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THE LIME-SINTER PROCESS FOR PRODUCTION OF ALUMINA FROM FLY ASH*

K. S. Chou[1/], W. A. Klemm[2/], M. J. Murtha[1/] and G. Burnet[1/]

INTRODUCTION

Fly ash, the product from burning pulverized coal in power plant furnaces, is produced in large quantities. In 1970, the U. S. production was 28 million tons, and it is expected that by 1980 the production will be around 40 million tons. With this large source of essentially waste material available at convenient locations, near power and transportation, one has the desire to obtain something of value from it.

Fly ash consists essentially of oxides. The oxide present in greatest amount is silica, either free, or combined as silicates and aluminates. The compositions vary, depending on the coal source, but a typical chemical composition of one that we shall designate C-1 is given in Table 1. The oxides of value are alumina and iron oxide.

BACKGROUND

A theoretical analysis of a particular fly ash, (designated here as C-1) by means of phase diagrams of ceramic oxides, indicated that several crystalline substances could be present.[1/] Equilibrium considerations would show mullite, trydimite, iron cordierite, anorthite, fayalite and possibly calcium and magnesium sulfates. In a quick-cooled, non-equilibrium system there could be other crystalline phases as well as a glassy phase or slag.

Since fly ash contains both iron and aluminum values, a process to segregate these components is desirable. Magnetic separation accomplishes this to a reasonable degree. Prior grinding of the

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1/ Levin, E. M., C. R. Robbins, and H. F. McMurdie, Phase Diagrams for Ceramists, American Ceramic Society, Columbus, Ohio, 1964.

Composition of C-1 Fly Ash and Fractions Obtained by Magnetic Separation

Constituent	Chemical Composition, Weight Percent				
	Whole Fly Ash 100 parts	Dry Separation		Wet Separation	
		Magnetics 23.6 parts	Non Magnetics 76.4 parts	Magnetics 26.1 parts	Non Magnetics 68.4 parts
SiO_2	42.36	20.31	47.89	20.83	53.0
Al_2O_3	17.91	10.21	20.04	9.95	22.83
Fe_2O_3	19.29	60.08	6.56	65.00	5.24
CaO	4.49	1.87	4.88	1.32	5.82
MgO	0.71	0.40	0.76	0.42	0.99
Na_2O	0.35	0.18	0.35	0.14	0.31
K_2O	1.72	0.81	1.85	0.71	1.91
SO_3	2.13	0.79	2.04	___c	___c
LOD[a]	0.58	0.13	0.45	0.12	0.56
LOI[b]	10.39	2.13	12.40	1.70	8.46

a. LOD is loss on drying at 110°C

b. LOI is loss on ignition from 110-800°C

c. not detected

Table 1

A B S T R A C T

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by

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A substantial background of literature on methods of extracting alumina from aluminous-siliceous raw materials shows that alumina may be released by addition of calcium oxide (lime) in a high-temperature treatment to produce a sinter or slag from which alumina is extracted using a sodium carbonate solution, the silica being converted to dicalcium silicate. The calcium oxide has a stronger affinity for silica than does alumina, thus leading to release of the alumina for extraction.

Work done at the Ames Laboratory on application of the lime-sinter process to fly ash has resulted in yields of over 50% of the alumina present. The primary variables are temperature, time and ratio of lime to fly ash. Tests have been run using a small number of pellets of lime-fly ash mixtures in a tube furnace at temperatures ranging up to 1400°C. The majority of the iron oxide in the ash is removed by magnetic separation prior to addition of lime. A solid phase transformation leads to a self-disintegrating sinter with proper selection of processing conditions.

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coarse particles to break the magnetic portion from the adhering non-magnetic portion enhances the separation. The magnetic fraction can be considered an iron ore. The non-magnetic fraction, low in iron, can be treated in various ways to extract alumina or another aluminum compound. Four proposed schemes for recovering aluminum values are:

1. Extraction of alumina by an acid process.
2. Lime sinter or lime-soda sinter processing followed by leaching to remove sodium aluminate from which alumina can be separated by crystallization.
3. Hydrochemical treatment in a modified Bayer process with added lime to separate insoluble calcium silicate and a sodium aluminate solution from which alumina can be crystallized.
4. Selective chlorination in several steps to remove aluminum chloride.

Any of the above processes could then lead to recovery of aluminum metal.

Acid processes have worked well in removing alumina from non-refractory, highly siliceous materials such as clays, in the raw state or when calcined up to 900°C.[2-5/] When the calcining temperature exceeded 900°C, the alumina recovery was drastically reduced. This was due to the formation of refractory forms of alumina and alumina-silica complexes, which did not exist in the raw clay. That these refractory forms of alumina and alumina-silica bonds already exist in fly ash was found in some earlier work. Cavin[6/] showed their presence by X-ray studies and some attempts at solution in acid. He obtained alumina recoveries of three to five percent in cold sulfuric acid at

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2/ Tilley, G. S., R. W. Millar, and O. C. Talston, Acid Processes for the Extraction of Alumina. U. S. Bur. Mines Bull. 267, 1927.

3/ Ozherel'ev, D. I. Extraction of Aluminum Oxide from Clay by Hydrochloric Acid. Trudy Khim - Technol. Fak. Donetsk, Ind. Inst., Nol., 1956, 87-95 (CA 53: 13522c, 1959).

4/ Tucker, Stanley, Aluminum from Siliceous Clays, U. S. Pat 2, 847, 279, Aug. 12, 1958 (CA 52: 18159h, 1958).

5/ Anaconda Company, Alumina from Clay, Fr. Pat. 1, 324, 189. June 2, 1962.

