the limit 0.015 g SiO_2/100 g clay of the analytical precision.

For extraction with sulfuric acid clay samples of about 5 g were weighed and treated at boiling temperature. For extraction with sulfurous acid samples of approximately 40 g were treated at the temperatures approximately indicated in Table 5.

The first group of tests (1-3) showed that prolonged boiling in water <u>does</u> extract small amounts of silica without dissolving any alumina. But for a satisfactory result it would be necessary (although not at all sufficient) to extract at least twenty times as much silica. This path was therefore abandoned.

In the second group (4-9) the combined influence of acid concentration and leaching time was examined. The results clearly show that the ratio SiO_2/Al_2O_3 increases with the leaching time and decreases with the acid concentration. One would conclude that short leaching with concentrated acid would give the best results. But this is not a very promising basis for a technical process.

Table 3. Leaching of Ione Kaolin with Sulfuric Acid.

No.	Leach time	H_2SO_4 leach vol ml	H_2SO_4 leach moles/liter	Al_2O_3 g extracted per 100 g of clay	SiO_2 g extracted per 100 g of clay	SiO_2/Al_2O_3 wt % in the leach liquor
1	8 hr	100	0	0	0.0039	---
2	10 hr	100	0	0	0.0059	---
3	15 hr	100	0	0	0.051	---
4	$3\frac{1}{2}$ hr	100	3	38.6	0.250	0.68
5	12 hr	100	3	40.7	0.377	0.98
6	$3\frac{1}{2}$ hr	100	1.5	37.3	0.500	1.20
7	12 hr	100	1.5	41.7	0.505	1.36
8	4 hr	100	0.5	26.2	0.787	4.10
9	12 hr	100	0.5	30.6	1.08	2.58
10	20 min	100	3	20.0	0.139	0.73
11	1 hr	100	3	27.4	0.253	0.92
12	15 min	100	1.5	10.2	1.329	3.2
13	1 hr	100	1.5	25.2	0.500	1.98
14	15 min	100	0.5	6.7	0.379	6.4
15*	1 hr	100	0.5	19.5	0.802	4.1
16	15 min	100	0.1	1.2	0.338	28.0
17	1 hr	100	0.1	4.4	0.665	15.0
18	1 hr	100	0.03	0.33	0.465	139.0
19	15 min	100	0.03	0.2	0.047	32.0
20	5 hr	100	0.03	1.6	0.525	32.0
21	1 hr	350	0.03	2.6	0.503	19.6
22	5 hr	350	0.03	2.8	0.690	24.5
23	1 hr	500	0.03	5.6	1.15	20.6

* Residue from the preceding leach.

Table 3. (cont.)

No.	Leach time	H_2SO_4 leach vol ml	H_2SO_4 leach moles/liter	Al_2O_3 g extracted per 100 g of clay	SiO_2 g extracted per 100 g of clay	SiO_2/Al_2O_3 wt % in the leach liquor
24	4 hr	500	0.03	10.7	1.49	13.9
25*	6 hr	100	1.5	29.4	0. 61	1.54
26	1 hr	500	0.01	0.32	0.635	198.0
27*	1 hr	100	3	26.6	0.278	1.05
28	6 hr	500	0.01	3.78	1.48	39.3
29*	4 hr	100	3	32.5	0.240	0.74
30	8 hr	500	0.005	.31	0.772	248.0
31*	40 min	100	6	25.8	0	0
32	13 hr	500	0.005	.29	0.890	306.0
33*	30 min	100	6	22.5	0	0
34**	1 hr	500	0.1	.17	0.108	61.5
35*	15 min	100	6	20.1	0.005	0.025
36	3 hr	100	6	34.8	0	0
37	12 hr	750	0.00375	.15	1.04	514.0
38*	9 hr	100	2	36.6	0.367	1.0
39	4 hr	750	0.00375	.15	0.916	445.0
40*	9 hr	100	1	36.4	0.715	1.96

* Residue from the preceding leach.

** Extracted with acetic acid.

Table 4. Leaching of Clay from Troy, Idaho, with Sulfuric Acid

No.	Leach time	H_2SO_4 leach vol ml	H_2SO_4 leach moles/liter	Al_2O_3 g extracted per 100 g of clay	SiO_2 g extracted per 100 g of clay	SiO_2/Al_2O_3 wt % in the leach liquor
41	4 hr	500	.01	.2	.518	235.0
42*	12 hr	100	1.5	36.5	.286	.78
43	$3\frac{1}{2}$ hr	500	.05	11.3	2.39	21.2
44*	$3\frac{1}{2}$ hr	100	1.5	25	0.456	1.83
45	3 hr	750	.02	6.2	0.623	1.0
46*	10 hr	100	2	34.2	0.362	1.06
47	12 hr	750	0.025	13.7	4.02	294
48*	6 hr	100	3	28.5	0.207	0.73
49	14 hr	750	0.01	5.9	2.99	50.7
50*	3 hr	100	4	27.7	0.037	0.29

* Residue from the preceding leach.

Time and concentration were studied again in the third group (10-19). Shorter times and lower concentrations were explored. It was found that considerable amounts of silica can be removed by long leaching with dilute acid.

