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ALUMINA FROM FLY ASH +

by

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Introduction

Known deposits of mineral raw material in the United States are seriously depleted. To meet demands to the end of this century will require not only recycling, conservation and new technology for finding and using mineral resources, but also use of new resources yet to be developed or previously evaluated and found to be subeconomic.

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One of the serious mineral raw material problems faced by our country relates to aluminum production. Present domestic production of aluminum ores accounts for only 13% of consumption. Lest they be caught in the same sort of raw material squeeze as the oil companies experienced in 1973, alumina producers are looking at non-bauxite* ores. Work to date has focused on alunite*, laterite*, kaolin clay*, and coal shales.

In 1972, work was started at the Ames Laboratory on the recovery of alumina from fly ash, yet a different non-bauxite raw material. Fly ash is a by-product derived from burning pulverized coal at electric power generating stations. If the fly ash is discharged to the atmosphere with the flue gases, it becomes a major air pollutant. To prevent air pollution, the fly ash is removed and collected from the flue gases using devices such as cyclone separators, electrostatic precipitators and bag filters.

Coal Ash Supply

Increasingly large amounts of fly ash are being produced. Because of the declining long-term availability of oil and natural gas, coal is assuming a larger role in the generation of electricity to meet national demands. The reduction in available fuel oil and natural gas, and the environmental and sociological problems which have slowed the development of nuclear power, have pushed coal consumption in 1975 to a level even higher than expected. Figure 1 shows actual and projected data on coal consumption and coal ash production for the United States electric utilities for the years 1950 through 1980 (1). Of the total coal consumed in 1975, 62% was used by the electric utilities, 20% was used in making coke and steel, 16% was used by other manufacturers, and 2% entered the retail market.

The accelerated rate of coal usage is producing a corresponding increase in the production of coal ash. In addition, higher ash-content coals are being burned and more efficient ash recovery systems are being installed.

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* Bauxite is a hydrated alumina, $Al_2O_3 \cdot 2H_2O$, with silica, clay and other impurities present; alunite is $KAl_3(SO_4)_2(OH)_6$; kaolin contains the clay mineral kaolinite, $Al_2(Si_2O_5)(OH)_4$; laterite is a more general term for red rocks that contain hydroxides of aluminum.

