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A STUDY OF THE EXTRACTABILITY OF ALUMINA FROM FLY ASH BY THE LIME-SINTER PROCESS

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MASTER

M.S. Thesis Submitted to Iowa State University

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by

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INTRODUCTION

Ever since the 1973 embargo on oil, not only have energy resources become a serious problem for most countries of the world, but also there is a clear warning of potential problems involving many other natural resources.

By forming the Organization of Petroleum Exporting Countries (OPEC), the oil-producing nations have raised their political influence in international affairs, and have become very wealthy in a very short period. The flow of huge amounts of capital to the oil exporting countries following the dramatic increase in oil prices three years ago has caused inflation and, even worse, economic depression in the whole world. Because of the tactics used, political factors have entered into the already complex international economic relations between nations. There could come a time when some countries will not be able to buy raw materials even if they have the money.

The United States has been a net importer of a variety of minerals for years. According to a new report by the United States Geological Survey (42), the United States is going to face a shortage of minerals in the "foreseeable future." And like the energy shortage, the cause stems from too much reliance on foreign imports.

In terms of domestic supply and demand, the report (42) says that the United States' oil reserves total about 36.3 billion barrels compared to domestic production in 1972 of 3.3 billion barrels. Natural gas consumption in the United States alone in 1972 totalled 22.5

trillion cubic feet. About 29% of the United States' requirements for oil and natural gas come from imports (42).

Among other mineral raw materials, the United States was, specifically in 1974, more than 90% dependent on imports of primary materials for seven commodities (manganese, cobalt, chromium, titanium, niobium, strontium, and sheet mica); 75 to 90% on eight other commodities (aluminum, platinum, tin, tantalum, bismuth, fluorine, asbestos, and mercury); and 50 to 75% on another eight commodities (zinc, gold, silver, tungsten, nickel, cadmium, selenium, and potassium). This dependence makes the United States vulnerable to cartel agreements among the major producing nations (1).

To ease the mineral shortages, the United States must turn to more recycling, conservation and new technology, as well as to processing low grade (low mineral bearing) ores. Research programs aimed at processing low grade ores include mining and extraction techniques that will raise the efficiency of the processes for obtaining vital materials from lower grade domestic ores and developing substitute materials and exploring their effects on product design and exploring their effects on product design and performance. Such research need not yield economic processes or products in the current market. Instead the research would give the United States an available technology that could be scaled up and brought on stream if normal supplies were in jeopardy for indefinite periods (72).

The usual ore from which aluminum is recovered is bauxite, an essentially silica-free alumina hydrate. As early as World War II, the United States began to research for substitute materials for bauxite because the domestic reserves of bauxite were very limited. Clay and other alumina bearing ores were the main materials studied. In 1945, the Illinois State Geological Survey made a broad study of the amenability of various types of clay minerals to alumina extraction by the lime-sinter and lime-soda sinter processes (25). Later, in 1962 and 1963, the U.S. Bureau of Mines evaluated several acid processes for extracting alumina from clay (53, 55). More recently a research firm, Applied Aluminum Research Corporation (AARC) at New Orleans, claimed a new process adaptable to many different aluminous raw materials to replace the universally used Bayer-Hall technology for bauxite (47).

Common to all current research into mineral resource supplies is the realization that current sources of domestic mineral deposits have only very limited duration before they are completely deleted. It is, then the purpose of this thesis to examine and explore the potential of utilizing power plant fly ash as an alternate source of aluminum and iron. The research is focused on the extraction process of alumina from the nonmagnetic part of fly ash, while the magnetic part, which is very rich in magnetite, can be used as a source of iron. Such a process would not only aid in creating a source of metals, but would utilize more efficiently the solid waste in the flue gases of coal burning furnaces and power plants.

LITERATURE REVIEW

Along with an increase in the standard of living goes an increase in the consumption of energy. Every family needs power to run various facilities in their house. Industry also needs power to produce the commodities people use. In the United States, the demand for electricity alone doubles every ten years (42). To meet this ever-growing demand for energy, several new sources, aside from the traditional coal, oil and gas, such as nuclear energy, solar energy and geothermal energy are being employed.

Historically, coal has been used as the fuel source for power generation. Steam production from coal combustion provides electricity for fulfilling power requirements. As early as the 1920's, pulverized-coal firing was developed for higher combustion volumetric rates and hence higher efficiency (4). However, the combustion of fossil fuels, even under efficient conditions of combustion, produces solid waste residues. When the solid wastes are discharged in the flue gases of fossil-fuel power generating facilities, they are termed fly ash.

Production of Fly Ash

The extraction of alumina from fly ash depends highly on the composition of the ash. Since there is a great difference in the properties of coal, there will also be some difference in the resulting fly ash. Broadly speaking, factors which influence fly ash properties are (32):

1. Origin and kind of mineral matter in the coal;

2. Coal processing methods and furnace conditions;
3. Methods of fly ash collection.

Origin and kind of mineral matter in the coal

As found in seams, coal is a heterogeneous mixture of organic and inorganic materials. Not only are there large differences in the properties of coal from different elevations but also of coal removed from different elevations and different locations in a single seam.

Some of the coal used in power plants may contain up to 25% incombustible mineral matter which forms ash when the coal is burned (32). The ash-forming mineral matter is usually classified as either inherent or extraneous (4, 46, 67).

Inherent mineral matter is usually defined as that portion of the mineral matter organically combined with the coal. It contains elements which have been assimulated by the living plant, such as iron, phosphorous, sulfur, calcium, potassium and magnesium (67). Generally the inherent mineral matter contained in coal is about 2% or less of total ash (4).

The extraneous mineral matter is considered to be that which became associated with the coal-forming system through outside agencies, such as by dust carried in the air, and by dissolved or suspended material brought in by water.

Although the type and amount of mineral matter will vary widely among coals, there is general agreement that major group associated with coal are as follows (5, 46, 67):

1. Clay and shale group: This is made up chiefly of clay, quartz and feldspar, Kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$,

and muscovite, $KNaO \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$ are two examples.

2. Sulfide group: This group comprises pyrite and marcasite, whose formula is FeS_2. With weathered high-sulfur coals, significant amounts of iron sulfate, $FeSO_4$, may also be present from oxidation of pyrite.
3. Carbonate group: Members of this group are commonly found in coal. Examples are calcite, $CaCO_3$, and dolomite, $CaCO_3 \cdot MgCO_3$.
4. Associated mineral groups: In addition to the minerals listed above, there are some which are found in minor quantities, such as gypsum, $CaSO_4 \cdot 2H_2O$, apatite, $9CaO \cdot 3P_2O_5 \cdot CaF_2$, zircon, $ZrSiO_4$, etc.

According to the studies of Ball (5) and Gumz (27), more than 95% of the mineral matter consists of three minerals, kaolinite, pyrite, and calcite. The general range of composition is indicated as follows: kaolinite 70-95%; pyrite 5-35%; calcite 0-20%. Higher percentages of pyrite and calcite are very rare in bituminous coals; however, lignites often have a higher proportion of calcite (27). Other secondary or trace minerals seldom exceed 5% (46).

Coal processing methods and furnace conditions

The presence of mineral impurities adversely affects the use of coal in combustion applications. In addition to serving as diluents with respect to the heating value of the coal substance, their presence also contributes to problems of slag formation, erosion and corrosion while the coal is being burned, and to costs of fly ash separation and ash disposal.

These factors have long been recognized by the consumers and miners of coal, and many processes for the mechanical cleaning of coal have been developed and put into use. The principal methods used in the U.S. for cleaning anthracite and bituminous coals are: (a) cleaning at mine face; (b) picking out impurities manually or mechanically; (c) froth flotation; (d) gravity concentration (4). The principle of separating these impurities is based largely on differences in specific gravity and shape of the particles. The types of equipment involved include cyclones, launders, jigs, classifiers, and concentrating tables.

When the coal is crushed, some of the mineral impurities are released from the coal and their separation is not difficult. Other mineral impurities consist of fine particles intimately mixed with the coal. These impurities cannot be separated from coal substance under ordinary circumstances.

The character of the inorganic residue is affected by the method of burning the fuel and by the conditions imposed upon combustion process. It is generally agreed that the thermal changes which mineral matter undergoes during the combustion of coal are influenced by the following factors (27, 32, 46, 50):

1. The size to which the coal is ground and the degree to which this influences the quantity and distribution of mineral matters;
2. The atmosphere in the furnace;

3. The temperature to which the mineral matter is subjected, the rate of heating and quenching, and the residence time at these temperatures;
4. Boiler load conditions.

The function of a pulverized coal system is to pulverize the coal, deliver it to the fuel-burning equipment, and accomplish complete combustion in the furnace with a minimum of excess air. In the grinding or pulverizing of coal, the mineral matter is also pulverized. It is generally believed that there is a direct relationship between the average size of fly ash particles and the degree to which the coal is pulverized.

Littlejohn (39) studied the variation of ash content with particle size and density fractions. On the basis of pulverized coal "as fired," he was able to classify particles as (a) clean coal particles containing less than 2% ash, (b) mixed particles each containing both coal and mineral, and (c) discrete mineral particles. He also discerned that there is a tendency for the ash content to be greater in the smaller size fractions with a corresponding increase in mineral particles and fragments.

Detailed descriptions of the atmosphere, temperature and particle residence times were made by Nelson (46) and Gumz (27).

Maximum temperatures in the flames of pulverized-coal-fired boiler furnaces have been reported to be in the range of 1300°C to 1700°C (46, 50, 74). The total available burning time for a particle of coal in a pulverized-coal furnace is 1 to 2 seconds (46). This means the mineral matter in the coal is heated to a maximum temperature within a fraction of a second, with accompanying physical and chemical changes, and thus little opportunity occurs for mixing of the various minerals or ash residence. The resulting ash particles are mainly glass spheres of one or at the most two mineral species (27, 46, 74).

Although complete combustion conditions exist in a suspension-fired furnace, the velocity of injected air is so high that 5% to 23% of the coal particles pass through the furnace unoxidized (16). Clendenning and Durie (16) also observed that a decrease in load, because of reduced velocity of primary air, results in an increase in carbon content and accompanying increase in fineness of fly ash particles. The unburned coal particles are irregular shaped and black in color. Microscopic studies of various fly ash samples (59, 74) indicate that the size of such unburned coal particles varies from 20 to 200 microns as compared to 0.1 to 100 microns for the spherical mineral particles.

Methods of fly ash collection

When pulverized coal is burned in a furnace, nearly all the ash particles are formed in suspension and tend to remain in suspension. With different types of furnaces, 30% to 80% of the ash originally in the coal leaves the furnace entrained in the flue gas (4). Other parts of the coal is found in the form of bottom ash and boiler slag.

Concern over environmental pollution and public health problems has made it a necessity to collect the fly ash from the stack. The usual types of particulate removal equipment may be classified electrostatic precipitators, mechanical dust collectors, fabric filters and wet scrubbers. Electrostatic precipitators can achieve an efficiency of 99% (4, 32). Mechanical dust collectors have an efficiency about 90%, but they are not very effective for particles of sizes below 10 microns (4).

The effect of the properties of fly ash particles on ash collection was noticed by Brackett (8) and Styron (70). They found that halloysite, $Al_2(Si_2O_5)(OH)_4 \cdot 2H_2O$, which is a hydrated analogue of kaolinite, is a very efficient electrical insulator. This material changes its form but not its properties as it passes through the combustion process. As it leaves the boiler and starts to cool, it picks up moisture which in turn causes it to plate out in a thick coat that completely covers and insulates the electrical components of electrostatic precipitators. This insulating coating makes it a very difficult ash to collect electrostatically. However, the halloysite is generally only a small percentage of the total fly ash.

Composition and Properties of Fly Ash

There have been many studies on the chemical composition of fly ash from various sources (14, 15, 32, 74). Chemical analysis of a large number of U.S. fly ashes show ranges in composition given in Fig. 1 (14).

Fly ash is comprised of compounds of silicon, aluminum, iron and calcium, smaller amounts of compounds containing magnesium, titanium, sodium and potassium, and traces of other elements. These compounds occur in fly ash primarily as silicates, oxides and sulfates, along with lesser amounts of phosphates and carbonates.

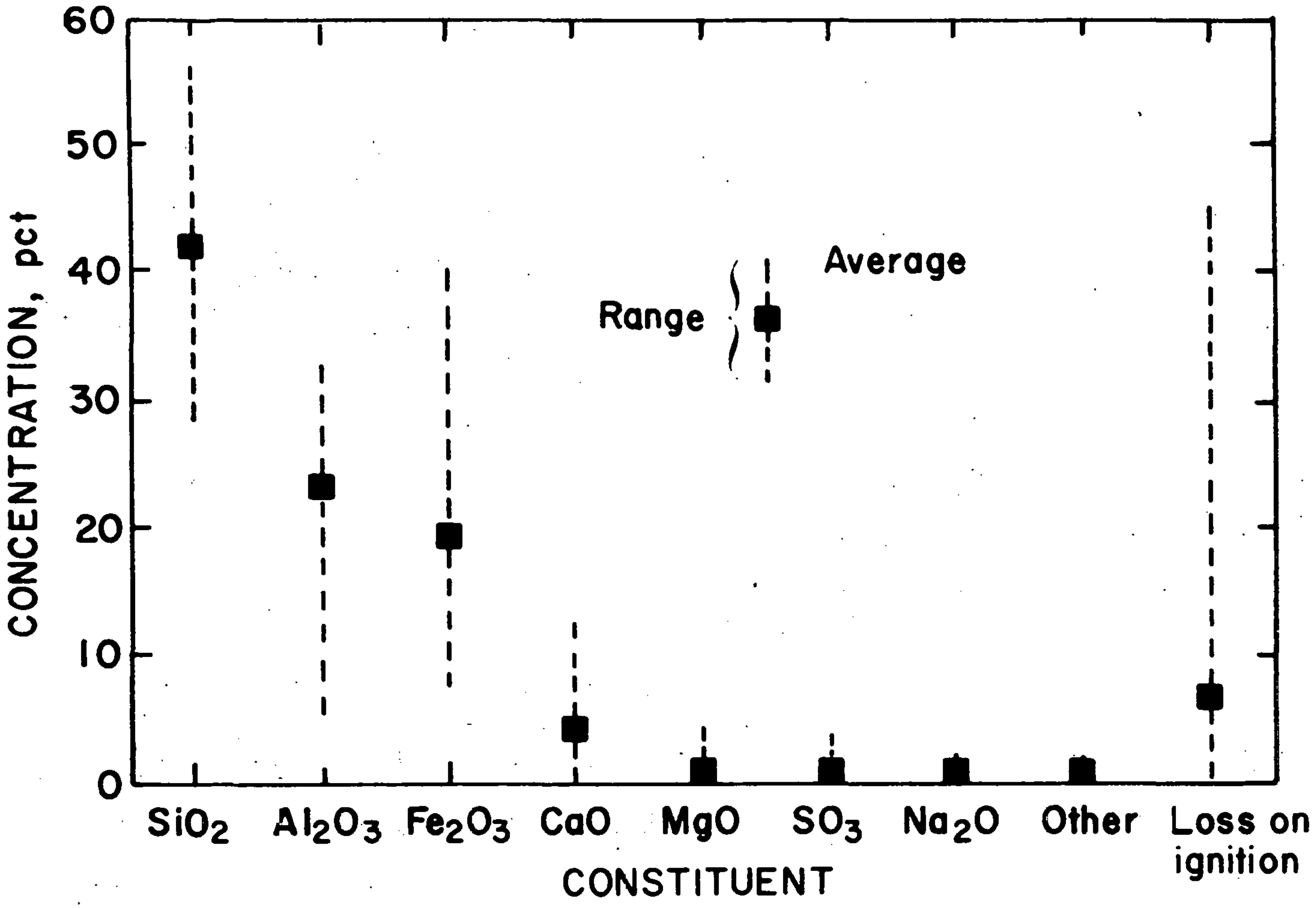


Fig. 1. Range and average of analysis of United States fly ashes

Silica and alumina are the main constituents in the majority of U.S. fly ashes most of which appear in a glassy form (43, 66, 75). Brindley and Nakahira (11, 12) studied the kaolinite-mullite reaction series and found that kaolinite, upon heating, transforms first to metakaolin and then transforms to a mullite phase of composition $3Al_2O_3 \cdot 2SiO_2$. The kaolinite is dehydrated at about 500°C according to the reaction:

$$\underset{\text{kaolinite}}{2Al_2Si_2O_5(OH)_4} \longrightarrow \underset{\text{metakaolin}}{2(Al_2O_3 \cdot 2SiO_2)} + 4H_2O. \qquad (1)$$

The metakaolin decomposes at 925°C to form a spinel-type phase of approximate composition $2Al_2O_3 \cdot 3SiO_2$ with discard of silica. At about 1050-1100°C, the spinel-type structure transforms to a mullite phase with further discard of silica, appearing visible as cristoballite. This reaction will continue until 1400°C. The presence of mullite and cristoballite in fly ash has been verified by X-ray diffraction studies (32, 41, 74). These two compounds in fly ash probably arise as a result of the kaolinite-mullite reaction series proposed by Brindley and Nakahira (11, 12).

Although the mullite is crystal in nature there are also spheroidal particles of alumino-siliceous glasses in fly ash (32). The mineral constituent in coal at the flame temperature can be fused (61). As the fused particles enter the flues the temperature drop is rapid enough to effectively quench the fluid minerals into glassy spheres. Joshi (32) was able to synthesize fly ashes with more mullite by prolonged heat treatment and a relatively slow rate of cooling. He also observed that there are present variable amounts of iron oxide and trace quantities of calcium and magnesium. In the original mineral fraction of coal, clay is the most important alumina bearing material. Consequently the glassy alumino-siliceous structures as well as the crystalline mullite contain the majority of the alumina in fly ash. Photomicrographs of fly ash show the mullite to be essentially acicular in form (32).

Iron is found in fly ashes in both glassy and crystalline forms. Hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) are present in a crystalline form (41, 43, 74). The formation of hematite and magnetite is a result of the oxidation of pyrites. Pyrites decomposes during the early stages of combustion. The primary reaction,

$$FeS_2 \longrightarrow FeS + S \tag{2}$$

begins at a temperature of about 300°C and reach a maximum rate in the range of 400-500°C (46, 77). In oxidizing atmospheres and at the higher temperature, the decomposition products are oxidized according to the following reactions:

$$S + O_2 \longrightarrow SO_2 \tag{3}$$

$$3FeS + 5O_2 \longrightarrow Fe_3O_4 + 3SO_2 \tag{4}$$

or

$$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2 \tag{5}$$

At higher rates of heating, the several reactions occur practically simultaneously (46).

According to Minnick (45) the magnetic fraction in fly ash is made up in part of extremely fine crystalloids of magnetite embedded in a siliceous glass matrix of high specific gravity. Watt and Thorne (74) studied some features of the magnetic material in fly ash. They applied a simple procedure of magnetic separation to five British fly ashes. The products contained opaque spheres and rounded particles which were shown by X-ray examination to be composed of magnetite and hematite. By heating the residue from the first magnetic separation in hydrogen at 400°C for 24 hours and repeating the magnetic separation, further small quantities were recovered. This second fraction, the reduced magnetic fraction, according to Watt and Thorne (74), is derived partly from a ferrite, $(CaMgFe)OFe_2O_3$, in the ash, this in turn probably derived from an ankerite, $(MgFeCa)CO_3$, a mineral commonly found in the coals.

The decomposition of calcite, dolomite and magnesite at high temperatures accounts for the formation of calcium oxide and magnesium oxide. The oxide may undergo further reactions, the type depending upon the proximity of the inorganic constituents and gases. For example, CaO can react with sulfur dioxide to form $CaSO_4$ (46, 77). Nelson (46) also pointed out that calcium sulfate begins to decompose at 1200°C and that in the presence of silica, alumina or ferric oxide, decomposition takes place at a lower temperature, 1000°C. Products of this decomposition are calcium oxide and sulfur trioxide.

In addition to the presence of silica, alumina, iron, calcium oxide and magnesium oxide and small quantities of sulfur trioxide is the presence of residial carbon. This is usually present as black vesicular particles distributed intimately throughout the mass (43, 74). This fraction usually varies with the efficiency and load of power plant (16). In general, it is present in most of the ashes produced in the United States in amounts ranging from about 2 to 12% (45).

When it is examined microscopically, collected fly ash may be observed to consist of particles varying in size and shape. The average size varies from less than 1 micron to approximately 80 microns (8, 39, 43, 61, 74). Watt and Thorne (74) and Cavin (15) found that the weight distribution of the samples of different sizes is approximately linear in a logarithmic probability plot. This implies that the particle size of the ashes has a Gaussian distribution. The finer particles are much more numerous than the coarse particles; they contribute much less to the weight. For example, more than 50% to 80% of the particles in fly ash, numerically, have a diameter less than 4 microns, but these particles account for less than 10% of the weight (15, 32, 74). The coarser material usually gives a dark color, indicating that these are the unburned or partially burned coal particles (15, 43). Agglomeration and intermixing of two or more primary particles in the furnace can also form large particles (32, 74). Minnick (43) inferred from his analysis that the fine fraction shows higher silica and alumina. Cavin (15) investigated the distribution of magnetic particles in each size fraction and found that the distribution is reasonably uniform, varying from about 22% in the coarse material (+210 microns) to about 29% in the fine material (-74 microns).

Most of the fly ashes are made up of three types of particles: clear glass spheres, spongy particles and brown to dark glass particles

(74). The clear glass spheres are generally smaller than the other particles. Some particles of this type contain crystalline matter varying from one or two needles up to substantially the whole particle; the crystalline phase is mullite. The spongy particles are larger and also contains crystals, generally very small and limited in amount. The other type, brown to black glass spheres, is the least abundant and the most heterogeneous; most of them are magnetic. There are some other types of particles, such as irregular black particles and clear angular particles, which occur in less important amounts.

Recently interest has been focused on certain spheroidal glass particles that show as hollow when viewed under the microscope (52, 60). These particles have an apparent density less than that of water, thus they separate from the dense ash in ash settlement lagoons. Raask (60) indicated that these cenospheres, as the particles are called, are formed at a temperature of 1400°C and that the formation and size are governed by the viscosity and surface tension of the fused silicate glass, by the rate of change in particle temperature, and by the rate of diffusion of gases in the silicate. The molten spheres freeze at 1000°C, trapping the gases which are formed internally through catalytic action of ferric oxide on carbonaceous material present. The gas in the cenospheres consists mainly of CO_2 and N_2. The chemical composition of cenospheres differs from that of the dense particles: the silica content is higher and that of calcium oxide is lower in the cenospheres than in the dense material.

Qualitative microscopic and X-ray diffraction studies show that most fly ashes contain only four crystalline phases in significant amounts viz., quartz, mullite, hematite and magnetite. The amounts vary from 11-48% of the total ash (32, 41, 66, 74). The rest consists of carbon particles and amorphous material, mostly siliceous, aluminous and ferruginous glasses (32, 59, 74).

Utilization of Fly Ash

Of the recoverable U.S. reserves of coal, oil, natural gas and shale oil as of January 1, 1970, coal represents 87.4%, petroleum 0.92%, shale oil 10.0% and natural gas and natural gas liquid 1.64% (4). These reserves of coal can last for 350-400 years (30). The United States consumed 600 million tons of coal in 1974 (17). Of this amount, 62% was used by the electric utilities; 20% was used in making coke and steel; 16% was used by other manufacturers; 2% went into the retail market (9). Thus the electric utilities use the majority of coal. It is estimated that production of fly ash in the United States will reach 40 million tons a year by 1980 (9).

Since the cost of fly ash disposal is not insignificant, there is economic incentive to convert fly ash from a liability into an asset. In 1971, 11.7% of the fly ash was used (9). This was the highest degree of utilization up to that time in this country, but figures indicate that there will be some increase in ash utilization in the future, but not of a high order of magnitude.

Capp and Spencer (14) have made a complete survey of the utilization of fly ash. They have found that the cement and concrete industry had 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 permeability, and helps control shrinkage and evolution of heat during settling. Fly ash is also used as a raw material in the manufacture of cement. The reason for fly ash being used in cement and concrete manufacture is because it is 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 (14).

Soil stabilization and base course construction has also consumed a large amount of fly ash. Soils that exhibit marked resistance to deformation under repeated or continuing loads are said to be stable. Treatment of a soil to improve its strength and deformation resistance is referred to as "stabilization". Stabilization is affected by mechanical, chemical, electrical, and thermal means. Fly ash can be used as a chemical soil-stabilization material. A lime-fly ash mixture is used in base course construction and outstanding performance from properly designed paving materials has been obtained (6). Pavements with lime-fly ash-stabilized soils exist in Iowa, Pennsylvania, Maryland, and other states (14).