6/ Cavin, D. C., A Study of Iron and Aluminum Recovery from Power Plant Fly Ash. M. S. Thesis, Ch. E. Dept., Iowa State University, Ames, Iowa, 1973.

all concentrations up to 98% H_2SO_4, and only slightly higher recoveries in boiling sulfuric acid solutions. Patel obtained only modest increases in solubilization by ball milling fly ash up to 16 hours and subsequently extracting with boiling 25% sulfuric acid solution. He obtained 3.3% recovery of alumina with no grinding, and 5.4% recovery with 16 hours of milling.[7]

Silica has the ability to form compounds with other oxides, greatly reducing their ability to react. Richardson[8] studied the calcium oxide-silicon dioxide system and showed that in the binary melt at 1600°C, when the calcium oxide mole fraction was less than 0.40, its activity was essentially zero, and that of silica was high. The fly ash used in this present investigation contained a high proportion of silica. By deduction we infer that this high fraction of silica would lower the activity of alumina many orders of magnitude, rendering it unavailable to reagents in the ordinary sense.

LIME-SINTER PROCESS

In order to release alumina from a refractory aluminosilicate compound, it is necessary to provide a reagent which has a stronger affinity for silica than does alumina. The chosen reagent is calcium oxide provided by limestone in the lime sinter or Pederson process used on highly siliceous bauxites. Investigators have found that to release the alumina from an aluminosilicate compound, the ratio of calcium oxide to silica should be 2.0 for the silica and also there must be sufficient calcium oxide to give a $CaO:Al_2O_3$ ratio of 5:3[9-12]

7/ Patel, G. G., Alumina from Fly Ash, A senior project report. Ch. E. Dept., Indiana Institute of Technology, Ft. Wayne, Indiana (1975).

8/ Richardson, R. D., Thermodynamic Aspects of Molten Slags. Symposium on Molten Slags and Salts, Inst. of Mining & Metallurgy, London, 1953, pp. 75-100.

9/ Zhukovetskii, V. V., Preparation of Alumina from Kyanite. Izv. vys. ucheb. Zavod, Isvet. Met. 4 (5), 1961, pp. 110-116.

10/ Khodak, L. P., S. I. Kuznetsov, A. I. Ivanov, O. V. Serebrennikova, and J. G. Moleva. The Recovery of Alumina from Alumin-Containing Blast Furnace Slag. Izvest. Sibir. Otdel. Akad. Nauk, S.S.S.R. No. 2, 1959, pp. 19-28 (CA 53: 19745d, 1959).

11/ Moleva, M. G., A. I. Ivanov and L. P. Khodak. Effect of Calcium Oxide Content on the Structure and Properties of Self-disintegrating Calcium Aluminate Slags. Igvest. Sibir. Otdel, Akad. Nauk, S.S.S.R. No. 8, 1959, pp. 58-61 (CA 54: 6443, 1960).

12/ Magyarossy, I., D. Bartok and A. Hejja. Utilization of Calcium-Aluminate Slags in the Aluminum Industry. Femipari Kutato Intezet Kozlemenyer, 1956, pp. 96-115, (CA 53: 13929g, 1959).

If less lime is used, the alumina recovery is less. In view of these required ratios, it is apparent that a high lime or limestone requirement is needed to release alumina from fly ash.

Extensive work has been done by Grim, Machin, and Bradley[13/] with the lime-sinter and lime-soda sinter processes. They studied the effects of $CaO:Al_2O_3$ ratios and of sintering temperatures on the recovery of alumina from various types of clays. Extraction of alumina from the sintered material was done with sodium carbonate solutions. In general, the highest extractions were obtained with a $CaO:Al_2O_3$ ratio of 5:3 in the sintered material, considering only that part of CaO beyond that required to react with silica to give dicalcium silicate, $2CaO \cdot SiO_2$. Generally the alumina yields were 80-95% when optimum sintering temperatures were used. For most of the clays, the optimum sintering temperature range was 1370-1390°C when the optimum calcium oxide:alumina ratio was used. On the basis of this and other work, similar treatment appeared promising for extraction of alumina from fly ash.

Cavin at Iowa State University[6/] in his work of 1973, performed some exploratory sintering experiments with fly ash C-1 at 1320°C (maximum temperature on the available furnace). With $CaO:Al_2O_3$ ratios of 1.2, 1.4 and 1.6, the extraction of alumina was less than 0.3%. At a ratio of 1.8, the extraction was 2.1%. Undoubtedly the low sintering temperature was responsible for the low yields.

The studies reported here concern the more extensive treatment of the same fly ash, C-1, by means of the lime-sinter process to render the alumina soluble in a sodium carbonate solution to give sodium aluminate. This work was done during 1975 at Ames Laboratory, ERDA, at Iowa State University. The purpose was to study the effect of the primary variables, sintering temperature, sintering time, and lime-fly ash ratio on alumina recovery. The effect of sodium carbonate leaching conditions on the sintered material was also investigated.

EQUIPMENT AND PROCEDURE

Since the iron and aluminum values both were of interest, magnetic separations were done first. Both wet and dry methods were used.

13/ Grim, R. E., J. S. Machin and W. S. Bradley, Amenability of Various Types of Clay Minerals to Alumina Extraction by the Lime Sinter and Lime-Soda Sinter Processes. Div. of State Geological Survey, Bulletin No. 65, Urbana, Illinois, 1945.

6/ Cavin, D. C., A Study of Iron and Aluminum Recovery from Power Plant Fly Ash. M. S. Thesis, Ch. E. Dept., Iowa State University, Ames, Iowa, 1973.

