EXTRACTION OF ALUMINA FROM CLAYS AND HIGH-SILICA BAUXITES

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ABSTRACT

Two processes for extracting alumina from low-grade ores are described, one applicable to both clays and high-silica bauxites, and the other only to bauxites. In the former process, a line-containing sinter is prepared and annealed by cooling it slowly through the range of 1,300° to 1,200° C. The annealed sinter dusts to a powder which requires no grinding. This material is extracted with a solution containing about 200 g of Na_2CO_3 and 150 g of NaCl/liter, and an extract is obtained in which the concentration of Al_2O_3 is 70 to 80 g/liter and that of SiO_2, 1 to 2 g/liter. By boiling the extract with a seed charge of synthetic sodalite, $3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaCl$, its silica content is reduced to 0.1 percent of the alumina content or less. Alumina, suitable for the manufacture of aluminum by electrolytic reduction, is precipitated by passing carbon dioxide into the desilicated solution. About 95 percent of the alumina in the clay is recovered by this method.

The other process developed in this investigation involves the extraction of alumina from high-silica bauxites with sodium hydroxide-sodium chloride solution and recovery of soda and alumina from the residues by a modified soda-lime-sinter method. Recoveries in excess of 90 percent of the alumina in high-silica bauxites are obtained.

In cyclical operation of each process, the spent solution from the alumina-precipitation step is used in the treatment of a fresh batch of material.

When the bauxites are extracted with solutions containing mixtures of sodium hydroxide and sodium carbonate, sodium sulfate, sodium bromide, or sodium nitrate, the quantities of silica present in the extracts are lower, the higher the concentration of the salt. This is caused by the formation and increased stabilization of slightly soluble compounds related to sodalite. Comparisons of the X-ray diffraction patterns of various sodalite type compounds are presented. By the extraction of bauxite with sodium hydroxide solution, in the absence of added salts, a relatively soluble hydrated nephelite, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, is formed, which has a crystal structure different from that of sodalite.

CONTENTS

CONTENTS—Continued

I. INTRODUCTION

The object of the investigations was to develop alkaline processes, of possible commercial application, for the extraction of alumina from clays and high-silica bauxites.

In the extraction of alumina from an ore as sodium aluminate there are three principal methods: (1) Direct extraction of the un-treated ore with sodium hydroxide solution, as in the Bayer process. [1][1]; (2) treatment of the ore to give a product containing solid sodium aluminate, which is extracted with water; and (3) treatment of the ore to give a product containing calcium aluminate, which can be decomposed with sodium carbonate.

The first part of this paper deals with the extraction of alumina from high-silica bauxites by a combination of methods (1) and (2). The remainder of the report is concerned with the extraction of alumina from clays and high-silica bauxites by method (3) used as a modified lime-sinter process. In the three methods developed at the National Bureau of Standards, the final desilication is effected by the formation of the very slighlty soluble compound sodalite, $3Na_2O.3Al_2O_3.6SiO_2.2NaCl$.

II. EXTRACTION OF ALUMINA FROM HIGH-SILICA BAUXITES WITH SODIUM HYDROXIDE-SALT SOLUTIONS

1. MATERIALS AND GENERAL PROCEDURE

Four bauxites of compositions given in table 1, ground to such fineness that 80 to 90 percent passed a No. 200 sieve, were chosen for extraction. Other materials used included sodium hydroxide, sodium carbonate, sodium sulfate, sodium bromide, sodium chloride, and sodium nitrate.

The procedure followed in most experiments involved boiling or autoclaving the finely ground bauxite with 100 to 400 ml of a sodium hydroxide solution containing various proportions of sodium salts.

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[1] Figures in brackets indicate the literature references at the end of this paper.

The experiments at boiling temperatures were made in iron containers fitted with reflux condensers, and those at 150° C in a bomb-type autoclave having a capacity of 1 liter. After a heating period of 1 to 3 hours, the residues were separated from the solutions by filtration and repulped at boiling temperature with 100-ml portions of water. Each residue was then washed on the filter with 100 ml of hot water and the combined extracts and washes made up to 1 liter in volumetric flasks. Analyses for silica were made by dehydration with sulfuric acid of aliquots large enough to contain 5 to 10 g of alumina. Alumina was determined in the filtrates from the silica determinations. In some cases the approximate concentrations of sodium hydroxide and carbonate in the extracts were determined by titration of aliquots with standard acid.

TABLE 1.—*Composition of bauxites*

Oxide	Bauxite			
	A	B	C	D
	%	%	%	%
SiO $_2$	10.22	19.80	19.89	11.08
Al$_2$O$_3$	50.78	44.14	50.57	56.18
Fe$_2$O$_3$	7.92	9.61	1.26	1.18
TiO$_2$	2.17	2.05	2.52	2.39
CaO	0.05		0.02	0.03
MgO	.02		.01	.01
Loss on ignition	28.80	23.58	25.30	28.38
Total	99.96	99.18	99.57	99.25

Extractions of the bauxites were made on both a laboratory and small pilot-plant scale. The solid residues from the pilot-plant extractions were dried, analyzed, and further treated to recover the alumina and soda they contained. This treatment consisted in mixing the residues with calcium carbonate, heating to suitable temperatures, and extracting the ground products with water or various alkaline solutions.

Studies were made of the structures, as revealed by X-ray diffraction patterns, and of the compositions of the solid residues remaining after extraction of the bauxites with sodium hydroxide solution alone and when various sodium salts were present. Synthetic preparations consisting of the various sodium salts were also investigated and compared with the residues from the extractions of the bauxites.

2. PRELIMINARY EXPERIMENTS

Because of an extensive background of research in this laboratory on the preparation and properties of the calcium aluminates and silicates [2], it was decided to investigate the recovery of alumina from various calcium aluminates. For this purpose quantities of 3 CaO.Al$_2$O$_3$, 5CaO.3Al$_2$O$_3$, CaO.Al$_2$O$_3$, and isometric hydrated tricalcium aluminate, 3CaO.Al$_2$O$_3$.6H$_2$O, prepared by the usual methods [3], were available. The preparations were ground to pass a No. 200 sieve, and 2-g samples were extracted for 2 hours with 100-ml portions of a solution containing 50 g of Na$_2$CO$_3$ per liter. The results of extractions of alumina at 25° C, 50° C, 85° C, and at boiling are given

in table 2. In making the extractions, mechanical stirring was employed at temperatures below boiling.

Because the hydrated calcium aluminate gave an appreciably better extraction than any of the anhydrous compounds, the possibility suggested itself of forming $3CaO.Al_2O_3.6H_2O$ from a mixture of bauxite and lime, for the purpose of subsequent extraction with sodium carbonate solution.

TABLE 2.—*Extraction of alumina from calcium aluminates*

[Extraction for 2 hours of 2-g samples, ground to pass No. 200 sieve, with 100 ml of sodium carbonate solution containing 5-g of Na_2CO_3. Mechanical stirring was used at temperatures below boiling]

Experiment	Temperature	Recovery of Al_2O_3 from—			
		$3CaO.Al_2O_3$	$5CaO.3Al_2O_3$	$CaO.Al_2O_3$	$3CaO.Al_2O_3.6H_2O$
1	25° C	33.8	66.1	84.6	89.4
2	50° C	27.5	77.2	92.2	94.3
3	85° C	28.7	72.9	95.5	98.6
4	Boiling	46.4	82.2	95.6	99.3

Accordingly, a slurry of bauxite and calcium hydroxide (molar ratio of CaO to Al_2O_3 in bauxite=3) was prepared and placed in an autoclave which was maintained at 150° C for 4 hours, with shaking at half-hour intervals. The product was removed, dried at 110° C, and examined microscopically. All the gibbsite originally in the bauxite had been converted to well-developed crystals of $3CaO.Al_2O_3$. $6H_2O$.

This product was boiled for 3 hours with 200 ml of a 20-percent Na_2CO_3 solution and filtered (experiment 1, table 3). Similar extractions with 20- and 30-percent Na_2CO_3 solutions were made of mixtures of the same quantities of $Ca(OH)_2$ and bauxite that had not been previously autoclaved. Sodium hydroxide extractions were also made of the bauxite with no added $Ca(OH)_2$. In all the experiments the quantity of material treated was equivalent to 58 g of bauxite per liter of solution.

TABLE 3.—*Recovery of alumina from bauxite A under various conditions*

The quantity of material extracted was equivalent to 58 g of bauxite A (29.5 g of Al_2O_3) per liter of solution. The extraction mixtures were boiled for 3 hr before filtering].

Experiment	Mix	Molar ratio CaO/Al_2O_3 in mix	Autoclave treatment of mix prior to extraction	Composition of extracting solution		Recovery of Al_2O_3	$\frac{SiO_2}{Al_2O_3} \times 100$ in extracted solution
				Na_2CO_3	NaOH		
				g/liter	*g/liter*	%	
1	Lime+bauxite	3	4 hr at 150° C	200	0	81	0.58
2	do	3	None	200	0	81	.52
3	do	3	do	300	0	71	.20
4	Bauxite only	0	do	0	74	77	1.29
5	do	0	do	0	200	81	1.33
6	do	0	do	0	300	83	1.44

Comparison of experiments 1 and 2, table 3, shows that there is no advantage in forming the tricalcium aluminate hydrate by preliminary autoclaving of the lime-bauxite mixture. It may be noted that there was less silica in the extracts in experiments 1 to 3 than in 4 to 6. In the first three experiments sufficient lime was present to convert

100 g of Na_2CO_3 per liter to 74 g of NaOH per liter on complete causticization, leaving 100 g of Na_2CO_3 per liter in excess in experiments 1 and 2, and 200 g of Na_2CO_3 per liter in excess in experiment 3. It appears that an increase in Na_2CO_3 is accompanied by a decrease in the concentration of silica in the extracts. This observation is in agreement with a statement by Pesin and Lileev [4] that sodium aluminate solutions can be desilicated by heating them in the presence of high concentrations of sodium carbonate.

Two series of extractions were made of bauxites B, C, and D with solutions containing mixtures of Na_2CO_3 and NaOH (tables 4 and 5). The purpose of the first series was to determine the molar ratios of the Na_2O (added as NaOH)[2] in the solution to the Al_2O_3 in the bauxites, that would dissolve the maximum quantities of alumina at the boiling temperatures of the solutions. In these experiments the volume of the extracting solution was 200 ml.

TABLE 4.—*Determination of optimum molar ratios of* Na_2O *(as NaOH) in extracting solution to* Al_2O_3 *in bauxites* [a]

Experiment	Baux-ite desig-nation	Quan-tity of baux-ite used	Composition of solutions						Al_2O_3 ex-tracted [b]
			Initial			Final			
			Na_2CO_3	NaOH	Molar ratio Na_2O (as NaOH): Al_2O_3 in bauxite	Na_2CO_3	NaOH	Al_2O_3	
		g/liter	*g/liter*	*g/liter*		*g/liter*	*g/liter*	*g/liter*	%
1	B	289	300	100	1.0	256.5	84.5	39.3	31
2	B	241	300	100	1.2	263.0	94.5	47.3	44
3	B	144	300	100	2.0	278.0	88.5	39.9	63
4	B	96.5	300	100	3.0	286.8	88.5	26.8	63
5	C	252.5	300	100	1.0	259.5	86.5	52.7	41
6	C	168	300	100	1.5	278.0	77.0	55.8	66
7	C	126	300	100	2.0	278.0	88.5	42.3	66
8	C	84	300	100	3.0	267.5	94.5	28.9	68
9	D	284	250	125	1.0	231.5	114.0	64.1	40
10	D	189.5	250	125	1.5	221.0	121.5	81.3	76
11	D	142	250	125	2.0	234.0	117.0	61.1	77
12	D	94.5	250	125	3.0	229.5	120.5	41.8	79

[a] Extracted by boiling for 3 hr.
[b] Based on original volume of extracting solution (200 ml).

Figure 1 shows the relationships between the percentages of Al_2O_3 dissolved from the bauxites and the molar ratios of Na_2O in the initial solutions to Al_2O_3 in the bauxites. It is evident that, at boiling temperatures, only very slight increases in the extraction of Al_2O_3 occur at molar ratios above 2.0.

It should be noted (table 4) that the concentrations of both Na_2CO_3 and NaOH remaining in solution are less than those initially present. This indicates that the solid residues must contain carbonate as well as Na_2O derived from both NaOH and Na_2CO_3.

A second series of extractions of the bauxites was made, both at boiling temperatures and 150° C, with solutions containing 125 g of NaOH per liter and various amounts of Na_2CO_3 as shown in table 5.

[2] Here and subsequently in the text, in the tables, and in figure 1, the designation Na_2O is intended to indicate the sodium hydroxide added to the mixtures as such, and does not include sodium hydroxide that may be formed by the partial hydrolysis of sodium carbonate.

The actual volume of the solutions used in the experiments was 400 ml, and the quantities of bauxite were such that the molar ratio of Na_2O (as NaOH) in the initial solutions to Al_2O_3 in the bauxites was 2.0. As before, the concentrations of Al_2O_3 and SiO_2 in the extracts are calculated on the basis of the original volume of the solutions and expressed in grams per liter.

The concentration of SiO_2 in the extracts is shown (in table 5) to decrease with increase in the Na_2CO_3 in the solutions, thus confirming

TABLE 5.—*Extractions of bauxites with solutions containing 125 g of sodium hydroxide per liter and various amounts of sodium carbonate[a]*

Experiment	Bauxite designation	Quantity of bauxite used	Na_2CO_3 in extracting solution	Temperature	Al_2O_3 in solution	SiO_2 in solution	Extraction of Al_2O_3 [b]	$\frac{SiO_2}{Al_2O_3} \times 100$ in solution
		g/liter	g/liter		g/liter	g/liter	%	
1	B	180	0	Boiling	50. 2	0. 228	63. 2	0. 45
2	B	180	125	___do___	42. 1	. 102	53. 0	. 24
3	B	180	250	___do___	48. 6	. 089	61. 1	. 18
4	B	180	375	___do___	48. 0	. 075	60. 3	. 16
5	B	180	0	150° C	48. 8	. 172	61. 5	. 35
6	B	180	250	150° C	50. 1	. 056	63. 1	. 12
7	C	157. 5	0	Boiling	54. 0	. 324	67. 9	. 60
8	C	157. 5	62. 5	___do___	53. 7	. 177	67. 5	. 33
9	C	157. 5	125	___do___	52. 5	. 147	66. 0	. 28
10	C	157. 5	250	___do___	55. 5	. 130	69. 8	. 24
11	C	157. 5	312. 5	___do___	53. 7	. 129	67. 5	. 24
12	C	157. 5	0	150° C	51. 6	. 146	64. 9	. 28
13	C	157. 5	250	150° C	53. 1	. 074	66. 8	. 14
14	D	142	0	Boiling	61. 8	. 340	77. 4	. 55
15	D	142	62. 5	___do___	61. 3	. 245	76. 8	. 41
16	D	142	125	___do___	61. 4	. 233	77. 0	. 38
17	D	142	250	___do___	61. 8	. 212	77. 4	. 34
18	D	142	0	150° C	61. 3	. 215	77. 0	. 35
19	D	142	250	150° C	60. 6	. 088	75. 9	. 14