Fly ash is also used as a filler for dams, mounds and construction. The material properties considered to be of major importance when considering fly ash as a fill material are grain size, density, compaction characteristics, shear strength and permeability (35). The physical and chemical characteristics of most fly ashes also make them adaptable as a raw material for brick manufacture. Four types of brick consisting mainly of fly ash or fly ash mixed with another material have been developed. They are catalogued as fly ash, fly ash-clay, fly ash-slag, and fly ash-sand (14). In agriculture, fly ash is used to ameliorate the soils (14, 57). There are some other possible uses of fly ash cited by Capp and Spencer (14). The fact remains that, according to recent reports, only about 20% of fly ash produced annually in the United States is utilized. Consequently it becomes imperative that other uses for fly ash be investigated.

Conventional Alumina Recovery Processes

In order to understand the basic ideas about the extraction of alumina from ores, a review of conventional alumina recovery processes is in order. The majority of alumina produced today comes from bauxite. The term bauxite refers to residual rocks, in which the alumina trihydrate (gibbsite, $Al_2O_3 \cdot 3H_2O$) and monohydrate (boehmite and diaspore, $Al_2O_3 \cdot H_2O$) predominate (19, 31, 51). The parent rocks are often nepheline ($3Na_2O \cdot K_2O \cdot 4Al_2O_3 \cdot 9SiO_2$), serpentine, granite, dolerite and limestone containing clay minerals (51). In the weathering or decomposition of rocks at the earth's surface, there is a gradual removal of the more soluble constituents; alkalies, lime and magnesia going first, followed later by silica, leaving iron oxide, titania, and alumina as relatively insoluble constituents. Thus the impurities in bauxite essentially consist of kaolinite, halloysite, goethite

(α-FeO(OH)), hematite, magnesite, anatase (tetragonal TiO_2) and quartz (19, 31, 51).

Production of alumina from bauxite is usually performed using the Bayer process. Raw bauxite is ground to 80- to 100-mesh and digested with hot caustic soda, usually under pressure, to produce a sodium aluminate solution, which leaves behind most of the impurities, predominantly iron oxide, titania and silica, as an insoluble residue. The solution is discharged from the digester and the insoluble residue ("red mud") is separated by filtration, sedimentation, or both. The residue is washed to remove as much soda as practicable. The wash water is added to the sodium aluminate solution and following further dilution the clear solution is cooled and stirred with a "seed" charge of previously prepared hydrated aluminum oxide to precipitate the soluble sodium aluminate as a hydrated aluminum oxide. The resulting precipitate is washed to remove soda and calcined at 1000°C to produce anhydrous alumina (19, 31, 51).

The most troublesome impurity in bauxite is silica, especially when the silica occurs as a silicate in a clay or other mineral. During the digestion there apparently is formed an insoluble sodium aluminum silicate which carries both soda and alumina into the red mud. Seimiya (64) found that the products formed in this process are sodalite compounds, $3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) \cdot Na_2X \cdot nH_2O$, where X is an anion dependent on the salt present in the solution. Titanium oxide is also said to combine with soda to form insoluble sodium titanates (19, 51) and still further increase the soda losses. It is quite essential, therefore, in selecting ore for the Bayer process, to keep the silica and titania as low as practical. Generally the bauxites employed contain less than 5% silica, or if titania is present, the ore should not contain more than 3% of total titania and silica.

With depletion of domestic reserves of high-grade bauxite, the aluminum industry has to consider the use of low-grade (high-silica) bauxites. Since the Bayer process is only economical for bauxites with low silica content, many other processes are being studied. These processes may be broadly classified (51) into two types: (a) dry processes in which the essential step is furnacing operation, e.g., sintering with lime or soda to produce soluble sodium or calcium aluminates; (b) wet processes in which the aluminum is directly extracted by means of an aqueous agent, e.g., the alkaline (Bayer process) or acid extractions.

Soda and lime are the two principal materials used in the dry processes. Finely ground bauxite is uniformly mixed with powdered soda ash and the charge thus prepared is sintered by heating to the reaction temperature. Fused sodium carbonate not only reacts with alumina to form sodium aluminate, but also with ferric oxide to form sodium ferrite, with titanium oxide to form sodium titante, and with silica to form sodium silicate (19). In the subsequent leaching process, the sodium ferrite reacts with water to form insoluble ferric hydroxide and sodium hydroxide, while silica is mostly precipitated as sodium aluminum silicate. The sodium aluminum silicate and sodium titanate formed represent real soda losses, and in addition, the silica may go into the solution and contaminate the product. Consequently, lime is usually added to form insoluble calcium salts with the impurities (e.g., $2CaO \cdot SiO_2$) and its addition is essential if the silica content of the raw material is high. Lime is sometimes used in the sintering process without any soda ash. The use of calcium carbonate instead of sodium carbonate has the advantage of eliminating loss of soda by votalization. A practical process of this type is the Pederson process. Edwards, et al. (19) describe the Pederson process as the smelting of a mixture of iron core, coke, lime and bauxite to produce a molten calcium aluminate of low silica content. Low-sulfur iron of a high grade is produced as a by-product. The alumina in the slag can be extracted by means of sodium carbonate solution which forms insoluble calcium carbonate and soluble sodium aluminate. This solution is filtered to permit the precipitation of an aluminum hydrate using carbon dioxide. The alumina hydrate is then calcined to free alumina.

If the lime-soda sintering operation is introduced as a cyclic step into the Bayer process, many of the difficulties of desilication can be overcome. This is the Alcoa Combination Process (20, 51). In this process, the high-silica bauxite is given the customary Bayer alkaline digestion without regard to the considerable amounts of alumina and soda that form insoluble silicates and pass into the red mud. The red mud is not discarded, however, but after the addition of limestone and soda ash is put through a sintering operation. The sinter is leached with caustic soda solution, which dissolves most of the alumina and soda but only a relatively small proportion of the silica. The leach liquor is then returned to the kiers for the next cycle in the treatment of fresh bauxite. This cyclic procedure has been found to have an economical extraction of about 85 to 90% of the alumina in high-silica bauxite and has been used on a large scale (20).

In wet processes, alkaline and mineral acids are used. Alkaline solutions are not practicable for raw materials other than bauxite owing to the poor extraction efficiency and silica content. Mineral acids, on the other hand, readily dissolve the aluminum both from bauxite and silicate bodies, while leaving behind the silica. All the acid processes are similar in principle; the roasted clay or mineral is treated with the chosen acid, aluminum, iron and some of the other impurities go partly or completely into solution, and the silica, together with other insoluble impurities, is filtered off. After treating the solution in some suitable way to remove the iron impurity, it is concentrated causing the aluminum salt precipitate. The solid phase is then dehydrated and decomposed thermally to produce alumina and the corresponding acid. The acid is removed and recycled (51).

Basically, the alumina processes may be divided into two classes by the reagent used: alkaline or acid (19). The Bayer process and the sintering process with soda ash or limestone are examples of alkaline processes. Iron causes no trouble in alkaline processes, ferric oxide being substantially insoluble in alkaline solutions. Iron is thus easily and cheaply eliminated. Silica, on the other hand, is always attacked by the alkaline processes and its elimination is always troublesome. Consequently alkaline processes require low silica content raw materials.

Acid processes, on the contrary, always dissolve more or less of the iron, but most of them do not dissolve the silica. Titanium is likely partly dissolved. Any colloidal silicic acid formed by acid attack on the mineral can be readily and quite completely removed, but the iron salts are so closely related to the aluminum salts in their chemical behavior that a complete separation is always difficult, expensive and commercially unattractive. From their nature, therefore, the acid processes are best adapted to the treatment of ores low in iron such as kaolin, feldspar, alunite or leucite.

Fly ash, however, contains an abundance of both silica and iron. In United States' fly ashes the ranges of silica and iron are 30-50% and 9-38% respectively (14). As a result of this nature of fly ash, it is felt that a study on alumina recovery processes developed for a material that affords some degree of chemical similarity to fly ash is necessary.

Recovery of Alumina from Clays

Since the reserve of bauxite is very limited in the U.S., government agencies and industry began to search for other sources for the production of alumina very early. Aluminum is the most abundant metallic element in the world. It is an important constituent in practically all common rocks except sandstone and limestone, and, even in these, it is nearly always present as an impurity. The principal alumina-bearing minerals are listed in Table 1 roughly in the order of their abundance as given by Edwards, et al. (19).

Of the minerals in Table 1, the feldspars are by far the most abundant because they are the principal constituents of igneous rocks. Feldspars, however, are not usually considered as a potential source of alumina. Tilley, et al. (71) give as reasons that feldspars does not

Table 1. Principal aluminum-bearing minerals

Name of mineral	Aluminum content calculated as Al_2O_3, weight percentage
Feldspars:	
Orthoclase, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$	18.4
Albite, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	19.5
Anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$	36.7
Micas:	
Muscovite, $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	28.5
Biotite, variable composition	15.0±
Phlogopite, variable composite	15.0±
Clay minerals:	
Kaolinite (kaoline), $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	39.5
Halloysite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$aq	36.9
Allophanite (allophane), $Al_2O_3 \cdot SiO_2 \cdot 5H_2O$	40.5
Leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$	23.5
Nephelite (nepheline), $3Na_2O \cdot K_2O \cdot 4Al_2O_3 \cdot 9SiO_2$	33.2
Analcite, $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$	23.2
Scapolite, calcium-sodium-aluminum silicate	30.0±
Spodumene, $CiO_2 \cdot Al_2O_3 \cdot 4SiO_2$	27.4
Pyrophyllite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$	28.3
Cyanite (kyanite), $Al_2O_3 \cdot SiO_2$	63.2
Sillimanite, $Al_2O_3 \cdot SiO_2$	63.2
Andalusite, $Al_2O_3 \cdot SiO_2$	63.2
Dumortierite, possibly $4Al_2O_3 \cdot 3SiO_2$	Variable
Staurolite, $2FeO \cdot 5Al_2O_3 \cdot 4SiO_2 \cdot H_2O$	55.9
Gibbsite (hydrargillite), $Al_2O_3 \cdot 3H_2O$	65.4
Diaspore, $Al_2O_3 \cdot H_2O$	85.0
Corundum, Al_2O_3	100.0
Alunite, $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$	37.0
Alunogen, $Al_2(SO_4)_3$: $18H_2O$	Variable
Pickeringite, $Al_2(SO_4)_3 \cdot MgO \cdot SO_4 \cdot 22H_2O$	Variable
Spinel, $MgO \cdot Al_2O_3$	71.8
Hercynite, $FeO \cdot Al_2O_3$	58.6
Gahnite, $ZnO \cdot Al_2O_3$	55.7
Warellite, $4AlPO_4$: $2Al(OH)_3 \cdot 9H_2O$	38.0
Cryolite (kryolith), $3NaF \cdot AlF_3$	24.3

occur in large high-grade deposits, its value for use in pottery and other industries is much more than that associated with its aluminum and potash after extraction, and all of the processes that have been proposed are expensive. Thus most of the investigations directed toward finding a substitute for bauxite are based on clays.

There are two general processes for extracting alumina from clays: An acid process that uses an acid to selectively dissolve the alumina and a sintering process that uses lime or lime and soad followed by a leaching step using water or dilute alkaline solutions. Other processes such as an ammonium sulfate process, ankalunite process and a newly developed AARC's chlorination process (47) will also be given a brief review here in order to fully understand the behavior of the constituents common in clays and fly ashes.

Acid processes for alumina recovery from clays

As mentioned earlier, the main difficulty in acid extraction processes has always been that iron in the aluminous raw materials dissolves coincidentally with the alumina. Besides the removal of the iron impurity, however, there are two minor difficulties inherent in acid extraction processes (71). The dissolution of the alumina from the mineral used and the problem of transforming the aluminum salts obtained to oxide along with the recovery of the acidic portion of the salts. Of the numerous acids, the only ones that seem to be able to extract alumina are sulfuric, sulfurous, nitric and hydrochloric acids. The neutral and acid salts of sulfuric and sulfurous acids are also used and sometimes included in this category. From the standpoint of the chemical engineer it could be most desirable to use sulfuric acid. Hydrochloric acid or nitric acid offers more difficulty in handling when compared with the use of normal sulfuric acid and the acid sulfates of alkalies or ammonia. In addition, sulfuric acid is the least expensive (53).

The preliminary treatment of clays comprises grinding, roasting and sometimes the extraction of impurities (51, 71). The grinding reduces the clay to a powder of a fineness of 80 to 100 mesh, a particle size necessary during extraction because the acid penetrates slowly through a coating of insoluble silica left on the outside of the grains by the action of the acid (71). Roasting follows and increases the extractability of alumina in clays. It is found (19, 71, 73) that the extractability is much increased by roasting at temperatures of 500 to 900°C, and is decreased by temperatures that are higher for any length of time. Clays go through a dehydration reaction at these temperatures to relate the moisture and form amorphous metakaolin in which the alumina is more extractable. But when the temperature goes higher than 900°C, metakaolin will gradually change into mullite which is very refractory (11, 12).

<u>Sulfuric acid processes</u> The acid leaching step may be described by the following reaction:

$$Al_2O_3 \cdot 2SiO_2 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 2SiO_2 \downarrow + 3H_2O \qquad (6)$$

Different concentrations of sulfuric acid have been tried and recommended (71, 73). The use of concentrated sulfuric acid is not favored because of the formation of insoluble hydrated acid aluminum sulfate which is believed to have the formula of $Al_2(SO_4)_3 \cdot H_2SO_4 \cdot 3H_2O$. There are several methods to remove the iron from the solution. Iron can be precipitated as metallic iron from the aluminum sulfate solution by electrolysis in mercury cathode cells (55). The second way is a chemical method. Iron in solution as ferric sulfate is precipitated as an iron-manganese complex by the addition of manganese sulfate and ozone to the solution (55, 73). Walthall, et al. (73) have cited the following reactions for the chemical removal of iron:

$$MnSO_4 + O_3 + 2H_2O \longrightarrow M_2MnO_3 + H_2SO_4 + O_2 \qquad (7)$$

$$6H_2MnO_3 + Fe_2(SO_4)_3 \longrightarrow 2Fe(HMnO_3)_3 + 3H_2SO_4 \qquad (8)$$

The overall reaction is then (55, 73):

$$Fe_2(SO_4)_3 + 6MnSO_4 + 6O_3 + 12H_2O \longrightarrow 2Fe(HMnO_3)_3 + 6O_2 + 9H_2SO_4 \qquad (9)$$

A third process has been investigated by Peters, et al. (55) which utilizes a 68% ethanol solution. Here a mixture of ethanol and aluminum sulfate solution forms a two phase system containing aluminum sulfate in an ethanol-water solution. Subsequent cooling results in the crystallization of aluminum sulfate hexadecahydrate, $Al_2(SO_4)_3 \cdot 16H_2O$, leaving ferric sulfate in the solution.

The removal of silica from the solution can be achieved by mixing iron-free aluminum sulfate solution with clay residue amounting to 1% of the solution at 85°C (73). Walthall, et al. (73) and Scott (63) also gave the effects of other variables such as temperature, pressure and particle size, etc. on the extraction.

Hydrochloric acid processes When compared with sulfuric acid processes, hydrochloric acid processes have the disadvantage of being more expensive. This process has been investigated by several researchers (29, 54). The extraction of alumina by hydrochloric acid is usually carried out at about 100°C under one atmosphere pressure using a dilute HCl solution. The leaching step can be expressed by the following reaction:

$$Al_2O_3 \cdot 2SiO_2 + 6HCl \longrightarrow 2AlCl_3 + 2SiO_2\downarrow + 3H_2O \qquad (10)$$

The solution resulting from leaching contains aluminum and iron chlorides and an insoluble residue consisting primarily of silica, which can be separated by filtration. Various processes to remove the iron were evaluated by Peters, et al. (54). Precipitation of hydrated aluminum chloride seems best. By saturating a cool hydrochloric acid solution of the soluble constituents of clay with hydrochloric acid gas, only aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, is precipitated. Practically all the other constituents remain in solution (29, 54). This is in contrast with the separation of iron by extraction with ether, whereby only part of the iron is removed, and almost all other impurities remain with the alumina (29, 54).

Nitric acid processes Nitric acid processes have been the least studied. Like the hydrochloric acid process, the nitric acid process is generally more expensive than the sulfuric acid process. Moreover, its salt on thermal decomposition does not regenerate the free acid unchanged, as the acid is largely decomposed into oxides of nitrogen, which require reoxidation to form nitric acid (19). Several investigations dealing with nitric acid processes were cited by Edwards, et al. (19) in their book.

Ammonium sulfate process for alumina recovery from clays

This process has sometimes been classified as an acid process. Various modifications (22, 65, 69) have been investigated since the process was first proposed. The process involves the following essential steps: (a) sulfating the alumina in the clay by baking with ammonium sulfate at approximately 400°C, (b) leaching with water to extract aluminum sulfate and ammonium sulfate, (c) crystallization of ammonium alum, (d) conversion of the alum to aluminum hydroxide by the ammonia gases given off during the baking, and (e) calcining the aluminum hydroxide to alumina (65, 69). St. Clair, et al. have proposed that the reaction between kaolinite and ammonium sulfate during the baking is as follows:

$$(NH_4)_2SO_4 \xrightarrow{400^oC} NH_3 + NH_4HSO_4 \qquad (11)$$

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 3NH_4HSO_4 \longrightarrow Al_2(SO_4)_3 + 3NH_3 + 5H_2O + 2SiO_2 \qquad (12)$$

$$Al_2(SO_4)_3 + (NH_4)_2SO_4 \longrightarrow (NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \qquad (13)$$

Reports of the extraction of alumina from clays show that 80% to 98% of the alumina can be recovered by this process (22, 65, 69).

Sintering processes for alumina recovery from clays

In general, the high temperature sintering processes for extraction of alumina from highly siliceous raw material make use of calcium oxide for fixation of the silica and fall into two classes with reference to the device for fixation of the alumina. In one group soda ash is added to the raw-material mix to form sodium aluminate, and in the other a further addition of lime is made for fixation of alumina, the two types being designated as soda-lime-sinter and lime-sinter processes, respectively. Since the lime-sinter process is experimentally investigated in this thesis with regard to its application to fly ash, the review of the sintering processes is limited to the use of lime only.

A complete sintering process involves several steps: (a) preparation and mixing of raw materials; (b) furnacing; (c) leaching; (d) purification of solution; (e) recovery of alumina trihydrate from solution; and (f) calcination of the hydrate to the oxide.

In the lime-sinter process, intimate mixing of the aluminous material and limestone is essential. The raw materials are generally ground to such fineness that 80 to 90% pass a 200-mesh screen (3, 24, 62). Mixing is usually carried out in the dry state. Archibald and Nicholson (3), however, found that results from dry blending even when the materials were ground together were never as satisfactory as from mixtures prepared by wet grinding. Dispersed clay slurry yielded better results than undispersed clay of equivalent grade (3).

The amounts of limestone used in this process is in the proper proportion to (2, 3, 24, 25):

1. Convert all SiO_2 to dicalcium silicate.

2. Convert all Al_2O_3 to calcium aluminates of mixed composition but approximately in a proportion of 1.5-1.7 moles CaO per mole Al_2O_3.

3. Convert minor constituents in part to ferrites, titanates, phosphates and the like. These compounds are irregular in formation and, if present in minor amounts, are usually disregarded in the calculation of proportions. For a more exact test, it is recommended that TiO_2 be assumed converted to $CaO \cdot TiO_2$ and Fe_2O_3 to $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, although $2CaO \cdot Fe_2O_3$ was also suggested (62).

The heat treatment of raw mix to produce satisfactory sinter, the reactions involved, and the possible phases developed in the lime-sinter process are very similar to those involved in the manufacture of Portland cement. In sintering a limestone-clay mixture the steps involved are (a) driving off all free and combined water, (b) driving off carbon dioxide, (c) conversion of all SiO_2 to properly developed β-dicalcium silicate, and (d) conversion of Al_2O_3 to calcium aluminates $5CaO \cdot 3Al_2O_3$ and $CaO \cdot Al_2O_3$. Although the proper maturing temperature varies with the raw and the rate of heating, it is usually between the limits 1300-1400°C for lime-sinter process (2, 3, 25, 62). It is at these temperatures that the proper phases develop and excessive liquid formation avoided. The importance of the time factor in this step is related not only to formation of the desired calcium aluminates, which appear to involve slower reactions than silicate formation, but also to completion the crystallization of dicalcium silicate and other components (3). It usually takes one hour or less (3, 25, 62).

When the sintered materials are cooled, they often decrepitate. This phenomenon is commonly called "dusting" (25). 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 gives the best alumina extraction and is the most easily handled in leaching. For those sinters, which do not disintegrate, grinding is required for subsequent extraction.

In the cement industry, the transformation of dicalcium silicate from β to γ form is, however, not desired. Preventing this transformation can also be important in certain alumina recovery processes. Many factors can influence this transformation (10, 49, 78). It is found that at each temperature below the bulk phase inversion point there is a critical size for the nuclei of the new phase. If a nucleus exceeds the critical size, it will grow and form a crystal; if it is less than the critical size it will revert to the old phase. This is one of the possible ways to stabilize the β-form of calcium orthosilicate. Another mechanism of stabilization involves the impurities present. Zerfoss and Davis (78) discuss the possible effects of the impurities under the heading of Physical and Crystal-Chemical Stabilization. The only way for impurities to cause physical stabilization is through an increase of strain due to glass formation or to affect the specific volume or surface energy by solid solution. Chemical stabilization is usually achieved by forming a solid solution. The most effective stabilizers for the β-form are B_2O_3, P_2O_5, and Cr_2O_3 (10, 49, 78). Reports of the effect of MgO, Fe_2O_3, CaO, Al_2O_3 and SiO_2 on stabilization are not all the same.

Nonetheless, they all have a stabilizing effect under certain conditions (10, 49, 78).

A 3 to 8% sodium carbonate solution is usually used for the leaching step. The reactions involved are as follows (36, 62):

$$5CaO \cdot 3Al_2O_3 + 5Na_2CO_3 + 2H_2O \rightleftharpoons 6NaAlO_2 + 5CaCO_3 \downarrow + 4NaOH \tag{14}$$

$$CaO \cdot Al_2O_3 + Na_2CO_3 \rightleftharpoons 2NaAlO_2 + CaCo_3 \downarrow \tag{15}$$

Sodium aluminate dissolves in water with great rapidity. Sodium ferrite is decomposed in accordance with the reaction:

$$2NaFeO_2 + 2H_2O \rightleftharpoons 2NaOH + Fe_2O_3 \cdot H_2O \downarrow \tag{16}$$

The reactions between sodium carbonate and calcium aluminates are reversible. They shift further to the right with increasing dilutions of the solutions, at elevated temperatures, and in the presence of an excess of Na_2CO_3 (24, 36).

Under the leaching conditions, the pregnant solution will usually contain silica up to approximately 2 to 3% of the dissolved alumina (3, 24, 62). This requires that a separate desilication operation be carried out on the solution to produce alumina of satisfactory grade in the following precipitation step. The desilication process involves the digestion of the solution at elevated temperatures in pressure vessels. This operation resembles the Bayer digestion process and the mechanism of silica inactivation is probably similar (3).

Kalunite process for alumina recovery from alunite

The kalunite process is restricted to aluminous material that can be converted to potassium alum or equivalent normal alum (23, 56). This process consists of dehydration of the alunite at 600°C, followed by leaching the ore with 10% sulfuric acid for dissolving the alumina. The reaction can be expressed as follows:

$$Al_2O_3 \cdot 2SiO_2 + 3H_2SO_4 + K_2SO_4 + 21H_2O \longrightarrow K_2SO_4 \cdot Al_2O_3 \cdot 3SO_3 \cdot 24H_2O + 2SiO_2 \tag{17}$$

The potassium alum is crystallized, separated from the mother liquor and washed. The dissolved alum is decomposed in autoclaves to the basic alum which is then calcined to produce a mixture of alumina and potassium sulfate (23, 56).

Toth process for alumina recovery

This process is dveloped at a research firm called Applied Aluminum Research Corporation (47). The Toth process begins with a chlorination step in the presence of a reductant such as coke. The usual products are chlorides of aluminum, iron and other metals such as titanium. In a subsequent step, fractional condensation separates the metal chlorides. Then the aluminum chloride reacts with manganese metal to produce aluminum metal and manganese chloride. Manganese chloride is then processed to recover and recycle manganese metal and chlorine (47).

After examining the various processes used to recover alumina from clays, a brief review is also given below to the recent work on the recovery of iron and alumina from fly ash.