Magnetic Separation

The wet method of separation consisted of making a slurry of 100 grams of fly ash in 500 ml of water in a separatory funnel placed between the poles of a strong horseshoe magnet. The magnetic material adhered to the inside of the funnel next to the poles of the magnet. The non-magnetic material, still suspended in the water was run out of the funnel into a container. The funnel was removed from the magnet and the magnetic material was washed out into another container. Each fraction was repeatedly treated by the same method until visual observation indicated no further separation.

The dry method consisted of using an electromagnet inclined so that a plastic board placed across the poles had a slope of 25-30° from the horizontal. After energizing the magnet and setting the board in motion by a mechanical vibrator placed against the bottom of the board, the fly ash was poured down the sloping board. The mechanical vibrations assisted the non-magnetic particles to slide down the board into a container. The magnetic particles which adhered to the board, were removed by de-energizing the magnet. Each portion was repeatedly treated until visual observation indicated no further separation.

The analyses of the magnetic and non-magnetic fractions obtained by these two methods are given in Table 1.

The wet method gave a higher iron concentration in the magnetic fraction and a higher alumina concentration in the non-magnetic fraction than the dry method. In the wet process the sulfur oxides were eliminated indicating they were water soluble. There was a total loss of weight of 5.5%. Previous work by Cavin[6/] showed a 4.33% loss of weight by water extraction.

The alumina recoveries were nearly the same, 85.53% in the dry process and 87.3% in the wet process. Because subsequent production was needed for more material, the dry process was used for preparation of the non-magnetic fly ash fractions used in sintering, since we found it difficult to justify the wet separation with its added filtration and drying operations.

Preparation of Sintered Samples

The dry powdered non-magnetic fly ash fraction was mixed with the calculated amount of calcium carbonate and milled in a ball mill for two hours. The mixtures prepared were calculated to give ratios of $CaO:Al_2O_3$ from 1.51 to 2.22. The compositions are given in Table 2.

6/ Cavin, D. C., A Study of Iron and Aluminum Recovery from Power Plant Fly Ash. M. S. Thesis, Ch. E. Dept., Iowa State University, Ames, Iowa, 1973.

COMPOSITION OF SINTERED PELLETS

Mix	Composition		Weight Percent*	Ratio†
	SiO_2	Al_2O_3	CaO	CaO/Al_2O_3
A	25.72	10.75	56.95	1.51
B	25.49	10.66	57.34	1.67
C	25.32	10.59	57.62	1.78
D	25.22	10.55	57.80	1.85
E	25.12	10.50	57.94	1.91
F	25.02	10.46	58.11	1.99
G	24.68	10.32	58.68	2.22

* Compositions made to these values by adding CaO as $CaCO_3$ before sintering. Other constituents not listed.

† Ratio after accounting for a ratio of 2.0 for CaO/SiO_2.

Table 2

About eight to nine percent water was added to make a good pellet. The various mixtures were pressed into pellets measuring ½ inch diameter by ¼ inch thick. A Carver press was used and the pressing pressure was 6000 psig.

The pellets were placed on a bed of alundum powder in an alumina boat. The powder was used to prevent sticking to the boat. After pre-drying the charge, the boat with pellets was pushed into the pre-heated alundum tube furnace with a high alumina refractory rod fast enough to prevent undue reaction during the heatup, but slow enough to prevent thermal shock to the refractories. The apparatus used is shown in Figure 1. During the sintering operation, the pellet temperature was measured with an optical pyrometer. The charge was held at the sintering temperature for the specified time. The furnace was then turned off and cooled at a rate of 200°C/hr. until it reached 1000°C. The boat was then pushed out of the furnace as quickly as practicable to avoid thermal shock. This removal took about 10 minutes. The pellets were cooled in air and then stored in a desicator until further processing. Some of the pellets disintegrated mechanically during cooling.

The chemical reactions which occur in the sintering process are:

(A) $CaCO_3 \longrightarrow CaO + CO_2\uparrow$

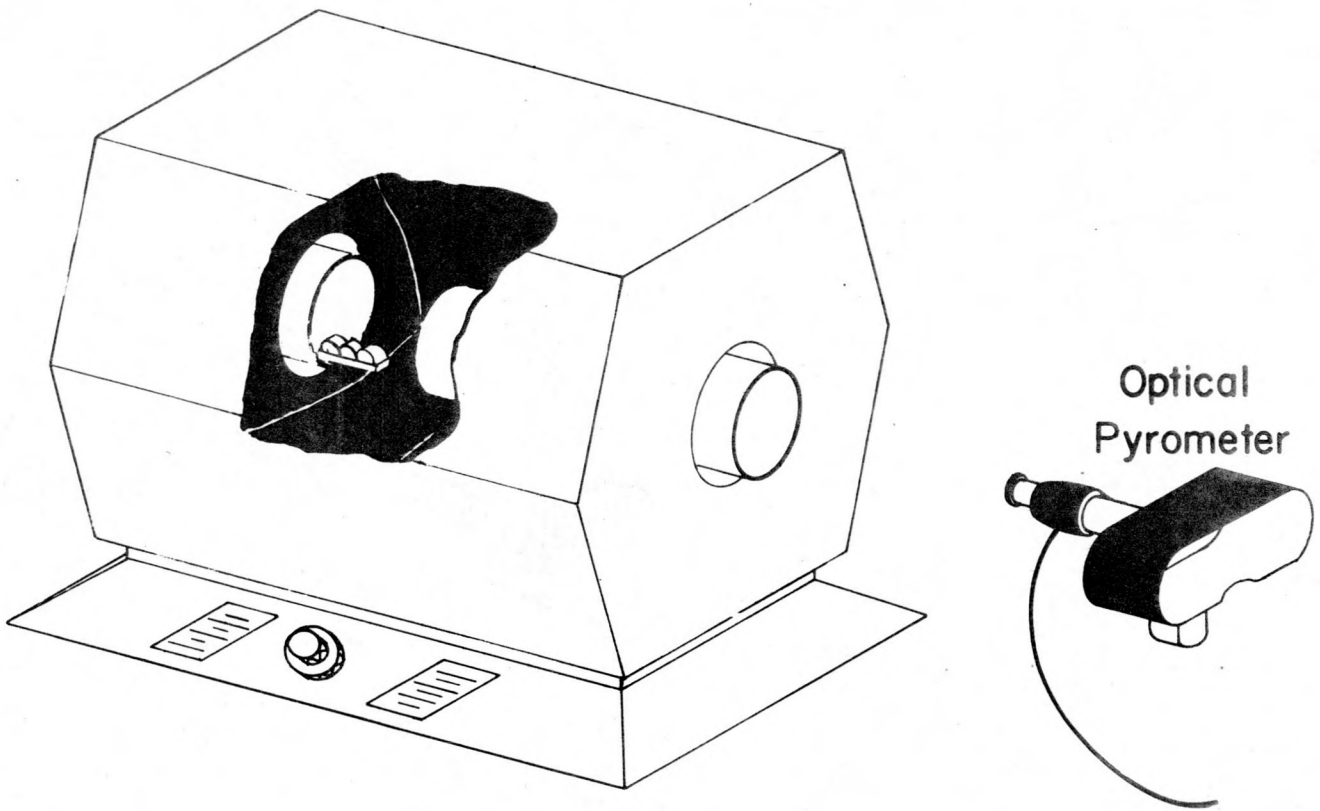
(B) CaO + aluminosilicates $\longrightarrow 2CaO\cdot SiO_2 + 5CaO\cdot 3Al_2O_3$

The dicalcium silicate formed in sintering is only slowly reacted in the subsequent leaching operation. The calcium aluminate is more readily soluble.

EXTRACTION OF ALUMINA FROM SINTERED MATERIAL

The extraction process used here was basically similar to that used by Grim and coworkers.[13/] The cooled pellets from the sintering operation were ground to pass a 200 mesh screen before leaching. Weighed amounts of powdered material were extracted with a three percent solution of sodium carbonate, stirring constantly to prevent settling. Sufficient sodium carbonate solution was provided to furnish 1.66 moles of Na_2CO_3 for each mole of Al_2O_3 present in the sintered material except where this ratio was studied as a variable. The extraction time was 15 minutes and the extraction temperature was 75°C except where temperature was studied as a variable.

13/ Grim, R. E., J. S. Machin and W. S. Bradley, Amenability of Various Types of Clay Minerals to Alumina Extraction by the Lime Sinter and Lime-Soda Sinter Processes. Div. of State Geological Survey, Bulletin No. 65, Urbana, Illinois, 1945.



Tube Furnace with Boat and Pellets

Figure 1

The extract was immediately filtered from the solids and the residue was washed with water to recover all extracted alumina. The combined extract and washings were analyzed for alumina and silica by accepted procedures.

The chemical reactions which occur in the leaching of the sintered material with sodium carbonate are:

$$(C)\quad (5CaO\cdot 3Al_2O_3) + 5Na_2CO_3 + H_2O \longrightarrow 5CaCO_3\downarrow + 6NaAlO_2 + 4NaOH$$

$$(D)\quad 3(2CaO\cdot SiO_2) + 6NaAlO_2 + 15H_2O \longrightarrow 3Na_2SiO_3 + 2(CaO\cdot Al_2O_3\cdot 6H_2O)\downarrow + 2Al(OH)_3$$

$$(E)\quad 2Na_2SiO_3 + 2NaAlO_2 + 4H_2O \longrightarrow (Na_2O\cdot Al_2O_3\cdot 2SiO_2\cdot 2H_2O)\downarrow + 4NaOH$$

Reaction "C" is the desired reaction. It is reasonably rapid giving the required solubilized alumina as sodium aluminate. The calcium carbonate is filtered off with the dicalcium silicate formed in the sintering operation. Reaction "D" which uses some of the product aluminate from reaction "C" adversely affects the alumina yield in that it precipitates some of the alumina. At the same time it solubilizes some of the dicalcium silicate. Reaction "E" also adversely affects the alumina yield since it precipitates more of the solubilized alumina. A proper optimization of leaching conditions is needed to give the greatest yield of alumina at the best purity.