[a] Extracted by heating for 3 hr.
[b] Based on original volume of extracting solution (400 ml).
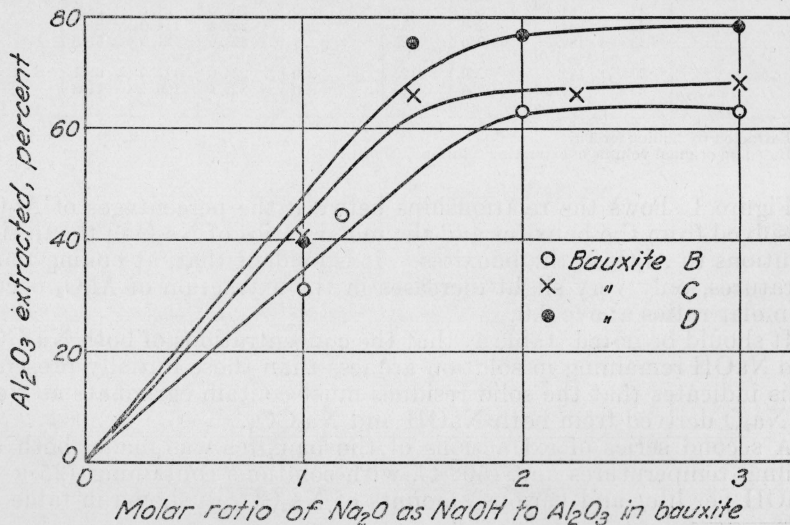
FIGURE 1.—*Effect of varying the molar ratio of Na_2O (as NaOH) in the extracting solutions to Al_2O_3 in the bauxites.*

Mixtures boiled or 3 hr.
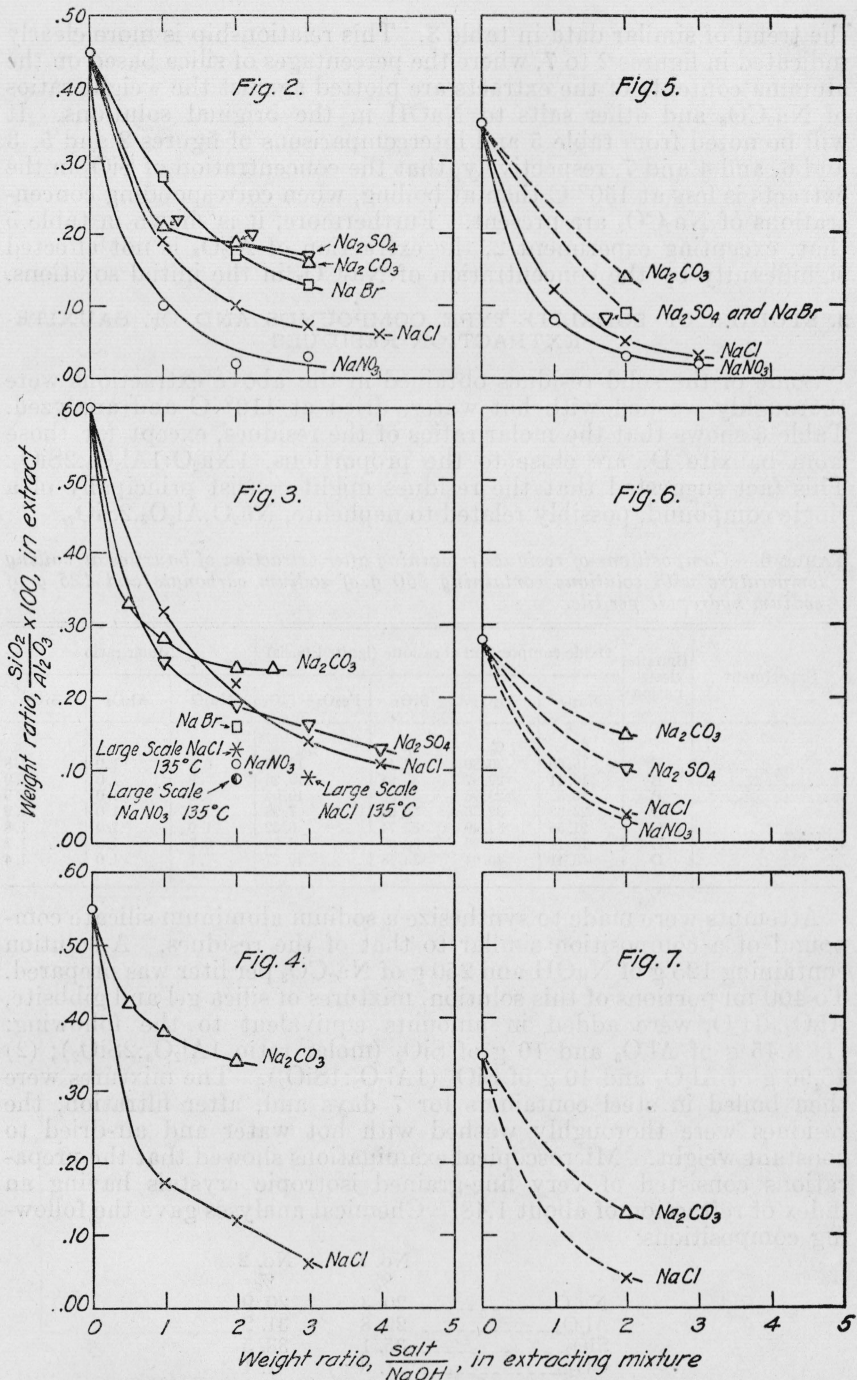
FIGURES 2 to 7.—*Effect of sodium salts on the silica-alumina ratio in sodium hydroxide extractions from high-silica bauxites.*

Molar ratio of Na_2O (as NaOH) to Al_2O_3 in bauxite=2.0. Figures 2, 3, and 4, mixtures boiled for 3 hr; figures 5, 6, and 7, mixtures autoclaved at 150° C for 3 hr; figures 2 and 5, bauxite B; figures 3 and 6, bauxite C; figures 4 and 7, bauxite D. Points marked "Large Scale" represent [data obtained in small-pilot-plant extractions at 135° C.

the trend of similar data in table 3. This relationship is more clearly indicated in figures 2 to 7, where the percentages of silica based on the alumina contents of the extracts are plotted against the weight ratios of Na_2CO_3 and other salts to NaOH in the original solutions. It will be noted from table 5 and intercomparisons of figures 2 and 5, 3 and 6, and 4 and 7, respectively, that the concentration of SiO_2 in the extracts is less at 150° C than at boiling, when corresponding concentrations of Na_2CO_3 are present. Furthermore, it is shown in table 5 that, excepting experiment 2, the extraction of Al_2O_3 is not affected significantly by the concentration of Na_2CO_3 in the initial solutions.

3. STUDIES OF SODALITE-TYPE COMPOUNDS AND OF BAUXITE-EXTRACTION RESIDUES

Some of the solid residues obtained in the above extractions were thoroughly washed with hot water, dried at 110° C and analyzed. Table 6 shows that the molar ratios of the residues, except for those from bauxite D, are close to the proportions, $1Na_2O:1Al_2O_3:2SiO_2$. This fact suggested that the residues might consist principally of a single compound, possibly related to nephelite, $Na_2O.Al_2O_3.2SiO_2$.

TABLE 6.—*Compositions of residues remaining after extraction of bauxites at boiling temperature with solutions containing 250 g of sodium carbonate and 125 g of sodium hydroxide per liter*

Experiment	Bauxite designation	Oxide composition of residue (ignited basis)				Molar ratio		
		Na_2O	Al_2O_3	SiO_2	$Fe_2O_3+TiO_2$	Na_2O	Al_2O_3	SiO_2
		%	%	%	%			
1	B	15.60	30.80	33.47	19.55	0.8	1.0	1.8
2	B	16.41	29.97	33.94	19.26	.9	1.0	1.9
3	B	16.32	29.96	34.00	19.04	.9	1.0	1.9
4	C	23.62	32.36	36.04	7.98	1.15	1.0	1.9
5	C	21.55	34.40	35.74	6.52	1.0	1.0	1.8
6	D	18.11	42.26	30.88	8.60	0.7	1.0	1.2
7	D	16.41	40.04	33.18	10.27	.7	1.0	1.4

Attempts were made to synthesize a sodium aluminum silicate compound of a composition similar to that of the residues. A solution containing 125 g of NaOH and 250 g of Na_2CO_3 per liter was prepared. To 400-ml portions of this solution, mixtures of silica gel and gibbsite, $Al_2O_3.3H_2O$, were added in amounts equivalent to the following: (1) 8.45 g of Al_2O_3 and 10 g of SiO_2 (molar ratio $1Al_2O_3:2SiO_2$); (2) 16.90 g of Al_2O_3 and 10 g of SiO_2 ($1Al_2O_3:1SiO_2$). The mixtures were then boiled in steel containers for 7 days and, after filtration, the residues were thoroughly washed with hot water and air-dried to constant weight. Microscopical examinations showed that the preparations consisted of very fine-grained isotropic crystals having an index of refraction of about 1.48. Chemical analyses gave the following compositions:

	No. 1	No. 2
	%	%
Na_2O	20.3	20.9
Al_2O_3	29.8	31.2
SiO_2	35.1	33.5
CO_2	1.8	1.1
H_2O	12.7	13.8
Fe_2O_3	0.1	0.0
Total	99.8	100.5

The corresponding $Na_2O:Al_2O_3:SiO_2:Na_2CO_3:H_2O$ molar ratios are 0.98:1.00:2.00:0.14:2.42 and 1.02:1.00:1.82:0.09:2.50 for preparations 1 and 2, respectively.

An X-ray diffraction pattern of sample 1 showed that the structure of the crystals was very similar to that of the mineral sodalite, $3Na_2O.3Al_2O_3.6SiO_2.2NaCl$. A sodium aluminum silicate preparation of similar composition (but containing neither carbonate nor chloride) was synthesized. In this experiment a mixture of 26 g of gibbsite and 20 g of SiO_2, as silica gel (in the molar ratio $1Al_2O_3:2SiO_2$) and 600 ml of solution containing 90 g of NaOH was heated in an autoclave at 150° C for 5 days. The resulting product was filtered and washed with a small amount of hot water, followed by alcohol and then by ether. It was dried overnight at 110° C. Analysis gave the following composition:

	%
Na_2O	21. 97
Al_2O_3	30. 74
SiO_2	35. 54
H_2O	11. 46
Total	99. 71

The corresponding molar ratios are $1.17Na_2O:1.00Al_2O_3:1.96SiO_2$: $2.11H_2O$. These ratios are in agreement with the composition of the hydrated nephelite, which has been reported formed in the desilication of sodium aluminate solutions [5]. The material gave an X-ray diffraction pattern distinctly different from that of the preparations containing sodium carbonate. Its pattern was identical, however, with that of the residue from extraction of bauxite C with sodium hydroxide solution containing no added carbonate (experiment 25, table 7).

In continuation of these studies, an analysis was made of the residue from a laboratory-scale extraction of bauxite C with a sodium hydroxide-sodium chloride solution (experiment 33, table 7). This residue had the following composition:

	%
Na_2O	22. 46
Al_2O_3	32. 75
SiO_2	33. 46
$Fe_2O_3 + TiO_2$	5. 80
Cl	5. 28
Total	99. 75

The corresponding molar ratios are $0.90Na_2O:1.00Al_2O_3:1.74SiO_2$: $0.46NaCl$. The X-ray diffraction pattern of this material was identical with that given by a sample of natural sodalite obtained from Canada.

Four minerals have been recognized as belonging to the sodalite group [6], as follows:

Sodalite _____ $3Na_2O.3Al_2O_3.6SiO_2.2NaCl$
Noselite _____ $3Na_2O.3Al_2O_3.6SiO_2.Na_2SO_4$
Hauynite _____ $3Na_2O.3Al_2O_3.6SiO_2.2CaSO_4$
Lazurite _____ $3Na_2O.3Al_2O_3.6SiO_2.2Na_2S.$

In a further investigation of sodalite-type compounds, mixtures of 26 g of gibbsite and 20 g of SiO_2 as silica gel (in the molar ratio $1Al_2O_3:2SiO_2$) were added to 600-ml quantities of solution containing

TABLE 7.—*Extractions of bauxites with solutions containing 125 g of sodium hydroxide per liter and various amounts of sodium salts* [a]

Experiment	Bauxite		Salt added		Temperature	Al_2O_3 in solution	SiO_2 in solution	Extraction of Al_2O_3 [b]	$\frac{SiO_2}{Al_2O_3} \times 100$ in solution
	Designation	Amount used	Kind	Amount					
		g/liter		g/liter		g/liter	g/liter	%	%
1	B	180	None		Boiling	50.2	0.228	63.2	0.45
2	B	180	Na₂SO₄	125	---do	50.2	.105	63.2	.21
3	B	180	Na₂SO₄	250	---do	50.0	.090	63.0	.18
4	B	180	Na₂SO₄	375	---do	48.2	.080	60.6	.17
5	B	180	None		150° C	48.8	.172	61.5	.35
6	B	180	Na₂SO₄	250	150° C	50.2	.046	63.2	.09
7	B	180	NaBr	125	Boiling	49.4	.140	62.2	.28
8	B	180	NaBr	250	---do	45.6	.078	57.4	.17
9	B	180	NaBr	375	---do	48.3	.061	60.8	.13
10	B	180	NaBr	500	---do	49.8	.025	62.7	.05
11	B	180	NaBr	250	150° C	50.2	.046	63.2	.09
12	B	180	NaCl	125	Boiling	46.4	.085	58.4	.19
13	B	180	NaCl	250	---do	47.2	.048	59.3	.10
14	B	180	NaCl	375	---do	47.5	.031	59.7	.07
15	B	180	NaCl	500	---do	46.3	.028	58.2	.06
16	B	180	NaCl	125	150° C	43.9	.054	55.3	.12
17	B	180	NaCl	250	150° C	37.5	.017	43.5	.05
18	B	130	NaCl	375	150° C	50.1	.016	63.1	.03
19	B	180	NaNO₃	125	Boiling	49.1	.048	62.0	.10
20	B	180	NaNO₃	250	---do	48.7	.010	61.5	.02
21	B	180	NaNO₃	375	---do	48.4	.013	61.1	.03
22	B	180	NaNO₃	125	150° C	46.2	.036	58.2	.08
23	B	180	NaNO₃	250	150° C	49.4	.009	62.2	.02
24	B	180	NaNO₃	375	150° C	42.6	.008	53.7	.02
25	C	157.5	None		Boiling	54.0	.324	67.9	.60
26	C	157.5	Na₂SO₄	125	---do	54.0	.135	67.8	.25
27	C	157.5	Na₂SO₄	250	---do	52.7	.102	66.2	.19
28	C	157.5	Na₂SO₄	375	---do	49.4	.080	62.0	.16
29	C	157.5	Na₂SO₄	500	---do	53.8	.071	67.8	.13
30	C	157.5	Na₂SO₄	250	150° C	53.0	.053	66.7	.10
31	C	157.5	NaBr	250	Boiling	47.7	.076	60.0	.16
32	C	157.5	NaCl	125	---do	51.3	.169	64.5	.33
33	C	157.5	NaCl	250	---do	51.2	.113	64.4	.22
34	C	157.5	NaCl	375	---do	50.4	.071	63.4	.14
35	C	157.5	NaCl	500	---do	50.5	.056	63.4	.11
36	C	157.5	NaCl	250	150° C	48.2	.021	60.6	.04
37	C	157.5	NaNO₃	250	Boiling	47.1	.057	59.3	.12
38	C	157.5	NaNO³	250	150° C	51.8	.018	65.2	.03
39	D	142	None		Boiling	61.8	.340	77.4	.55
40	D	142	NaCl	125	---do	59.2	.102	74.4	.17
41	D	142	NaCl	250	---do	56.8	.069	71.5	.12
42	D	142	NaCl	375	---do	52.6	.032	66.2	.06
43	D	142	None		150° C	61.3	.215	77.0	.35
44	D	142	NaCl	250	150° C	56.0	.024	70.2	.04

[a] Extracted by heating for 3 hr. [b] Based on original volume of extracting solution (400 ml).

75 g of NaOH and 150 g of NaCl, NaBr, NaNO₃, or Na₂SO₄. The mixtures were kept in the autoclave at 150° C for 5 days and were shaken twice daily. The resulting products were then filtered, washed thoroughly with hot water, alcohol, and ether, and dried at 110° C overnight. Analysis of the preparations gave the results shown in table 8.