Iron and Alumina Recovery from Fly Ash

Iron in the fly ash not only occurs in ferruginous glasses but also as crystalline hematite and magnetite. Being highly magnetic in nature (7, 39, 43, 44, 48, 74) the iron in fly ash can be removed by magnetic separation. The magnetic fraction is made up in part of extremely fine crystalloids of magnetite imbedded in a siliceous glass of high specific gravity. In addition to the magnetite, iron is also present in this glass in several forms including dissolved iron oxides, together with amorphous or crystalloidal iron compounds (44).

Minnick (44) describes a magnetic separation that produces a unique, rotating magnetic field ideally suited to the dry fractionation of very fine powders. When finely divided ferromagnetic and nonferromagnetic particles are introduced into the rotating magnetic field, the rotating magnetic component of the field brings the particles into synchronous rotation which imparts random motion to the particles. The random motion of the particles will in turn place them in an expanded state relative to each other effectively filtering out the magnetic iron-rich particles from the iron-deficit particles (44).

Boux (7) uses a permanent magnet drum separator to separate iron from fly ash. He reports that up to 65% of the iron is concentrated in the magnetically separated particles. Nowak (48) separates the magnetic constituents in fly ash with an electromagnetic plate separator with a travelling magnetic field.

By separating the fly ash magnetically, one cannot only recover iron from fly ash but also eliminate to a marked degree the majority of contamination from iron that frequently occurs in the recovery of alumina.

Basically, acid process and sintering process are the two general methods to recover alumina from the nonmagnetic part of fly ash, which is low in iron. However, Klemm (34) suggested that two other processes may also work for fly ash. One of them is a hydrothermal treatment as in the Bayer process but with lime added to the autoclave and more severe conditions of temperature, pressure and alkali concentration used to satisfactorily separate alumina from fly ash. The other one is actually a chlorination process like the one described before (47).

Nowak (48) states in his paper that in Poland both acid and sintering processes can successfully extract alumina from the nonmagnetic fraction of fly ash. In his acid process, sulfuric acid is added to the aluminous material and the suspension is heated by high pressure steam in a direct contact system. In this way leaching is already achieved at this stage. A two-stage separation of the pure aluminum salts by crystallization follows and there the hydrolysis of the aluminum salts. The product is heated to 1300°C to yield metallurgical aluminum oxide and sulfur dioxide which can be used for recycle (48).

In the sintering process, lime is used. It is said (48) that the control of the disintegration process, which is based on the polymorphis of the β-phase of calcium orthosilicate, is the main factor on which the whole process of the alumina production depends. Nowak (48) also found that certain ions occurring in fly ash have a stabilizing action on the β-form of dicalcium silicate. This auto-disintegration dust with a high specific surface area is the basic material for the further process of alumina production by extraction with soda solutions.

Based on the above review of alumina recovery processes from high silica materials and fly ash, an experimental investigation of iron and alumina recovery from a particular power plant fly ash was undertaken. Such a study was intended to characterize the fly ash as a potential source of alumina and iron.

EXPERIMENTAL PROCEDURE

It is well known that fly ashes from different sources may have different chemical composition and physical properties. In fact, it is also difficult to characterize a typical fly ash from a power plant. In view of the widely varying nature of fly ash, a particular sample was sought that represented as closely as possible the average chemical composition of nine available midwestern power plant fly ashes.

By comparing the data on chemical composition from Cavin (15), a sample of fly ash from a power plant in Milwaukee, Wisconsin was chosen for this research work. Both Leonard (37) and Cavin (15) have provided the physical properties and chemical composition as well as other information on this sample. As a matter of convenience, this sample has been designated as C-1 fly ash throughout this thesis.

Material

The Milwaukee fly ash (C-1) was collected by mechanical precipitators from a dry bottom type of boiler fired with coal from western Kentucky and southern Illinois. The boiler was located at the Lakeside power plant in Milwaukee, Wisconsin.

Leonard (37) provided the following physical characteristics for sample C-1 fly ash (Table 2).

From Cavin's (15) study, more information was provided. The chemical composition of C-1 fly ash, which is shown in Table 3, was given in his thesis.

Table 2. Physical characteristics of fly ash sample C-1 (37)

Total specific gravity[a]	Ignited specific gravity[b]	Percent passing 325 sieve[a]	Mean diameter, microns[c]	Specific surface area, cm^2/gm[d]
2.42	2.55	81.0	31.0	3370

[a] Total sample as received was used.

[b] Total sample ignited in a muffle at 600°C was used.

[c] Based on hydrometer and sieve analysis of ignited samples.

[d] Supplied by the Robert W. Hunt Co. of Chicago, Illinois. Based on a gas adsorption method, total sample used.

Table 3. Chemical composition of C-1 fly ash (15)

Component (weight percent)									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	C	Other	L.O.D.[a]	L.O.I.[b]
42.36	17.63	19.29	4.73	0.62	1.54	8.37	4.88	0.58	10.39

[a] L.O.D. is loss on drying to 110°C.

[b] L.O.I. is loss on ignition from 110-800°C.

Cavin (15) also tried water leaching of various size fractions of the fly ash sample to ascertain the water soluble content of each size fraction. The data showed that the soluble portion varied from 2.65% for the course particles (+ 65 mesh) to 4.88% for the fine particles (- 200 mesh). A magnetic separation of each particle size fraction was also performed by Cavin (15) in order to find the distribution of magnetic particles in the fly ash sample C-1. He found that this distribution in various size fractions is reasonably uniform. Variations occur from about 22% in the course (+ 65 mesh) to about 29% in the fines (- 200 mesh) (15). This would indicate that a simple screening alone would not reduce the iron content to any significant degree.

In order to study the extractability of alumina from this special sample by the lime-sinter process, the following experiments were performed.

Magnetic Separation

From previous studies of alumina recovery process, it is clear that iron acts as a contaminant in the lime-sinter process. In order to provide suitable material for experimental work on lime sintering, a magnetic separation was performed on C-1 fly ash. In view of the uniform distribution of magnetics in various size fractions (15), this separation was done on the whole C-1 fly ash instead of on any particular fraction of the ash.

The magnetic separation was performed in both dry and wet states to determine which method would give better separation.

The wet magnetic separation was done as follows: 100 gm of C-1 fly ash was dispersed in 500 ml of water in a separatory funnel which was placed between the poles of a strong horseshoe magnet. The magnetic particles were attracted to the funnel walls adjacent to the poles of the magnet, and the suspension containing nonmagnetic particles was drained into a large beaker. The magnetic particles were then washed down into a separate beaker. The two fractions were repeatedly subjected to this process until visual observation indicated that no more separation occurred. The water from the two beakers was removed by decantation and evaporation and the two fractions were weighed separately.

Magnetic separation in the dry state was accomplished by an electromagnet and a mechanical vibrator. The magnet, about 5" X 8", was put at about 25 to 30 degrees from the horizontal on a table. A thin plastic board of approximately the same size as the magnet was put on top of the magnet; the C-1 fly ash was then poured on the plastic board and an adjustable vibrator was placed against the bottom of the board. The rapid vibration of small amplitude of the plastic board made the nonmagnetic particles slide down the board, while the magnetic particles were held in place by the magnet. After being collected, both portions were separated in the same way again until no more magnetics remained on the board. Each portion was then weighed and sent for chemical analysis. The nonmagnetic C-1 fly ash was preserved for use in the lime-sinter process. It was anticipated that the iron deficient particles would provide better alumina recovery by eliminating to a degree the contamination from iron.

Quantitative Analysis

Both the magnetic and nonmagnetic portions of C-1 fly ash from the wet and then the dry magnetic separation were analyzed quantitatively for their oxide constituents, carbon and loss on drying and ignition. Techniques employed for these analyses were developed from analytical procedure set forth in the 1974 Annual Book of the American Society for Testing and Materials Standards (68).

The general procedures for these analyses are as follows (68). The sample to be analyzed is ashed under standard conditions and ignited to constant weight. Two solutions are prepared from the ash. Solution A is obtained by fusing the ash with sodium hydroxide followed by a final dissolution of the melt in dilute hydrochloric acid. Solution B is prepared by decomposition of the ash with sulfuric, hydrochloric and nitric acids. Solution A is used for the analysis of SiO_2 and Al_2O_3, and Solution B for the remaining elements.

The two solutions are analyzed by a combination of methods: (a) spectrophotometric procedures are used for SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and P_2O_5, (b) chelatometric titration for CaO and MgO and (c) flame photometry for Na_2O and K_2O.

Preparation of Pellets

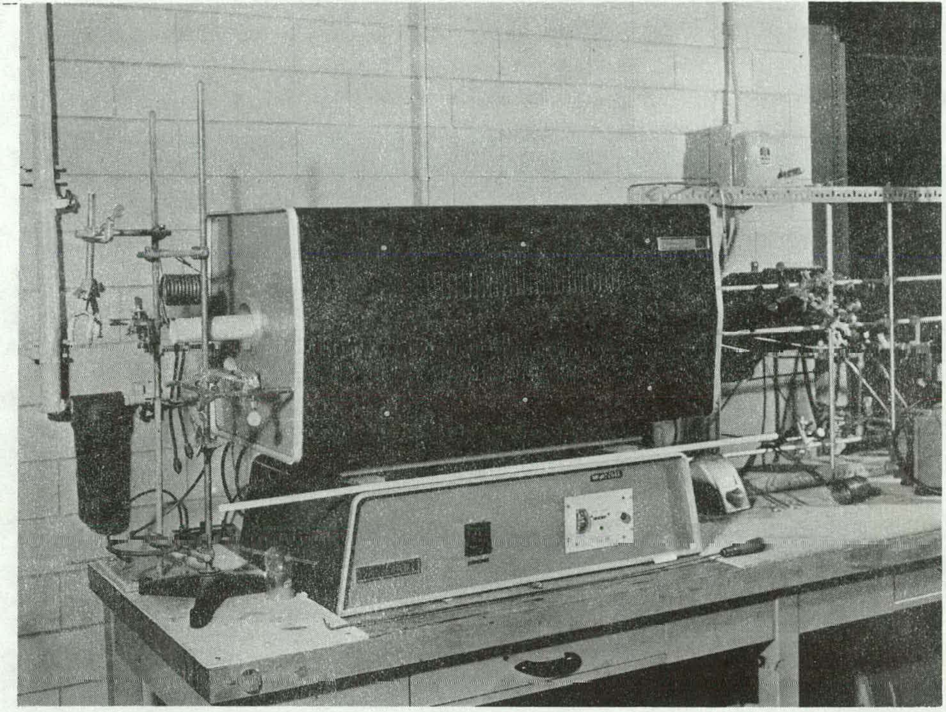
Proportioned nonmagnetic C-1 fly ash from dry separation and calcium carbonate were mixed and ground in a ball mill for two hours. Then pellets were made out of this mixture. In order to hold the particles together, water of about 8% to 9% of the total mixture by weight was added as a binder. Pellets were formed using a hydraulic pressing machine of Model B manufactured by Fred S. Carver, Inc. A load of 6000 lbs was used for most of the pellets, but other loads were also tried. The pellets had a diameter of 1/2 inch and a height of about 1/4 inch.

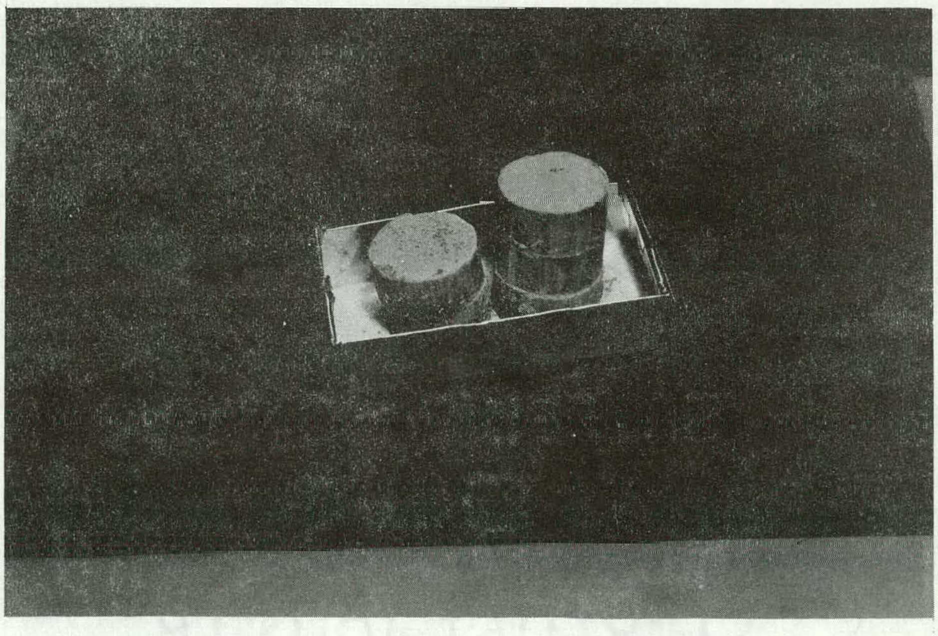
Furnacing

The furnace used in this sintering process is a product of Type 59545 from Lindberg Hevi-Duty Division of Sola Basic Industries (Figure 2). The control systems of this furnace are capable of controlling the temperatures to better than $\pm 1^{\circ}C$. The furnace uses silicon carbide as the heating element and is designed such that the temperature of a wide region in the center is maintained at the established setpoint.

Figure 2. The Lindberg hevi-duty furnace used in the sintering tests

Figure 3. The platinum boat and pellets (1/2 inch diameter). A layer of alundum powder was used to prevent the pellets from sticking to the boat





The temperature distribution along the tube in the furnace was measured once with a thermocouple and it was as shown in Figure 4.

The pellets were held in a platinum "boat" with a layer of about 1/8 inch of corundum powder which was added to prevent the pellets sticking to the boat after the furnacing step (Figure 3). The corundum powder is a refractory material with a low reactivity even at high temperatures (33). It was felt that the possibility of contamination from this powder was very small because of its inertness.

In view of the fact that the furnace takes a very long time to reach a temperature of 1340°C, the boat containing the pellets was pushed into the furnace little by little using a high-alumina rod instead of putting it in the center of the tube at the beginning. By so doing it is possible to avoid thermal shock in the tube and yet simulate a heating treatment as might occur in a continuously operated industrial process. The thermal history of the pellets was measured using an optical pyrometer (Figure 5). This treatment was kept roughly the same in all the runs.

After keeping the sample at the desired temperature for a desired period, the furnace was cooled down at a constant rate of 200°C/hr until it reached 1000°C. Then the boat was pushed out of the tube as soon as possible, usually within ten minutes, using care to avoid any thermal shock to the tube. The pellets were allowed to cool in the air and were then transferred to a desiccator and held for further experiments. Sometimes the pellets partially disintegrated during the cooling process.

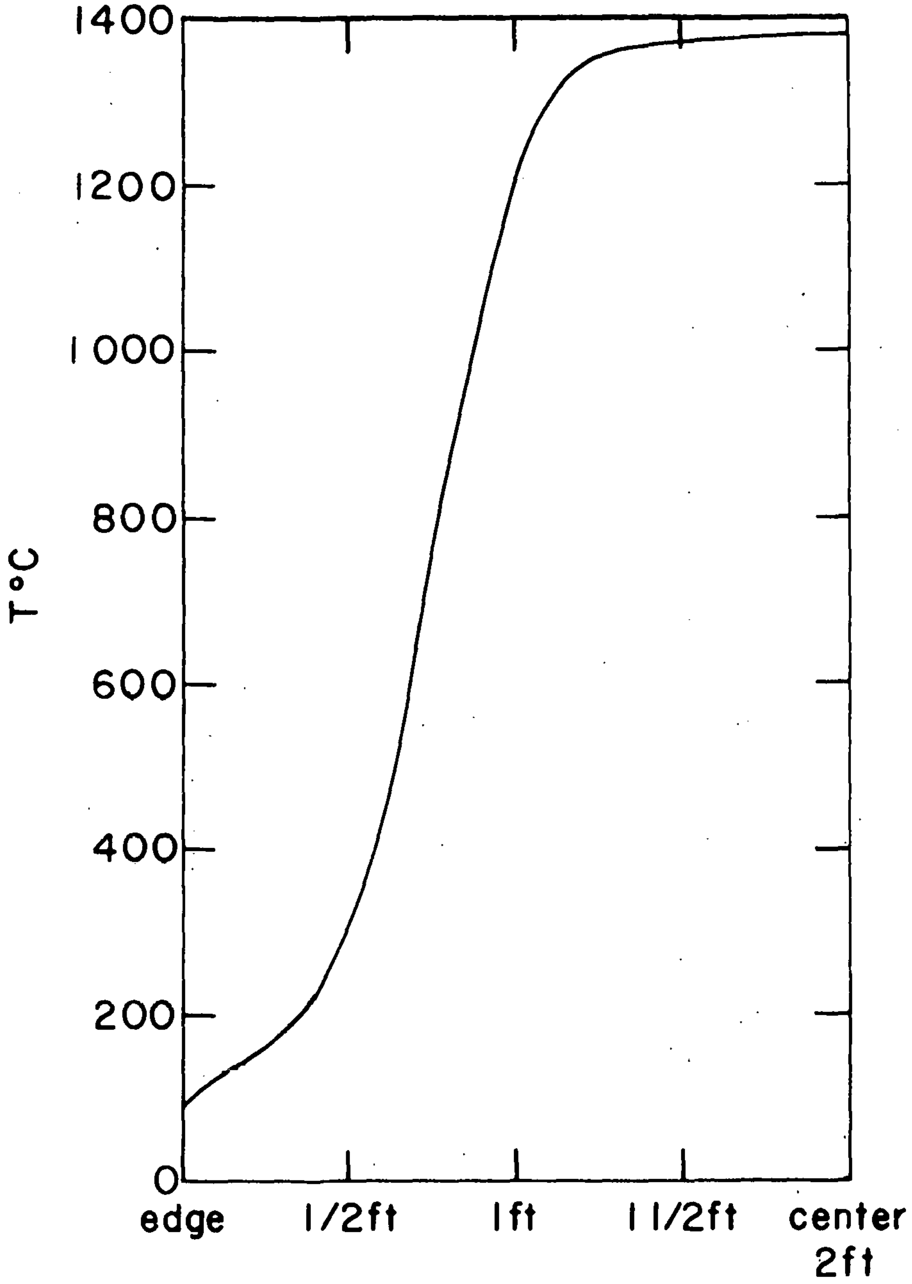


Figure 4. The temperature distribution along the tube when the furnace is at 1370°C

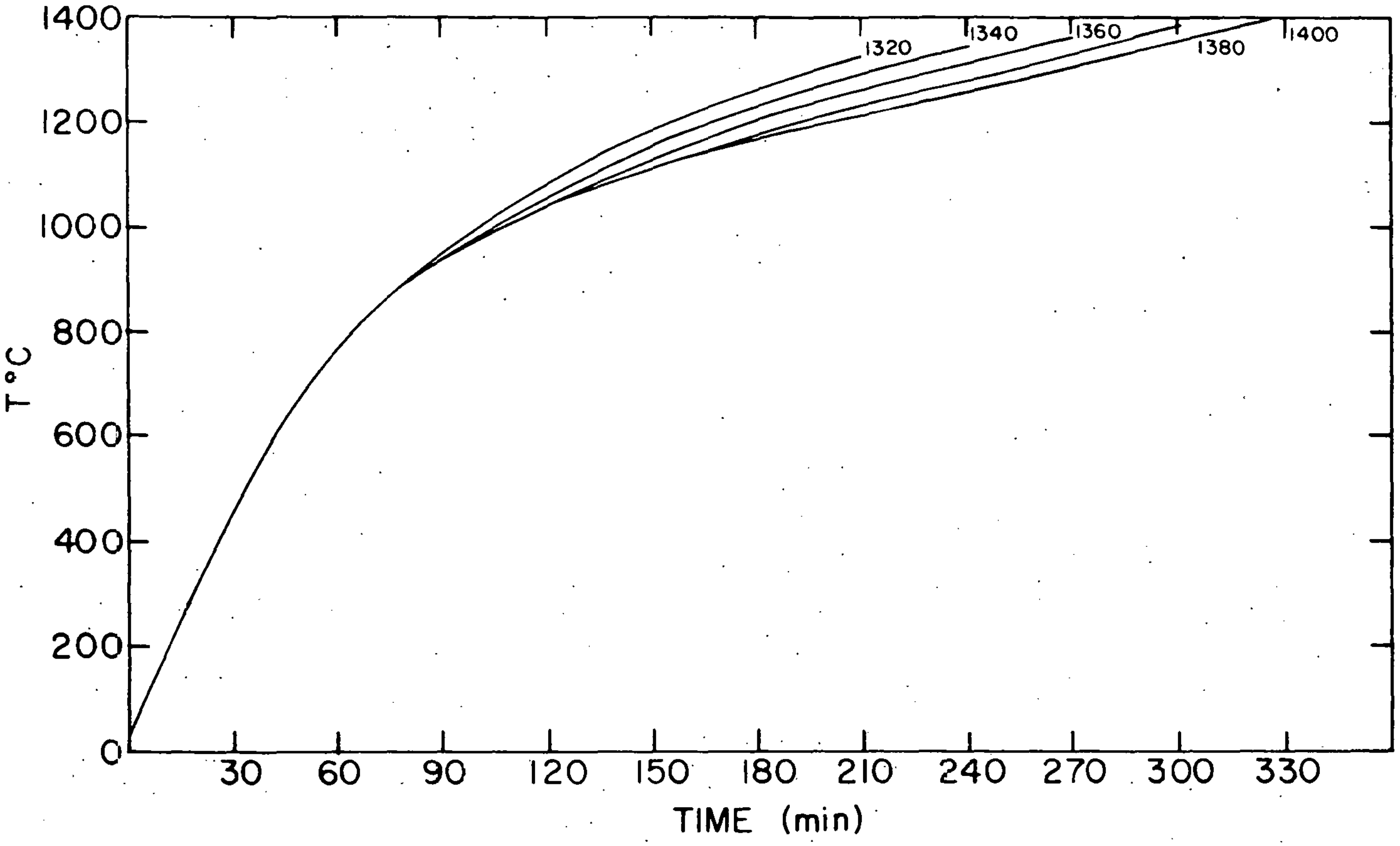


Figure 5. The temperature history of the pellets from ambient temperature to the desired sintering temperature

Qualitative Analysis of the Sintered Materials

In an attempt to understand the chemical reactions taking place during the sintering process, a qualitative analysis was carried out. It was expected that both calcium orthosilicate and calcium aluminates should have been formed in fairly large amounts. Their appearance was one of the principal factors required for the successful extraction of alumina. In order to identify the compounds formed after the high temperature treatment, the following experiments were performed.

Electron microprobe analysis

Scanning electron micrographs of the nondisintegrated pellets of the sinters were taken in order to better understand the morphology of the individual particles. A Hitachi XMA-S Electron Microprobe Analyzer was employed in this study. In this method a beam of electrons from an electron gun is focused by magnetic lenses to a fine spot on the surface of a specimen. At the point of impact several processes take place including secondary electron emission, electron backscattering and the generation of the characteristic X-ray spectrum. Both qualitative and quantitative analysis can be made with this X-ray spectrum. The sintered pellets were subjected to this energy dispersive X-ray elemental analysis to determine where aluminum, iron, calcium and silicon reside were in the pellets after the heat treatment. Electron micrographs were also taken at specific sites on the surface.

Photomicroscopic observations

Representative samples of the sinters were dispersed in alcohol and treated with ultrasonic waves to prevent agglomeration. Then photomicrographs of the samples were taken using a Bausch and Lomb camera-microscope arrangement under polarized light.

X-ray diffraction

The X-ray diffraction patterns for the sinters were obtained by using a basic Simens Kristalloflex 4 diffraction unit, an electronic circuit panel including a liner scale recorder, and a wide angle goniometer with a Geiger-Muller counter. The X-ray unit was operated using stabilized line power at 40 Kv and 20 ma for operating a copper target X-ray tube. Samples of sinters for X-ray analysis were reground to a uniform size to pass 300 mesh and were held in a milled mount of bakelite. Samples were slightly compacted and smoothed level with a glass slide. The divergent and scatter slits were 1°, the detector was a 0.2° slit and a strip nickel filter was used. The scanning speed was 2° 2θ/min. from 15° to 60°. The compound phases of the samples were identified by reference to the ASTM data file (1957) and the corresponding data cards.

Leaching of the Sinters

The sinters were ground to pass 200 mesh before they were extracted. Weighed samples of most sinters were extracted with 3% sodium carbonate solutions using constant stirring to prevent settling. The extraction time was 15 minutes and the temperature was $75^{\circ}C$. Sufficient sodium carbonate solution was added to provide 1.66 mole of Na_2CO_3 for each mole Al_2O_3 calculated to be present in the weighed sample. The extract was immediately filtered off and the residue washed. The extract was analyzed for alumina and silica.