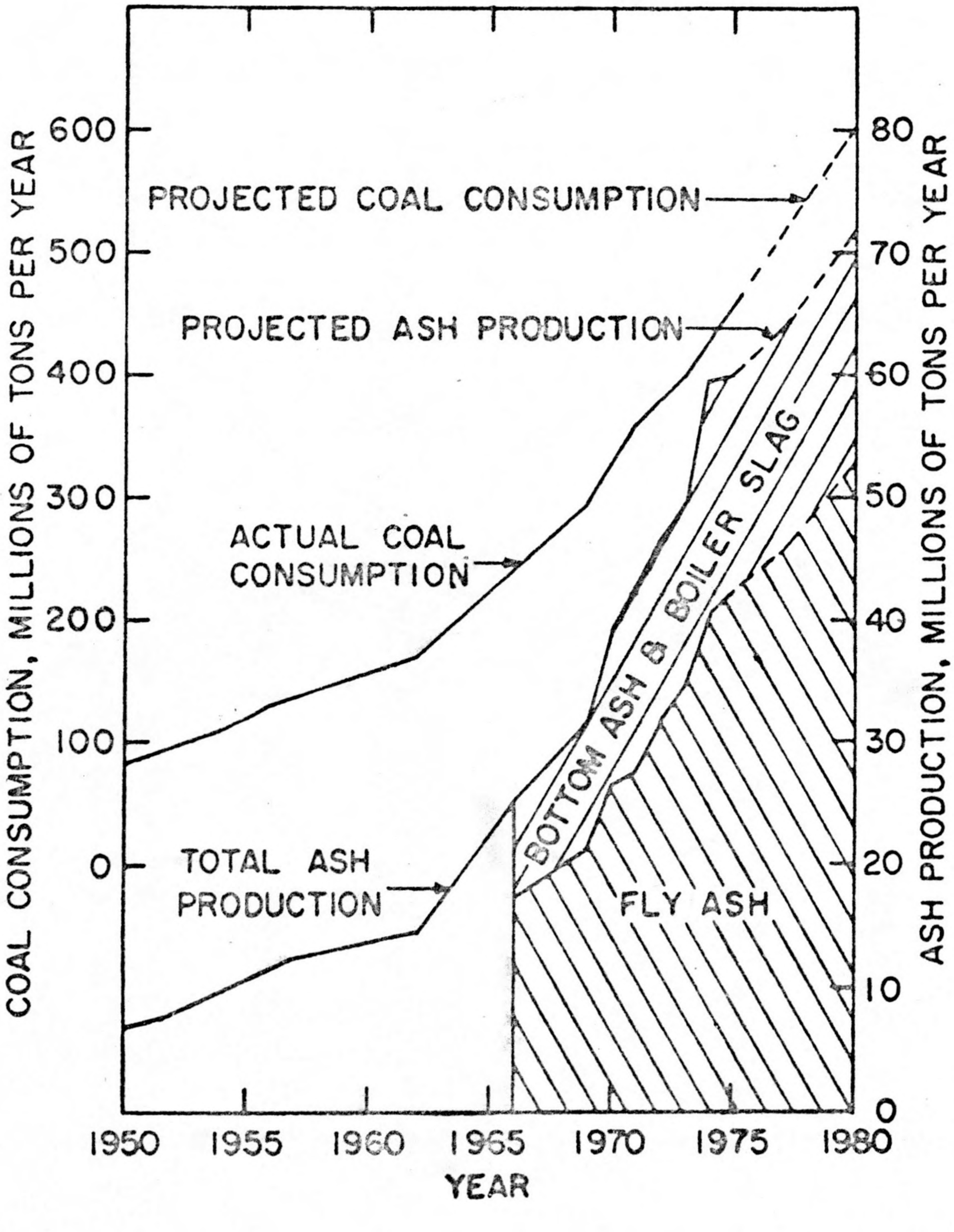

Figure 1. Coal Consumption and Ash Production by U.S. Electric Utilities. (1)

At the present time only 11% of the fly ash collected in the U.S. is being utilized; the remainder constitutes a waste disposal problem (1). The principal uses are partial replacement of cement in concrete or concrete products, soil stabilization, road surfacing, as light weight aggregate and cement manufacture. Over two-thirds of the power plants in the U.S. have dry collecting and loading facilities for fly ash.

Coal Ash Composition

The amount of ash in coals varies over a wide range. This variation is not just in coal from different parts of the world, but in coal from different areas of a given mine. Of significance to work on ash utilization, however, is the fact that the composition of the ash is much less variable.

Coal may be classified into two groups based on the composition of the ash. One group is the bituminous type ash coals; the other is the lignite-type ash coals. The term "lignite-type" ash refers to an ash which has a larger percentage by weight of calcium oxide (CaO) plus magnesium oxide (MgO) than it contains ferric oxide (Fe_2O_3). The bituminous-type ash has more ferric oxide than calcium oxide plus magnesium oxide.

Composition data for United States coal fly ashes are shown in Figure 2 (2,3). Although the constituents are reported as oxides, they occur in the ash as a mixture of silicates, oxides, carbonates, and sulfates, with small amounts of phosphates and other compounds. In Figure 2, the average fly ash analysis for the three major constituents is shown to be 44 wt.% silica (SiO_2), 21 wt.% alumina (Al_2O_3), and 17 wt.% ferric oxide (Fe_2O_3). These three constituents comprise about 90 wt.% of the fly ash from bituminous coals. The alumina content of coal ashes from Central states coals generally is somewhat lower than average while the iron oxide content of many of these ashes will be above the average. Lignite ashes and some Western states coal ashes have relatively higher percentages of CaO and MgO, and have larger amounts of the sulfur in the ash in the form of sulfates (4).