The compositions of the chloride, bromide, and nitrate double salts in table 8 are similar to that of sodalite and the composition of the sulfate compound corresponds approximately with noselite. All the synthetic preparations contain less sodium salt than corresponds to the theoretical compositions and are hydrated, whereas the pure compounds should be anhydrous.

TABLE 8.—*Composition of sodalite-type compounds* [a]

Experiment	Sodium salt (NaX[b]) in molecule	Oxide composition					Molar ratios				
		Na_2O	Al_2O_3	SiO_2	X[c]	H_2O	Na_2O	Al_2O_3	SiO_2	NaX[b]	H_2O
		%	%	%	%	%					
1	None	21.97	30.74	35.54	------	11.46	1.17	1.00	1.96	------	2.1
2	NaCl	22.71	30.28	35.20	5.53	5.76	0.96	1.00	1.97	0.53	1.1
3	NaBr	22.39	29.80	33.46	11.45	3.43	.99	1.00	1.91	.49	0.7
4	NaNO3	21.22	32.06	34.64	8.24	3.64	.85	1.00	1.83	.49	.6
5	Na2SO4	22.14	29.86	34.18	6.53	7.12	.94	1.00	1.94	.28	1.3

[a] Prepared from mixtures (heated at 150° C for 5 days) of 26 g of gibbsite and 20 g of SiO_2 as silica gel ($1Al_2O_3:2SiO_2$, molar) in 600 ml of solution containing 75 g of NaOH and 150 g of NaCl, NaBr, NaNO3, or Na2SO4.
[b] NaX=NaCl, NaBr, NaNO3, or Na2SO4.
[c] X=Cl, Br, N_2O_5, or SO_3.

Table 9 shows the results of comparisons of the X-ray diffraction patterns of the various synthetic preparations and of the extraction residues from bauxite C with the pattern of natural sodalite. The patterns of the separate compounds within groups 1, 2, 3, 4, and 5 were identical with each member of the group, but each group pattern differed in various degrees from the pattern of sodalite. In the case of the NaBr preparations, the patterns were different from that of sodalite only in indicating a slightly larger unit-cube size, whereas for the NaNO3 preparations, slight variations from the sodalite pattern were noted. The sulfate preparation had a pattern different from that of sodalite and also from that of naturally occurring noselite. Unexpectedly, the pattern of the residue of bauxite C, extracted with NaOH-Na2SO4 solution, fell in group 5 with sodium aluminum silicate hydrate and showed no similarity to the pattern of the synthetic sulfate compound.

TABLE 9.—*Comparison of X-ray diffraction patterns of sodalite-type compounds*

Experiment	Sodium salt in molecule	Source of preparation	Degree of similarity with X-ray pattern of sodalite as given in literature
1a	NaCl	Natural sodalite, Canada	Identical.
1b	do	Synthetic	Do.
1c	do	NaOH-NaCl extraction residue of bauxite C	Do.
2a	NaBr	Synthetic	Almost identical.
2b	do	NaOH-NaBr extraction residue of bauxite C	Do.
3a	NaNO3	Synthetic	Very similar.
3b	do	NaOH-NaNO3 extraction residue of bauxite C	Do.
4	Na2SO4	Synthetic	Different.
5a	None	do	Do.
5b	do	NaOH extraction residue of bauxite C	Do.
5c	Na2SO4	NaOH-Na2SO4 extraction residue of bauxite C	Do.

4. COMPARISON OF EFFECTIVENESS OF VARIOUS SALTS IN DEPRESSING THE CONCENTRATION OF SILICA IN SODIUM ALUMINATE SOLUTIONS

These experiments suggested that the decreased concentrations of silica obtained in sodium aluminate solutions in the presence of sodium carbonate might be caused by the formation of a compound similar to sodalite and having a lower solubility than that of the sodium aluminum silicate formed in the absence of sodium carbonate. They

suggested also that under the conditions of extraction other sodium salts, particularly sodium chloride, might form sodalitic-type compounds, possibly having lower solubilities than the carbonate compound. Accordingly, the investigation was extended to determine which sodium salt would be more effective in depressing the solubility of silica in sodium aluminate solutions.

A considerable number of extractions of bauxites B, C, and D were made with a solution containing 125 g of NaOH per liter and various added salts in the amounts shown in table 7. Exactly the same procedure was followed in these experiments as in those reported in table 5.

Figures 2 to 7, based on data in tables 5 and 7, indicate the purity of the Al_2O_3 in solution with respect to SiO_2 in the presence of the various salts. It is evident that sodium nitrate is the most effective, of the salts tried, in reducing the concentration of SiO_2 in the sodium aluminate extracts. Next in order are the halide salts, and of these the chloride is shown to be more effective than the bromide where comparable data are available. The behavior of sodium sulfate and sodium carbonate is somewhat erratic, but in most cases the former causes the larger reductions in the concentration of SiO_2. Generally, the amounts of SiO_2 found in the 150° C extracts are considerably lower than those obtained at boiling at atmospheric pressure, but with bauxite B in the presence of $NaNO_3$, boiling appears to be almost as effective as treatment at 150° C.

The economic advantages and effectiveness of sodium chloride are such that it seemed desirable, in the remainder of this investigation, to concentrate on the use of common salt as a desilication agent.

5. PILOT-PLANT EXTRACTIONS

A number of extractions of bauxites B, C, and D were made in a small pilot plant. This equipment consisted of 30-gallon iron digester fitted with a mechanical stirrer and having steam, water, and air inlets. The digester was connected with a filter press from which the filtrate flowed to two 50-gallon storage drums. A centrifugal pump in the circuit permitted transfer of the solution from one storage drum to another or back to the digester.

The quantities of materials used and data obtained in some representative extractions are given in table 10. The solution containing sodium hydroxide and dissolved sodium salt was heated to boiling by passing steam into the digester. The bauxite then was added, and the mixture was heated at the desired temperature for 3 hours while stirring constantly. In experiments 1, 2, and 3 of table 10 the extractions were made at atmospheric pressure and, in experiments 4, 5, and 6, at approximately 30-lb/in.^{2} gage pressure (135° C). At the completion of the heating period each mixture was filtered, the filter cake thoroughly washed with hot water, and the volume of the extract plus wash water determined. Analyses of the solutions were made for Na_2CO_3, NaOH, Al_2O_3, and SiO_2.

It will be noted that the recoveries of Al_2O_3 reported in table 10 are slightly lower than those obtained in laboratory-scale extractions. This was caused by an accumulation of minor losses that could not be avoided in the pilot plant setup. The percentages of silica in experiments 4, 5, and 6, based on the Al_2O_3 content of the solutions,

TABLE 10.—*Pilot-plant extractions of bauxites* [a]

Experiment	Bauxite		Salt added		NaOH added	Volume of—		Composition of extract plus wash				Recoveries of—			$\dfrac{SiO_2}{Al_2O_3}\times100$ in solution	$\dfrac{SiO_2}{Al_2O_3}\times100$ in precipitated $Al_2O_3.3H_2O$
	Designation	Quantity used	Kind	Amount		Initial solution	Extract plus wash	Na_2CO_3	NaOH	Al_2O_3	SiO_2	Na_2CO_3	NaOH	Al_2O_3		
		lb		*lb*	*lb*	*gal*	*gal*	*g/liter*	*g/liter*	*g/liter*	*g/liter*	*%*	*%*	*%*		
1	B	20.0	Na_2CO_3	27.8	13.9	13.1	32.9	77.5	39.2	18.6	0.046	75	77	58	0.25	0.20
2	D	17.25	do	30.0	15.0	13.2	29.4	105.4	56.0	29.8	.089	86	92	75	.30	.27
3	D	17.25	do	30.0	15.0	14.0	36.4	81.3	43.8	22.6	.072	82	89	71	.32	.21
4	C	15.8	NaCl	25.0	12.5	11.0	23.5	_____	_____	24.5	.034	_____	_____	60	.14	.14
5	C	15.8	do	37.5	12.5	10.9	21.4	_____	_____	26.7	.024	_____	_____	60	.09	.09
6	C	12.6	$NaNO_3$	20.0	10.0	9.0	30.3	_____	_____	14.2	.013	_____	_____	63	.09	.09

[a] Experiments 1, 2, and 3 were made at the boiling temperatures of the solutions at atmospheric pressure, and experiments 4, 5, and 6 at 135° C (30-lb gage pressure). Time of extraction was 3 hr.

are plotted in figure 3. These values are comparable with those obtained in the small-scale extractions.

On completion of each extraction, the combined filtrate and wash contained in the storage drum was heated to boiling. Carbon dioxide was then passed slowly into the solution, which was kept in continuous agitation. Addition of carbon dioxide was continued over a period of 8 to 10 hours, until less than 0.5 g of Al_2O_3 per liter remained in solution. The mixture of precipitate and solution was then pumped into the digester, from which it was filtered on the filter press, and the precipitate was washed four times with 10-gallon portions of hot water. The material was removed from the filter press and dried overnight.

Microscopical examinations of the products showed that they consisted of irregular or prismatic crystals having the refractive indices of gibbsite. Analyses of the material for SiO_2 and Al_2O_3 gave the ratios shown in the last column of table 10. These values are the same or somewhat lower than those for the solutions before precipitation of the alumina. The soda contents of gibbsite from experiments 2 and 3 were 0.3 and 0.4 percent, respectively, and the Fe_2O_3 content of the latter was 0.09 percent. This relatively high value for Fe_2O_3 was undoubtedly caused by mechanical contamination. This was extremely difficult to prevent because the same equipment had to be used both for the extractions and for precipitation and handling of the hydrated alumina.

The precipitation of alumina from silica by differential precipitation was not investigated as this problem has received considerable study in connection with commercial operation of the Bayer process. McCulloch [7] has shown that by means of carbon dioxide, alumina containing 0.02 to 0.03 percent of silica can be precipitated from solutions containing 75 to 80 g of Al_2O_3 and 0.15 to 0.25 g of SiO_2 per liter, provided precipitation is stopped when about 75 percent of the alumina has been removed from solution.

As separation of alumina from silica by differential precipitation is most effective when the alumina concentration is high, extracts similar to those obtained in this study should not be diluted by excessive quantities of wash water prior to separation of the alumina.

6. RECOVERY OF SODA AND ALUMINA FROM BAUXITE-EXTRACTION RESIDUES

A number of experiments were performed on the recovery of Na_2O and Al_2O_3 from the bauxite-extraction residues. As shown previously, such residues contain Na_2O, Al_2O_3, and SiO_2 in molar ratios approximating 1:1:2 as an insoluble sodium aluminum silicate complex.

In most of the experiments, the residues were mixed with approximately the quantities of $CaCO_3$ required to form dicalcium silicate with the silica, leaving the Na_2O and Al_2O_3 as sodium aluminate. A few mixtures were also prepared in which lime and silica were present in molar ratios of 1 and 3. In some experiments, data for which are included in table 11, Na_2CO_3, as well as $CaCO_3$, was added. This was also done in the treatment of a bauxitic clay, experiment 11, table 11. The mixtures in 25 to 30-g quantities were heated in an electric furnace and held for 1 hour at the temperatures indicated in the table. The products were ground to pass a No. 80 sieve.

TABLE 11.—*Extractions of Al₂O₃ and Na₂O from sinters prepared from bauxite-extraction residues*

Experiment	Material	Temperature of heating[a]	Composition of sinter					Molar ratio CaO/SiO_2 in sinter	Molar ratio Na_2O/Al_2O_3 in sinter	Extraction[b] of—		$\frac{SiO_2}{Al_2O_3} \times 100$ in solution
			CaO	SiO₂	Al₂O₃	Fe₂O₃+TiO₂	Na₂O			Na₂O	Al₂O₃	
		° C	%	%	%	%	%			%	%	
1	Residue from B	1,260	24.2	25.9	28.1	4.7	17.0	1.0	1.0	2	0	
2	do	1,200	38.7	20.9	22.7	3.9	13.1	2.0	1.0	85	62	2.05
3	do	1,300	40.4	21.5	19.3	4.8	12.0	2.0	1.0	92	81	1.23
4	do	1,325	50.4	17.8	16.0	3.9	10.4	3.0	1.1	62	2	
5	Residue from C	1,280	22.5	24.2	32.8	5.9	14.5	1.0	0.7	3	0	
6	do	1,225	36.8	19.7	26.8	4.8	12.2	2.0	.8	97	68	
7	do	1,225	35.2	18.9	25.6	4.6	c 15.3	2.0	1.0	93	82	
8	do	1,230	32.6	17.5	23.8	4.3	c 20.5	2.0	1.4	67	87	
9	Residue from D	1,300	38.9	20.8	19.6	11.4	8.9	2.0	0.8	94	55	1.42
10	do	1,325	48.9	17.4	16.4	9.5	7.0	3.0	.7	47	0	
11	Bauxitic clay	1,225	25.8	13.8	33.5	3.8	c 22.0	2.0	1.1	85	85	0.22

[a] Heated for 1 hr. and ground to pass No. 80 sieve.
[b] Two-gram samples of the sinters were extracted by boiling for 2 hrs with 100-ml quantities of water.
[c] Na₂CO₃ added to raw mix before calcination.

Two-gram samples of the sinters were extracted by boiling for 2 hours with 100-ml quantities of water. The results in table 11 show that the CaO/SiO_2 ratio is rather critical and that at values of 1.0 and 3.0 the amounts of Al_2O_3 and Na_2O extracted are sharply reduced from the quantities obtained at a CaO/SiO_2 molar ratio of 2.0. When Na_2O and Al_2O_3 are present in molar ratios below unity, unsatisfactory extractions of Al_2O_3 are obtained even at the optimum molar ratios of CaO to SiO_2 (experiments 6 and 9).

A quantity of sinter No. 3, table 11, was calcined at 1,300° C for 1 hour, and the product ground to pass a No. 80 sieve. Samples of the sinter were extracted with 100-ml portions of solutions containing the amounts of NaOH shown in table 12. At temperatures below boiling, mechanical stirring was employed.

The percentage extractions of Al_2O_3 and Na_2O from this sinter are only slightly affected by an increase in the amount of sinter treated from 50 to 200 g/liter. For an agitation period of 30 minutes, the maximum extractions of Na_2O and Al_2O_3 are about 90 and 85 percent, respectively.

TABLE 12.—*Extraction of Al_2O_3 and Na_2O from sinter prepared from residue of bauxite B and ground to pass a No. 80 sieve*

[Volume of extracting solution, 100 ml; mechanical stirring used at temperatures below boiling.]

Experiment	NaOH in extracting solution	Weight of sample extracted	Temperature of extraction	Time of extraction	Extraction of—		$\frac{SiO_2}{Al_2O_3}\times100$ in solution
					Na_2O	Al_2O_3	
	g/liter	g/liter	° C	min	%	%	
1	0	50	50	30		65	
2	2	50	50	30		76	
3	10	50	50	30		83	
4	0	50	85	30	91	72	
5	0	200	85	30	90	72	0.33
6	2	50	85	30		85	
7	12	50	85	30		85	
8	100	50	85	30		82	
9	12	200	85	30		80	.75
10	0	50	Boiling	1	81	69	
11	2	50	---do-----	1		66	
12	0	50	---do-----	120	91	71	
13	2	50	---do-----	120		79	
14 ᵃ	0	50	70	30		84	1.93
15 ᵃ	0	200	70	30		82	2.42

ᵃ In these experiments the extracting solution contained 150 g of Na_2CO_3 and 200 g of NaCl per liter. Sinters ground to pass a No. 200 sieve.

Experiments 14 and 15, table 12, were made to determine the effect of high concentrations of Na_2CO_3 and NaCl in the extracting solution on the recovery of Al_2O_3 from the sinter. The samples of sinter used in these experiments were ground to pass a No. 200 sieve. It is evident that the high concentrations of the salts do not diminish the recovery of Al_2O_3 from the sinter. This fact makes it possible to use the spent solution from the initial extraction of the bauxite for extraction of the soda-lime sinter prepared from the bauxite-extraction residue, as will be illustrated in the following section.