Most of the leaching work was done under the conditions mentioned above, except those in which the effect of leaching on the extraction of alumina was investigated. Different temperatures, different concentrations of Na_2CO_3 solution, and also different ratios of Na_2O_3/Al_2O_3 were used. The total amounts of Al_2O_3 in the sinters were calculated from the chemical analysis of the nonmagnetic fly ash and the amount of CaO used. No further chemical analysis was performed on the sinters.

Analysis of Extracts

The amount of aluminum in the extract was determined by a complexometric titration (58). This is a simple and rapid procedure to determine iron and aluminum in mixtures. The extracts were acidified at first, then excess 0.05 M CDTA (1,2-diaminocyclohexane tetra-acetic acid) was added. The pH was brought to 5-5.5 by hexamethylenetetramine. Several drops of 0.5% Xylenol Orange was used as an indicator. The solution was titrated with 0.05 M lead nitrate. The consumption of CDTA gave the sum of Fe and Al. The amount of Fe can be determined as follows: To an aliquot of the extract add 1 M ammonium flouride (0.5-0.8 ml for 1 mg Al). After 5 minutes add a measured volume of CDTA, adjust the pH to 5-5.5 and titrate with 0.05 M lead nitrate. This consumption of CDTA gives the content of Fe. The amount of aluminum can be obtained by subtraction. Actually little iron entered the extract under the leaching conditions. For most of the time, no second titration was done to determine the iron content.

The silica content of the extract was determined spectrophotometrically. This procedure employs ammonium molybdate solution, a reducing solution and a tartaric acid solution and was well described in the 1974 Annual Book of ASTM Standards (68). Only a few extracts were analyzed for their silica content.

DISCUSSION OF RESULTS

The exploratory experiments conducted in this research were intended to provide some information on alumina and iron recovery from power plant fly ash. The design of this particular set of investigations enabled an evaluation of the extraction of alumina from a particular fly ash based on a lime-sinter process. In so doing, the results of each experiment are presented and discussed on the basis of observed experimental trends and direct experimental results.

Results of Magnetic Separation

The data presented in Table 4 give the chemical composition of both the magnetic and nonmagnetic parts of C-1 fly ash for both the wet and dry methods of separation. Both methods leave some iron in the nonmagnetic fractions. This is a consequence of the fact that some of the iron in the fly ash occurs as a dissolved oxide in the glassy particles (44). The magnetite, however, is readily separated and usually appears as very fine grains dispersed in a siliceous glass which is the principal constituent of alumino-siliceous material in the magnetic part of fly ash. A significant difference, as seen in Table 3, exists between these two methods is the disappearance of sulfur during the wet separation, which apparently results from the dissolution of all the compounds containing sulfur.

Photomicrographs of both parts of C-1 fly ash by dry separation are shown in Figures 6 and 7. In the picture of the nonmagnetic fraction, large, glassy particles are dominant, while the existence of some dark

Table 4. Composition of C-1 fly ash and its magnetic and nonmagnetic fractions

Sample		Chemical composition (weight percent)									
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	L.O.D.[a]	L.O.I.[b]
Whole fly ash		42.36	17.91	19.29	4.49	0.71	0.35	1.72	2.13	0.58	10.39
Dry separation	Magnetic	20.31	10.21	60.08	1.87	0.40	0.18	0.81	0.79	0.13	2.18
	Nonmagnetic	47.89	20.04	6.56	4.88	0.76	0.35	1.85	2.04	0.45	12.40
Wet separation	Magnetic	20.83	9.95	65.00	1.32	0.42	0.14	0.71	–[c]	0.12	1.70
	Nonmagnetic	53.0	22.83	5.24	5.82	0.99	0.31	1.90	–[c]	0.56	8.46

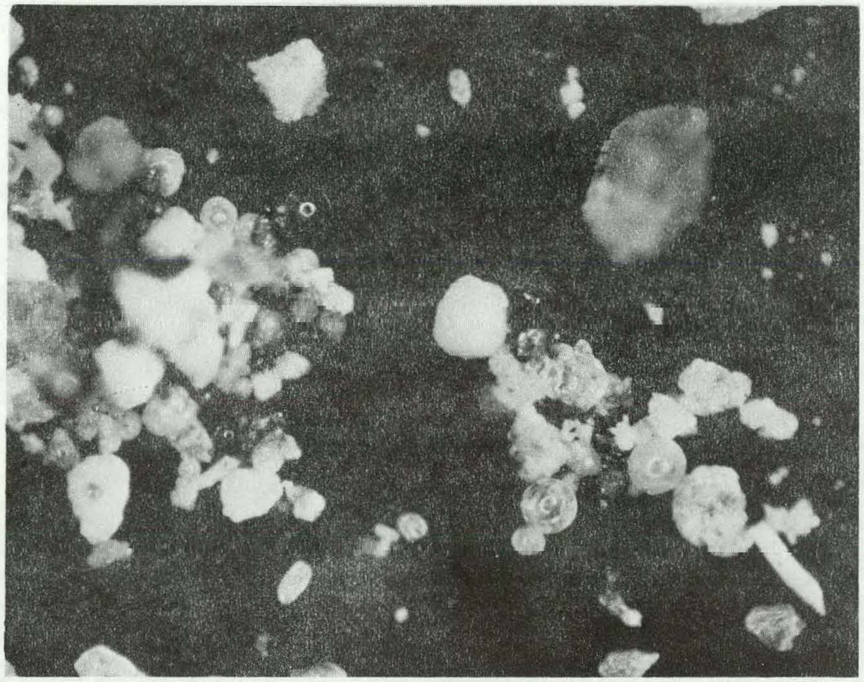
[a] L.O.D. is loss on drying to 110°C.

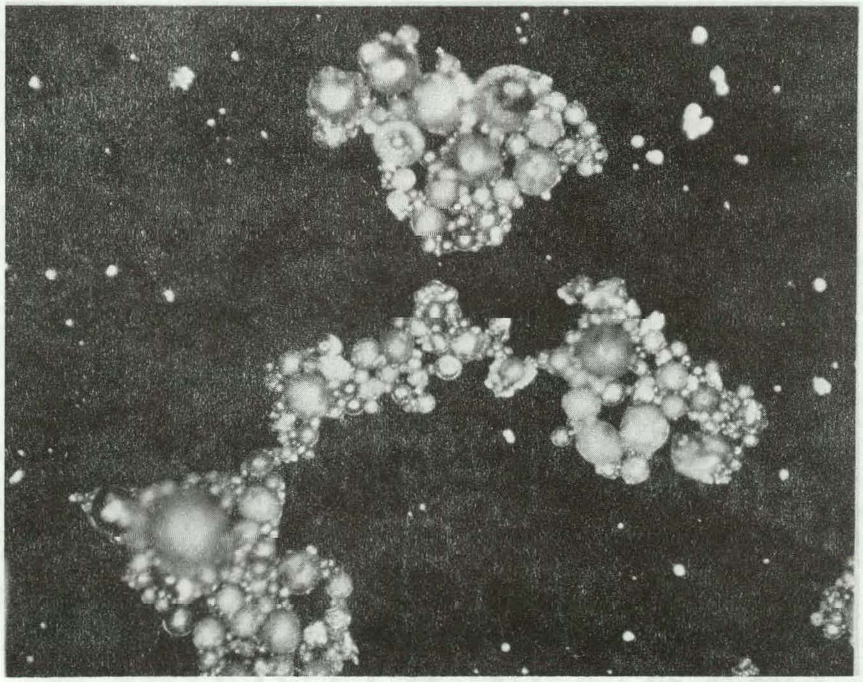
[b] L.O.I. is loss on ignition from 110-800°C.

[c] Not detected.

Figure 6. Photomicrograph of the nonmagnetic fraction of C-1 fly ash at 100X. There is an abundance of glassy particles which consist of the principal alumino-siliceous material in the fly ash

Figure 7. Photomicrographs of the magnetic fraction of C-1 fly ash at 100X. The dark iron oxide particle inclusions in the clear glassy material contribute to the magnetic susceptibility of the clear particles





particles of irregular shape indicates unburned carbon. The observations of the magnetic particles show an abundance of black spherical particles rich in iron. These particles give the magnetic fraction a dark-gray appearance which is darker than that of the nonmagnetic portion.

A brief comparison of the results from both separations is made in Table 5. The data show iron recovery and alumina "loss".

Table 5. Comparison of magnetic fractions from both dry and wet separations

Separation method	Magnetic fraction as weight percent of whole C-1 fly ash	Iron[a,b] content wt %	Iron[c] recovery wt %	Alumina[a] content wt %	Alumina[c] loss wt %
Wet	26.1[d]	65.00	87.9	9.95	14.5
Dry	23.6	60.08	73.5	10.21	13.5

[a] Iron content and alumina content are based on the magnetic fraction only.

[b] Iron as Fe_2O_3.

[c] Iron recovery and alumina loss are based on the total amount in the original whole fly ash.

[d] There is about 5.5% loss during the wet separation.

Results of the Effect of Furnacing Variables

The factors which may be varied at the will of the operator of a plant producing alumina by the lime-sinter process are the lime-to-fly ash ratio, the furnace temperature, the duration of the heating period, and the load applied to make pellets. Proper adjustment of these variables with respect to one another might be expected to result in an optimum yield for a given fly ash, assuming good extraction. Data showing the effects of these variables are presented in the sections that follow. Qualitative analysis of some of the sinters was also tried in order to give an explanation of the phenomena which occurred during the high temperature treatment. All the pellets used were made of the nonmagnetic portion of C-1 fly ash from a dry separation. The leaching conditions for recovering alumina from the sinter were 75°C, 15 minutes and a 3% Na_2CO_3 solution concentration.

Effect of the load used for making pellets

Eitel (21) has defined the sintering process as the mechanism whereby the grains in powders of defined particle properties, under the influence of a given temperature and, eventually, additional pressure adhere to one another. Sintering processes can occur with or without melt present and are usually referred to respectively as "wet" or "dry" sintering.

In modern atomic understanding of matter, sintering may be viewed as a function of a mobility of the structural particles of the solid reagents which sets in during a period of heating at a temperature above a well-defined threshold value (21). The atomic forces acting in the solids are manifested in the sintering process to produce inner or surface diffusion at phase boundaries. More precisely, the reacting particles must first be in close contact with one another, in order that attractive forces may interchange their atomic electrostatic field forces and their electrons. This is the reason why the pre-pressing during pellet formation is the essential factor in bringing about such contacts which enable the sintering material to increase its adhensive forces between particles and bring about diffusion phenomena.

The data showing the effect of the load used in pellet preparation on the overall recovery of alumina are shown in Figure 8.

It was observed during the experiments that the pellets made under higher loads gave more complete disintegration upon cooling. This fact would indicate that the calcium orthosilicate formed during heat treatment in the pellets of higher load had grains large enough to produce the desired dusting effect. However, the extraction percentage did not go up with the load. On the contrary, it showed a maximum at 8000 psig. This fact suggests that additional load is not necessary for higher extraction of alumina. Because the calcium oxide is added as calcium carbonate or limestone which decomposes upon heating to liberate CO_2 gas, this reaction product could be the reason for the extraction of alumina not increasing with the load.

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow \qquad (18)$$

According to the LeChatelier's principle, if a pressure is imposed upon the reaction above, the system will shift the equilibrium to the left. Thus the amount of CaO available to react with Al_2O_3 and SiO_2 will be decreased, and the extraction percentage of alumina also decreased. But when the load or pressure is just high enough to bring particles close together without causing this negative effect, the extraction of alumina will increase as shown in Figure 8. This is at least one possible reason for the effect of pressure used in pellet formation on alumina recovery.

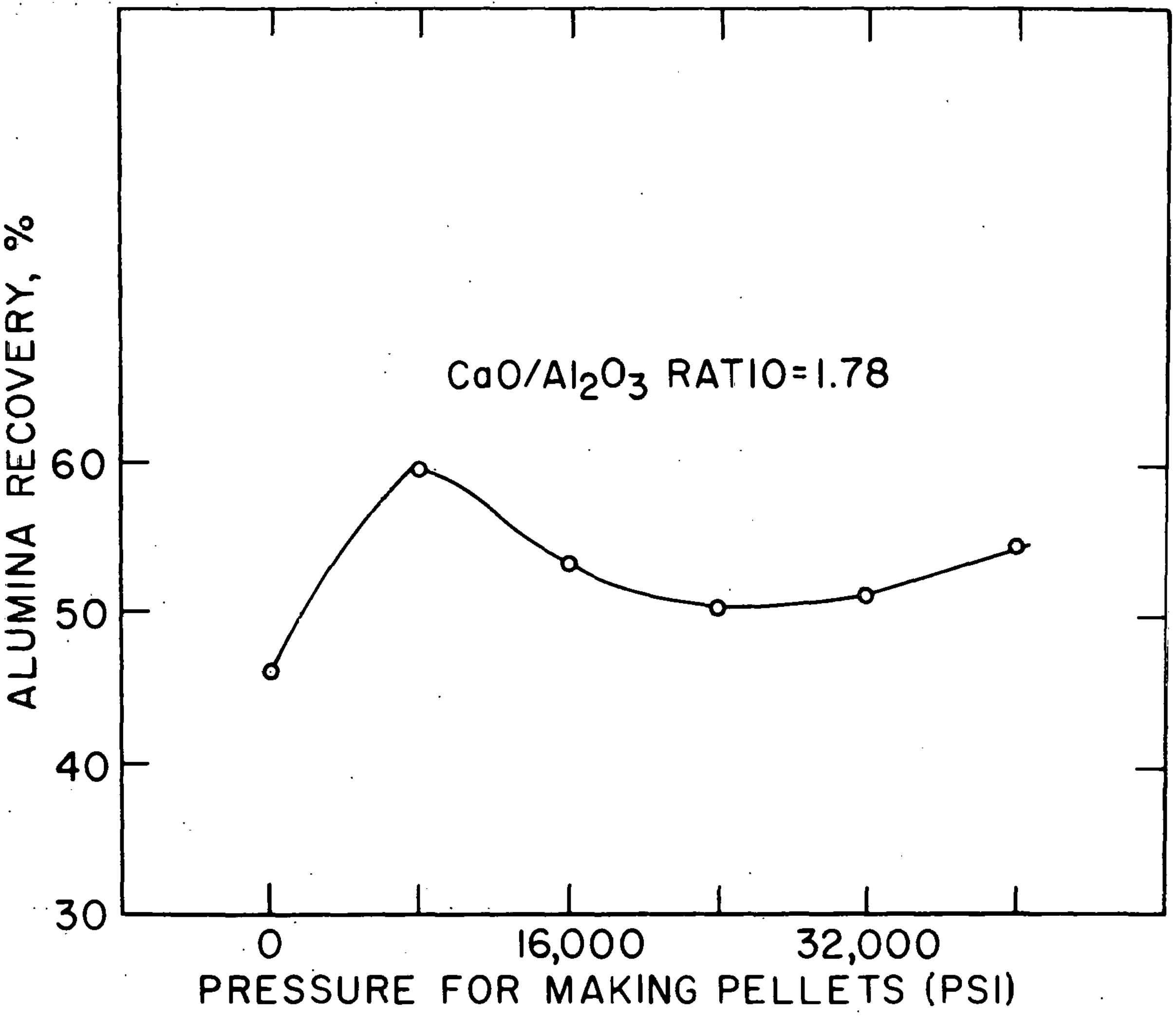


Figure 8. The effect of the pressure used for making the pellets on alumina recovery. All runs were carried out at 1380°C for 1 hour

Effect of lime to alumina ratio

Data presented graphically in Figure 9 show the effect of varying the CaO/Al_2O_3 ratio on the percentage of alumina extracted from nonmagnetic C-1 fly ash. The CaO/Al_2O_3 ratios consider only that part of the total CaO above that required to react with the silica to produce dicalcium silicate. The data show that ratios between 1.7 and 2.0 appear to be favorable with the nonmagnetic C-1 fly ash. All the compositions used in this thesis are listed in Table 6.

The mixture of nonmagnetic C-1 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 we look at the phase diagram of $CaO\text{-}Al_2O_3\text{-}SiO_2$ (Figure 10) (38), we find that the composition of nonmagnetic C-1 fly ash lies in the primary region of mullite near the SiO_2 end (shown as point A in Figure 10). 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 $2CaO\cdot SiO_2\text{-}12CaO\cdot 7Al_2O_3\text{-}CaO\cdot Al_2O_3$ and $2CaO\cdot SiO_2\text{-}12CaO\cdot 7Al_2O_3\text{-}3CaO\cdot Al_2O_3$. It is anticipated that 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 CaO to Al_2O_3. It was earlier believed that the compound formed had the formula $5CaO\cdot 3Al_2O_3$ (40), which is the principal compound responsible for alumina extraction. Grim, et al. (25) have studied the lime-sinter process by using various clays and they report that feed ratios of $CaO\cdot Al_2O_3$ between 1.5 and 1.8 appeared to be favorable for most kaolins.

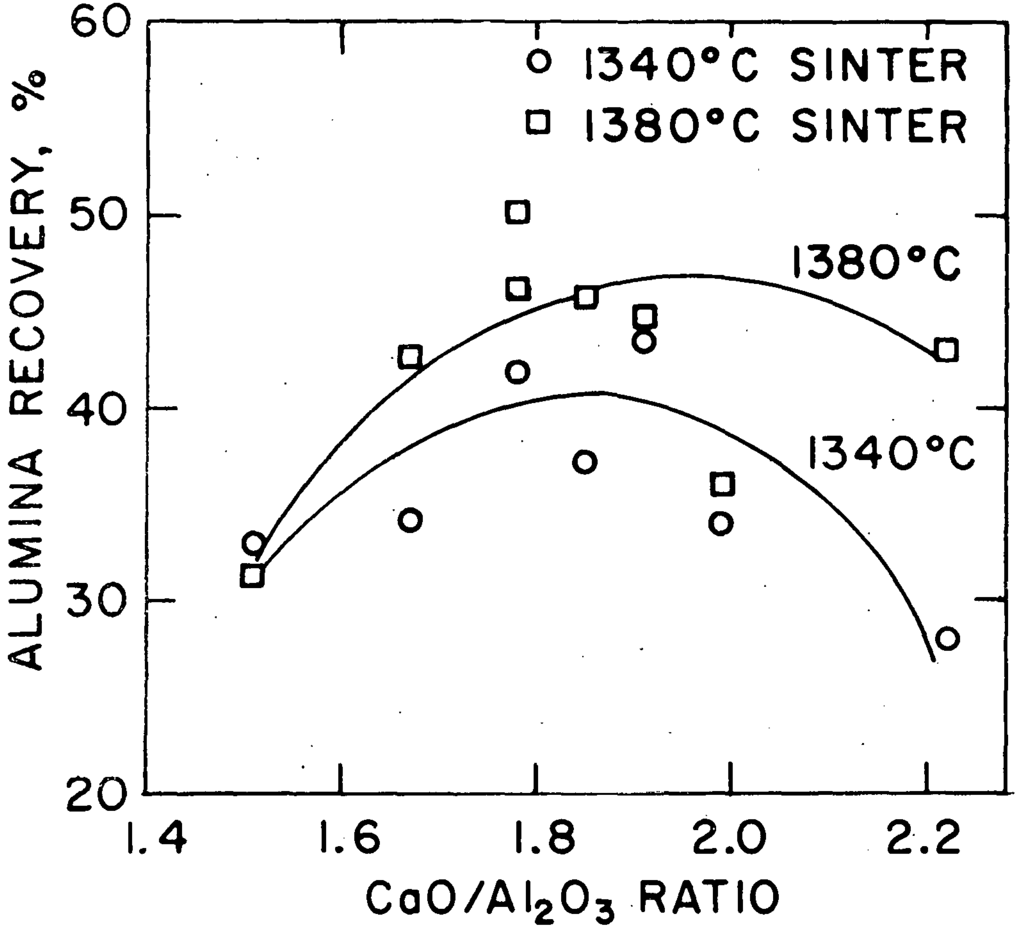


Figure 9. The effect of lime to alumina ratio on alumina recovery

Table 6. Composition of sintered pellets

Mix	Composition SiO_2	Composition Al_2O_3	Weight percent[a] CaO	Ratio[b] 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

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

[b] Ratio after accounting for a ratio of 2.0 for CaO/SiO_2.

In the author's case, with C-1 fly ash, the favorable ratios lie between 1.7 and 2.0. The additional amount of CaO needed is probably due to the higher content of iron in C-1 fly ash compared to that of most clays.

Effect of sintering temperature

Mixtures of compositions C and D (as shown in Table 6) were chosen for this investigation. The data are shown in Figure 11. Testing temperatures were varied from 1320°C to 1400°C. In both cases, the alumina recovery percentage rose to a maximum at 1380°C and then dropped a little bit as the temperature was raised to 1400°C. Sinters from 1380°C and 1400°C showed rounded corners on the pellets. This

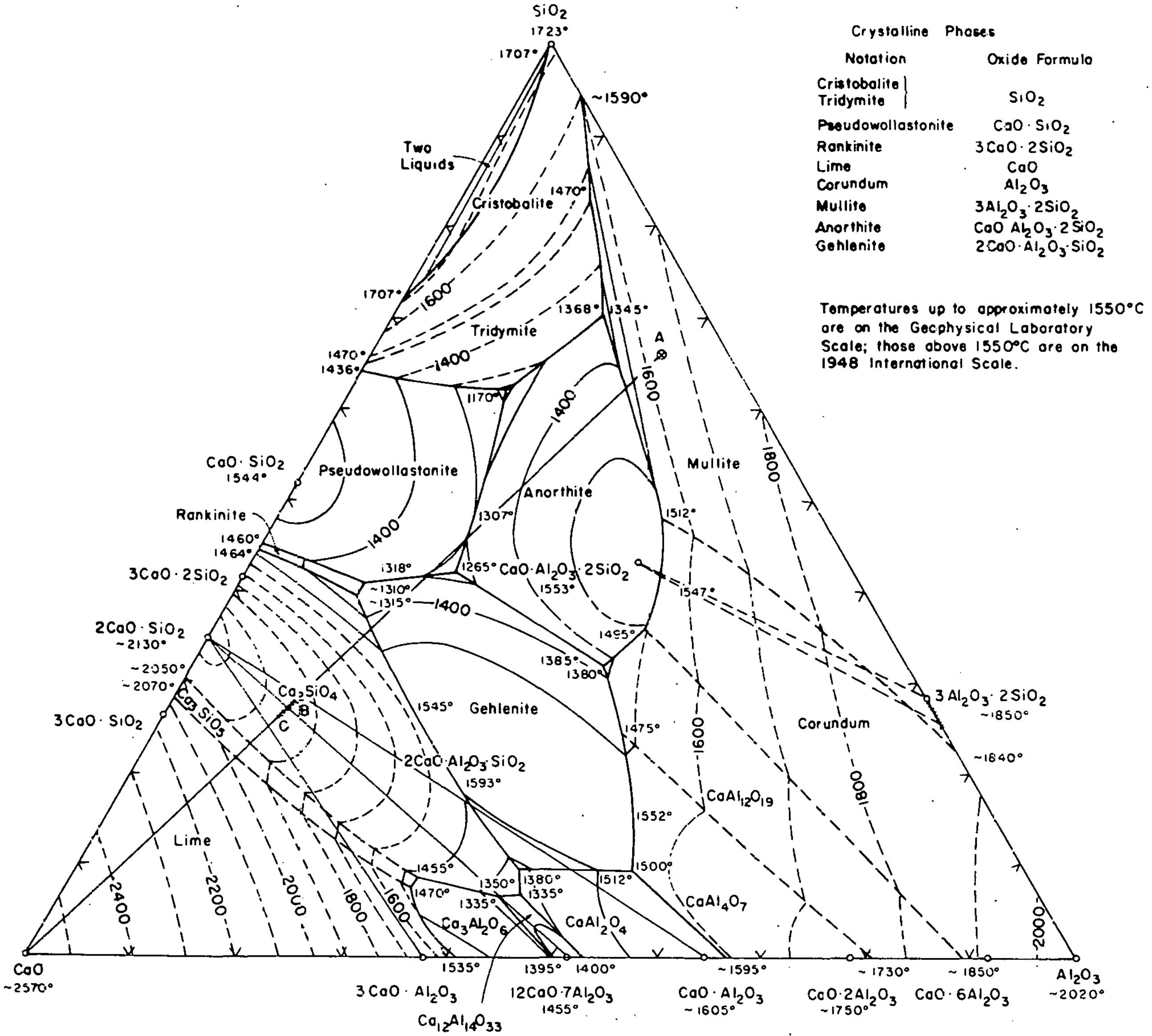


Figure 10. The phase diagram for the system SiO_2-Al_2O_3-CaO. Point A represents the composition of non-magnetic C-1 fly ash. The compositions between points B and C were used in this research

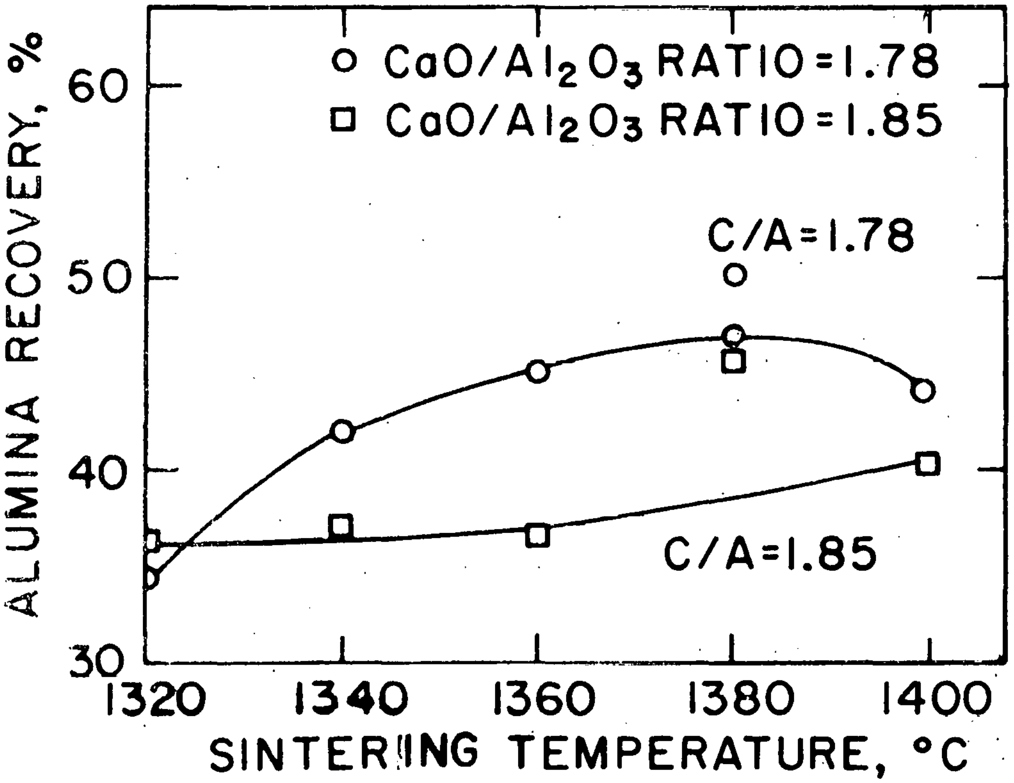


Figure 11. The effect of sintering temperature on alumina recovery

observation suggests that quite a bit of the pellets melts during this sintering treatment. Other pellets kept their shape, but shrunk to some extent, indicating that only very small amounts of melt or no melt at all formed. Usually, the pellets from higher sintering temperatures showed higher extents of auto-disintegration, while those from 1320°C and 1340°C failed to disintegrate.