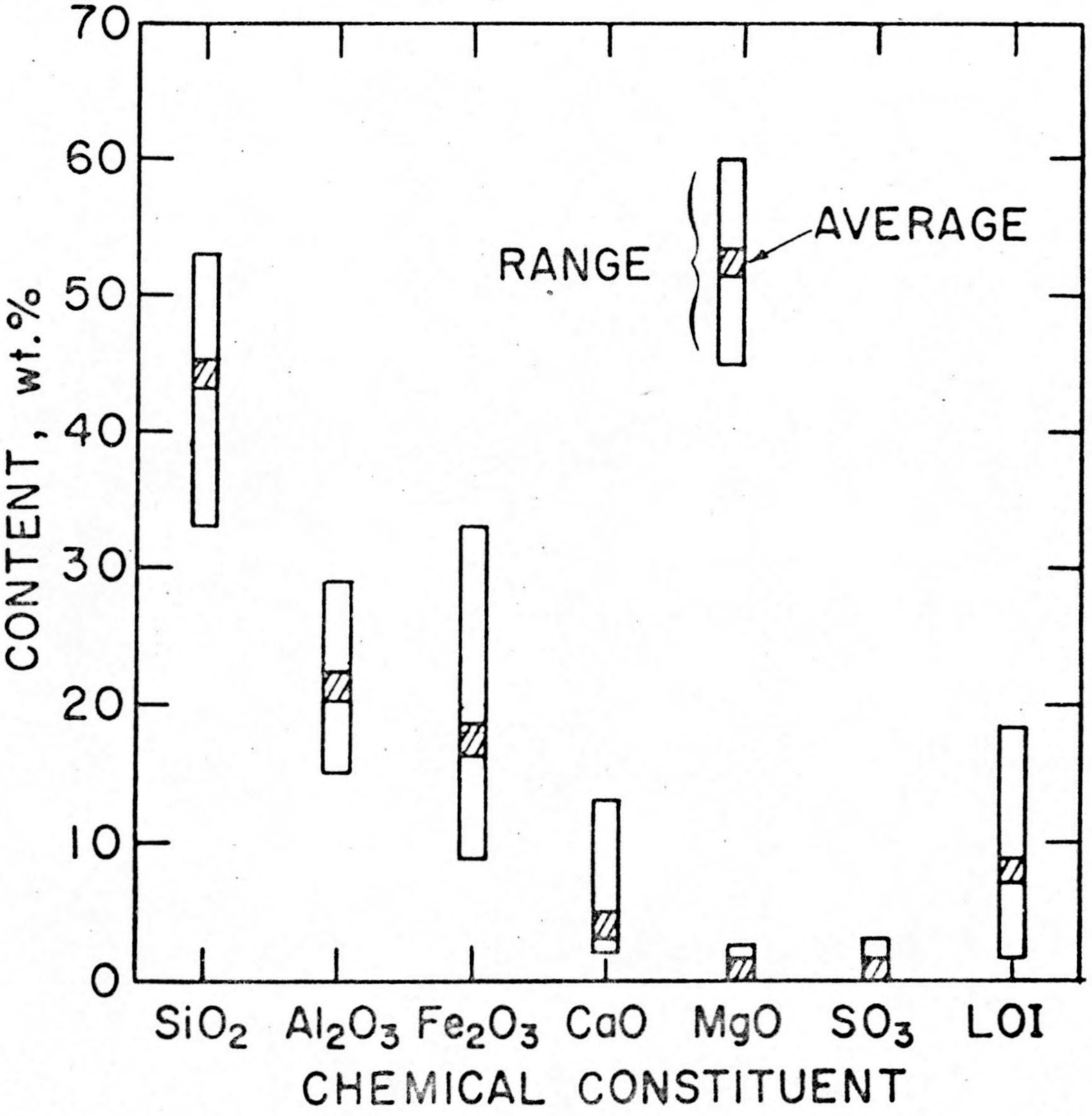

Figure 2. Range and Average Content of Different Chemical Constituents in United States Fly Ashes (2,3).