The data contained in this section obviously do not represent a thorough study of the soda-lime-sinter method of alumina extraction. This process has recently received considerable study elsewhere [8].

7. FLOW SHEET AND SUMMARY OF PROCESS

A suggested commercial process for the extraction of alumina from high-silica bauxites, developed from experiments described in the preceding sections, is illustrated by a flow sheet, figure 8.

The composition of the bauxite shown in the flow sheet is approximately that of bauxite C, with minor constituents such as Fe_2O_3 and TiO_2, omitted for simplification. The finely ground material is digested for a suitable time with a sodium hydroxide-sodium chloride solution, either at the boiling temperature of the solution at atmospheric pressure or at a higher temperature and pressure. On completion of the heating period, the mixture is filtered and the residue washed with water or salt solution. Washing need not be thorough because the residue is reserved for further treatment to recover the soda and alumina that it contains.
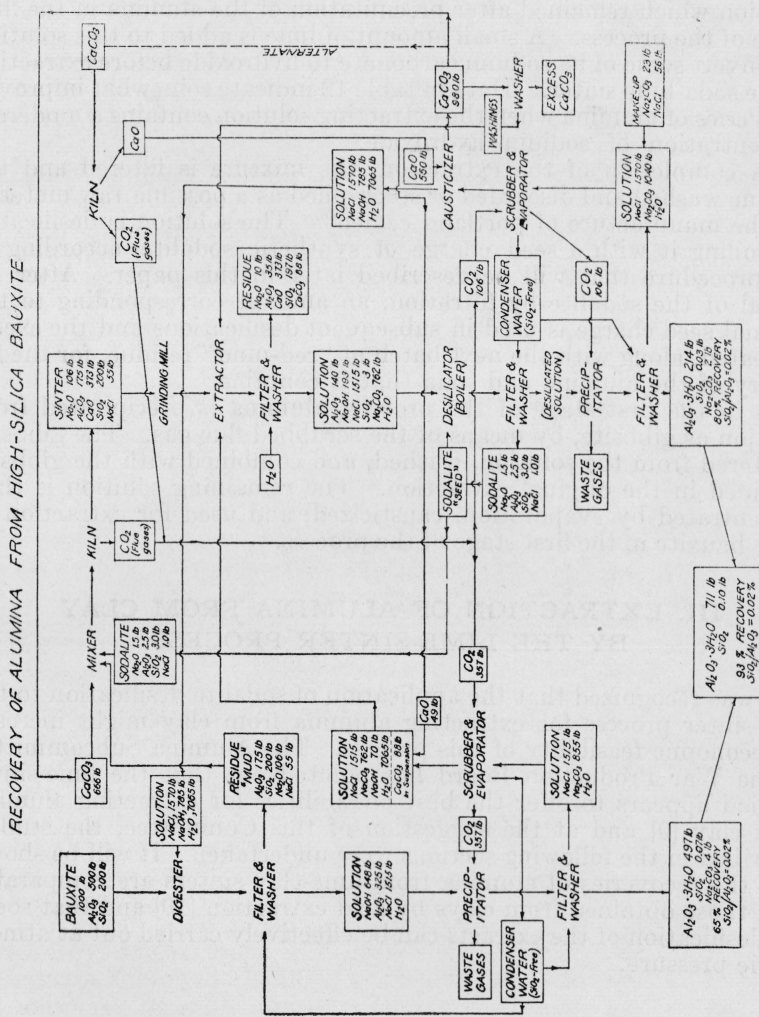
FIGURE 8.—*Flow sheet of suggested process for extracting alumina from high-silica bauxite.*

The alumina may be removed from the extract by controlled precipitation with carbon dioxide in the presence of a seed charge of gibbsite. In the flow sheet the scrubbed gas is shown as the source of carbon dioxide. By passing the kiln gas into the solution, the major part of the alumina can be precipitated without undue contamination by the small amount of silica in the extract. In the flow sheet, complete precipitation of the alumina is indicated as this would be accomplished in cyclical operation of the process.

The residue from the initial extraction contains soda, alumina, silica, and sodium chloride in proportions approaching those of the mineral sodalite, as well as the relatively inert constituents of the bauxite, such as Fe_2O_3 and TiO_2. Ground limestone is added to the residue to give a CaO/SiO_2 molar ratio of 2.0, and the mixture is then heated to a suitable temperature to bring about clinkering or sintering. After grinding the sinter, it is extracted at 70° to 80° C with the solution which remained after precipitation of the alumina in the first stage of the process. A small amount of lime is added to this solution to convert some of its sodium carbonate to hydroxide before extraction of the soda-lime sinter. Data in table 12 indicate somewhat improved recoveries of alumina when the extracting solution contains a moderate concentration of sodium hydroxide.

On completion of the extraction, the mixture is filtered and the residue washed and discarded or stock-piled as a possible raw material for the manufacture of portland cement. The solution is desilicated by boiling it with a seed charge of synthetic sodalite, according to the procedure that will be described later in this paper. After removal of the sodalite by filtration, an amount corresponding to the original seed charge is used in subsequent desilications and the excess is treated, along with the next batch of "red-mud" residue, for the recovery of the alumina and soda that it contains.

As in the first stage of the process, alumina is precipitated from solution as gibbsite, by means of the scrubbed flue gas. The gibbsite is filtered from the solution, washed, and combined with the gibbsite obtained in the original extraction. The remaining solution is then concentrated by evaporation, causticized, and used for extraction of more bauxite in the first stage of the process.

III. EXTRACTION OF ALUMINA FROM CLAY BY THE LIME-SINTER PROCESS

It was recognized that the application of sodalite desilication to the lime-sinter process for extracting alumina from clay might increase the economic feasibility of this process. The Alumina Subcommittee of the War Production Board has pointed out that the lime-sinter method appears to offer the best possibilities for extracting alumina from clay [9] and at the suggestion of this Committee, the studies described in the following sections were undertaken. It will be shown that the recoveries of alumina from lime-clay sinters are comparable with those obtained from clays by acid extraction [10] and that sodalite desilication of the extracts can be effectively carried out at atmospheric pressure.

1. MATERIALS AND PROCEDURE

The raw materials were a Georgia kaolin and a ground limestone of the following compositions:

	Kaolin, %	Limestone, %
SiO_2	45. 77	0. 88
Al_2O_3	37. 23	. 12
Fe_2O_3	1. 00	. 21
TiO_2	1. 12	-----
CaO	-----	54. 98
MgO	-----	0. 35
Na_2O	0. 06	-----
Loss on ignition	14. 01	43. 44
Total	99. 19	99. 98

The other materials included sodium carbonate, sodium chloride, and sodium hydroxide.

Sinters were prepared from properly proportioned mixtures of the ground limestone and kaolin by burning under various conditions. Extractions of the finely powdered sinters were made with solutions containing sodium carbonate or mixtures of sodium carbonate and sodium chloride. In the preliminary experiments listed in the following section the mixtures were agitated in 750-ml Erlenmeyer flasks placed on a slow-speed shaking machine which was kept in an air thermostat. In all other experiments, extractions of the sinters were made with a high-speed stirrer. The extraction vessel was a 500-ml three-neck flask, with the stirrer inserted in the middle neck and a thermometer and funnel for adding the sinter in the side necks. The temperature was maintained within ±1 degree centigrade of the values specified, by controlled heating.

On completion of the extraction, the mixtures were filtered and the residues washed with water or NaCl solution. In the preliminary experiments the extracts and washes were mixed, but in subsequent work they were stored separately. The combined extracts and washes were desilicated by boiling in iron containers with seed charges of synthetic sodalite, and the solutions were separated from the insoluble material by filtration.

In order to ascertain yields and the purity of the extracted alumina with respect to silica, analyses of the solutions were made for Al_2O_3 and SiO_2 and, in some cases, for Na_2O and NaCl. Determinations of SiO_2 were made in samples containing 5 to 10 g of Al_2O_3.

2. PREPARATION OF SINTERS

To obtain a sinter which would be free from unreactive aluminate compounds such as gehlenite, $2CaO.Al_2O_3.SiO_2$, a mixture of ground limestone and kaolin was prepared in such proportions that, after burning, the composition of the resulting material corresponded to a point on a line joining the composition of $2CaO.SiO_2$ and the quintuple point $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, and $2CaO.SiO_2$ in the CaO-Al_2O_3-SiO_2 diagram [16]. Allowance was made for the lime and alumina required for the formation of $CaO.TiO_2$ and $4CaO.Al_2O_3$-Fe_2O_3 with any TiO_2 and Fe_2O_3 in the raw materials. About 80

pounds of this mixture were burned in a brick kiln at 1,300° to 1,350° C for 5 hours. The composition of this product, which will be referred to as sinter R, was

	%
SiO_2	22. 82
Al_2O_3	18. 38
Fe_2O_3	0. 70
TiO_2	. 64
CaO	56. 84
MgO	0. 56
Na_2O	. 10
Loss on ignition	. 11
Total	100. 15

Because preliminary experiments showed that this product did not give satisfactory extractions, it was ground to an average particle size of 5 microns.

A number of small-batch sinters were prepared by burning 100-g quantities of the original mix in a muffle until the products gave no test for free lime. This material (sinter S) was only slightly sintered and required no grinding. It contained dicalcium silicate largely in the beta form.

A third batch of lime-clay calcine (sinter T) was obtained. Details of the preparation of this material were not available. Petrographic examination of the sinter showed the presence of about three times as much gamma- as beta-dicalcium silicate. The beta-dicalcium silicate grains appeared to be surrounded by thin films of low-index, isotropic material, presumably glass. The composition of the sinter was

	%
SiO_2	22. 38
Al_2O_3	18. 00
Fe_2O_3	1. 34
TiO_2	0. 98
CaO	54. 44
MgO	0. 99
Na_2O	. 76
Loss ignition	1. 15
Total	100. 04

3. EXTRACTION OF SINTERS WITH DILUTE SODIUM CARBONATE SOLUTIONS

The extractions listed in table 13 were made on samples of sinter S. The volume of the extracting solution was 400 ml in all experiments and the quantity of material extracted was such that the molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter was 2.0. The mixtures were shaken for 2 hours at the temperatures indicated in table 13, filtered, and the residues washed with 100 ml of hot water. Some of the combined extracts and washes were then analyzed for Al_2O_3 and SiO_2, giving the results shown in table 13 under the heading "Not desilicated." Other combined extracts and washes were boiled for 2 hours with seed charges consisting of 5 g of synthetic sodalite. After removal of the sodalite by filtration, the solutions were analyzed for Al_2O_3, SiO_2, and in some cases, Na_2O. The results of determinations of Al_2O_3 and SiO_2 and calculated recoveries of Na_2O are given in the last five columns of table 13.

TABLE 13.—*Extractions of sinter S with dilute* Na$_2$CO$_3$ *solutions containing* NaCl

[Volume of extracting solution, 400 ml; time of extraction, 2 hr]

Experiment	Composition of extracting solution		Quantity of sinter used	Temperature of extraction	Composition of extracts plus washes, and percentage of Al$_2$O$_3$ recovered								Recovery of Na$_2$O in desilicated solution
	Na$_2$Co$_3$	NaCl			Not desilicated				Desilicated				
					Al$_2$O$_3$ concentration	Al$_2$O$_3$ recovered	SiO$_2$	$\frac{SiO_2}{Al_2O_3} \times 100$	Al$_2$O$_3$ concentration	Al$_2$O$_3$ recovered	SiO$_2$	$\frac{SiO_2}{Al_2O_3} \times 100$	
	g/liter	g/liter	g/liter		g/liter	%	g/liter		g/liter	%	g/liter		%
1	100	0	261	35° C	31.7	80	0.761	2.4					
2	100	160	261	35° C	28.6	72	1.087	3.8					
3	50	0	130	50° C	15.8	81	0.411	2.6	14.6	76	0.035	0.24	
4	50	40	130	50° C					14.6	76	.023	.16	98
5	50	80	130	50° C	15.0	78	.285	1.9	14.8	77	.015	.10	98
6	50	120	130	50° C					14.2	74	.014	.10	97
7	50	160	130	50° C					13.3	69	.007	.05	
8	100	0	261	50° C	31.8	80	.763	2.4	30.4	79	.082	.27	98
9	100	160	261	50° C	27.3	71	.546	2.0	26.9	70	.027	.10	97
10	100	240	261	50° C					25.0	65	.022	.09	
11	100	160	261	85° C					10.3	26	.016	.16	
12	50	0	130	Boiling	13.5	70	.216	1.6					
13	100	160	130	____do					9.5	24	.017	.18	

It will be noted that the initial extracts contained SiO_2 in amounts corresponding to 1.6 to 3.8 percent of the weight of Al_2O_3 in solution. For extractions made at 50° C the purity of Al_2O_3 with respect to SiO_2 in the desilicated solutions increased as the ratio of NaCl to Na_2CO_3 increased, but the higher concentrations of NaCl caused diminished recoveries of Al_2O_3 in the initial extractions. The higher extractions of Al_2O_3 were obtained at both 35° and 50° C.
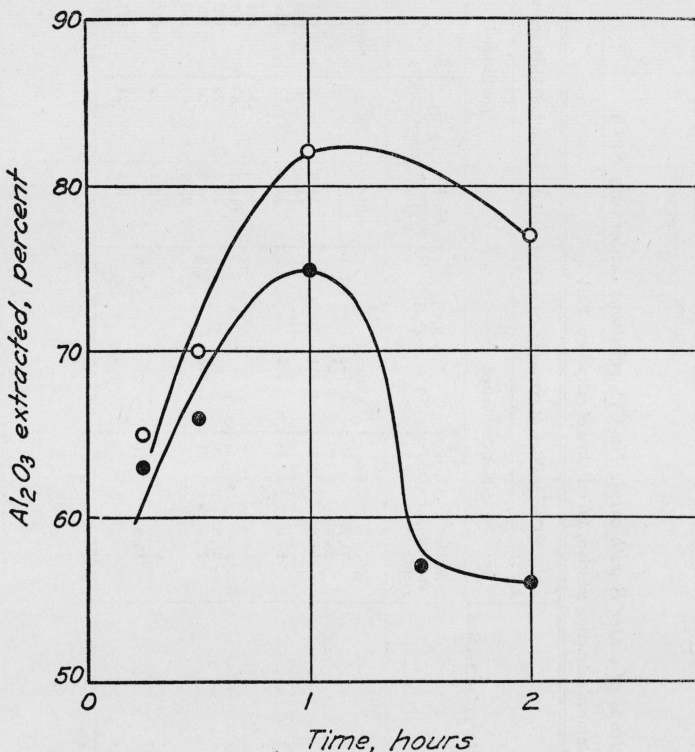

FIGURE 9.—*Effect of time of extraction at 40° C on the recovery of alumina from sinter R.*

The extracting solutions contained 50 g/liter of Na_2CO_3, 200 g/liter of NaCl (open circles); and 100 g/liter of Na_2CO_3, 200 g/liter of NaCl (closed circles). Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter=2.5

Although the data of table 13 indicate that the losses of soda amounted to 2 to 3 percent, it should be mentioned that these values are not particularly accurate, because of the very small aliquots of solution that had to be taken. A better method of measuring soda losses is by analysis of the solid residues. Such analysis indicated a loss of 0.05 percent of NaCl and 1.5 percent of Na_2CO_3. With some raw materials this loss in sodium carbonate might be made up, wholly or in part, by the amount of alkali usually found in clay.

The results of experiments on sinter R, which were made to determine the optimum values for time of extraction and molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter, are shown in figures 9 and 10, respectively. Both 5- and 10-percent Na_2CO_3 solutions, containing 200 g of NaCl per liter, were used and the extraction temperature

was 40° C. In the experiments illustrated by figure 9 the molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter was maintained constant at 2.5.