Effect of sintering time

Two series of runs were made to test the effect of sintering time. Pellets of composition C and D were held at 1380°C and 1340°C respectively with sintering time varied from 0.5 to 2.0 hours. The data are presented in Figure 12. The extractability of alumina generally increased with time for both compositions, while pellets with a CaO/Al_2O_3 ratio of 1.78 showed a decrease in alumina recovery percentage when the sintering time was longer than 1.5 hours.

Results of Qualitative Analysis of the Sinters

In an attempt to understand what happened to the fly ash during the furnacing stage, a series of qualitative analyses were undertaken. Only sinters of composition C were used for this purpose. After the pellets were taken out of the furnace, the nondisintegrated pellets were first taken for electron microprobe analysis, Then the pellets were ground and mixed with disintegrated powder for photomicrographs and X-ray diffraction studies. Since the results from various runs did not show any significant difference, only selected results are shown here for discussion.

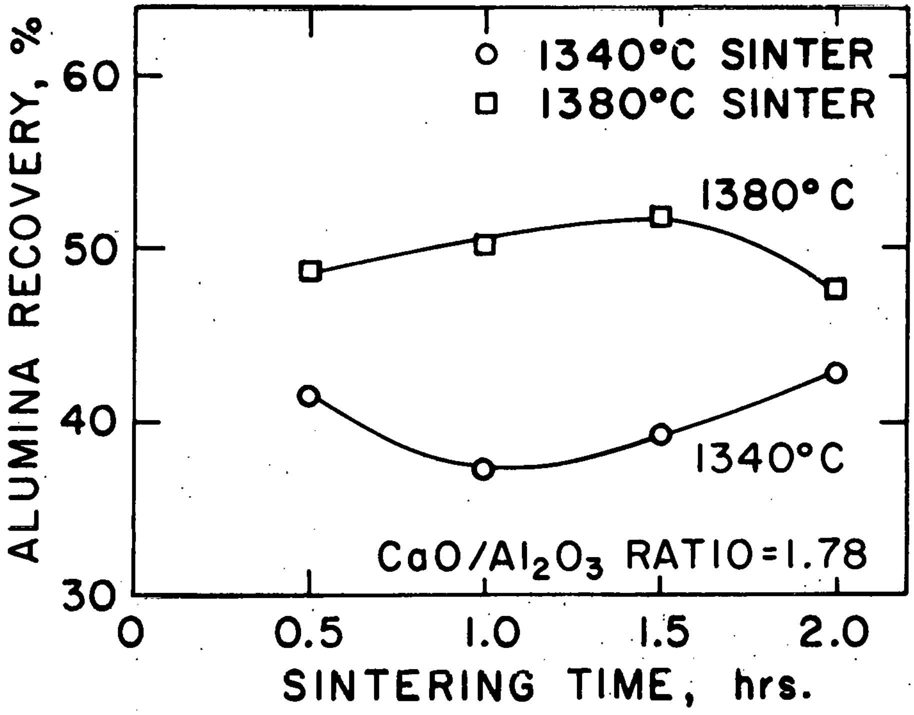


Figure 12. The effect of sintering time on alumina recovery

Photomicrograph observations

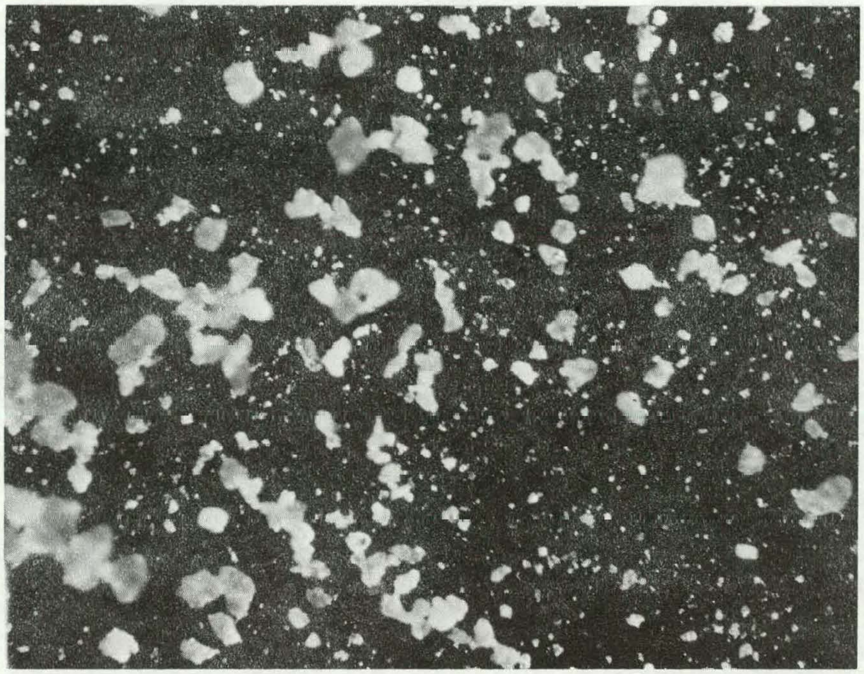
Two representative examples of photomicrographs of sinters are shown in Figures 13 and 14. The sample in Figure 13 was sintered at 1380°C for 1 hour and the other one was held at 1340°C for 1 hour. There were obviously two different sizes of particles in both pictures. The smaller particles have diameters under 10 microns, compared with the large particles which have an average diameter of about 100 microns. Generally speaking, those particles with a diameter less than 10 microns, were obtained when the pellets auto-disintegrated. For those nondisintegrated pellets, reasonable effort is required to crush those powders of suitable size.

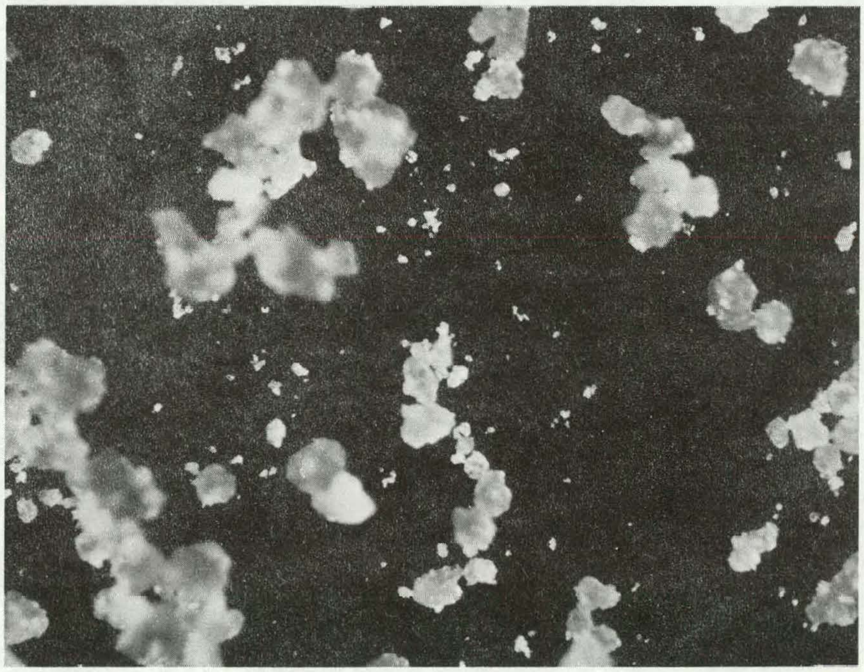
For a fixed amount of material, we know that the smaller the particle diameter, the larger the surface area these particles can provide. Thus the disintegrated samples are favorable for the purpose of leaching, because they can provide more area to react with the leaching agent. Nowak (48) states in his paper that the dusting effect is the key factor in the whole lime-sinter process.

As reviewed previously in this thesis, the dusting effect is due to the polymorphic transformation of β-C_2S into γ-C_2S. In the industrial production of self-disintegrating sinter we are faced with many parameters that influence the degree of self-disintegration. The most important ones of these are the chemical and mineralogical composition of the original raw materials, the amount and type of stabilizers, firing temperature and time, type of atmosphere in the furnace during firing, the cooling conditions, etc. (26). In view of the importance

Figure 13. Photomicrograph (at 100X) of sinter of composition C heated at 1380°C for one hour. There are particles of two general sizes in the crushed sinter. The orders of magnitude are 10 and 100 microns respectively

Figure 14. Photomicrograph (at 100X) of sinter of composition C heated at 1340°C for one hour. The sinter is very similar to the one in Figure 13





and complexity of the dusting phenomenon, it is recommended that more effort be devoted to this specific portion of the lime-sinter process.

Electron microprobe analysis

The electron microprobe analysis enables us to make energy dispersive X-ray elemental analysis to determine where the three principal elements, i.e. aluminum, calcium and silicon, reside were in the pellets both before and after the heat treatment. The pellets were sintered at 1360°C for one hour. Photomicrographs are presented in Figures 15 to 22.

In Figures 15 and 16, the sites where this analysis was made are shown. The pellets have a porous and rough surface before the heat treatment and the surface becomes rigid and smooth after the sintering. The porosity of the pellets decreases and the volume shrinks during the sintering. The small holes observable in Figure 16 indicate possible trapping of carbon dioxide liberated from calcium carbonate upon heating.

The energy dispersive X-ray calcium analysis of a pellet is shown in Figures 17 and 18. There are certain areas in the before sintering photograph in Figure 17 showing lack of calcium, indicating that these areas are occupied by fly ash particles. However, after the heat treatment, the photograph of the pellet shows a rather homogeneous distribution of calcium. The next two photographs in Figures 19 and 20 give the aluminum and silicon analysis of a pellet before sintering. We find from these two pictures that areas rich in aluminum are always also rich in silicon and are evidently occupied by fly ash particles. In Figures 21 and 22, the pictures of the aluminum and silicon analysis of a sintered pellet show a significant difference from those of the

Figure 15. Electron micrograph (500X) of a pellet before sintering

Figure 16. Electron micrograph (1000X) of a pellet after the sintering. The surface of the pellet looks more smooth than the one in Figure 15

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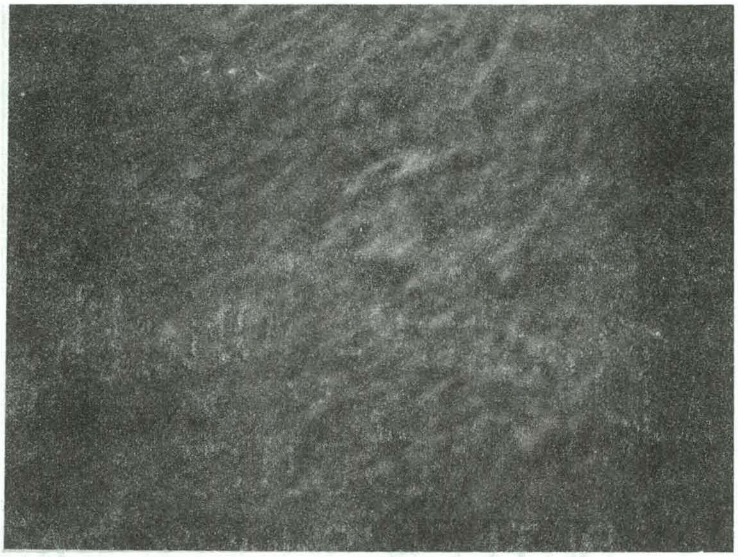

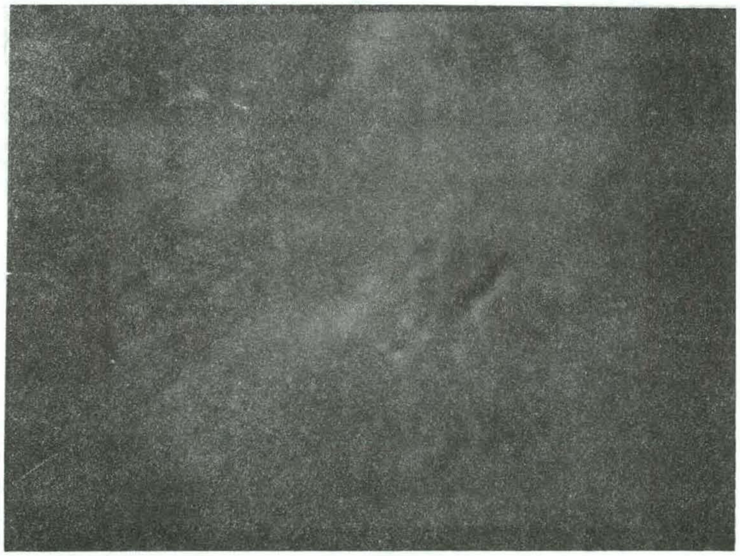

Figure 17. Energy dispersive X-ray calcium analysis of Figure 15

Figure 18. Energy dispersive X-ray calcium analysis of Figure 16. As a result of the heating, the calcium is found to be homogeneously distributed in the pellet

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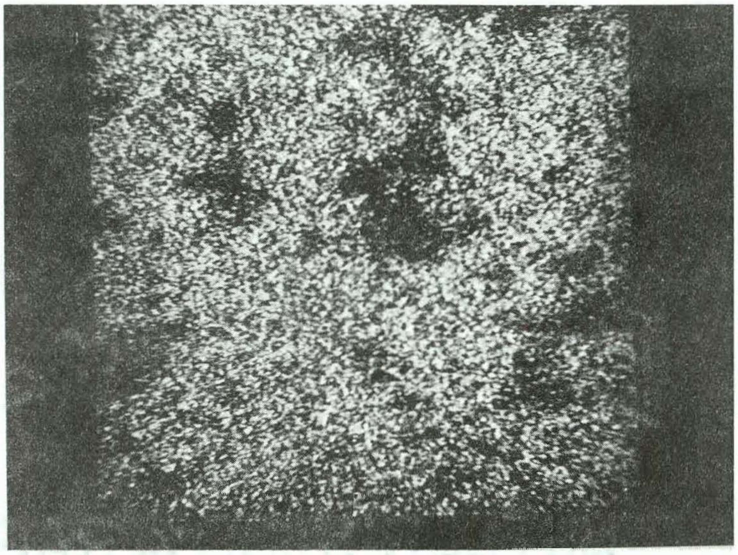

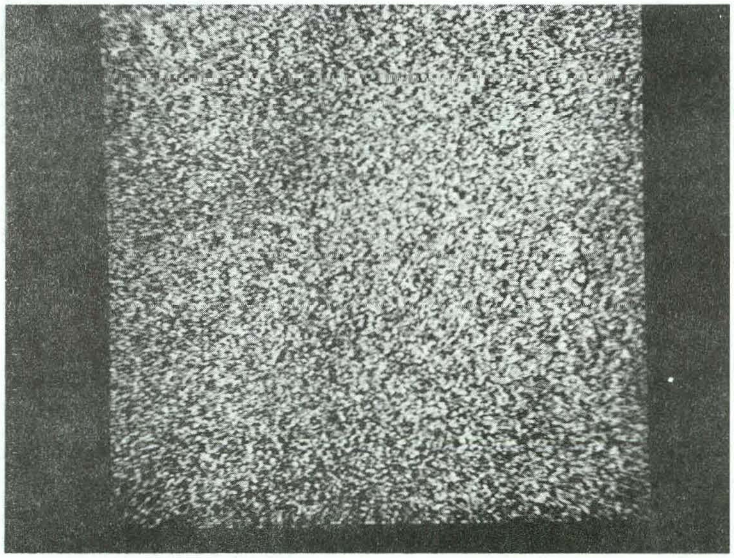

Figure 19. Energy dispersive X-ray aluminum analysis of Figure 15

Figure 20. Energy dispersive X-ray silicon analysis of Figure 15. The silicon is found to be in the same area in the pellet as aluminum

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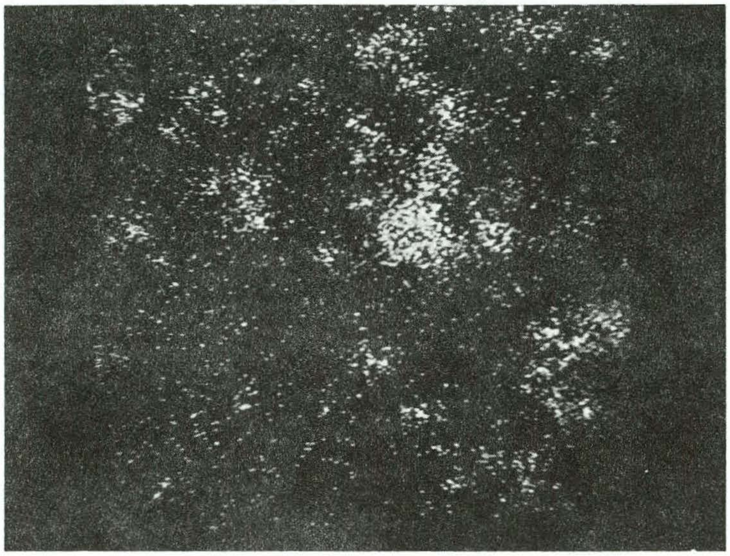

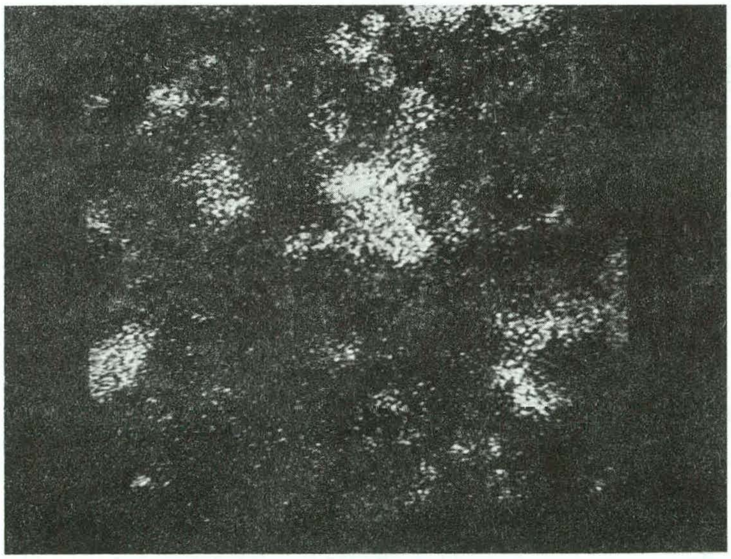

Figure 21. Energy dispersive X-ray aluminum analysis of Figure 16

Figure 22. Energy dispersive X-ray silicon analysis of Figure 16. There is a partial segregation between silicon and aluminum as a result of sintering

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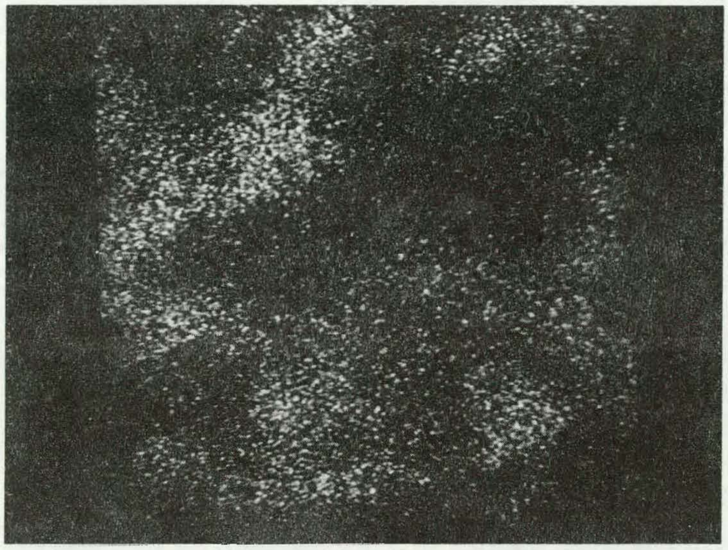

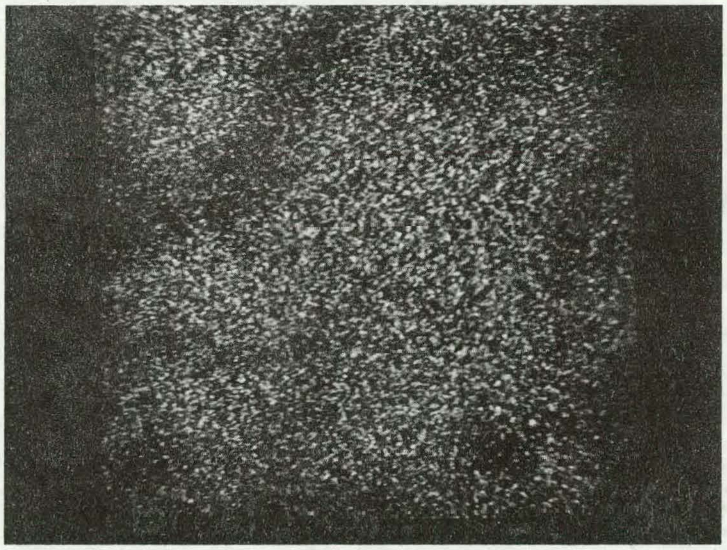

nonsintered pellet. The areas rich in aluminum are no longer rich in silicon. This fact indicates that segregation between these two elements occurred during the heat treatment, although it is by no means a complete segregation.

As we know, the lime-sinter process starts with the mixing of non-magnetic fly ash particles with the calcium carbonate powders. The temperature is then brought up to 1320°C to 1400°C, well below the melting point of the composite mixture as judged from the phase diagram of the $CaO-Al_2O_3-SiO_2$ system shown in Figure 10. Basically, the furnacing stage in the process is a solid state reaction. The rate of chemical reaction is generally much slower than the rate for liquid or gas reactions. Since the reactants are usually not mixed on an atomic scale, the reaction rate depends not only upon the rate of reaction itself but also upon the transport of material in the solid phase to a reaction site, it may also frequently depend upon nucleation of a new phase.