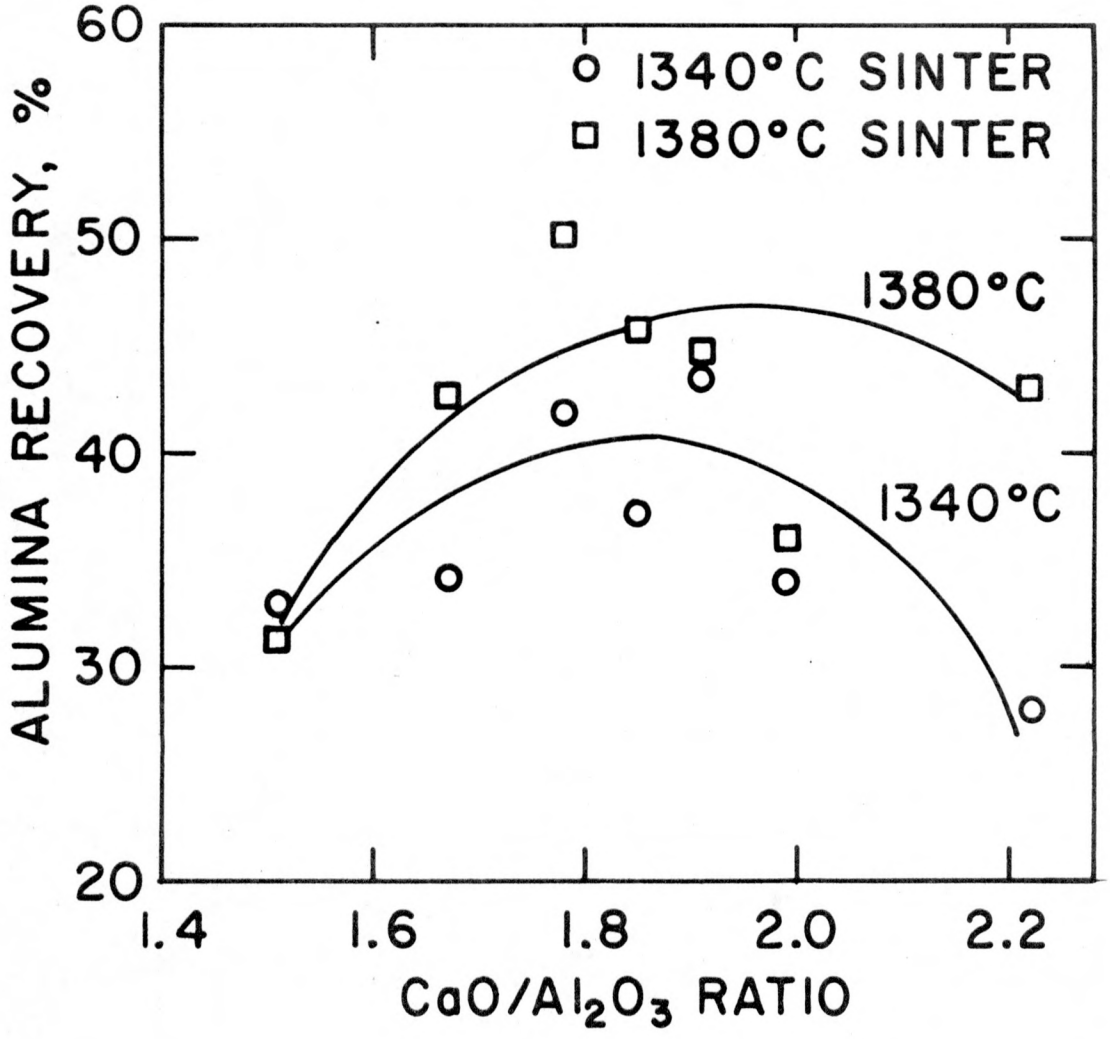
RESULTS AND DISCUSSION

As stated earlier in this paper, it was the purpose of this work to investigate the effect of main variables, sintering temperature, sintering time, and $CaO:Al_2O_3$ ratio during sintering on the alumina recovery from fly ash.

Effect of Lime-Alumina Ratio

Since previous work of this type on clay and shale indicated that the lime-alumina ratio greatly influenced the alumina recovery in the lime sinter process, the first runs investigated here were to explore the effect of ratio at two temperatures, 1340 and 1380°C. The sintering time was kept constant at one hour. The results of these runs are shown in Figure 2. A maximum alumina extraction of 50.2% at a $CaO:Al_2O_3$ ratio of 1.78 was achieved at 1380°C. At 1340°C

EFFECT OF CaO/Al_2O_3 RATIO ON ALUMINA RECOVERY



the maximum extraction was 43.1% at a ratio of 1.91. Furthermore, the recovery at 1380°C was higher than at 1340°C for all ratios from 1.6 to 2.22, indicating that sintering at 1380°C is more complete.

Effect of Sintering Temperature

To study the effect of sintering temperature, two series of runs were made at different but constant $CaO:Al_2O_3$ ratios. The sintering time was held constant at one hour with sintering temperatures ranging from 1320 to 1400°C. The results of these runs are given in Figure 3. For a ratio of 1.78, the maximum alumina recovery was 50% at a sintering temperature of 1380°C. For a ratio of 1.85, the maximum recovery was 45.7% at a temperature of 1380°C.

Effect of Sintering Time

Since the optimum sintering temperature was found to be 1380°C, and a $CaO:Al_2O_3$ ratio of 1.78 gave a higher alumina recovery than a ratio of 1.85, a series of runs was made at 1380°C and a ratio of 1.78 with the sintering time varied from 0.5 to 2.0 hours. The results of these runs are shown in Figure 4. The maximum alumina recovery of 52% was obtained with a sintering time of 1.5 hours.

Effect of Leaching Temperature

It was shown earlier that three reactions can occur in the leaching of the sintered material with sodium carbonate solution. Because the reactions are successive, it would appear that a short leaching time would be desirable to extract alumina as the soluble aluminate with minimum reduction of yield and minimum contamination by solubilized silica. Prolonged contact of the sodium aluminate solution with the dicalcium silicate would reduce the amount of alumina in solution. The extraction time was therefore kept short at 15 minutes. To determine the best conditions for this time, extractions were made at four different temperatures--58, 65, 75, and 85°C on a given sintered material. The effect of sodium carbonate concentration and ratio of sodium carbonate to alumina were also studied.