As shown in figure 9 the optimum extraction time appears to be about 1 hour. Longer periods gave much reduced extractions for the 10-percent Na_2CO_3 solution, appreciable reductions for the 5-percent solution. It should be pointed out, however, that the optimum
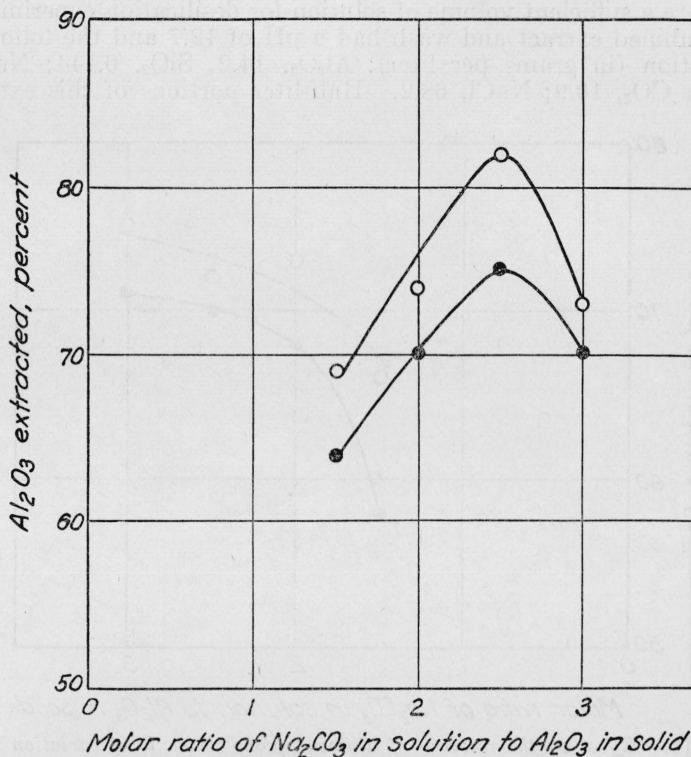

FIGURE 10.— *Effect on the recovery of alumina from sinter R of variation of the molar ratio of sodium carbonate in the extracting solution to alumina in the sinter.*

The extracting solutions contained 50 g/liter of Na_2CO_3, 200 g/liter of NaCl (open circles); and 100 g/liter of Na_2CO_3, 200 g/liter of NaCl (closed circles). Mixtures shaken for 1 hr at 40° C.

time of extraction will be determined by the type of agitator used as well as by the nature of the sinter. In a later section it will be shown that when more vigorous agitation was employed the optimum extraction period was considerably less than that indicated in figure 9.

Figure 10 shows that a molar ratio of $2.5Na_2CO_3/Al_2O_3$ gave the highest extractions of alumina from sinter R, with a marked decrease occurring at a $3.0Na_2CO_3/Al_2O_3$ molar ratio.

The effect of excess sodium hydroxide on extractions of alumina from sinter R is shown by comparison of figures 10 and 11. The compositions of the mixtures in the experiments illustrated by figure 11 were the same as those on which figure 10 is based, except that they contained a quantity of added NaOH, which corresponded to

10 percent of the weight of Na_2CO_3 in the initial solutions. Poorer extractions were obtained in these experiments than in comparable ones shown in figure 10, except where the molar ratio of Na_2CO_3 to Al_2O_3 was 3.0.

4. DESILICATION OF DILUTE SODIUM ALUMINATE SOLUTIONS

An extraction of sinter R was made in the small pilot plant in order to prepare a sufficient volume of solution for desilication experiments. The combined extract and wash had a pH of 12.7 and the following composition (in grams per liter): Al_2O_3, 14.2; SiO_2, 0.144; NaOH, 18.6; Na_2CO_3, 10.9; NaCl, 68.2. Half-liter portions of this extract,
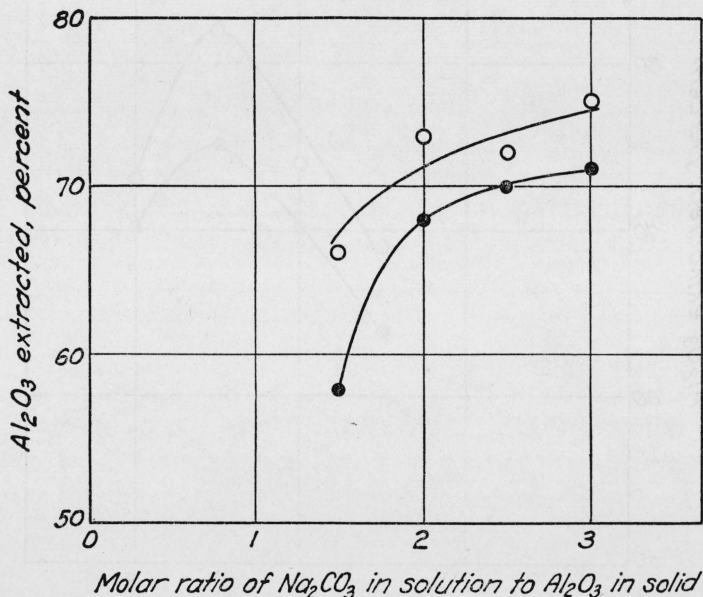

Figure 11.—*Effect on the recovery of alumina from sinter R of variation of the molar ratio of sodium carbonate in the extracting solution to alumina in the sinter, in the presence of sodium hydroxide.*

The extracting solutions contained 50 g/liter of Na_2CO_3, 5 g/liter of NaOH, 200 g/liter of NaCl (open circles); and 100 g/liter of Na_2CO_3, 10 g/liter of NaOH, 200 g/liter of NaCl (closed circles). Mixtures shaken for 1 hr at 40° C.

with and without added sodium chloride, were boiled with seed charges of synthetic sodalite prepared in the autoclave from gibbsite plus silica gel. The seed was removed by filtration, and the solutions were analyzed. The results are summarized in table 14.

When the quantity of seed added was 2 g/liter, the greatest lowering in SiO_2 concentration was obtained after boiling for 2 to 3 hours, as shown in experiments 2 to 5. This quantity of seed is insufficient, however, and if the amount of sodalite is increased to 10 g/liter, the desilication proceeds further, as shown in experiment 6. Increases in the concentration of NaCl in solution also bring about decreases in the SiO_2 concentration (experiments 7 to 10). The values of the SiO_2/Al_2O_3 ratio, both in the solution and in the alumina after complete precipitation by means of carbon dioxide, are shown in figure 12.

TABLE 14.—*Desilication (by boiling with synthetic sodalite) of dilute sodium aluminate solution containing 14.2 g of Al_2O_3, 0.144 g of SiO_2 per liter, and various amounts of sodium chloride*

Experiment	NaCl in extracting solution	Amount of seed added	Time of boiling	SiO_2 in solution	$\frac{SiO_2}{Al_2O_3} \times 100$ in—	
					Solution	Precipitated Al_2O_3
	g/liter	*g/liter*	*hr*	*g/liter*		
1	68	0	----------	0.1440	1.01	-----------
2	68	2	0.5	.0442	0.31	-----------
3	68	2	1	.0376	.26	-----------
4	68	2	2	.0238	.17	-----------
5	68	2	3	.0238	.17	-----------
6	68	10	2	.0110	.08	0.10
7	114	10	2	.0100	.07	.07
8	162	10	2	.0049	.035	.05
9	204	10	2	.0047	.03	.04
10	243	10	2	.0024	.02	02

The point at zero concentration of NaCl is taken from experiment 3 of table 13.

To obtain information on the effect of treating larger quantities of solution, a 26-liter portion of the undesilicated extract containing 200 g of NaCl per liter was boiled for 2 hours with 260 g of sodalite (10 g/liter). The sodalite was removed by filtration and carbon dioxide was passed into the boiling solution in the presence of gibbsite seed. Precipitation was continued for 8 hours when only 0.1 g of Al_2O_3 per liter remained in solution. After filtration, washing, and drying, analysis of the gibbsite showed its SiO_2 content to be 0.014 percent (on the basis of the anhydrous Al_2O_3).
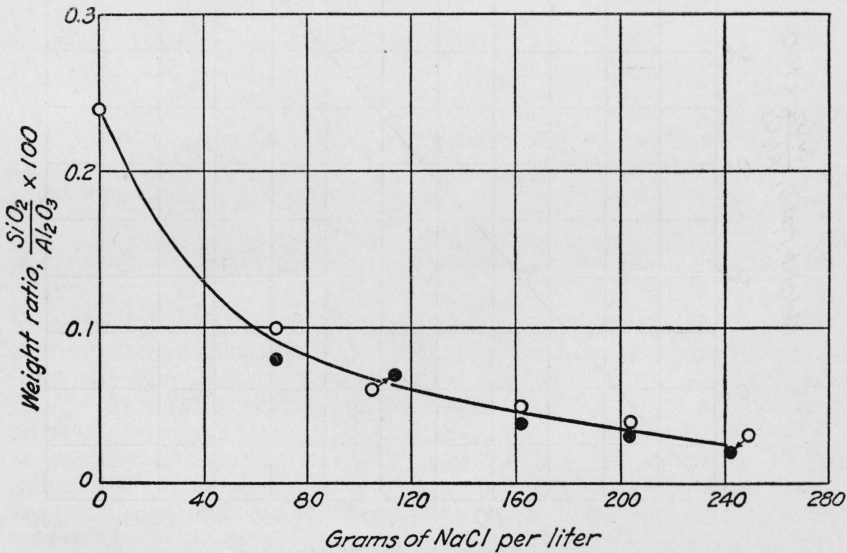

FIGURE 12.—*Effect of sodium chloride concentration on the sodalite desilication of an extract, from sinter R, containing 14 g/liter of Al_2O_3 and 0.14 g/liter of SiO_2.*

Values of $\frac{SiO_2}{Al_2O_3} \times 100$ determined by analysis of solutions (closed circles) and of hydrated alumina after complete precipitation from solution (open circles).

A few experiments were made in which various amounts of sodium hydroxide were added to portions of the extract described in the first paragraph of section C. After the pH of the resulting solutions had been measured, 500-ml portions were boiled for 2 hours with 5-g quantities of sodalite, the sodalite removed by filtration, and the

TABLE 15.—*Effect of sodium hydroxide concentration on the desilication of 500-ml portions of a sodium aluminate solution containing approximately 14 g of* Al_2O_3 *and 0.14 g of* SiO_2 *per liter*

[Desilication effected by boiling with 5 g of synthetic sodalite for 2 hr]

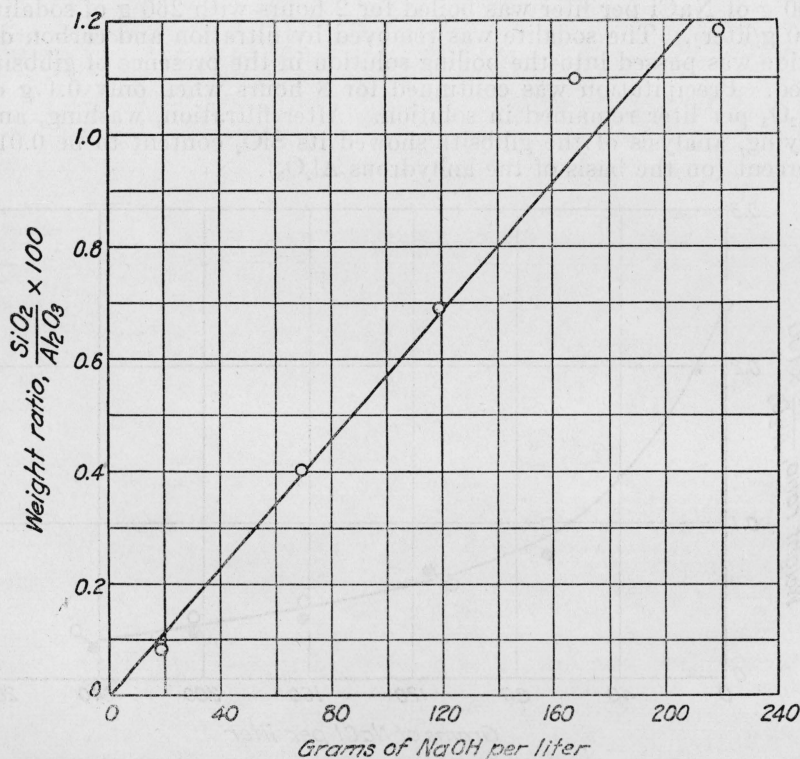| Experiment	NaOH in extracting solution	pH	Composition of solution after desilication		
			Al_2O_3	SiO_2	$\dfrac{SiO_2}{Al_2O_3}\times100$
	g/liter		g/liter	g/liter	
1	18.6	12.7	14.2	0.011	0.08
2	69	13.4	14.0	.056	.40
3	119	14.0	14.5	.097	.67
4	169	14.2	14.8	.163	1.10
5	219	14.4	14.7	.174	1.18

FIGURE 13.—*Effect of sodium hydroxide concentration on the sodalite desilication of an extract, from sinter R, containing approximately 14 g/liter of* Al_2O_3 *and 0.14 g/liter of* SiO_2.

solutions analyzed for Al_2O_3 and SiO_2. The data, given in table 15 and figure 13, show that desilication becomes less efficient as the sodium hydroxide concentration increases. Decomposition of the sodalite seed in the solutions containing the larger amounts of NaOH is indicated by increases in the Al_2O_3 contents of the solutions following desilication.

Thugutt [11] synthesized sodalite by autoclaving kaolinite at 212° C with a solution containing NaCl and NaOH. Other investigators have reported that sodalite is formed in fusions of large excesses of NaCl with (a) nephelite [12]; (b) mixtures of kaolinite and Na_2CO_3 [13]; or (c) mixtures of SiO_2, Al_2O_3, and NaOH [14].

As it had been observed in this study that some sodalite preparations were more effective desilicating agents than others, the various methods of preparation given in table 16 were tried.

TABLE 16.—*Comparison of desilication effectiveness of sodalites prepared by various methods*

[Initial solution contained 18.3 g of Al_2O_3 and 0.146 g of SiO_2 per liter.   Desilication effected by boiling with sodalites for 1 hr]

Experiment	Method [a] of preparing sodalite	Quantity of sodalite used	NaCl added to solution	$\frac{SiO_2}{Al_2O_3} \times 100$ in desilicated solution
		g/liter	*g/liter*	
1	None used	0	0	0.80
2	1	5	0	.36
3	1	5	50	.14
4	1	5	100	.08
5	1	5	200	.03
6	1	10	0	.19
7	1	10	50	.08
8	1	10	100	.037
9	1	10	200	.004
10	2	10	50	.28
11	3	10	50	.36
12	4	10	50	.11
13	5	10	0	.57
14	5	10	50	.21
15	5	10	100	.10
16	5	10	200	.033
17	6	10	50	.40
18	7	10	50	.12

[a] (1) Dehydrated kaolin+NaOH+NaCl+H_2O heated in autoclave at 150° C for 4 days.
(2) Undehydrated kaolin+NaOH+NaCl+H_2O heated in autoclave at 150° C for 4 days.
(3) Undehydrated kaolin+Na_2CO_3+NaCl heated in muffle at 820° C for 16 hours.
(4) Preparation (1), above, heated with excess NaCl in muffle at 820° C for 16 hours.
(5) Gibbsite+silica gel+NaOH+NaCl+H_2O heated in autoclave at 150° C for 4 days.
(6) Gibbsite+silica gel+Na_2CO_3+NaCl heated in muffle at 820° C for 16 hours.
(7) Preparation (5), above, heated with excess NaCl in muffle at 820° C for 16 hours.