Recovery of Minerals from Fly Ash

The large volume of coal ash being produced, largely in centralized locations, and the composition of the ash present unique opportunities for the recovery of minerals. The total amount of fly ash produced per day from a 1,000 megawatt power plant will be about 1,500 tons. Recovery of all of the alumina from the fly ash from one 1,000 megawatt facility would produce approximately 60,000 tons of aluminum metal per year or just over 1% of the present annual consumption in the United States. The iron oxide can also be recovered and theoretically would produce 60,000 tons of steel per year or just under 0.05% of the U.S. annual production. A 1974 listing (5) stated that there were 82 privately owned, coal-burning steam power plants with capacities of 1,000 megawatts electricity generated, or greater. These plants are located nationwide but a large percentage are in the Eastern states.

The utilization of fly ash as a source of minerals should be an energy conservative process because there will be no mining or crushing required and probably only a small transportation requirement. The technology developed for fly ash will be able to be applied to some degree to other coal wastes which also have a potential for alumina and iron recovery. Processing of fly ash-lime sludges from scrubbing towers should be investigated, although the sulfur content may present special problems. In addition, coal utilization in the future will involve both coal gasification and coal liquefaction processes. Both of these methods will produce ash-like wastes in large quantities.

A substantial background of literature on methods for extracting alumina from aluminous-siliceous raw materials such as fly ash shows that alumina may be released by addition of calcium oxide (lime) in a high-temperature treatment to produce a sinter or slag containing calcium aluminate. In a succeeding step sodium aluminate is extracted from the sinter using a sodium carbonate solution, the silica remaining behind as insoluble dicalcium silicate. The sodium aluminate solution is separated from the insoluble residue and contacted with CO_2 to form a precipitate of aluminum hydroxide which is calcined to form the alumina product.

In order to release alumina from a refractory aluminosilicate compound by sintering, it is necessary to provide a reagent which has a stronger affinity for silica than does alumina. 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 $CaO:Al_2O_3$ mole ratio of 5:3. (6,7,8,9) 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 will be needed to release alumina from fly ash.

Extensive work has been done in this country by the Bureau of Mines and by Grim, Machin, and Bradley (10) on the lime-sinter and lime-soda sinter processes. These studies have dealt with 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 $CaO:Al_2O_3$ mole 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 percent 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 work already done at the Ames Laboratory, similar treatment appears promising for extraction of alumina from fly ash.

Work at the Ames Laboratory

Since the iron and aluminum values both are of interest, magnetic separation has been used to first separate an iron-rich fraction. This fraction consists mostly of very small spheroidal particles of magnetite and represents about 25 wt.% of the total ash but only about 10 volume %. It contains 70% to 80% of the iron present. The fraction of the fly ash which consists of particles which contain both iron and aluminum is relatively small.

The magnetic fly ash fraction has immediate potential market application as magnetite for high density coal washing processes. The material is heavy, 3.0 to 3.5 g/cc, yet very fine; 70 wt.% of the particles is smaller than 40 micron particle diameter. These properties allow the preparation of high-density coal washing solutions with a minimum amount of mixing required to maintain a suspension. In addition, the magnetic fraction contains about 55 wt.% iron. With further treatment to reduce the silica concentration, pellets having compositions similar to taconite pellets can be produced which should be suitable for blast furnace feed.

For the sintering work the dry non-magnetic fly ash fraction was mixed with the calculated amount of calcium carbonate and milled in a ball mill. The mixtures prepared were calculated to give mole ratios of $CaO:Al_2O_3$ from 1:51 to 2:22. About eight to nine percent water was added and the various mixtures were pressed into pellets measuring ½ inch diameter by ¼ inch thick.

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 predrying the charge, the boat with pellets was placed in a pre-heated alumdum tube furnace. During the sintering operation, the pellet temperature was measured with an optical pyrometer. The charge was held at the sintering temperature for a specified time. The chemical reactions which take place are:

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

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

The mixture of nonmagnetic fly ash and lime is primarily made up of three major components: CaO, SiO_2 and Al_2O_3. Iron can be considered as an impurity, which amounts to about 3% of the total mixture. If one examines the phase diagram of CaO-Al_2O_3-SiO_2 (Figure 3) (11), it is noted that the composition of nonmagnetic fly ash lies in the primary region of mullite near the SiO_2 end (shown as point A in Figure 3). After the lime is added, the overall composition moves along the straight line connecting point A and the CaO vertext to points between the marked section. This section is in the subsystems of $2CaO\cdot SiO_2$-$12CaO\cdot 7Al_2O_3$-$CaO\cdot Al_2O_3$ and $2CaO\cdot SiO_2$-$12CaO\cdot 7Al_2O_3$-$3CaO\cdot Al_2O_3$. The final equilibrium product will be $2CaO\cdot SiO_2$ and other corresponding calcium aluminates. The compounds $12CaO\cdot 7Al_2O_3$ and $5CaO\cdot 3Al_2O_3$ have very similar stoichiometric ratios of