In order for a solid phase reaction leading to a solid product to continue, there must be diffusion through the solid, so that one or both reactants move through the product layer and maintain contact. A schematic of such a diffusion dependent reaction is shown below.

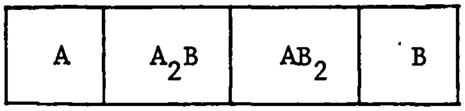

Figure 23. Reaction in the system of A and B on the boundary surface.

As mentioned before, the solid state chemical reactions are controlled by diffusion. Stated simply, diffusion is the movement of chemical species through matter. When there is a permanent preferential displacement of chemical species so that a local change in composition occurs with time, it is called chemical diffusion or interdiffusion (33). Since the impetus for this movement of atoms is thermal energy in the matter, the diffusion is referred to as a thermally-activated process.

As a gradient in temperature causes heat flow, a gradient in chemical potential is the driving force for chemical diffusion — chemical species move from regions of high chemical potential to regions of low chemical potential. Diffusion can be expected to continue until equilibrium is reached, i.e. the chemical potential of all species is uniform throughout the system.

A phase diagram is actually constructed on the basis of measured or calculated equilibrium states among elements. As discussed earlier, the overall composition of the pellets lies within the two subsystems of calcium orthosilicate and corresponding calcium aluminates. This means that the equilibrium products of this mixture will be the calcium orthosilicate and other corresponding calcium aluminates. However, the diffusion rates in either crystalline solids or glasses are very small and the equilibrium state can never be reached but only approached in a reasonable period. The partially segregated distribution of aluminum and silicon in Figures 21 and 22 can serve as evidence of this fact.

X-ray diffraction

Two representative X-ray diffraction patterns of sinters are shown in Figures 24 and 25. Abbreviations are used to simplify the

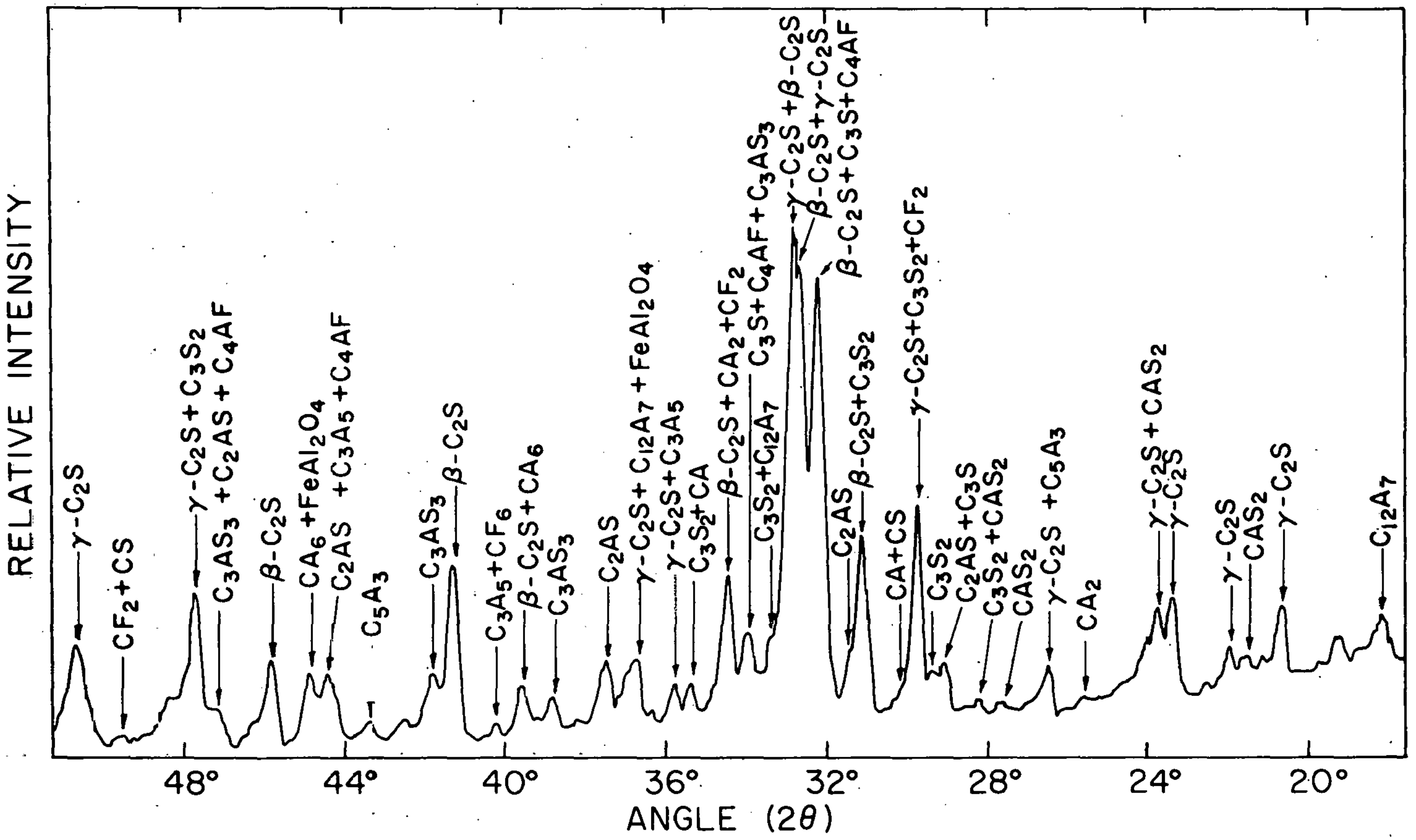

Figure 24. X-ray diffraction pattern of sinter of composition C sintered at 1380°C for 1 hour. β- and γ-C_2S are two principal crystalline compounds in the sinter. Some of the peaks are indistinguishable between compounds

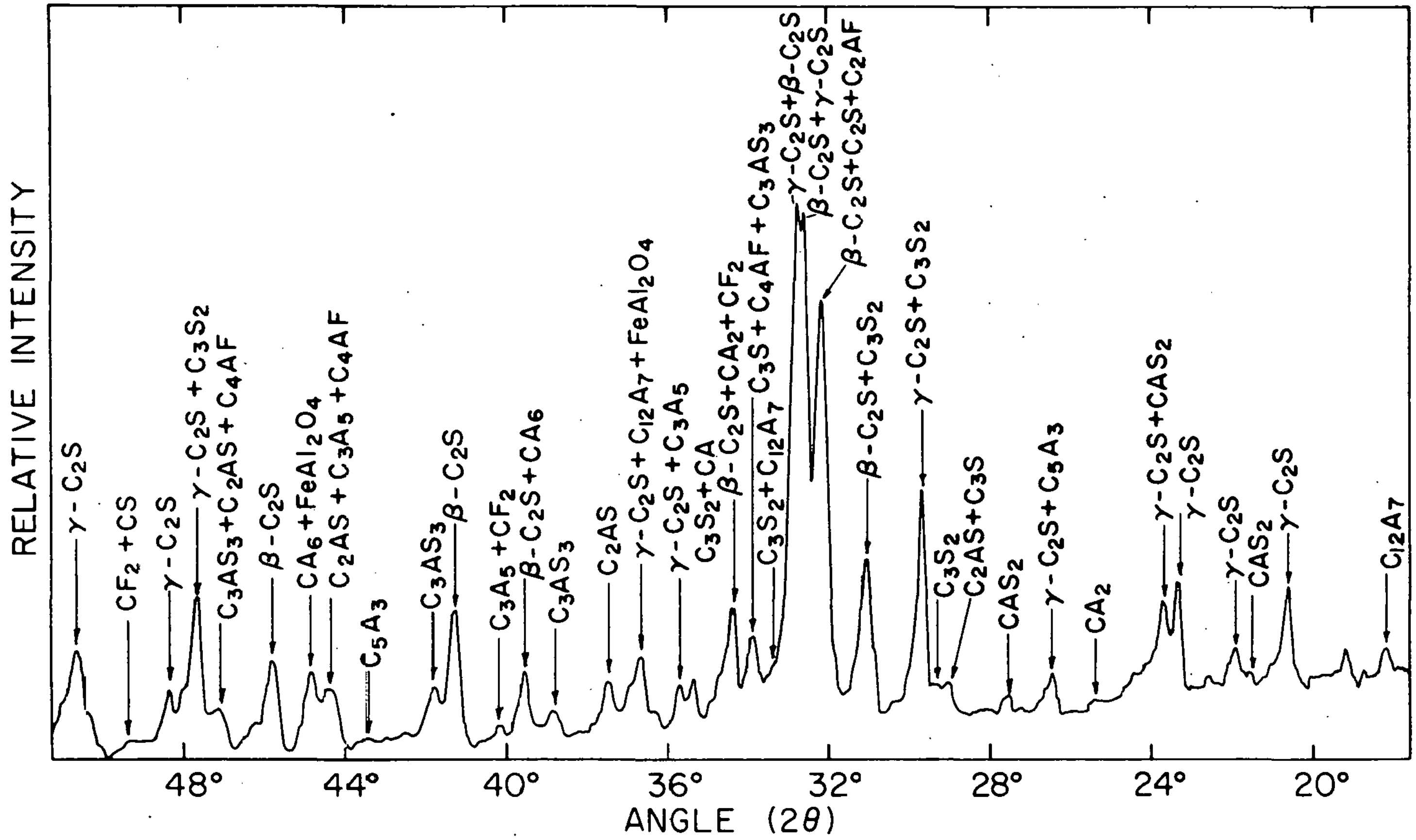

Figure 25. X-ray diffraction pattern of sinter of composition C sintered at 1360°C for 1 hour

names of compounds: A for Al_2O_3, C for CaO, F for Fe_2O_3 and S for SiO_2. Thus C_4AF is the abbreviation for $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$.

In both figures, most of the peaks belong to β- and γ-C_2S which is the compound responsible for dusting. There are also characteristic peaks showing the existence of $C_{12}A_7$, CA, C_4AF, etc. However, the author has to admit that many of the characteristic peaks of different compounds are too close to be distinguished without using a more sensitive scanning speed. Thus the two X-ray patterns shown here are only aimed at illustrating the complexity of the system.

Since the solid state chemical reaction is usually far from the equilibrium situation described by the principles of thermodynamics, the kinetics of the reaction need also to be considered. An excellent example of the use of the $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}Fe_2O_3$ system is the production of Portland cement and aluminous cement. Budnikov and Ginstling (13) have reviewed the chemistry of those systems in their book on solid state chemistry. Before the system reaches 600-800°C one can usually observe the well-known dissociation of carbonates and the very slow reaction between CaO and SiO_2. The rate of these reactions markedly increases with temperature, and in the range of 800-1000°C intensive formation of $CaO{\cdot}Al_2O_3$ occurs. The amount of primary formed $2CaO{\cdot}SiO_2$ is still relatively low. With a gradual rise in temperature to 1200°C, the $CaO{\cdot}Al_2O_3$ reacting with unreacted lime forms $5CaO{\cdot}3Al_2O_3$. Also at around 900°C, reaction commences between the CaO and Fe_2O_3 to form, as a primary product, $2CaO{\cdot}Fe_2O_3$. At 1200°C and somewhat above, intensive formation occurs of dicalcium silicate, which is completed at this stage of the process, and possibly $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$. All the above reactions are completed with a temperature rise to 1280-1300°C. Further increase of the temperature may produce the liquid phase which creates conditions for reaction between $2CaO \cdot SiO_2$ and CaO leading to the formation of $3CaO \cdot SiO_2$ (13). Two other possible ternary compounds are anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). However, the reactions leading to these compounds are very slow and thus they do not occur in any appreciable amount.

So far, the qualitative analysis conducted here helps to reveal not only some aspects of the process but also the complexity of the system. It is still believed that a better understanding of the behavior of this system can lead to a better alumina recovery.

Results of the Effect of the Leaching Variables

The leaching step plays another important role in the lime-sinter process for the production of alumina. Pellets came out of the furnace with extractable alumina tied up by calcium oxide. There are three principal calcium aluminates formed, i.e. $3CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$ (or $5CaO \cdot 3Al_2O_3$) and $CaO \cdot Al_2O_3$. All of these three compounds show more or less solubility in dilute sodium carbonate solution. Flint, et al. (24) found that $CaO \cdot Al_2O_3$ showed the greatest solubility in Na_2CO_3 solution, with about 95% of the alumina in this compound recoverable, while $5CaO \cdot 3Al_2O_3$ dissolved about 75% of its alumina into the solution and $3CaO \cdot Al_2O_3$ dissolved only 28%.

The formation of calcium aluminates from pure components were studied by Macias (40). It was found that $CaO \cdot Al_2O_3$ tended to form at lower temperatures (900-1000°C), no matter what ratio of CaO/Al_2O_3 was used. Then came the formation of $12CaO \cdot 7Al_2O_3$ on the $CaO/CaO \cdot Al_2O_3$ phase boundary. A new phase $3CaO \cdot Al_2O_3$ appeared within the 1100-1200°C temperature range. Under the effect of additional heating of the mixture at elevated temperatures, the synthesis ended with only appearance of the special compound of CaO/Al_2O_3 ratio as prepared at the beginning. Generally, the high temperature used in the sintering stage gives rise to the formation of those aluminates of a high degree of stability; this has an unfavorable effect on the extraction yield of Al_2O_3.

The principal reactions involved during the leaching are as follows:

$$CaO \cdot Al_2O_3 + Na_2CO_3 \rightleftharpoons 2NaAlO_2 + CaCO_3 \downarrow \qquad (19)$$

$$12CaO \cdot 7Al_2O_3 + 12Na_2CO_3 + 5H_2O \rightleftharpoons 14NaAlO_2 + 12CaCO_3 \downarrow + 10NaOH \qquad (20)$$

Both reactions are reversible. They shift further to the right with increasing dilution of the solutions, at elevated temperatures, and in the presence of an excess of sodium carbonate (36).

The behavior of dicalcium silicate during the leaching stage was investigated by Lecis and Guidi (36). In the presence of calcium aluminate, the following reaction tends to take place, with extremely unfavorable effects:

$$3(2CaO \cdot SiO_2) + 6NaAlO_2 + 15H_2O \rightleftharpoons 3Na_2SiO_3 + 2(3CaO \cdot Al_2O_3 \cdot 6H_2O) \downarrow + 2Al(OH)_3 \qquad (21)$$

and this is followed by a further reaction unfavorable to the process:

$$2Na_2SiO_3 + 2NaAlO_2 + 4H_2O \rightleftharpoons Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \downarrow + 4NaOH \qquad (22)$$

Thus, in the overall reaction, four molecules of Al_2O_3 are lost for every five molecules of silicate that react. It was also found (36) that the use of a high temperature during sintering appears to give a more stable dicalcium silicate. This means that a high temperature treatment in the sintering stage has a beneficial effect on the formation of dicalcium silicate and its subsequent resistance to sodium carbonate solution, while it has a detrimental effect on the formation of calcium aluminates and their subsequent decomposition.

In order to study the effect of leaching variables on alumina recovery from nonmagnetic C-1 fly ash, pellets of composition C were used. These pellets were heated at 1380°C for one-half hour before being leached. The variables studied were the temperature, concentration of Na_2CO_3 solution and the ratio of Na_2O/Al_2O_3. The data are presented in Figures 26, 27 and 28. In Figure 26, the alumina recovery from the sinters shows a maximum when the sinters are leached at 65°C. This recovery ratio would decrease somewhat if the leaching temperature was increased and would decrease significantly if the temperature was lowered. These sinters also showed a slight increase in alumina recovery when a higher concentration of Na_2CO_3 solution or an excess of sodium carbonate was used.

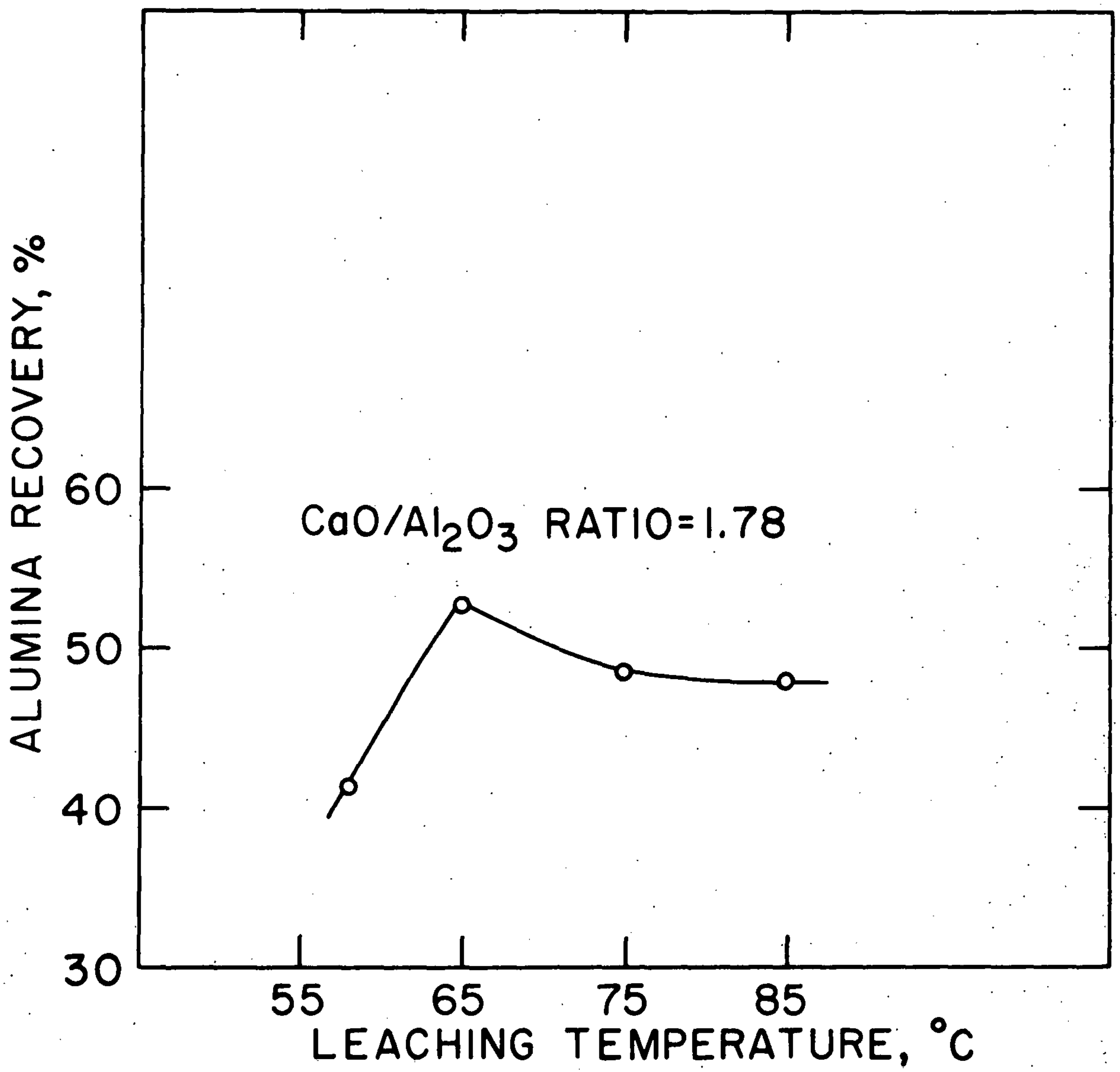

Figure 26. The effect of leaching temperature on alumina recovery. Pellets were sintered at 1380°C for one-half hour before leaching

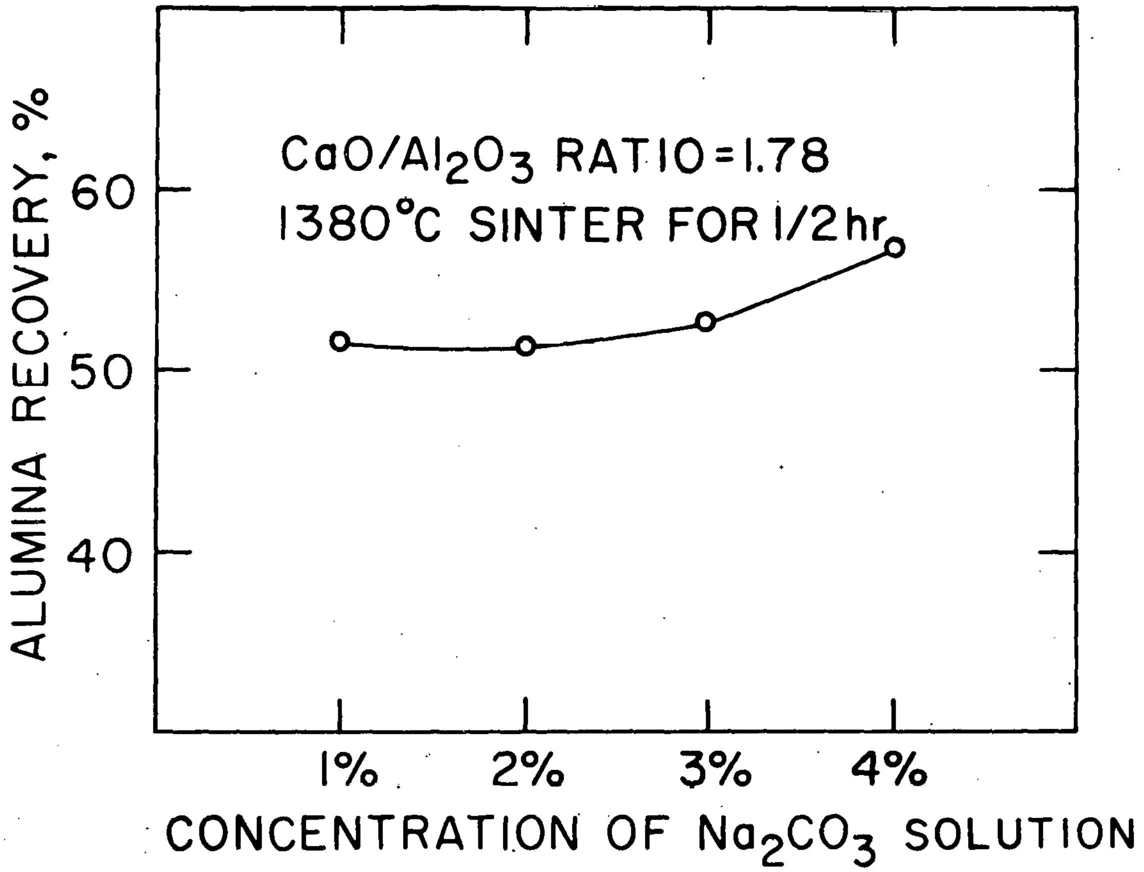

Figure 27. The effect of concentration of Na_2CO_3 solution on alumina recovery. The amount of solution for each run was selected so as to provide a Na_2O/Al_2O_3 ratio of 1.66. All sinters were leached at 65°C for 15 minutes

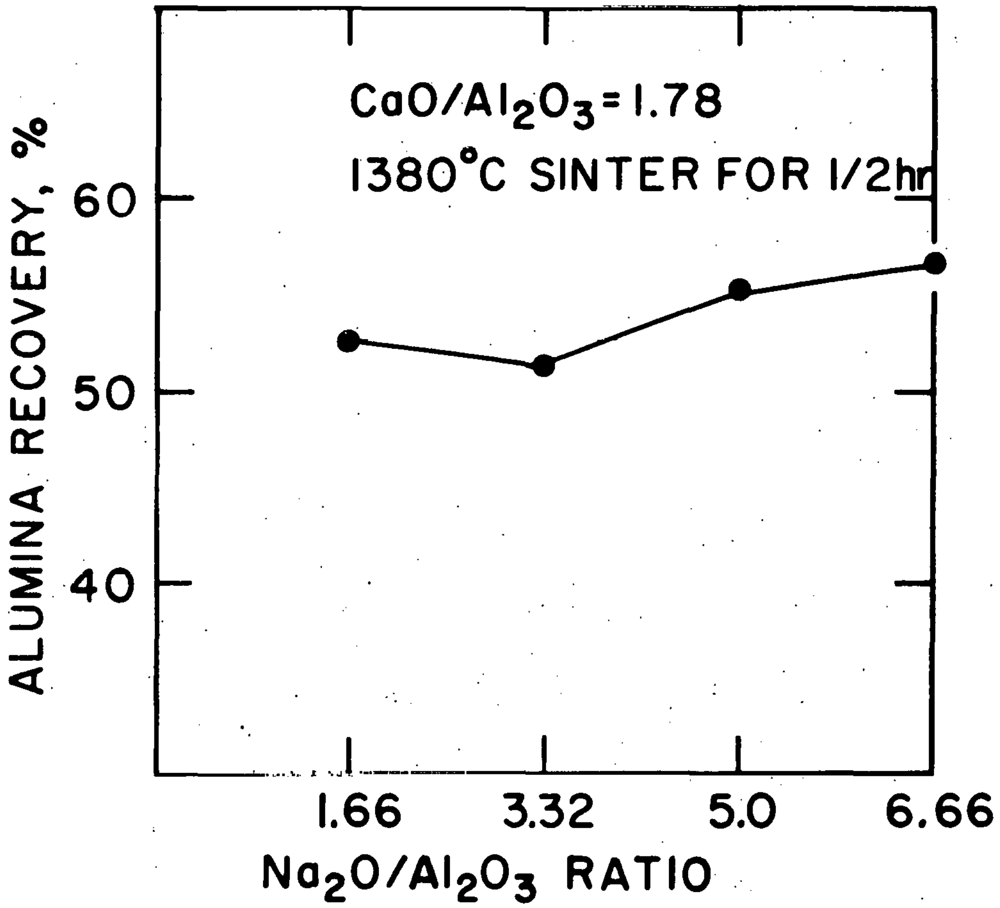

Figure 28. The effect of Na_2O/Al_2O_3 ratio on alumina recovery. Only 3% Na_2CO_3 solution was used. The leaching was performed at 65°C for 15 minutes

The silica content of the filtrate was only tested for some cases and the data are shown in Figures 29, 30 and 31. The silica content is expressed as weight percentage of the alumina present in the filtrate. As seen in these figures, the value of the silica content did not change very much when either the furnacing or leaching variables were changed. It averaged about 2.5% of the alumina in solution. This value is apparently too high for any industrial production of alumina. A desilication step is then necessary to eliminate the silica and produce alumina of satisfactory purity.