In these experiments, the quantity of sodium hydroxide or sodium carbonate used was in moderate excess of the amount theoretically required to form sodalite, and the sodium chloride was present in greater excess. As an example of the procedure, a batch of sodalite was prepared by method 1 as follows:

The kaolin was first activated by heating it at 700° C for 1 hour. A batch of 200 g of this dehydrated kaolin, 150 g of NaCl, 100 g of NaOH, and 400 ml of water, was kept at 150° C in an autoclave for 4

days. The product was then removed, washed with hot water, and dried at 110° C. Analysis showed the following composition:

	%
Na_2O	18. 32
Al_2O_3	30. 47
$Fe_2O_3 + TiO_2$	1. 67
SiO_2	36. 06
$NaCl$	10. 58
H_2O	2. 73
Total	99. 83

Ignoring the $Fe_2O_3 + TiO_2$, this analysis corresponds to the following molar ratios: $0.99Na_2O:1.00Al_2O_3:2.01SiO_2:0.61NaCl:0.51H_2O$, in good agreement with the theoretical molar ratios of sodalite: $1.00Na_2O:1.00Al_2O_3:2.00SiO_2:0.67NaCl$.

To compare the effectiveness of the various sodalite preparations, a large quantity of sodium aluminate solution containing 18.3 g of Al_2O_3 and 0.146 g of SiO_2 per liter was prepared by extraction of sinter R. Various amounts of sodium chloride were dissolved in 400-ml portions of this extract, and these were boiled for 1 hour with the quantities of the various sodalite preparations indicated in table 16.

The results show that the sodalite made by Method 1 is the most active preparation. Comparison of experiments 6 to 9 with 2 to 5 reveals that 10 g of sodalite per liter brought about a more complete desilication than 5 g.

Sodalite prepared in the autoclave from undehydrated kaolin gave poor desilication (experiment 10), and that prepared in the muffle was even less effective (experiment 11). However, when the sodalite obtained by method 1 was heated in the muffle with excess sodium chloride, its desilication capacity was not much impaired (experiment 12).

Experiments 13 to 18, inclusive, show that sodalite prepared from gibbsite and silica gel and the product obtained by method 6 were less active than that prepared from dehydrated kaolin. There was considerable improvement (experiment 18) when the sodalite prepared by method 5 was heated in the muffle at 820° C, method 7.

Comparison of the effectiveness of the various sodalite preparations may be facilitated by reference to figure 14.

For the dilute sodium aluminate solutions obtained in this portion of the investigation, the best conditions for desilication appear to require a concentration of sodium chloride of 200 g/liter and boiling for 1 hour with 10 g of sodalite seed per liter prepared in the autoclave from dehydrated kaolin. Under these conditions the concentration of silica in solution can be reduced to less than 0.01 percent of the alumina concentration.

5. EXTRACTION OF SINTERS WITH CONCENTRATED SODIUM CARBONATE SOLUTIONS

All extractions described in this and following sections were made with high-speed stirring. The extraction mixtures were 100-ml portions of solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride. The quantity of sinter added was such that the molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter was 2.0. At the end of each extraction the residue was

filtered off and washed with a solution containing the same concentration of sodium chloride as that in the original extraction. A 100-ml portion of this solution was used to wash the residue on the filter. The residue was then subjected to two successive repulpings, for 3 minutes each time, in 200-ml portions of the wash solution. Analyses of the combined extracts and washes were made for Al_2O_3 and also for SiO_2 in some cases.
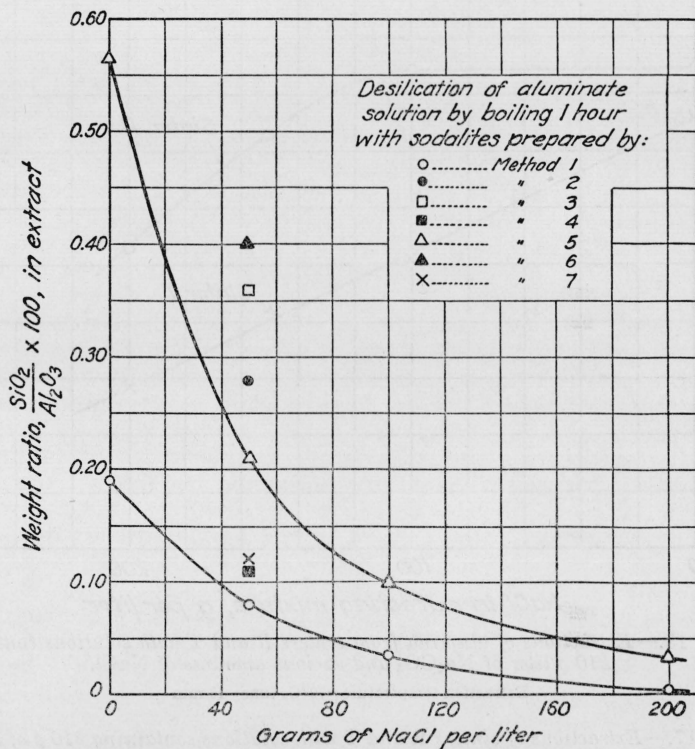

FIGURE 14.—*Comparison of effectiveness of various sodalite preparations (described in table 16) in desilicating an extract, from sinter R, containing 18 g/liter of Al_2O_3 and 0.15 g/liter of SiO_2.*

Figure 15 is based on data in table 17 for the 10-minute extractions of the sinters at 70° C. It shows that the extraction of alumina from sinter *R*, though considerably diminished at a sodium chloride concentration of 200 g/liter, is not affected adversely at 100 g of NaCl per liter. The recovery of alumina from sinter T, however, shows an approximately linear decrease as the NaCl concentration increases from 0 to 200 g/liter. Table 17 shows that variations from an extraction time of 10 minutes or temperature of 70° C did not improve the recoveries appreciably. No beneficial results were obtained by prolonged grinding of sinter T.

As mentioned in the preceding section, the dicalcium silicate in sinter T was present as a mixture of the gamma and beta modifications, and grains of the latter were surrounded by glassy films. Sinter *R*, however, was practically free of beta-dicalcium silicate and glass. It

was thought that the difference in behavior of the sinters might be due in part to these factors, particularly to the presence of the reactive beta-dicalcium silicate in sinter T, which might interfere with the reaction between sodium carbonate and calcium aluminate. Accordingly, an annealing procedure for eliminating glass and beta-dicalcium silicate from the sinter was investigated.
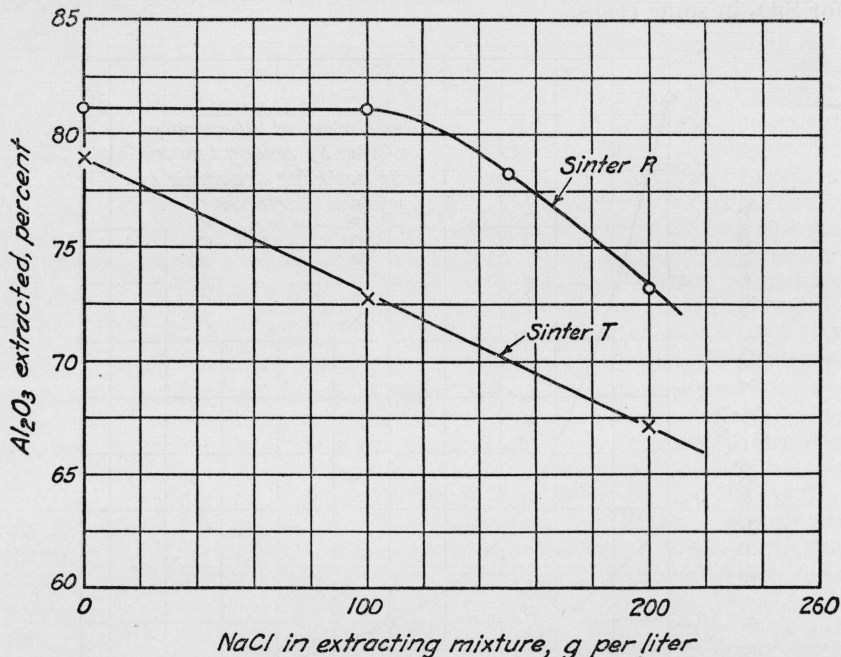

FIGURE 15.—*Extractions of alumina from sinters R and T with solutions containing 210 g/liter of* Na_2CO_3 *and various amounts of* NaCl.

Extraction temperature=70°C; time=10 min

TABLE 17.—*Extractions of sinters R and T with solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride*

[Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter=2.0.   High-speed stirring.]

Experiment	Sinter	Quantity of sinter extracted	NaCl in extracting solution	Temperature of extraction	Time of extraction	Al_2O_3 recovery
		g/liter	*g/liter*	*° C*	*min*	*%*
1	R	550	0	70	10	81.1
2	R	550	100	70	10	81.0
3	R	550	100	70	15	81.8
4	R	550	100	70	20	79.2
5	R	550	150	70	10	78.2
6	R	550	200	70	10	73.2
7	T	561	0	70	10	78.9
8	T	561	100	70	5	72.0
9	T	561	100	70	10	72.7
10	T	561	200	70	10	67.0
11	T	561	200	70	30	66.1
12	T	561	200	40	10	61.5
13	T	561	0	80	5	76.3
14	T	561	100	80	5	73.5
15	T	561	100	90	5	76.4

6. ANNEALING OF SINTERS

Lerch and coworkers [15] have shown that complete crystallization of cement clinkers may be induced by heating them to 1,400° C and allowing the temperature to drop slowly to a value below the solidus in the system. Such "annealed" products were found to be practically free from glass and to contain dicalcium silicate exclusively in the gamma form.

The alumina content of the clinkers studied by Lerch and Brownmiller [15] was distributed between the compounds $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$. The temperature of liquid formation when $CaO.Al_2O_3$ is substituted for $3CaO.Al_2O_3$, as in the sinters studied in this investigation, is unknown but in all probability is above 1,200° C.

Accordingly, to eliminate the glassy material and beta-dicalcium silicate as completely as possible from sinter T, a 3-pound sample of the material was reheated and annealed. This was accomplished by reburning the sinter at 1,300° C for 1 hour in a gas-fired furnace and then causing the temperature of the charge to drop at a uniform rate to 1,200° C over a period of 1½ hours. The charge was then removed from the furnace and allowed to cool rapidly, whereupon it "dusted" completely because of the inversion of the beta form of dicalcium silicate to the gamma form. A 3-pound batch of sinter R was also reburned and annealed similarly. In the following section the annealed sinters will be designated as R_a and T_a, respectively.

Another portion of sinter T was reburned and annealed after adjusting its composition. It had been noted that this sinter had a relatively low lime content compared with sinter R. Thus, after allowing for the lime and alumina required to form $2CaO.SiO_2$, $CaO.TiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and $Na_2O.Al_2O_3$ with the SiO_2, TiO_2, Fe_2O_3, and Na_2O in the sinters, the molar ratio of residual lime to alumina in sinter T was 1.15, whereas in sinter R it was 1.30. Sinter T was therefore mixed with 2 percent of added lime, reburned, and annealed as before. Analysis of the product, which will be referred to in the following section as sinter T'_a, gave the following composition:

	%
SiO_2	22. 14
Al_2O_3	17. 69
Fe_2O_3	1. 28
TiO_2	0. 93
CaO	56. 06
MgO	0. 93
Na_2O	. 64
Loss on ignition	. 23
Total	99. 90

All of the annealed sinters were extremely fine-grained and passed completely through a No. 200 sieve. Petrographic examinations indicated that they were free of glass and beta-dicalcium silicate.

7. EXTRACTION OF ANNEALED SINTERS WITH CONCENTRATED SODIUM CARBONATE SOLUTIONS

Samples of sinter T_a, which had been annealed without adjustment of composition, were extracted at 70° and 80° C with solutions containing 210 g of Na_2CO_3 per liter, with and without added NaCl.

Table 18 shows that the extractions were better than those made on the original sinter (table 17), but they were still unsatisfactory in the presence of NaCl.

TABLE 18.—*Extraction of annealed sinter T_a with solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride*

[Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter=2.0. Weight of sinter per liter of extracting solution = 561 g. High-speed stirring]

Experiment	NaCl in extracting solution	Temperature of extraction	Time of extraction	Al_2O_3 recovery
	g/liter	° C	min	%
1	0	70	20	82.7
2	100	70	10	76.5
3	100	70	20	76.7
4	0	80	10	79.6
5	100	80	10	76.0

However, annealing caused a considerable improvement in extractions of alumina at 70° C from sinter R_a, as shown by comparison of tables 17 and 19. A corresponding improvement resulted from the annealing of sinter T'_a. Furthermore, the extractions of alumina from both sinters were not seriously affected by high concentrations of sodium chloride when the molar ratio of sodium carbonate in the solutions to alumina in the sinters was increased from 2.0 to 2.5.

The extractions shown in table 19 were unexpectedly large, especially for sinter R_a, which even before annealing contained very little beta-dicalcium silicate and glass. It is known, however, that dicalcium silicate forms extensive solid solutions with various oxides, and a possible cause of the increased extractions might be the elimination of calcium aluminate from solid solution in dicalcium silicate. Such ex-solution would be favored by annealing. Rankin and Wright in

TABLE 19.—*Extractions at 70° C of annealed sinters, R_a and T'_a, with solution containing 210 g of sodium carbonate per liter and various amounts of sodium chloride*

[High-speed stirring]

Experiment	Sinter	Quantity of sinter extracted	Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter	NaCl in extracting solution	Time of extraction	Al_2O_3 recovery	$\frac{SiO_2}{Al_2O_3} \times 100$ in solution
		g/liter		g/liter	min	%	
1	R_a	550	2.0	0	10	93.5	2.48
2	R_a	550	2.0	100	10	89.6	1.91
3	R_a	550	2.0	200	10	83.9	1.54
4	T'_a	571	2.0	0	10	90.2	2.41
5	T'_a	571	2.0	100	10	86.6	2.17
6	T'_a	571	2.0	200	10	81.0	1.51
7	R_a	440	2.5	0	10	92.9	2.96
8	R_a	440	2.5	100	10	92.4	1.89
9	R_a	440	2.5	200	10	90.4	1.21
10	R_a	440	2.5	200	20	90.2	1.34
11	R_a	440	2.5	200	30	92.9	1.50
12	T'_a	457	2.5	0	10	94.6	2.39
13	T'_a	457	2.5	100	10	94.4	1.49
14	T'_a	457	2.5	200	10	92.9	1.09
15	T'_a	457	2.5	200	20	92.2	1.23
16	T'_a	457	2.5	200	30	89.8	1.33

TABLE 20.—*Compositions of extracts and washes from extractions of annealed sinters, with solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride*

[High-speed stirring]