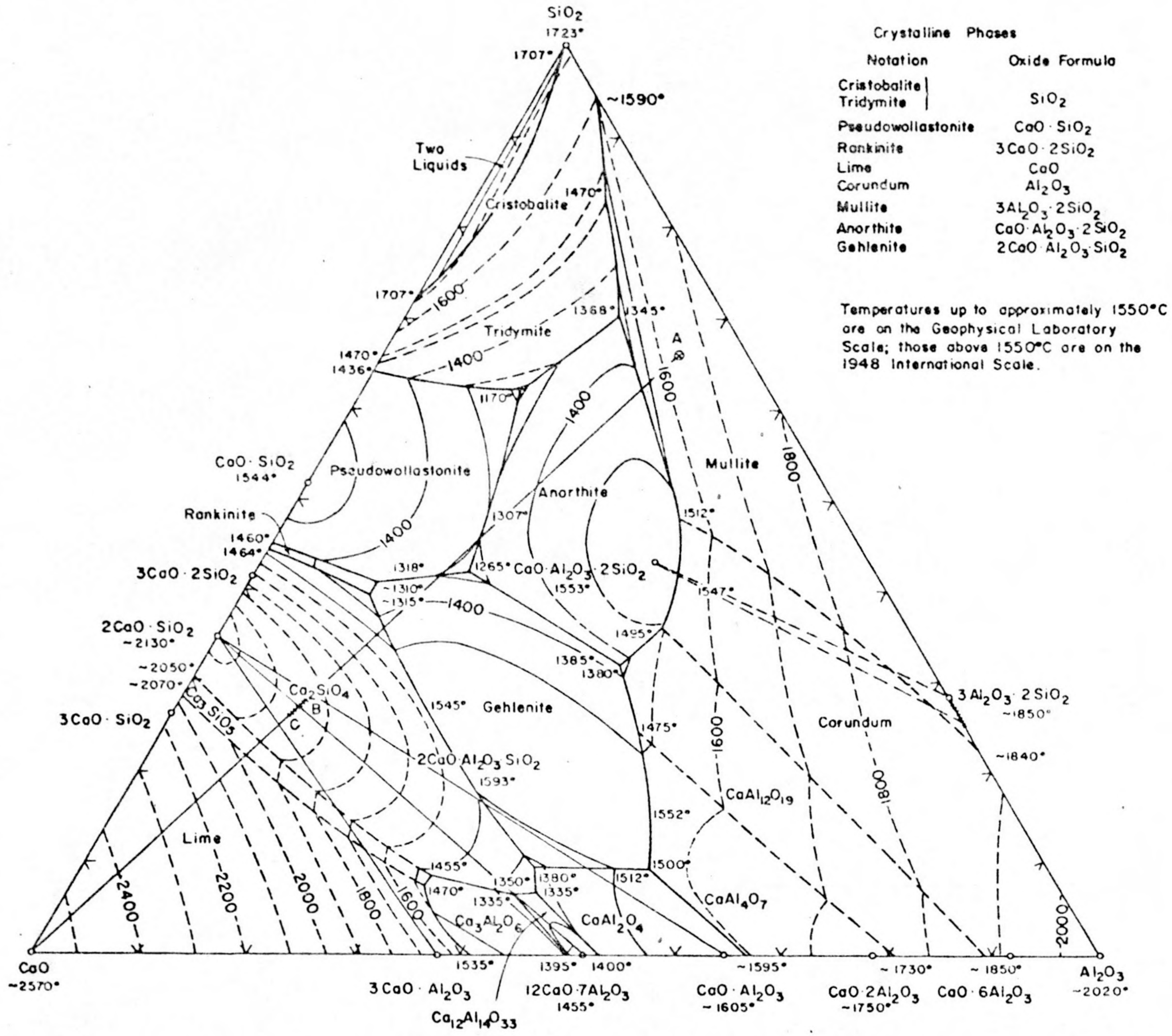

Figure 3. The phase diagram for the system SiO_2-Al_2O_3-CaO (11). Point A represents the composition of non-magnetic C-1 fly ash. The compositions between points B and C were used in this research.