Economics

In order to have some idea of the economic feasibility of this lime-sinter process, a brief cost estimate was prepared. The estimate was partly based on the results obtained from the author's research on the sintering and leaching steps and partly on the data from Henn, et al. (28) for other steps in the process. The complete lime-sinter process for producing alumina is shown in Figure 32.

Process description

In the process, the whole fly ash is first separated magnetically to obtain both magnetic and nonmagnetic fractions. The magnetic fraction can be used as a source for iron recovery, while the nonmagnetic part is used in this process to produce alumina.

Limestone is crushed to a suitable size before mixing with nonmagnetic fly ash in ball mills. The mixture is then pelletized and sent to a rotary kiln for high temperature treatment. Since only

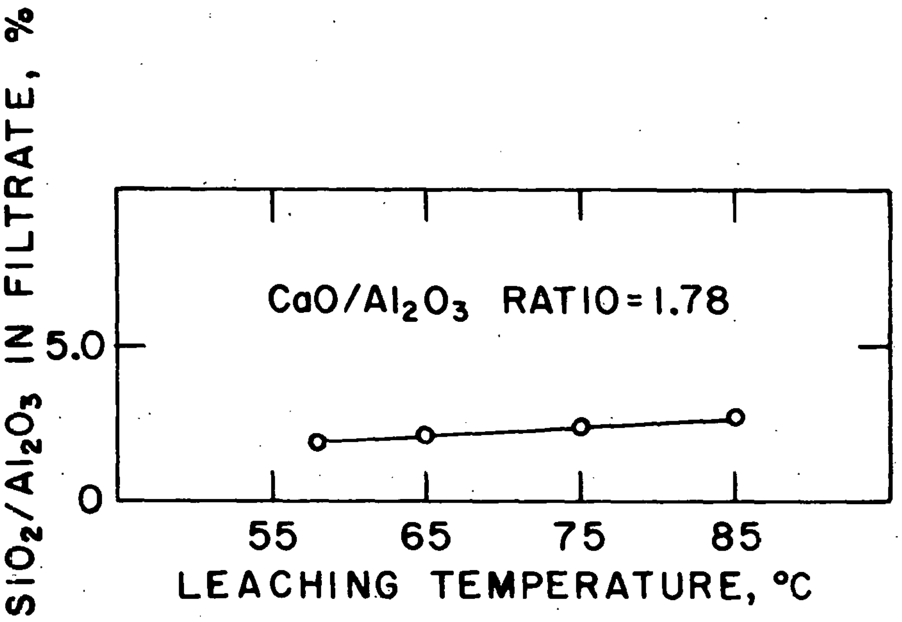

Figure 29. The effect of leaching temperature on silica content in the filtrate. Sinters were obtained by holding the pellets at 1380°C for one-half hour

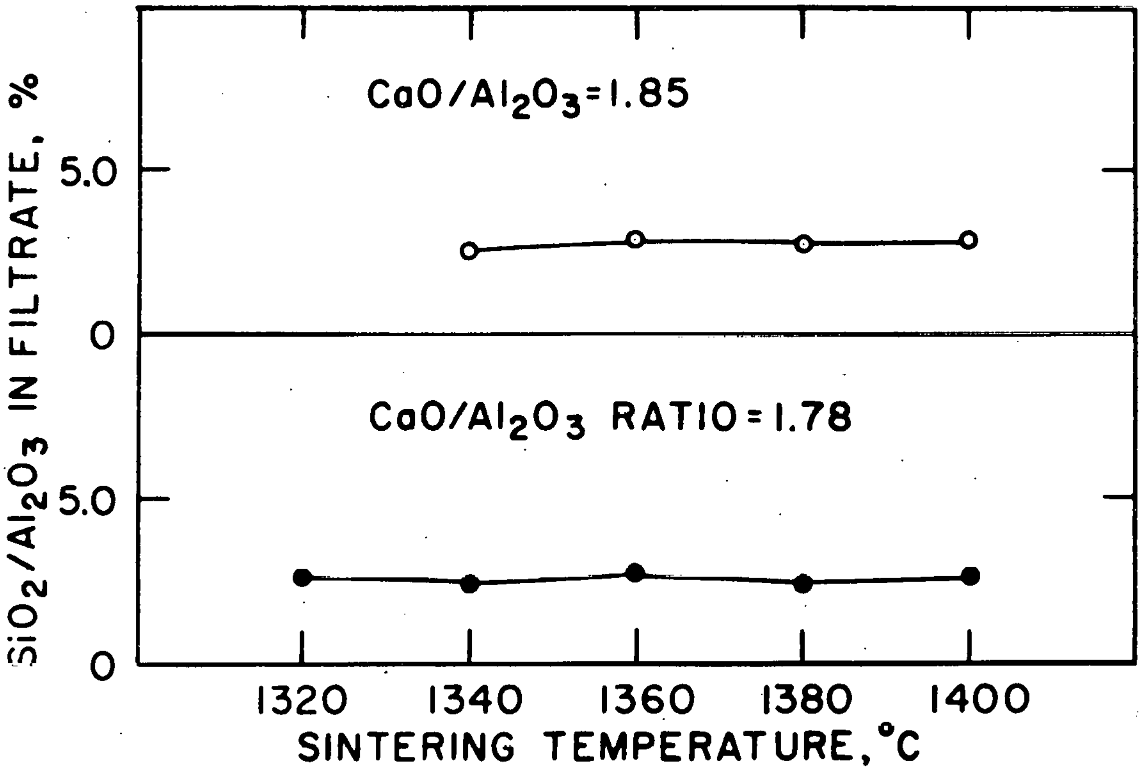

Figure 30. The effect of sintering temperature on the silica content of the filtrate. Sinters were leached at 75°C for 15 minutes

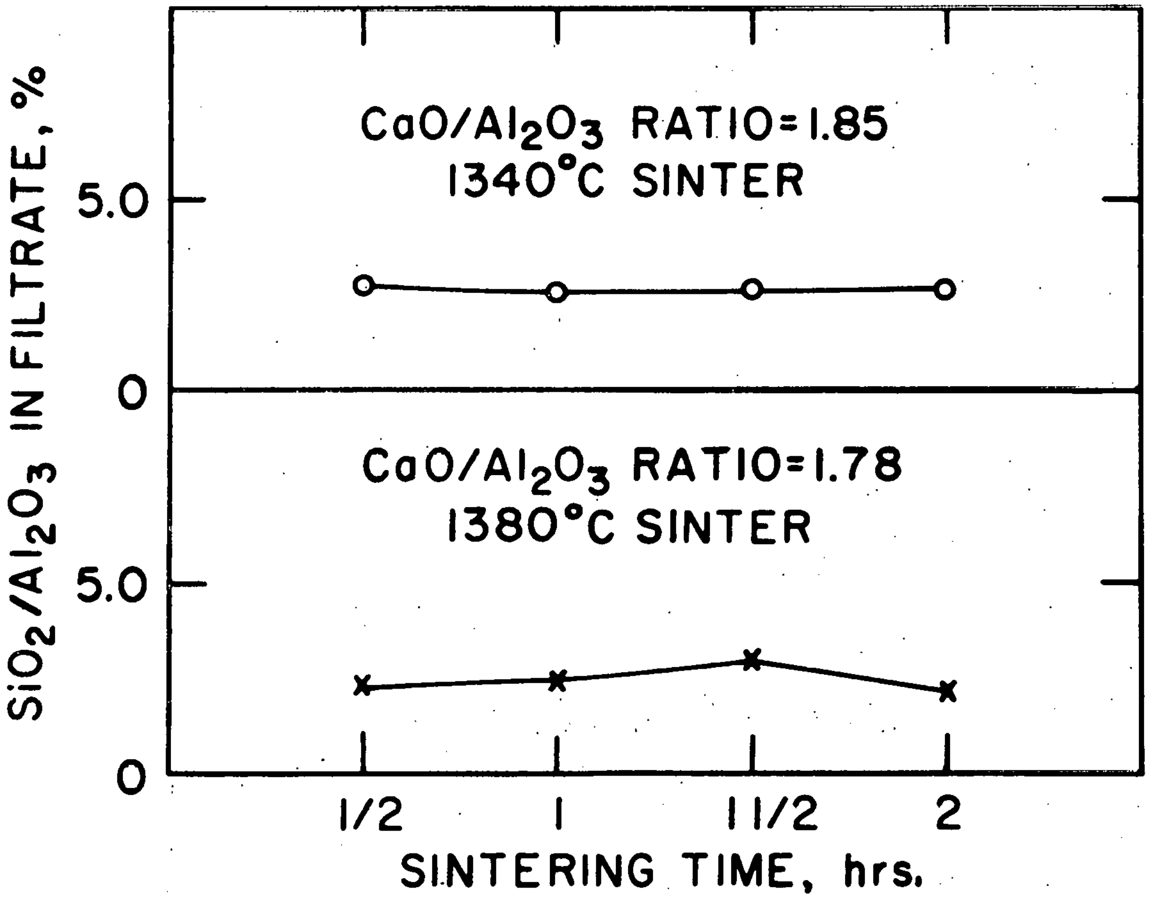

Figure 31. The effect of sintering time on the silica content of the filtrate. Sinters were leached at 75°C for 15 minutes

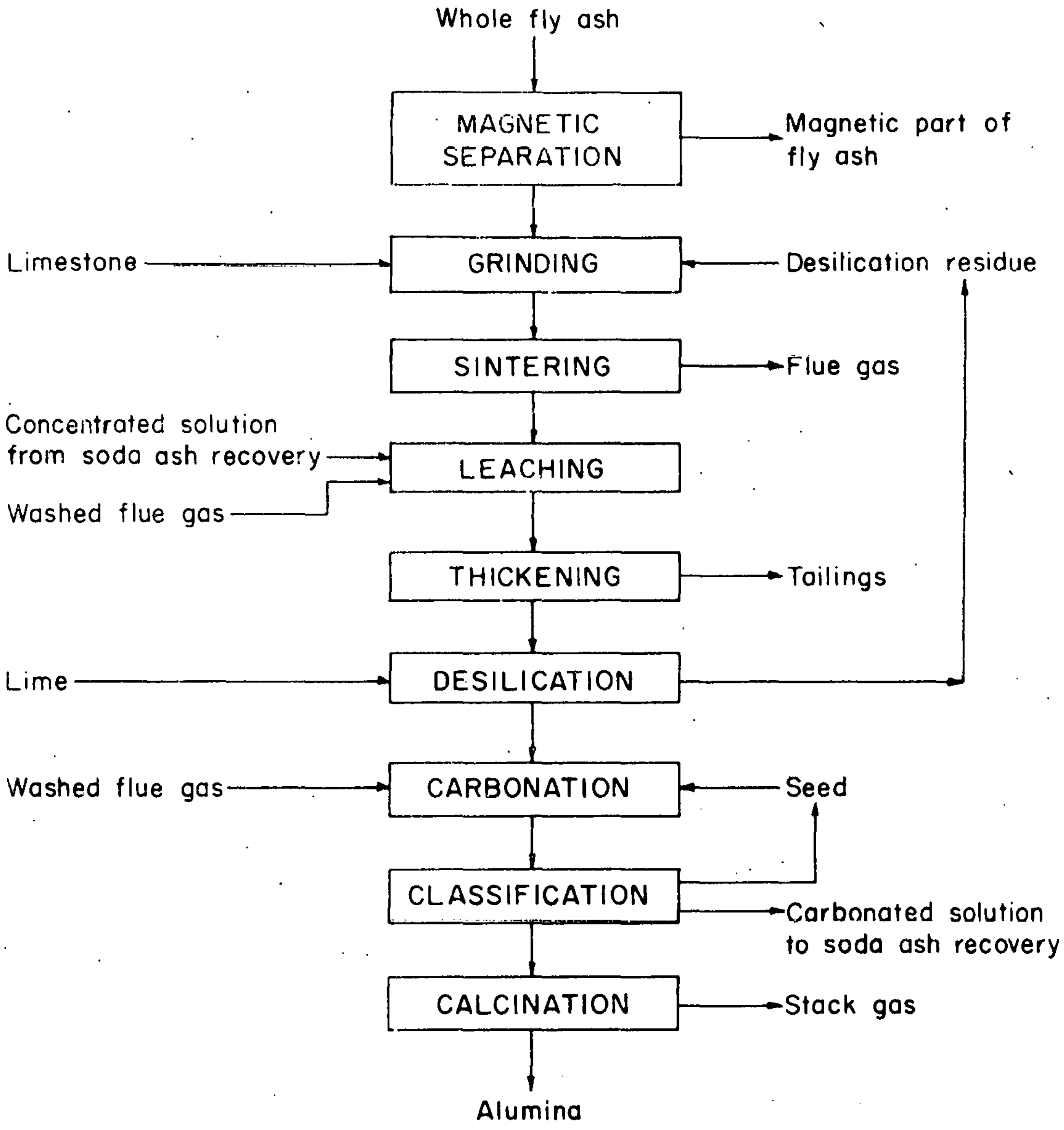

Figure 32. Lime-sinter process

incomplete disintegration of the pellets during cooling, the pellets need to be crushed before leaching.

The crushed sinter is leached with dilute sodium carbonate solution in leaching tanks. The pregnant solution is then separated from the tailings in a thickener. To maintain the proper concentrations of soda, alumina and carbonate in the pregnant liquor, carbon dioxide gas is added to the solution. The sludge from the thickener is washed nearly free of soluble soda, alumina and carbonate in a countercurrent washing system and can be used to produce Portland cement (48).

Desilication of the pregnant solution is necessary due to the relatively high concentration of silica in the solution. The method of desilication is to bring the pregnant solution in contact with lime at 100 psig and 177°C (350°F) for about two hours. The desilicated solution and the desilication residue are separated by thickening and filtration. The wet residue is recycled to the sintering section and the desilicated solution is carbonated to precipitate alumina trihydrate by the following reaction:

$$Na_2O \cdot Al_2O_3 + CO_2 + H_2O \longrightarrow Al_2O_3 \cdot 3H_2O + Na_2CO_3 \qquad (23)$$

The alumina trihydrate crystals are then calcined at 1100°C in rotary kilns to form alpha-alumina. A soda ash recovery unit is necessary in order to recycle the leaching solution and a flue-gas processing unit is necessary for recovering heat from the flue gas.

Estimation method

The standard estimation methods employed for this evaluation are the same as those used by Henn, et al. (28). Although the geographic location is not considered, it is assumed that the plant is located adjacent to either a fly ash source or a limestone deposit.

Brackett (9) estimated that the annual production of fly ash in the U.S. in 1980 will be 40 million tons. Based on this figure, a plant processing 1000 tons of whole fly ash a day seems to be reasonable. From this figure and the data of the author's research, the plant could produce 90 tons of alumina per day, which is smaller than the nominal size of alumina plant.

The capital cost estimates are of the general type called "study estimates" (76), which can be expected to be within 30% of the actual cost. Equipment capacity-cost data are based on a Marshall and Stevens chemical equipment index of 445.6 (18).

The cost estimate

The estimated operating costs are based on 350 days of operation per year, allowing 15 days down time for inspection, maintenance, and interruptions. The costs are divided into direct, indirect and fixed. The results of the estimation are summarized in Tables 6, 7 and 8. The supporting calculations are given in the Appendix.

The estimated cost per ton of alumina from this process is about $320 which is apparently higher than the cost of calcined alumina listed at $148 per ton. Although this evaluation indicates that the lime-sinter process using fly ash as the raw material is not economical at the

Table 7. Raw materials, utilities and labor requirements per ton of alumina

Item	Quantity
Fly ash------------tons	11.36
Limestone----------tons	19.00
Soda ash-----------lb	39.77
Electric power-----kwhr	600
Steam, 250 psig----Mlb	20.80
Water, cooling-----Mgal	48.60
Water, process-----Mgal	9.46
Water, raw---------Mgal	1.10
Natural gas--------MMBtu	100.05
Operating labor----man-hr	2.25

present time, the process might, however, with an increase in the production of fly ash, a decrease in reserves of bauxite and an improvement in extraction technique, become a major source of alumina at sometime in the future.

Table 8. Estimated capital cost for a 1000 tons of fly ash per day plant

Sintering section[a]	$ 9,821,400
Leaching section	2,694,600
Desilication section	2,438,300
Carbonation section	1,414,500
Calcination section	1,628,600
Soda ash recovery section	1,557,900
Flue-gas processing section	753,100
Total section costs	$20,308,400
Steamplant[b]	1,749,900
Subtotal	$22,058,300
Plant facilities, 10% of subtotal	2,205,800
Plant utilities, 12% of subtotal	2,647,000
Total physical cost	$26,911,100
Engineering and construction, 15% of total physical cost	4,036,700
Total direct cost	$30,947,800
Contractor's fee, 5% of total direct cost	1,547,400
Contigency, 15% of total direct cost	4,642,200
Total plant cost	$37,137,400
Interest during construction period[c]	2,228,300
Fixed capital cost	$39,365,700

[a] Including magnetic separation cost.

[b] Estimated from the steam requirements.

[c] Estimated at 6% of the total plant cost.

Table 9. Estimated annual operating cost for a 1000 tons of fly ash per day plant

	Annual cost	Cost per ton of alumina
Direct cost —		
Raw materials —		
Whole fly ash at $1.50 per ton	$ 525,000	$ 17.04
Limestone at $2.00 per ton	1,170,400	38.00
Soda ash at $57.00 per ton	69,800	2.27
Total	$ 1,765,200	$ 57.31
Utilities —		
Electric power at 1.3 cent per KWHR	$ 240,200	$ 7.80
Steam 250 psig at $1.50 per MLB	960,700	31.19
Steam recovered at 30 cents per MLB	384,400	6.24
Water, cooling at 3.66 cents per MGAL	55,100	1.79
Water, progress at 22.3 cents per MGAL	65,000	2.11
Water, raw at 1.83 cents per MGAL	600	0.02
Natural gas at 55 cents per MMBtu	1,694,700	55.02
Total	$ 3,400,700	$104.17
Direct labor —		
Labor at $4.20 per hour	$ 290,800	$ 9.44
Supervision, 15% of labor	43,600	1.42
Total	$ 334,400	$ 10.86
Plant maintenance, 5% of total section costs	1,015,400	$ 32.97
Operation supplies, 15% of plant maintenance	152,400	4.95
Total direct cost	$ 6,668,100	$210.26
Indirect cost —		
50% of direct labor and maintenance	$ 675,000	$ 21.91

Table 9. Continued

	Annual cost	Cost per ton of alumina
Fixed cost —		
Taxes and insurance, 2% of total plant cost	$ 742,800	$ 24.12
Depreciation[a], 5% of total fixed capital cost	1,968,300	63.90
Total operating cost	$10,054,200	$320.19

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[a] Depreciation is calculated using the straight-line method and a 20-year life.

CONCLUSIONS

The exploratory work presented in this thesis combined with the derived results enabled the following conclusions to be reached.

1. Magnetic separation of fly ash in water will dissolve all the sulfur contained in the original fly ash. Although it will recover less iron in the magnetic fraction than the wet separation, the dry separation is more convenient.

2. It is not necessary to use a very high pressure to make pellets, since the alumina recovery percentage does not increase with the pressure. A pressure of 8000 psi should be good enough for this process.

3. The best lime to alumina ratio for the lime-sinter method for recovering alumina from C-1 fly ash lies between 1.7 to 2.0. The most favorable sintering temperature is 1380°C and one hour of sintering time appears sufficient.

4. Qualitative analysis of the sinter reveals the complexity and heterogeneity of the system. The system does not reach equilibrium and a variety of products are found by X-ray study including the calcium aluminates from which the alumina is subsequently recovered by leaching. Pictures based on the electron microprobe analysis show the partial segregation of calcium and aluminum. This fact may suggest that chemical diffusion occurs during sintering.

5. Results of leaching of the sinters with sodium carbonate solution show maximum recovery at 65°C and an increase in recovery with more concentrated Na_2CO_3 solutions or an excess of this solution.

6. Economic evaluation shows the process to be economically unattractive based on the present degree of development and costs. As bauxite keeps on being consumed and the lime-sinter process is improved, fly ash has the potential of becoming a source of alumina in the future.

RECOMMENDATIONS

From the results of this exploratory work the following recommendations are offered for future research:

1. Investigate more intensively the optimum conditions for alumina extractability by the lime-sinter process. One such study should focus upon the optimization of the load used for making pellets. A lower load seems to be favorable. Investigations of the effect of leaching time and a stronger leaching solution such as NaOH are also recommended for better extraction of alumina. Based on previously reported work with clays it is believed that the alumina recovery can go up to at least 80% of that present in the raw ash.

2. Desilication of the solution is also important to the production of alumina by this process. It is recommended to find a satisfactory method to eliminate the silica from the final product.

3. Investigate the methods to eliminate the stabilizing effects of β-calcium orthosilicate formed in this sintering stage so as to cause dusting effect (auto-disintegration) to take place.

4. Addition of a small amount of fluxing material to the lime-ash mixture opens another field of study. This fluxing material (mineralizer) can help the system to form more liquid or to increase the diffusion rate at lower temperatures, thus accelerating the reaction rates in the system. A good mineralizer could lower the melting temperature and/or time necessary for good alumina recovery.

5. The lime-soda-sinter process is also recommended for the extraction of alumina from fly ash. Studies of this process should

be similar to those of the lime-sinter process. An optimization of operating conditions is necessary. Instead of using sodium carbonate solution for the leaching stage, but water could be used for this purpose in this method.

6. Investigate other processes such as the chlorination process as potential methods for alumina recovery from fly ash. Optimization studies of reaction temperature and residence time in the chlorination process would be of extreme importance to research in this area.