The fourth group (20-23) showed that the amount of silica extracted by a dilute acid increased with the volume and also with the time. But the amount of alumina also increased with the volume.

As a result of the information obtained at this point the idea of a preliminary leach of silica with a large volume of very dilute acid and a subsequent shorter principal leach of alumina with a stronger acid appeared to offer a good chance. The fifth group (24-40) shows the results of such double leachings. With acids below 0.01 moles/lit the alumina losses in the preliminary leach were reasonably low. With acids containing 6 moles/lit the alumina extraction efficiency was perhaps acceptable though not very satisfactory. The silica content of the extracted alumina was below the precision of the analytical method, i.e., below 0.01% in the SiO_2/Al_2O_3 ratio. Only in a short leach (15 minutes) a ratio 0.025 was found. Replacement of sulfuric acid by acetic acid (test 34) did not lead to any improvement.

Thus a positive result of some kind was obtained with Ione clay. But the use of a fairly concentrated sulfuric acid for leaching would hardly be attractive in a technical process. Moreover, tests (41-50) with clay from Troy, Idaho, furnished much less promising results. With a principal leach acid containing 4 moles/lit the SiO_2/Al_2O_3 ratio was 0.29, still an order of magnitude above the accepted specification.

From the beginning the main objective has been the examination of

the combined sulfurous-sulfuric acid method. The last group of tests (Table 5, 51-58) was conducted with sulfurous acid as a principal leaching agent after preliminary leaches with a large volume of dilute sulfuric acid. The preliminary leaches were carried out with portions of 20 g clay in 3 liters acid. For the principal leaches the residues were kept under water in a vertical glass tube (20 mm diameter) and sulfur dioxide was bubbled through. No particular effort was made to obtain high leaching efficiency for alumina since this question had been amply examined in previous work[18].

The results show that the preliminary leaching with dilute sulfuric acid does not lower the SiO_2/Al_2O_3 ratio of the principal extraction. The low efficiency of alumina extraction exaggerates the SiO_2/Al_2O_3 ratio. But even so the results show no promise of a satisfactory solution of the problem of silica elimination.

5. CONCLUSIONS

It has been found that the ratio SiO_2/Al_2O_3 can be modified in extraction by sulfuric acid within a wide range. Acid containing 6 moles/lit extracts alumina from clay very efficiently and practically free of silica. On the other hand, acid containing only 0.005 moles/lit extracts appreciable amounts of silica and little alumina.

These results invite a consideration of practical applications in a process of producing alumina from clay. The conditions for a differential leaching of silica and alumina, however, are still not favorable. The use of a large volume of very dilute acid in a prolonged preliminary leach does not present any serious difficulty. But leaching with a strong

Table 5. Clay Leaching with Sulfurous Acid Following a Preliminary Leaching with Dilute Sulfuric Acid.
(Clay from Troy, Idaho)

No.	Temp. °C	Leach time	Acid vol ml	Acid moles/lt	Al_2O_3 g extracted per 100 g clay	SiO_2 g extracted per 100 g clay	SiO_2/Al_2O_3 in the leach liquor
51	100	18 hr	6000	0.01 H_2SO_4	4.5	1.87	41.7
52*	22	213hr	250	sat. SO_2	15.6	0.344	2.2
53	100	16 hr	6000	0.02 H_2SO_4	10.9	2.37	22.6
54*	22	120hr	250	sat. SO_2	10.6	0.345	3.24
55	100	17 hr	6000	0.01 H_2SO_4	5.0	2.14	42.7
56*(1)	55	20 hr	250	sat. SO_2	8.8	0.405	4.5
57(2)	100	15 hr	6000	0.0075H_2SO_4	0.57	0.858	154.0
58*(1)	55	24 hr	250	sat. SO_2	13.8	0.375	2.52

* Leaching was performed with sulfurous acid and residue from the preceding leach.

sulfuric acid solution involves obvious problems of reactor design and recovery of the acid. Moreover, according to present results different clays may behave differently; a special study will be required for every clay deposit.

Sulfurous acid as a fairly weak acid cannot be expected to furnish the same results as a strong sulfuric acid solution. This is confirmed in direct tests. No beneficial influence of extraction of silica in preliminary leaches with dilute sulfuric acid has been observed. The nature of the tests would not permit the safe observation of a minor effect of preliminary leaching. But the results definitely indicate no promise for a technical process that would sufficiently eliminate silica in the leaching of clay by removal of silica in a preliminary leach.

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APPENDIX

Check for Phosphorus

Since the presence of phosphorus would disturb the colorimetric analysis (p.10), two silica samples were examined before as well as after fuming with hydrofluoric acid.

The results shown in Table 6 indicate that any phosphate residue is of the order of magnitude of the other analytical errors. An indirect check is also given by the decrease of the obtained silica with increasing concentration of sulfuric acid. Presence of phosphate would have caused an apparent increase rather than decrease of the found silica.

Table 6. Ione Clay Leached with Sulfuric Acid.

Leaching time hours	vol ml	H_2SO_4 moles/lit	SiO_2 g extracted per 100 g clay	SiO_2 g/100 g clay after fuming
14	100	3	0.246	0.048
9	100	1	0.515	0.032

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