CaO to Al_2O_3. The primary compound formed has the formula $5CaO{\cdot}3Al_2O_3$ and is the principal compound responsible for alumina extraction.

When the sintered materials are cooled, they often decrepitate. This phenomenon is commonly called "dusting" (10). The dicalcium silicate formed undergoes a crystallographic transformation on cooling below about 675°C with an increase in volume which results in reduction of the sintered mass to a powder. The powder thus formed gave the best alumina extraction and was the most easily handled in leaching. For those sinters, which did not disintegrate, grinding was required for subsequent extraction.

The process used to extract the alumina from the sinter was basically similar to that used by Grim and coworkers (10). Weighed amounts of powdered material were extracted with a 3% solution of sodium carbonate. 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.

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:

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

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

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

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 produces an insoluble precipitate which contains 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.

The purpose of the work to date has been to investigate in an exploratory way the effect of what appear to be the main variables: sintering temperature, sintering time, and $CaO:Al_2O_3$ ratio during sintering. The optimum temperature was 1380°C, the optimum time was about 1 hour and the maximum alumina extraction corresponded to an overall mole ratio of 1.9 for $CaO:Al_2O_3$.

Flow Sheet for Proposed 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 presented in flow sheet form. The steps in the process are as given below:

A. Grinding of fly ash to separate magenetics adhering to non-magnetics
B. Magnetic separation: send magnetic fraction to be used as iron ore, heavy media, etc.
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
G. Separation of sodium aluminate solution for dicalcium silicate sludge and other impurities by filtration
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"