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APPENDIX. MATERIAL AND HEAT BALANCES AND EQUIPMENT COST FOR LIME-SINTER PROCESS

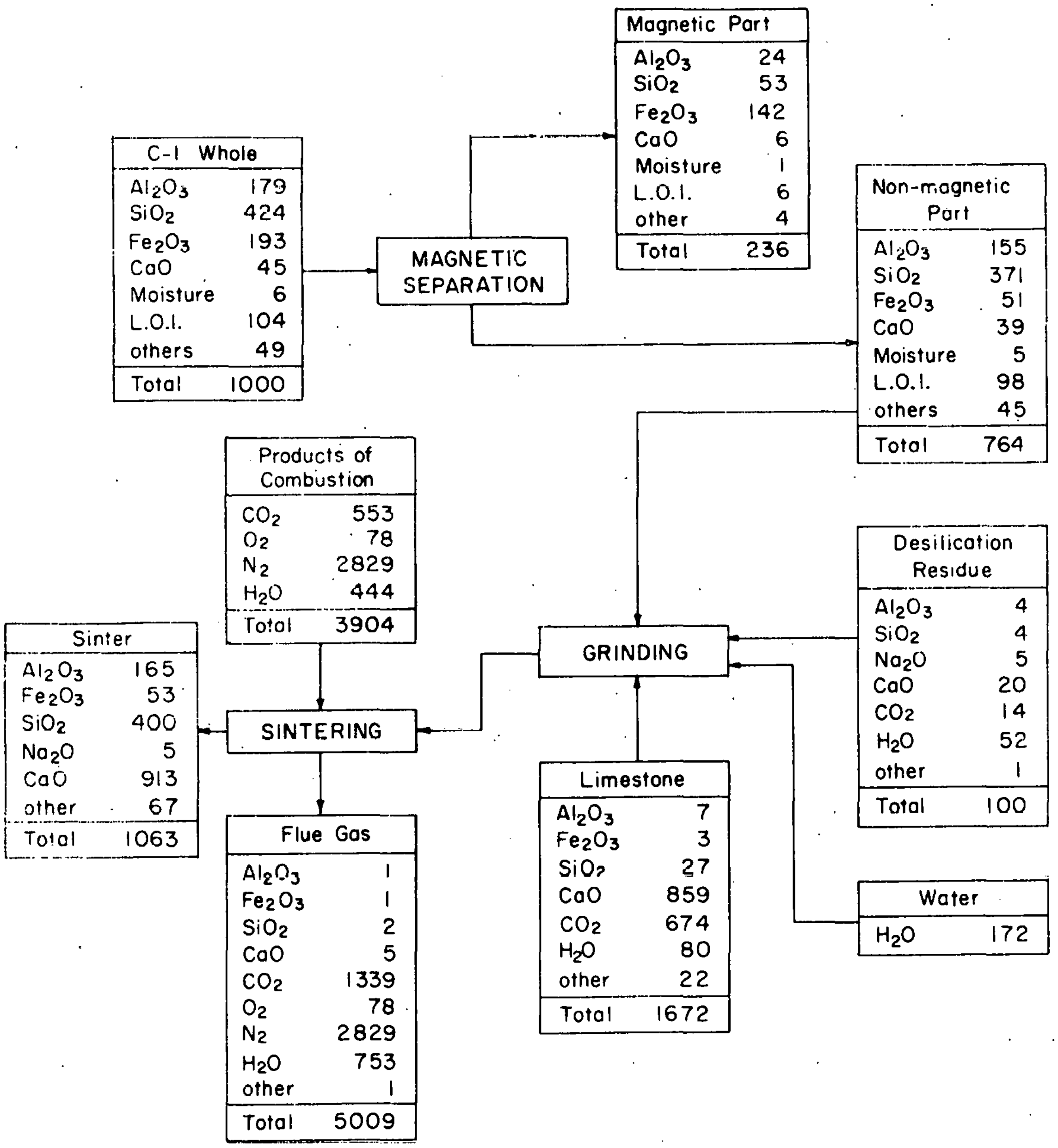


Figure A-1. Material balance, sintering section (tons per day) (including magnetic separation)

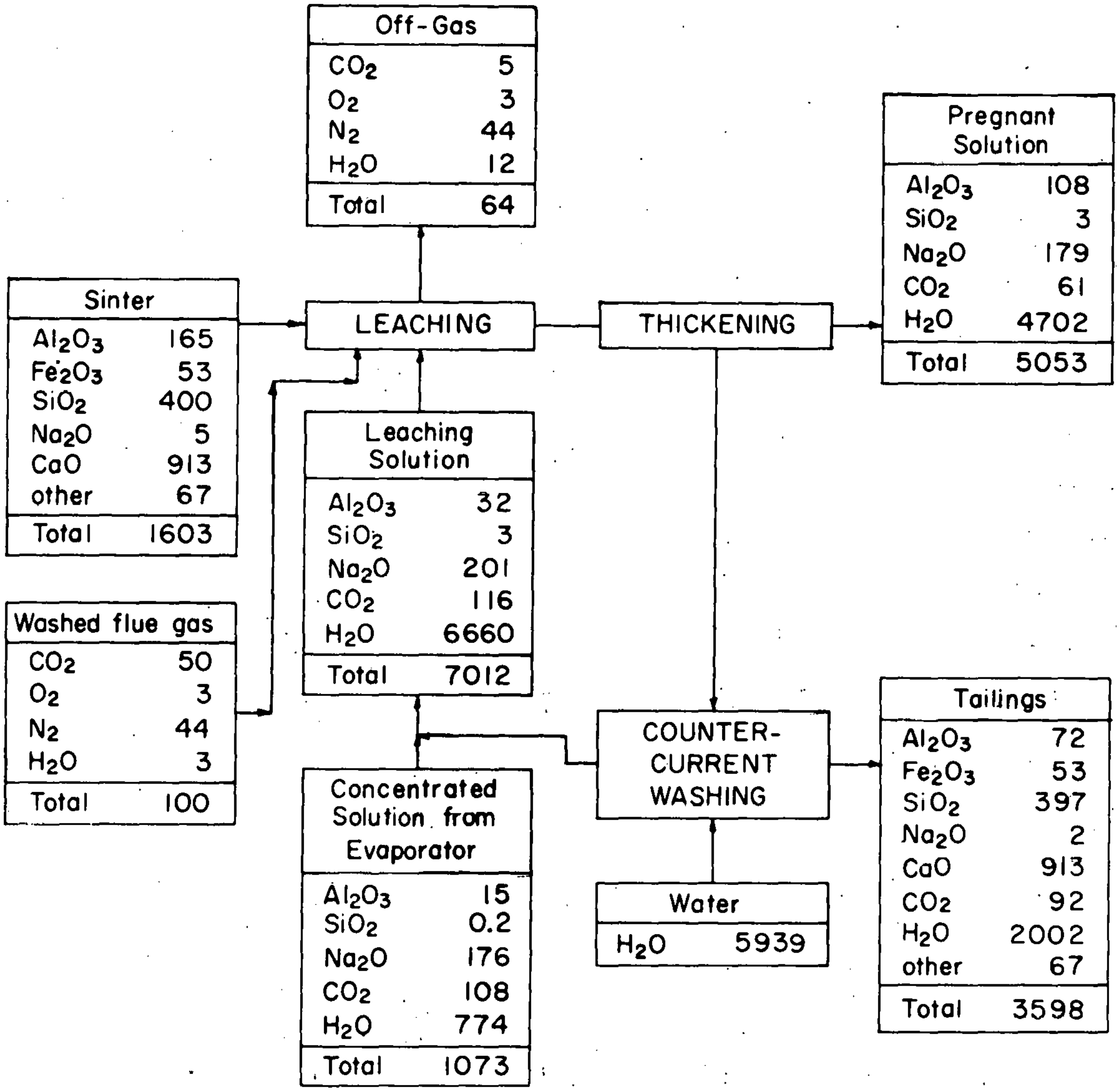


Figure A-2. Material balance, leaching section (tons per day)

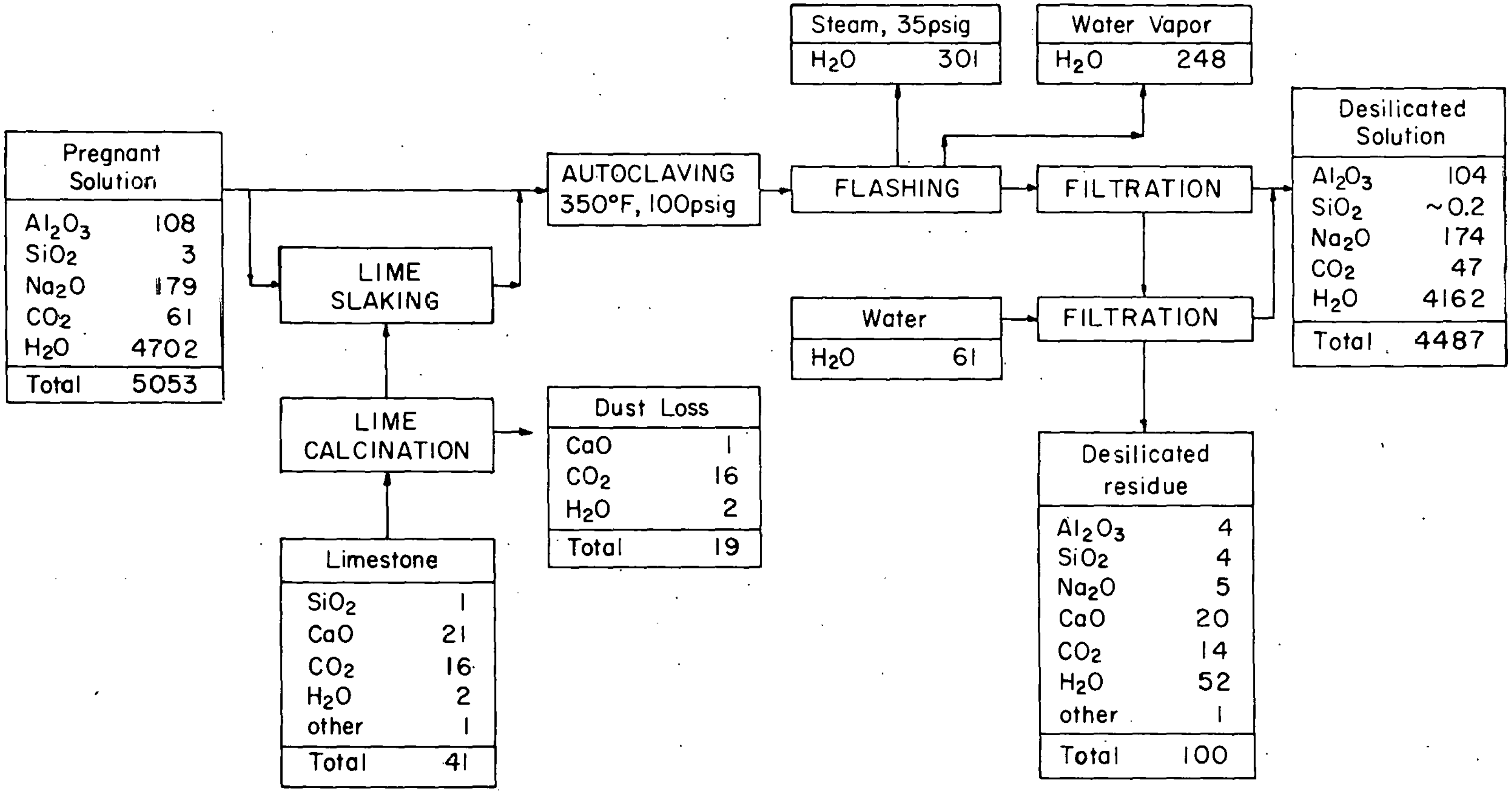


Figure A-3. Material balance, desilication section (tons per day)

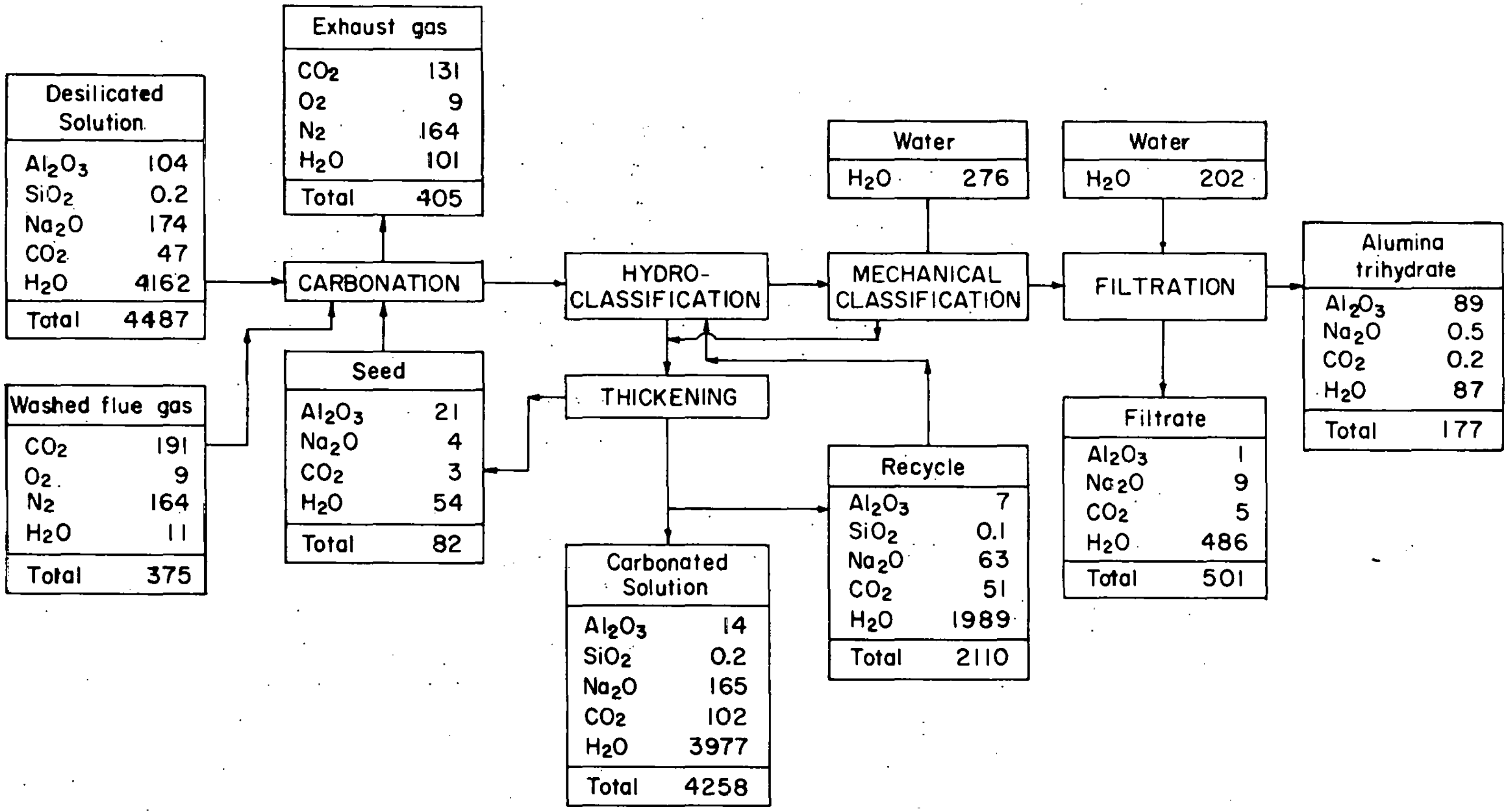


Figure A-4. Material balance, carbonation section (tons per day)

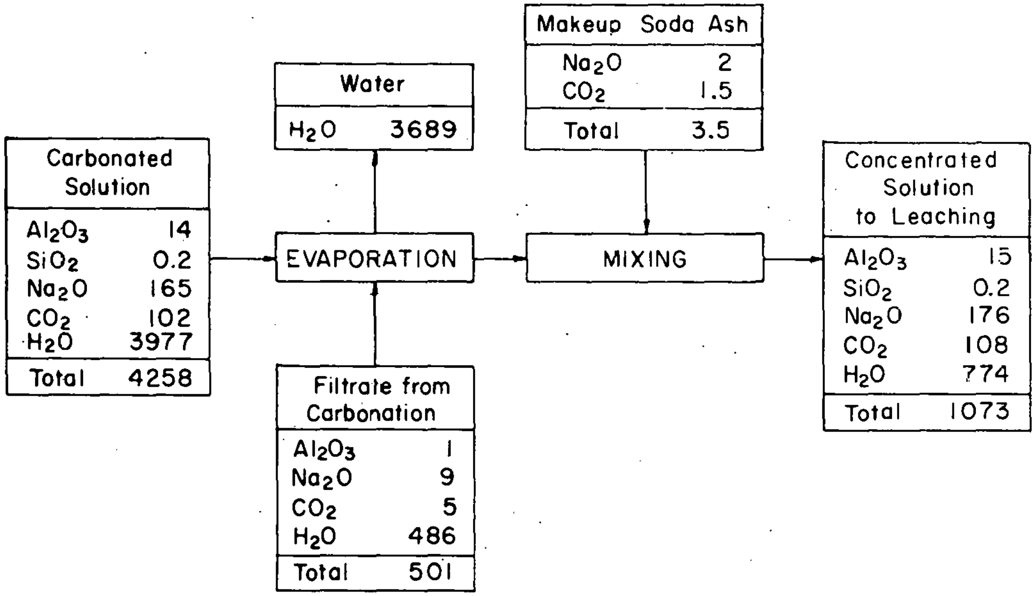


Figure A-5. Material balance, soda ash recovery section (tons per day)

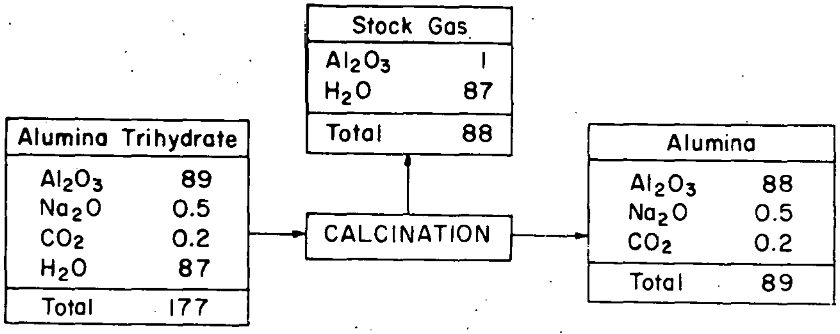
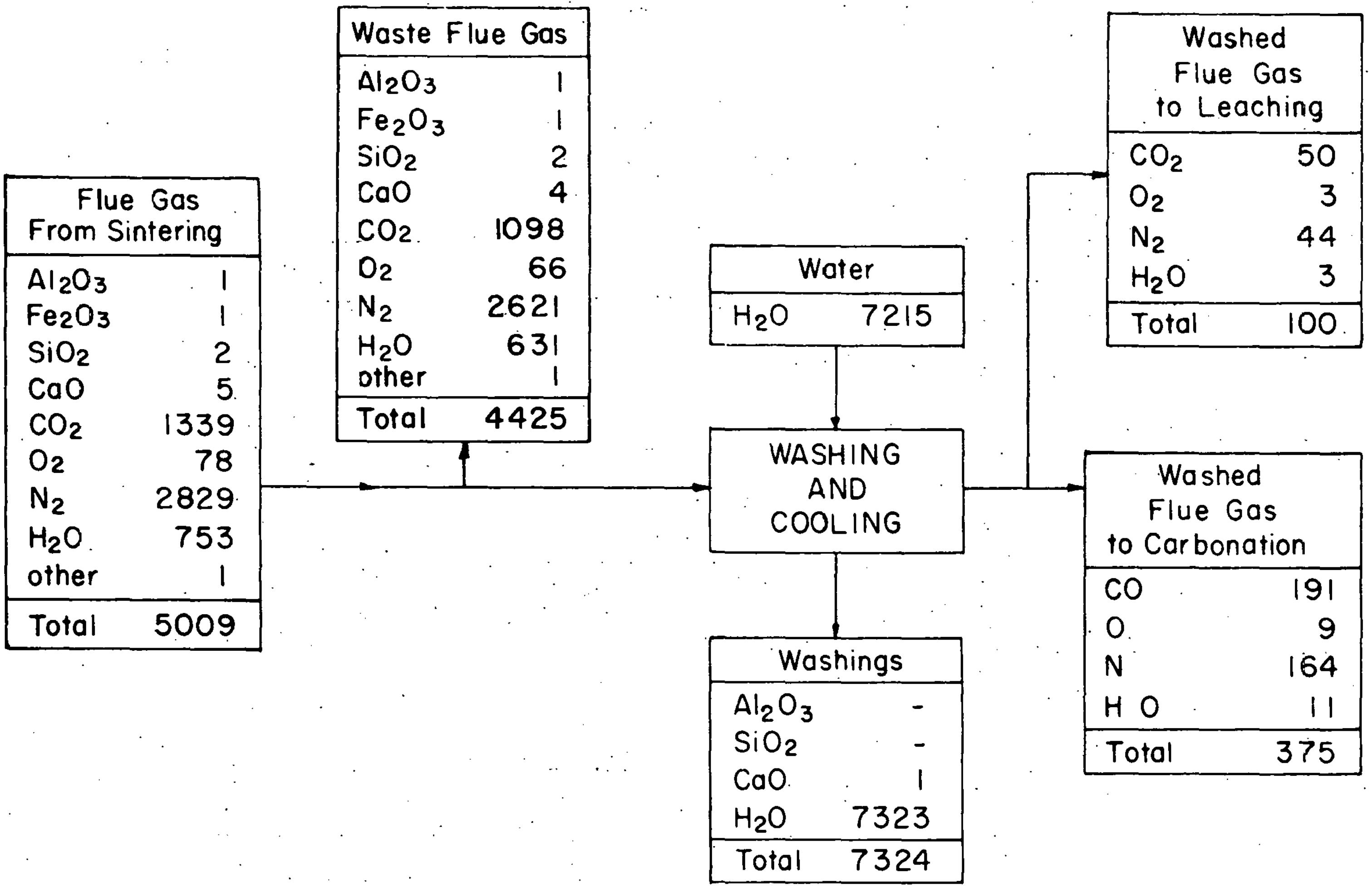


Figure A-6. Material balance, calcination section



Flue Gas From Sintering	
Al_2O_3	1
Fe_2O_3	1
SiO_2	2
CaO	5
CO_2	1339
O_2	78
N_2	2829
H_2O	753
other	1
Total	5009

Waste Flue Gas	
Al_2O_3	1
Fe_2O_3	1
SiO_2	2
CaO	4
CO_2	1098
O_2	66
N_2	2621
H_2O	631
other	1
Total	4425

Water	
H_2O	7215

Washings	
Al_2O_3	-
SiO_2	-
CaO	1
H_2O	7323
Total	7324

Washed Flue Gas to Leaching	
CO_2	50
O_2	3
N_2	44
H_2O	3
Total	100

Washed Flue Gas to Carbonation	
CO	191
O	9
N	164
H O	11
Total	375

Figure A-7. Material balance, flue-gas processing section (tons per day)

Table A-1. Daily thermal requirements

Section and unit	Steam, 1000 pounds			Natural gas MMBtu	Cooling water 1000 gallons
	30 psig	100 psig	250 psig		
Sintering: sintering kilns	—	—	—	8309	—
Leaching: leach tanks	—	361	—	—	—
Desilication:					
Heat exchangers	671	—	—	—	—
Autoclaves	—	—	1830	—	—
Hash tanks	602[a]	—	—	—	—
Lime kiln	—	—	—	139	—
Calcination: calcining kiln	—	—	—	356	—
Soda ash recovery:					
Evaporator, 7-effect	—	1734	—	—	2546
Flue-gas processing:					
Waste heat boiler	69[b]	2095[b]	—	—	—
Coolers	—	—	—	—	1730
Total thermal requirements			1830	8804	4276

[a] Steam credited at 30 psig.

[b] Steam credit of 2,164,000 pounds at 100 psig and reduced to required pressures.

Table A-2. Major items of equipment for the lime-sinter process

Section	Items
Magnetic separation	Magnetic separator
Sintering	Gyratory crusher, standard cone crusher, short-hand cone crusher, ball mill, pelleting mill, sintering kiln, hammermill
Leaching	Leaching tank, thickener
Desilication	Heat exchanger, autoclave, flask tank, thickener, rotary vacuum filter, pressure leaf filter, lime kiln
Carbonation	Carbonator, hydroclassifier, rake classifier, thickener, internal drum filter
Calcination	Calcining kiln
Soda ash recovery	7-effect evaporator
Flue-gas processing	Waste heat boiler, spray chamber, compressor

Table A-3. Study estimate using factors for process plant component costs

Items considered	Percentage factor assumed						
	Section						
	Sintering	Leaching	Desilication	Carbonation	Calcination	Soda ash recovery	Flue-gas processing
Process equipment	57.9	50.9	44.3	43.5	54.9	43.4	72.8
Process equipment labor	12.3	4.4	7.8	4.3	14.5	4.4	1.6
Foundation	4.0	3.1	3.1	3.0	3.2	3.0	2.0
Building	8.6	8.9	13.1	8.7	9.3	8.7	7.8
Insulation	0.6	3.6	3.5	3.5	0.5	3.5	2.2
Instrumentation	2.3	4.5	4.3	4.4	1.9	4.3	0.2
Electrical	0.6	4.5	4.3	4.3	4.6	4.4	2.7
Piping	5.1	13.4	13.1	21.8	4.2	21.7	7.8
Painting	2.9	2.2	2.2	2.2	2.3	2.2	0.2
Miscellaneous	5.7	4.5	4.3	4.3	4.6	4.4	2.7