Experiment	Sinter	Quantity of sinter extracted	Molar ratio of Na₂CO₃ in solution to Al₂O₃ in sinter	NaCl content	Temperature of extraction	Time of extraction	Extract Volume	Extract Al₂O₃ content (g)	Extract Al₂O₃ content (g/liter)	Extract $\frac{SiO_2}{Al_2O_3}\times100$	Wash Al₂O₃ content	Wash $\frac{SiO_2}{Al_2O_3}\times100$	First repulp Al₂O₃ content	First repulp $\frac{SiO_2}{Al_2O_3}\times100$	Second repulp Al₂O₃ content	Second repulp $\frac{SiO_2}{Al_2O_3}\times100$	Third repulp Al₂O₃ content	Third repulp $\frac{SiO_2}{Al_2O_3}\times100$	Over-all Al₂O₃ extraction	Over-all $\frac{SiO_2}{Al_2O_3}\times100$ in solution
		g/liter		g/liter	°C	min	ml	g	g/liter		g		g		g		g		%	
1	Rₐ	440	2.5		70	30	58	5.39	93	4.35	2.29	3.82	0.071	6.7	0.019	8.1			95.2	4.23
2	Rₐ	440	2.5	100	70	10	67	3.70	55	2.45	2.01	1.74	.800	0.90	.194	0.26	0.101	1.3	84.3	1.97
3	Rₐ	440	2.5	100	70	20	65	4.20	65	2.71	2.20	2.46	.652	.94	.206	.20	0.104	1.3	91.2	2.39
4	Rₐ	440	2.5	100	70	30	51	4.27	84	3.30	2.72	2.93	.554	1.32	.174	.86	.045	3.3	96.0	2.98
5	Rₐ	440	2.5	150	70	10	67	4.24	63	2.43	2.20	2.12	.536	0.80	.584	.50	.096	1.1	94.9	2.07
6	Rₐ	440	2.5	150	70	20	58	4.23	73	2.59	2.52	2.31	.370	1.22	.666	.63	.190	0.74	97.5	2.23
7	Rₐ	440	2.5	150	70	30	50	4.12	82	2.78	2.64	2.44	.432	0.95	.700	.57	.214	.56	98.2	2.34
8	Rₐ	440	2.5	200	70	10	64	3.74	58	1.79	2.14	1.65	.548	.40	1.000	.40			89.7	1.49
9	Rₐ	440	2.5	200	70	20	58	3.89	67	2.10	2.55	1.80	.380	.95	0.585	.51			90.7	1.80
10	Rₐ	440	2.5	200	70	30	56	3.63	65	2.17	2.66	1.83	.842	1.09	.360	.70	.168	.71	93.9	1.83
11	T'ₐ	457	2.5	0	70	30	46	4.22	92	3.84	3.22	2.73	.268	7.8	.024	31.0	.008	46.0	95.8	3.64
12	T'ₐ	457	2.5	100	70	30	54	3.84	71	3.02	2.45	2.57	.994	1.13	.148	0.20	.032	1.2	92.4	2.56
13	T'ₐ	457	2.5	150	70	20	62	3.70	60	2.27	2.23	2.11	.730	0.70	.424	.45	.166	0.84	89.7	1.92
14	T'ₐ	457	2.5	150	70	30	52	3.65	71	2.70	2.50	2.32	.780	.76	.608	.62	.087	1.0	94.3	2.19
15	T'ₐ	457	2.5	200	70	10	64	3.50	55	2.02	1.92	1.98	.418	.62	1.174	.42			87.6	1.64
16	T'ₐ	457	2.5	200	70	20	65	3.76	58	2.06	1.98	1.82	.374	1.04	1.045	.42			89.5	1.70
17	T'ₐ	457	2.5	200	70	30	54	3.64	67	2.22	2.13	2.04	.468	1.03	0.974	.44			90.2	1.94
18	T'ₐ	457	2.5	150	80	30	40	3.20	80	2.47	2.72	2.61	.568	0.92	1.084	.44	.131	1.1	95.4	2.10
19	T'ₐ	457	2.5	150	90	30	24	2.17	90	2.92	3.26	2.45	2.262	.72	0.330	.76	.041	1.5	99.8	2.02
20	T'ₐ	507	2.25	100	70	30	45	3.52	78	3.13	3.29	2.81	1.182	.81	.202	.24	.084	1.8	92.2	2.55
21	T'ₐ	507	2.25	150	70	30	54	3.77	70	2.69	2.67	2.34	1.128	.76	.484	.17	.070	1.0	90.4	2.14

their study of the system CaO–Al$_2$O$_3$–SiO$_2$ [16] were not able to detect solid solution of aluminates in dicalcium silicate, but Green [17] has shown that in the more complex systems containing Fe$_2$O$_3$, Na$_2$O, etc., the occurrence of rather extensive solid solution of alumina-bearing compounds in dicalcium silicate is possible.

To ascertain the distribution of alumina between the extracts from the sinters and successive washings of the residues, the experiments listed in table 20 were performed. Each extraction was made with
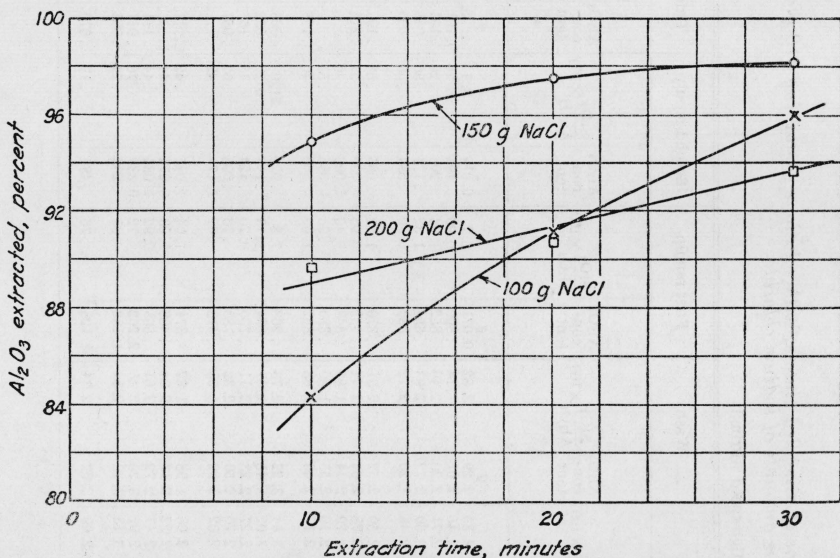

FIGURE 16.—*Rate of extraction at 70° C of alumina from sinter R$_a$ (i. e., sinter R after annealing) with solutions containing 210 g/liter of Na$_2$CO$_3$ and various amounts of NaCl.*

a 100-ml portion of a solution containing 210 g of Na$_2$CO$_3$ per liter and the indicated amounts of NaCl. After removal of the extract by filtration, the residue was washed with a solution containing the same concentration of sodium chloride as that in the original extraction. The residue was washed with a 100-ml portion of the solution and then was repulped two or three times, for 3 minutes each time, in 200-ml portions of the wash solution. The four or five filtrates thus obtained in each experiment were analyzed separately for SiO$_2$ and Al$_2$O$_3$.

Figure 16 shows the rate of extraction of alumina from sinter R$_a$ at various concentrations of sodium chloride in the extracting solutions. The best extractions at 10, 20, and 30 minutes were obtained when the sodium chloride concentration was 150 g/liter. At 100 g of NaCl per liter a longer extraction period than 30 minutes is apparently necessary. Figure 17 permits comparisons of the effects of various concentrations of sodium chloride on the 30 minute extractions. A concentration of 150 g of NaCl per liter appears to be the optimum, and above this a marked decrease in extraction occurs. As shown in this figure, the quantity of SiO$_2$ in the extracts decreases linearly with increase in the NaCl concentration of the solutions.

Extraction of sinter R_a with Na_2CO_3-NaCl solution of suitable concentration thus has a twofold advantage over extraction with Na_2CO_3 solution alone, in increasing the quantity of Al_2O_3 dissolved and decreasing that of SiO_2. If it is assumed that SiO_2 and Al_2O_3 will be removed from solution in approximately equal percentages during desilication, the net recoveries of alumina in experiments 1 (no NaCl) and 7 (150 g of NaCl per liter), table 20, will be 91 and 96 percent, respectively.
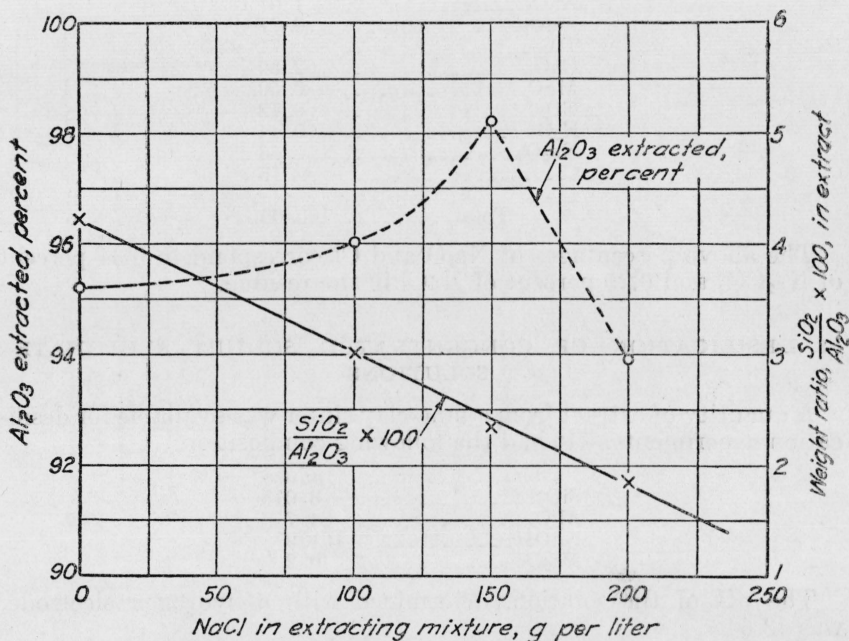

FIGURE 17.—*Effect of sodium chloride on recovery of* Al_2O_3 *and on silica-alumina ratio in extracts from sinter* R_a.

Initial solutions contain 210 g/liter of Na_2CO_3 and various amounts of NaCl. Extraction temperature = 70° C; time = 10 min.

A slight disadvantage of the use of sodium chloride is the reduction it causes in the Al_2O_3 contents of the extracts. Thus, with 0 and 150 g of NaCl per liter in the initial solutions, the concentrations of Al_2O_3 in the extracts from sinter R_a are 93 and 82 g of Al_2O_3 per liter, respectively. The corresponding values for sinter T'_a are 92 and 71 g of Al_2O_3 per liter, respectively.

The extractions of Al_2O_3 from sinters R_a and T'_a are practically identical in the absence of NaCl, but most of the extractions of sinter T'_a with Na_2CO_3-NaCl solutions are several percent less than those of sinter R_a. In order to determine the effect of increased temperature, extractions of sinter T'_a were made at 80° and 90° C (experiments 18 and 19). At 90° C practically all the Al_2O_3 in the sinter was obtained in solution. The volumes of the extracts obtained at the higher temperatures were considerably less than those at 70° C.

Extractions 20 and 21 were made using a molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter of 2.25 instead of 2.5. Comparison of

corresponding extractions shows that the lower molar ratio is satisfactory at 100 g of NaCl per liter in the initial solution but not at 150 g of NaCl per liter.

An analysis was made of the residue from extraction 4 after washing with hot water and drying at 110° C. The following values were obtained:

	%
SiO_2	24. 77
Al_2O_3	1. 01
Fe_2O_3	0. 77
TiO_2	. 71
CaO	62. 69
MgO	0. 50
CO_2	8. 72
H_2O	0. 44
Na_2O	. 33
Cl	. 15
Total	100. 09

The above percentages of Na_2O and Cl correspond to 0.34 percent of Na_2CO_3 and 0.25 percent of NaCl in the residue.

8. DESILICATION OF CONCENTRATED SODIUM ALUMINATE SOLUTIONS

A quantity of extract from a lime-clay sinter was available for desilication experiments. It had the following composition:

	g/liter
SiO_2	3. 015
Al_2O_3	84. 7
NaOH	101. 9
Na_2CO_3	40. 2

The pH of the solution, determined with a hydrogen electrode, was 13.64.

Sodium chloride was added to 500-ml portions of this extract to give 100, 150, and 200 g of NaCl per liter of solution. These portions and like volumes of the original extract were placed in iron containers fitted with reflux condensers and each solution was boiled for 2 hours with various amounts of synthetic sodalite prepared from dehydrated kaolin. Analyses of the resulting solutions for SiO_2 and Al_2O_3 gave the values shown in table 21.

TABLE 21.—*Desilication of concentrated sodium aluminate extract containing various amounts of sodium chloride, by boiling for 2 hr with synthetic sodalite*

Experiment	NaCl in solution	Sodalite added as seed	Composition of solution after desilication		
			SiO_2	Al_2O_3	$\frac{SiO_2}{Al_2O_3} \times 100$
	g/liter	g/liter	g/liter	g/liter	
1	0	10	0. 344	81. 4	0. 42
2	100	10	. 211	81. 1	. 26
3	150	10	. 220	81. 1	. 27
4	200	0	. 371	80. 7	. 46
5	200	10	. 139	80. 9	. 17
6	200	20	. 081	81. 0	. 10
7	200	50	. 040	80. 9	. 05

Although the desilication improved as the sodium chloride concentration increased, undesirably large amounts of silica remained dissolved when the quantity of seed used was 10 g/liter of solution. It was thought that this amount of seed might be insufficient in view of the large amount of silica in the extract. To eliminate the silica completely from 500 ml of solution would require the precipitation of 8.1 g of sodalite. Accordingly, the amount of seed was increased to 20 and 50 g/liter in experiments 6 and 7, respectively, and improved desilications were obtained.

In experiment 4, the extract containing 200 g of NaCl per liter was boiled without the addition of seed. The precipitate that was formed was separated by filtration, washed with alcohol and ether, and examined microscopically. It was composed entirely of very small isotropic crystals having an index of refraction close to that of sodalite. Analysis gave the following composition expressed in molar ratios: $1.03 \, Na_2O:1.00Al_2O_3:1.67SiO_2:0.23NaCl:3.06H_2O$. The composition of this precipitate differs considerably from the theoretical proportions of sodalite, $Na_2O.Al_2O_3.2SiO_2.0.67NaCl$. If the material precipitated in the presence of seed shows a corresponding departure from the composition of sodalite, it might be anticipated that the seed charge would become less effective as it is used in successive desilications.

To determine whether such deterioration occurs, the experiments recorded in table 22 were carried out. The same desilication procedure as before was followed, using 500-ml portions of the extract containing 100 g of NaCl. In the first cycle, 25 g of sodalite was used. The sodalite recovered after this desilication was washed with hot water, alcohol, and ether, and dried in air. A 25-g charge of this material was then used for desilication of a second batch of solution. The same procedure was repeated in a third desilication.

The original sodalite had a composition corresponding to the following molar ratios: $0.99Na_2O:1.00Al_2O_3:2.01SiO_2:0.61NaCl:0.54H_2O$. After this material had been used in three successive desilications, as indicated in table 22, it was reanalyzed and the following molar ratios obtained: $1.00Na_2O:1.00Al_2O_3:2.04SiO_2:0.56NaCl:1.96H_2O$. Thus, it appears that the material precipitated in the presence of seed has very nearly the theoretical composition of sodalite. However, a slight decrease in NaCl content and increase in water of hydration of the mixture of seed and precipitate had occurred.

It seemed possible that the sodium chloride content of the sodalite, and also its desilication efficiency, might be restored by treating the

TABLE 22.—*Effectiveness of sodalite on repeated use for desilicating a concentrated sodium aluminate solution (cycles 1, 2, and 3), and the subsequent improvement caused by boiling the used sodalite for 2 hr with a solution saturated with NaCl (cycle 4)*

[Volume of sodium aluminate solution, containing 100 g of NaCl, 500 ml; quantity of sodalite, 25 g; time of boiling, 2 hr.]

Cycle	$\dfrac{SiO_2}{Al_2O_3} \times 100$ in desilicated solution
1	0.053
2	.067
3	.080
4	.037

used preparation with sodium chloride solution. Accordingly, the seed charge recovered from cycle 3, table 22, was boiled for 2 hours with a saturated salt solution, and 25 g of this product was used to desilicate another batch of extract. As shown in table 22, the seed charge than gave a more effective desilication than the original sodalite.

The desilications recorded in table 23 were made on duplicates of extracts, having the same numbers, listed in table 20. These extracts, in volumes of 120 to 150 ml, were boiled with synthetic sodalite, in the proportion of 25 g/liter of solution. It was found to be advantageous to disperse the sodalite in the extracts by high-speed stirring before boiling.

All of the desilicated extracts (table 23) are sufficiently low in silica and high in alumina to permit differential precipitation of alumina containing about 0.02 percent of silica, according to the method described by McCulloch [7].