The maximum alumina extraction was 52.8% at a temperature of 65°C when a 3% Na_2CO_3 solution was used. Lesser amounts were extracted at lower and higher temperatures. The results are shown in Figure 5.

When the sodium carbonate concentration was varied at a constant leaching temperature of 65°C the alumina extraction increased only from 51.5% for a one percent solution to 52.8% for a three percent solution. The $Na_2O:Al_2O_3$ ratio was kept constant at 1.66. However, when the sodium carbonate concentration was kept constant at 3%, the alumina extracted increased from 52.8% at a $Na_2O:Al_2O_3$ ratio of 1.66 to 55% at a ratio of 5.0.

EFFECT OF SINTERING TEMPERATURE ON ALUMINA RECOVERY

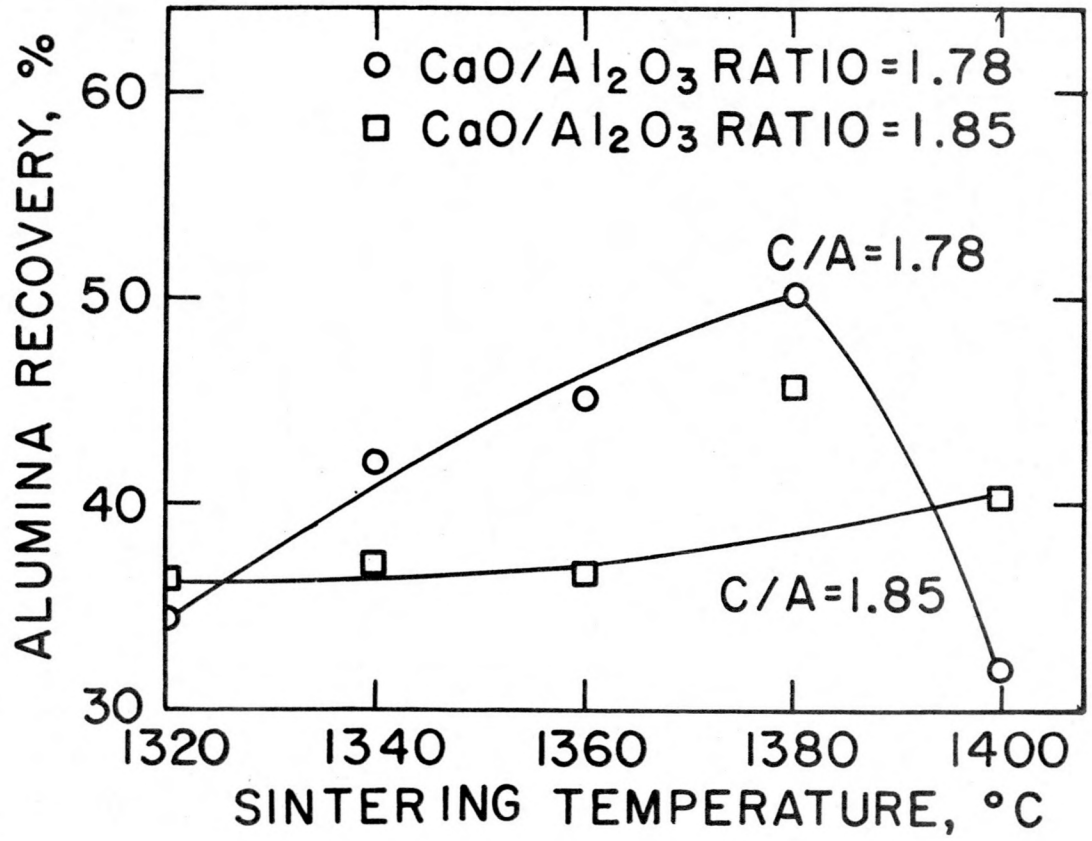


Figure 3

EFFECT OF SINTERING TIME ON
ALUMINA RECOVERY

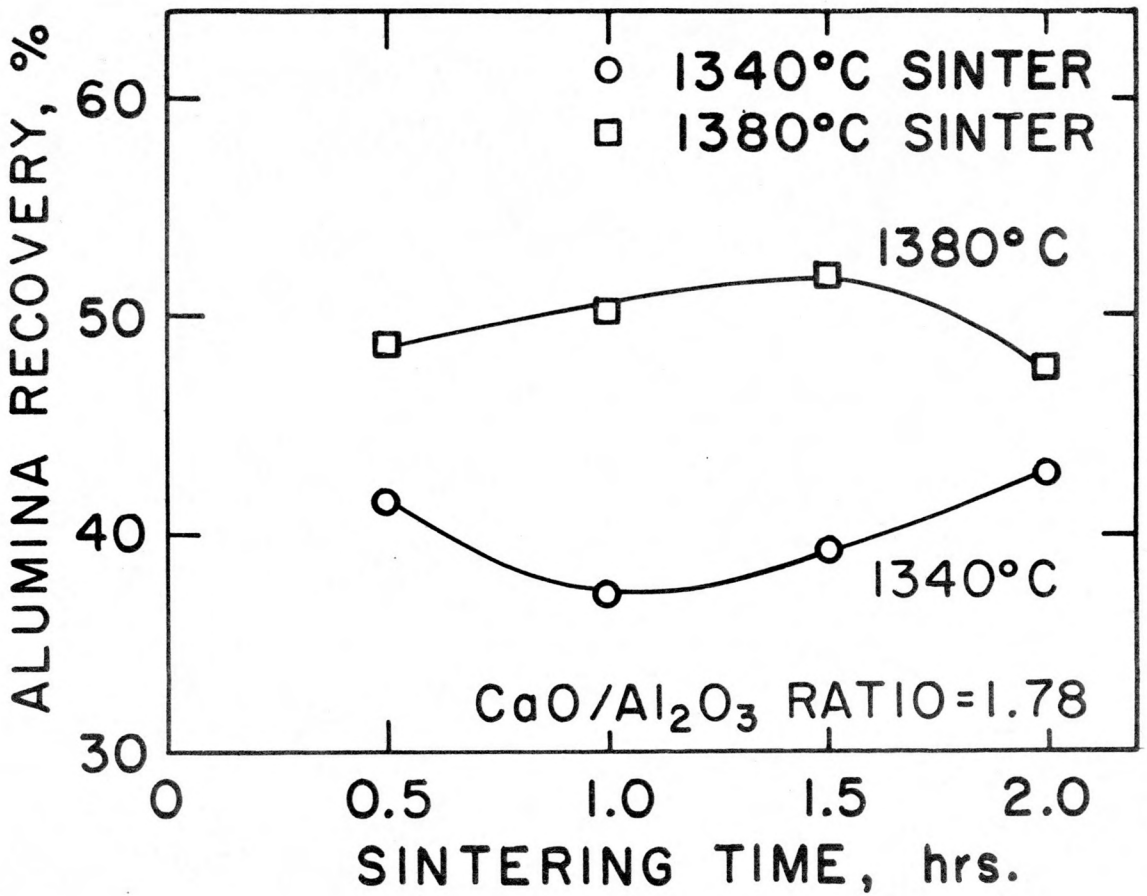