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

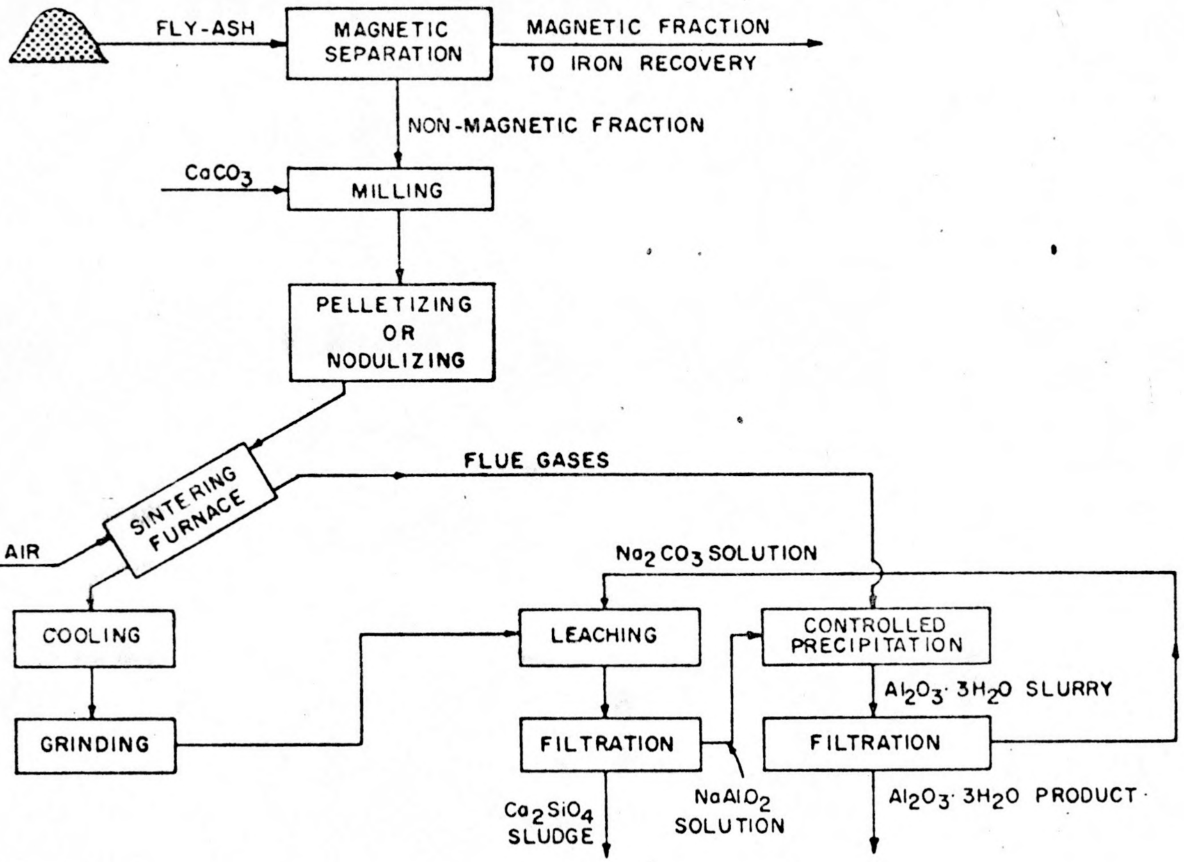

Figure 4

Use of Siliceous Residue in Cement Manufacture and in Concrete

The cement and concrete industry have been the biggest consumer of fly ash for many years. The addition of fly ash to concrete improves or imparts certain properties, including strength, resistance to sulfate attack, workability, and impermeability, and helps control shrinkage and evolution of heat during setting. Fly ash is also used as a raw material in the manufacture of cement. It is used in cement and concrete because it is a pozzolan. Pozzolans are siliceous or siliceous-aluminous materials that have little or no cementitious value themselves but, in finely divided form and in the presence of moisture, are able to chemically react with calcium hydroxide and other alkaline earth hydroxides to form compounds that possess this property.

It has been proposed that the residue from the leaching step in the lime-sinter process be dried, mixed with gypsum and calcined to produce a cement clinker. Fragmentary references in the literature suggest that this has been investigated in Hungary and Poland. If the use of the residue to manufacture cement proved technically feasible, it would mean the entire fly ash would be put to use.

Summary

The results of the exploratory work done so far show that with the lime-sinter process, more than 50 percent of the alumina in a typical fly ash can be made soluble by sodium carbonate extraction of the sintered product. Based on the work reported for other non-bauxite materials, there is every reason to expect increased yields. Fly ash can become a potential, easily available domestic resource for alumina. At the present rate of production of fly ash, this could supply approximately 35 percent of the alumina needs of the United States at a 50 percent recovery level. With an increase in alumina recovery to 75-80 percent, which appears attainable as further research leads to better processing conditions, the fly ash could supply even a greater share of the country's needs.

References

1. Faber, J. H. U.S. overview of ash production and utilization. Proceedings of the 4th International Ash Utilization Symposium, Al, March 24-25, St. Louis (1976).
2. Kokubu, M. Fly ash and fly ash cement. Proc. 5th Internation Symposium of Cement, Tokyo, Japan, v. 4, pt. 4, Oct. 7-11, 75 (1968)
3. Capp, J. P. and J. D. Spencer. Fly ash utilization. A summary of applications and technology. Bur. of Mines Inf. Circ. No. 8483 (1970).
4. Abernathy, R. F., M. J. Peterson, and J. F. Gibson. Major Ash Constituents in U.S. Coals. Bur. of Mines Rep. of Invest. No. 7240 (1969).
5. Statistics of Privately Owned Electrical Utilities in the United States. Federal Power Commission (1974).
6. Zhukovetskii, V. V. Preparation of Alumina from Kyanite. Izv. vys. ucheb. Zavod, Isvet. Met. 4 (5), pp. 110-116 (1961).
7. 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).
8. 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 (CA54: 6443, 1960).
9. 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).
10. 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. 29, Urbana, Illinois (1945).
11. Levin, E. M., Robbins, C. R., and McMurdie, M.F. Phase diagrams for ceramists. American Ceramic Society, Columbus, Ohio (1964).