TABLE 23.—*Desilication of extracts from sinters R_a and T'_a, by boiling with synthetic sodalite*

[Sodalite, 25 g/liter]

Experiment	Sinter	NaCl in extracting solution	Al$_2$O$_3$ in extract	Time of boiling for desilication	$\frac{SiO_2}{Al_2O_3} \times 100$ in extract	
					Before desilication	After desilication
		g/liter	g/liter	hr		
4	R$_a$	100	84	2	3.30	0.10
7	R$_a$	150	82	1	2.78	.082
7	R$_a$	150	82	2	2.78	.077
10	R$_a$	200	65	2	2.17	.057
12	T'$_a$	100	71	1	3.02	.15
14	T'$_a$	150	71	1	2.70	.085
16	T'$_a$	200	58	2	2.06	.060

9. THEORY OF SODALITE DESILICATION

It has been shown that desilication of a sodium aluminate solution is favored by the following factors: (1) The presence of a high concentration of sodium chloride in the solution, (2) the presence or formation of a seed charge of sodalite, (3) a boiling temperature at atmospheric pressure or higher temperatures and pressures, and (4) sufficient time for precipitation of sodalite to approach completion.

In the initial extraction of the lime-clay sinters, the above conditions must be avoided, insofar as possible, to prevent losses of soda and alumina that would result from formation of sodalite at this stage. Because economical operation of the process requires a high concentration of sodium chloride in the extracting solution, the precipitation of sodalite is prevented by using a short extraction time at a temperature below boiling, and with the exclusion of material that might serve as seed.

Sodalite liberates sodium chloride to solution when in contact with boiling water [6] and thus is incongruently soluble. The end product resulting from complete liberation of the sodium chloride in sodalite is probably the comparatively soluble hydrated sodium aluminum silicate formed in the Bayer process. At high concentrations of sodium chloride in solution, the solubility of sodalite becomes increas-

ingly congruent and diminishes to very low values. Sodium hydroxide, however, has an effect opposite to that of sodium chloride, and sodalite becomes less stable as the alkalinity of the solution rises.

The function of the seed charge during desilication is to induce the precipitation of crystalline sodalite. As shown in the preceding section, the material precipitated from solution in the absence of seed has a composition differing considerably from that of sodalite but, when seed is present, the precipitate has very nearly the theoretical composition.

10. FLOW SHEET AND SUMMARY OF PROCESS

A suggested commercial process for the extraction of alumina from clay, by the lime-sinter method developed in this study, is shown in figure 18.

The composition of the clay given in the flow sheet is that of a kaolin used in this investigation. Minor constituents of the kaolin are omitted in order to simplify the diagram. A mixture of clay and limestone is prepared by either wet or dry process grinding and mixing. The composition of the resulting material on an ignited basis should correspond approximately to a point on the line joining $2CaO.SiO_2$ and the quintuple point $CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $2CaO.SiO_2$ in the CaO-Al_2O_3-SiO_2 diagram. Allowance is made for the lime and alumina required for the formation of $CaO.TiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, or $Na_2O.Al_2O_3$ with any TiO_2, Fe_2O_3, or Na_2O in the raw materials.

The equipment described by McLarmour, McMaster, and Jacques [18] appears to be particularly well adapted for burning the raw mix and annealing the resulting clinker. This apparatus consists of an ordinary rotary kiln in series with a rotary cooler carrying a burner installed at its feed end. The clinker discharged from the primary kiln can be annealed in the cooler at a rate determined by its speed of rotation and by adjustment of the burner.

Complete dusting of the annealed clinker obviates the need of grinding. The material is extracted for about one-half hour at 60 to 80° C with a solution containing approximately 200 g of Na_2CO_3 and 150 g of $NaCl$ per liter. High-speed stirring of the slurry is used.

On completion of the extraction period, the mixture is filtered and an extract containing 70 to 80 g of Al_2O_3 and 1 to 2 g of SiO_2 per liter is obtained. By subjecting the residue to counter-current washing with salt solution, it is anticipated that the concentration of Al_2O_3 in the wash water can be built up to approach that in the extract. The residue may then be washed with water and stock-piled as a raw material for the manufacture of portland cement.

The solution, plus concentrated washings, is next desilicated by boiling it for 1 hour with a seed charge of synthetic sodalite (25 g/liter of solution). After filtration, the sodalite in excess of that required for seed for the next batch is returned to the first stage of the process, allowance for its addition being made in calculation of the amount of limestone to be used in the subsequent batch. By this means, the alumina and soda in the excess sodalite are recovered.

Alumina is precipitated as gibbsite by passing carbon dioxide into the desilicated solution. Scrubbed gases from the kiln are the source of carbon dioxide. In order to avoid contamination by silica, the precipitation of alumina is not carried to completion. However, in
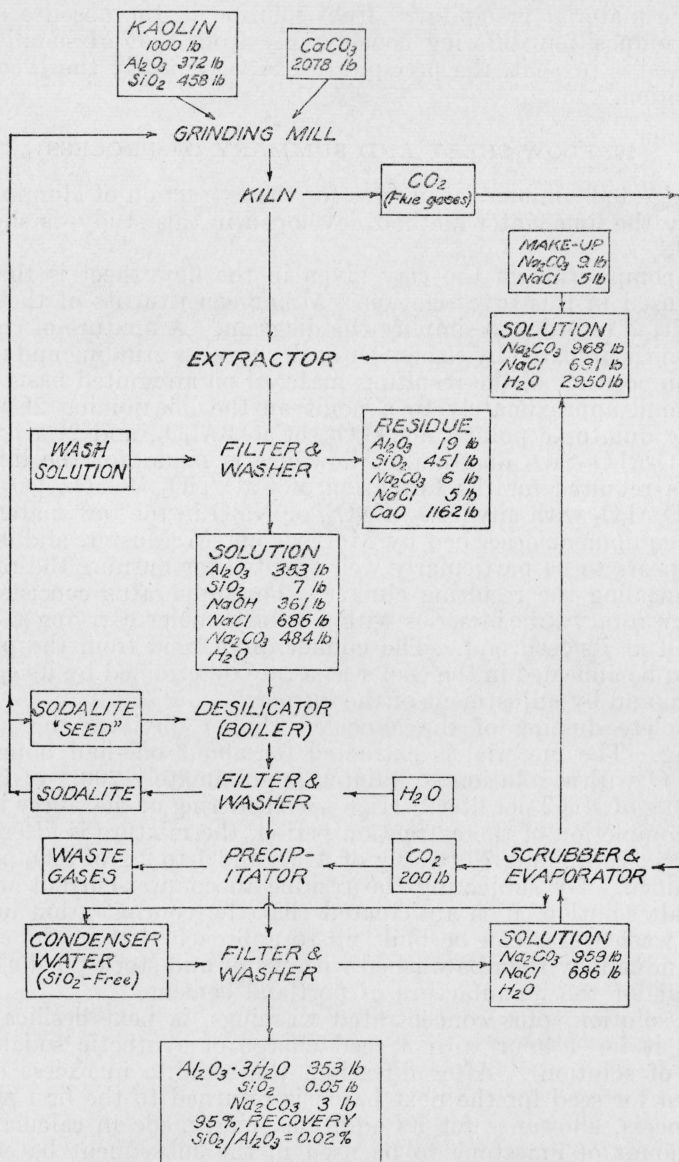
RECOVERY OF ALUMINA
FROM KAOLIN

KAOLIN
1000 lb
Al_2O_3 372 lb
SiO_2 458 lb

$CaCO_3$
2078 lb

GRINDING MILL

KILN → | CO_2 (Flue gases) |

MAKE-UP
Na_2CO_3 9 lb
NaCl 5 lb

SOLUTION
Na_2CO_3 968 lb
NaCl 691 lb
H_2O 2950 lb

EXTRACTOR ←

| WASH SOLUTION | → | FILTER & WASHER |

RESIDUE
Al_2O_3 19 lb
SiO_2 451 lb
Na_2CO_3 6 lb
NaCl 5 lb
CaO 1162 lb

SOLUTION
Al_2O_3 353 lb
SiO_2 7 lb
NaOH 361 lb
NaCl 686 lb
Na_2CO_3 484 lb
H_2O

| SODALITE "SEED" | → | DESILICATOR (BOILER) |

| SODALITE | ← | FILTER & WASHER | ← | H_2O |

| WASTE GASES | ← | PRECIP-ITATOR | ← | CO_2 200 lb | | SCRUBBER & EVAPORATOR |

CONDENSER WATER (SiO_2-Free)	→	FILTER & WASHER	→	SOLUTION

SOLUTION
Na_2CO_3 959 lb
NaCl 686 lb
H_2O

$Al_2O_3 \cdot 3H_2O$ 353 lb
SiO_2 0.05 lb
Na_2CO_3 3 lb
95% RECOVERY
SiO_2/Al_2O_3 = 0.02%

FIGURE 18.—*Flow sheet of suggested process for extracting alumina from kaolin.*

cyclical operation of the process, complete recovery of the alumina from solution would be obtained and this is indicated in the flow sheet. The hydrated alumina is filtered and washed with water, low in silica to avoid contamination. The residual solution and the washings are used to scrub the kiln-flue gases. This procedure effects evaporation of water from the combined solution and washings, and dust is removed from the gases. Make-up quantities of sodium carbonate and sodium chloride are added to the evaporated and carbonated solution, which is then used for extraction of a fresh batch of sinter. The precipitated gibbsite is dried and calcined for electrolytic reduction to aluminum.

IV. EXTRACTION OF ALUMINA FROM HIGH-SILICA BAUXITES BY THE LIME-SINTER PROCESS

1. MATERIALS

Bauxite B, the composition of which is given in table 1, was selected for study. Other experiments were made on a diaspore bauxite (bauxite E) having the following composition:

	%
SiO_2	18. 16
Al_2O_3	50. 62
Fe_2O_3	11. 37
TiO_2	3. 23
CaO	0. 00
MgO	. 04
Na_2O	. 07
Loss on ignition	16. 27
Total	99. 76

The major part of the iron oxide content of this material was in the ferrous state, as siderite.

Other materials included calcium carbonate, sodium carbonate, sodium chloride, and sodium hydroxide.

2. PROCEDURE, RESULTS, AND DISCUSSION

Calcium carbonate-bauxite mixtures were prepared which, after burning, would contain Al_2O_3 as $CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $4CaO.-Al_2O_3.Fe_2O_3$; SiO_2 as $2CaO.SiO_2$; and TiO_2 as $CaO.TiO_2$. The mixture made from bauxite B, in 100-g batches, was heated in an electric furnace at 1,300° C for 1 hour and cooled slowly, but without careful control of annealing temperatures. Complete dusting of the product occurred on cooling.

Extractions were made of the dusted sinter at 50° C for 2 hours, using a slow-speed shaking machine. Table 24 shows the recoveries of Al_2O_3 obtained after desilication of the extracts with sodalite. The highest extraction was obtained when the molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter was 4.0. Small amounts of NaOH in the initial solutions had little effect on the extractions, but a concentration of 50 g of NaOH per liter (experiment 4) gave a greatly reduced recovery of Al_2O_3.

A sample of sinter B was reheated to 1,300° C, in an electric furnace, held at that temperature for 1 hour, and cooled to 1,150° C at a uniform rate of 1 degree per minute. The dusted sinter was ex-

tracted for ½ hour at 70° C with a solution containing 50 g of Na_2CO_3 and 150 g of NaCl per liter, using high-speed stirring. The residue was washed by the multiple repulping procedure described previously. An over-all recovery of 97 percent of the Al_2O_3 in this sinter was obtained in solution and the over-all SiO_2 was 1.22 percent. The recovery of Al_2O_3 is approximately the same as those obtained from sinters R_a and T_a' under corresponding conditions.

A 3-pound batch of the mixture of calcium carbonate and bauxite E was burned in a gas-fired furnace at 1,300° C for 1 hour and cooled to 1,200° C in 1½ hours. The product, which failed to dust, was ground to pass a No. 200 sieve. Only 71 percent of the alumina in this sinter was obtained in solution by the procedure given in the preceding paragraph.

TABLE 24.—*Extraction at 50° C of lime sinter prepared from bauxite B (84.6 g of sinter per liter of extracting solution)*

[Time of extraction, 2 hr]

Experiment	Composition of extracting solution			Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter	Al_2O_3 on recovery	$\frac{SiO_2}{Al_2O_3}\times100$ in solution
	Na_2CO_3	NaOH	NaCl			
	g/liter	*g/liter*	*g/liter*		%	
1	38	5	136	1.5	76	0.03
2	50	0	179	2.0	80	.07
3	99	5	317	4.0	84	.04
4	38	50	297	1.5	25	.09

To compare the behavior of the lime sinters of bauxites B and E, parallel experiments were made in which samples of the raw mixes were heated to 1,300° C in an electric furnace, held at that temperature for 1 hour, and cooled to 1,150° C at the rate of 2 degrees per minute. The sinter from bauxite B dusted completely, but that from bauxite E failed to dust. As both sinters contained approximately the same amount of Fe_2O_3, the difference in behavior was attributed to the presence of about 37 percent of dicalcium silicate in the bauxite B sinter as compared with 30 percent in that of bauxite E.

It was concluded that bauxite E would have to be mixed with a material of higher silica content to obtain a sinter that would dust satisfactorily. For this purpose a mixture of 75 percent of bauxite E and 25 percent of kaolin (based on ignited weights) was prepared. A sample was heated in an electric furnace to 1,300° C, held at that temperature for 1 hour, and cooled to 1,150° C at 1 degree per minute. The product, which contained about 41 percent of dicalcium silicate, dusted completely. Extractions, made as before, dissolved 88 percent of the Al_2O_3 from the sinter.

It is not known why the extractions of the bauxite E sinters are inferior to those of bauxite B. Analysis of bauxite E for P_2O_5 and Cr_2O_3 showed only traces of these oxides, which, in small amounts, might prevent the complete beta-gamma inversion of dicalcium silicate.

The above experiments appear to indicate that the suitability of an aluminous ore, as a raw material for the extraction of alumina by the lime-sinter method, cannot be accurately predicted without actual laboratory tests. This is because of the numerous factors

which affect the completeness of the beta-gamma inversion of dical-
cium silicate, on which the success of the method depends. In general,
it appears that annealing must be the more prolonged, the higher the
proportion of fluxing oxides in the sinter and the lower the dicalcium
silicate content. Sinters containing as little as 20 percent of dical-
cium silicate can be made to dust, as shown by Lerch and Brownmiller
[15], but a 17-hour annealing schedule was required.

V. POSSIBLE COMMERCIAL SIGNIFICANCE OF METHODS

The principal advantage of preparing sodium aluminate solutions
by the method described in section II consists in the attainment of
a more complete separation of alumina and silica than is given by
the Bayer process. This fact makes it possible to precipitate a con-
siderably greater proportion of alumina from the salt-containing
extract than from the Bayer solution, before contamination of the
precipitated alumina by silica becomes excessive.

In the recovery of soda and alumina from the "red-mud" residues,
the use of an extracting solution containing sodium chloride permits
the subsequent desilication to be carried out at atmospheric pressure
rather than in autoclaves as has been the practice heretofore.

It is believed that the lime-sinter process developed in this study
has considerable commercial promise, particularly as applied to clay,
for the following reasons:

1. Recoveries of approximately 95 percent of the alumina in clay
can be obtained from annealed lime-clay sinters. Such recoveries
are comparable with those obtained by acid extraction of kaolin
clays [10] and exceed values that have been reported for other alkaline
processes [5].

2. Losses of alkali are small.

3. All steps of the process can be carried out at atmospheric pressure.

4. As shown in the flow sheet, the process is simple and no unusual
equipment is required.

In common with other alkaline methods for the extraction of alumina
from clay, this process suffers from the disadvantage of requiring
calcination of the clay with somewhat more than twice its weight of
limestone. Only large-scale operation will show whether the cost
of this step will be sufficiently compensated by the factors listed above·

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