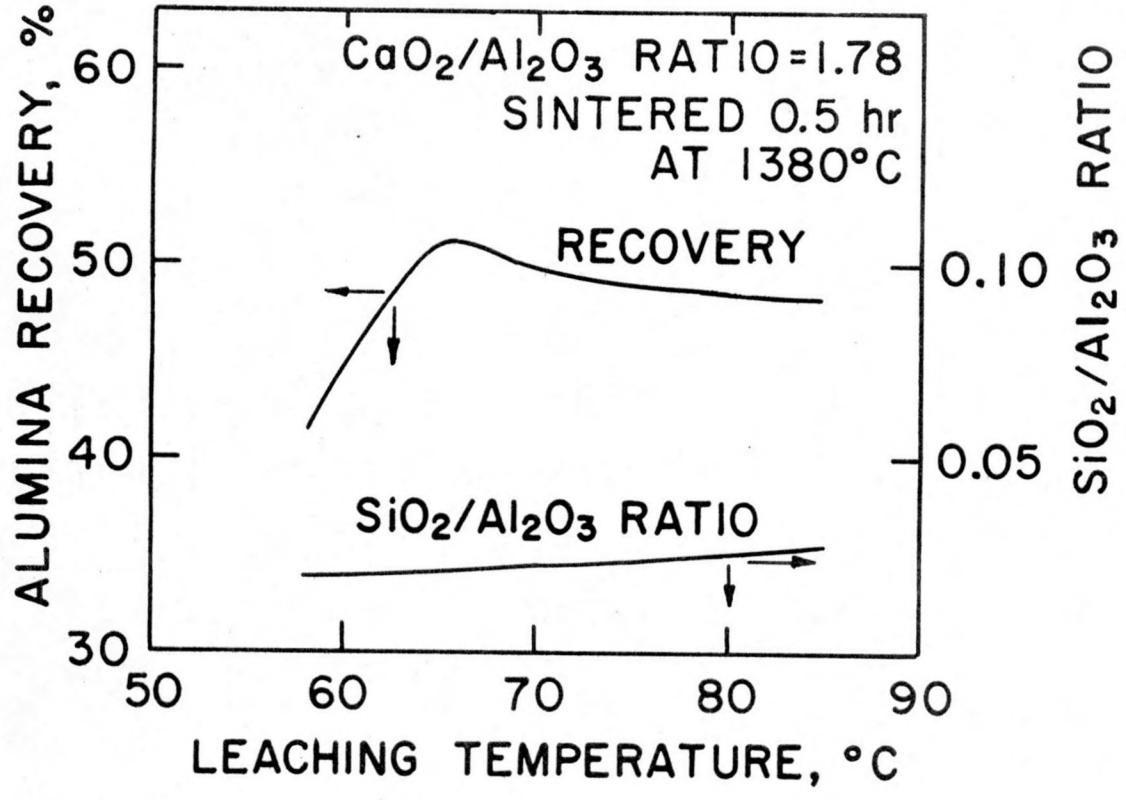


Figure 4

EFFECT OF LEACHING TEMPERATURE ON ALUMINA RECOVERY AND SiO_2/Al_2O_3 RATIO IN PRODUCT



Silica in the Alumina Extract

Previous workers, Grim, et al[13], reported that high sintering temperatures resulted in lowered solubility of silica and low temperatures favored increased solubility of silica. Our work showed no such trend, but a constant amount of silica solubilization with sintering temperature. Our work showed a slightly increased silica solubility with increased leaching temperature. At a leaching temperature of 58°C the SiO_2:Al_2O_3 ratio in the extract was 0.019 and there was essentially a linear increase to a ratio of 0.026 at 85°C. This is shown as the lower curve of Figure 5. It is apparent that some work needs to be done further on leaching to obtain a higher purity of recovered alumina.

CONCLUSIONS

The results of the exploratory work done so far show that with the lime sinter process, more than 50% of the alumina in a typical fly ash can be made soluble by sodium carbonate extraction of the sintered material. Fly ash then becomes a potential, easily available domestic resource for alumina. At the present rate of production of fly ash, this could supply approximately 35% of the alumina needs of the United States at a 50% recovery level. With an increase in alumina recovery to 90%, which we believe attainable as further research leads to better processing conditions, the fly ash could supply 63% of the country's needs.

FLOW SHEET OF PROCESS FOR ALUMINA FROM FLY ASH

Based on the research reported here and looking to the future, a proposed process for recovery of alumina from fly ash by the lime sinter method is outlined here and given in the flow sheet in Figure 6.

A. Grinding of fly ash to separate magnetics adhering to non-magnetics
B. Magnetic separation; send magnetic fraction to be used as iron ore
C. Milling of fly ash with limestone
D. Sintering of limestone-fly ash mixture
E. Cooling and grinding of sintered material
F. Leaching of sintered material with sodium carbonate solution

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13/ Grim, R. E., J. S. Machin and W. S. Bradley, Amenability of Various Types of Clay Minerals to Alumina Extraction by the Lime Sinter and Lime-Soda Sinter Processes. Div. of State Geological Survey, Bulletin No. 65, Urbana, Illinois, 1945.

EXTRACTION OF ALUMINA FROM FLY-ASH
(LIME-SINTER PROCESS)

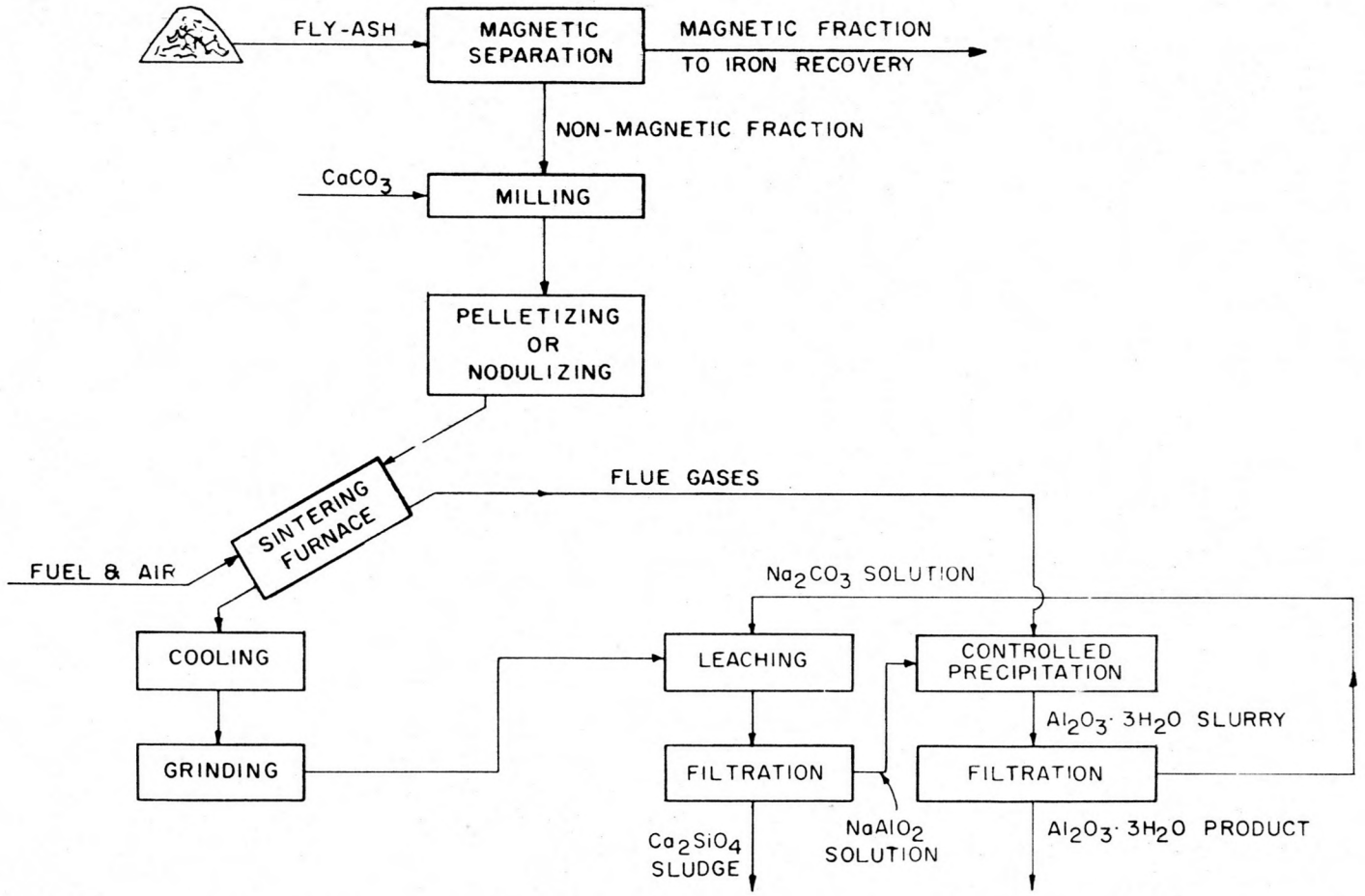

Figure 6

G. Filtration of sodium aluminate extract from dicalcium silicate sludge and other impurities.
H. Controlled precipitation of alumina trihydrate from the extract
I. Filtration of the alumina trihydrate from the extract
J. Calcination of the alumina trihydrate to the anhydrous form
K. Recycle of the sodium carbonate from "I" back to the leaching stage "F"