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RECOVERY OF ALUMINA FROM FLY ASH
BY HIGH-TEMPERATURE CHLORINATION

by

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Abstract. The large volume of fly ash being produced, largely in centralized locations, and the composition of the ash present unique opportunities for the recovery of minerals. A typical United States fly ash will contain about 21 percent alumina and 17 percent iron oxide, the balance being primarily silica. Up to 85 percent of the iron oxide can be removed from the ash by magnetic separation.

Since 1972, three different processes for recovering alumina from the non-magnetic fraction of fly ash have been under investigation at the Ames Laboratory. The processes are lime-sinter, hydrochemical and high-temperature chlorination. Significant progress has been made with the latter and it will be discussed in detail.

In the chlorination process, the non-magnetic fraction of the fly ash is mixed with carbon and chlorinated in a fixed bed. Because the iron has a high chlorine affinity, the iron remaining in the ash can be removed as volatile iron chloride at 400°C to 600°C; very little aluminum and silicon react. The temperature is then raised to 850°C to 950°C where a mixture consisting mostly of volatile aluminum and silicon chlorides forms. When the vapors are cooled, solid aluminum chloride condenses at 120°C to 150°C while the silicon tetrachloride remains in a vapor state because of its low condensation temperature. The silicon tetrachloride can be easily decomposed to form silica and HCl thus recycling the chlorine.

Introduction

With the declining long-term availability of oil and natural gas, coal is assuming a major role in the generation of electricity to meet national demands. The reduced availability of fuel oil and natural gas, and the environmental, sociological, and regulatory problems which are slowing the development of nuclear power, have pushed coal consumption to unexpected levels. As the demand for coal increases, lower grade, higher ash content coals will be burned. At the same time, better ash removal facilities are more effectively removing ash particles from the combustion gases. These factors tend to further increase coal ash production. Data which illustrate the extent of the continuing increase in the rate of coal consumption and resultant ash production are shown in Figure 1.¹

Most of the coal used in power generation plants is burned in pulverized form. The coal particles burn in the fire box of the boiler and about two-thirds of the residual ash leaves in the furnace gas stream in the form of suspended, finely-divided particles which are collected as a fine powder known as fly ash. The remainder leaves as bottom ash, the portion of the ash which slags and falls into the pit below the burner. The data in Figure 1 show that the coal burned in 1975 contained

an average of 15 wt. percent ash, of which 70 wt. percent was collected as fly ash.

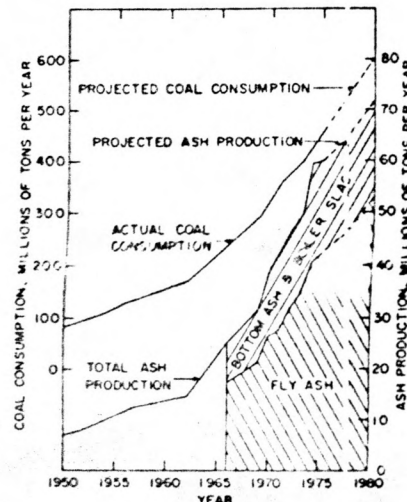


Figure 1. Coal Consumption and Ash Production by U.S. Electric Utilities.¹

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Coal Ash Composition

The amount of ash in coal varies over a wide range. This variation occurs not only in coals from different locations, but in coals from different areas of a mine. The composition of the ash, however, is much less variable.

Composition data for the major ash constituents have been collected in a study in which commercial samples of coals produced throughout the United States were analyzed.² Similar data have been collected for the fly ash fraction only. These data are shown in Figure 2.^{3,4} Although the constituents are reported as oxides, they occur in the ash as a mixture of silicates, oxides, carbonates, and sulfates, with small amounts of phosphates and other compounds. From Figure 2, the average fly ash analysis for the three major constituents is shown to be 44 wt. percent silica (SiO_2), 21 wt. percent alumina (Al_2O_3), and 17 wt. percent ferric oxide (Fe_2O_3). These constituents comprise about 90 wt. percent of the fly ash from bituminous coals; lignite coal ashes contain larger amounts of calcium oxide (CaO) and magnesium oxide (MgO) and less ferric oxide.

Minerals from Coal Fly Ash

The large volume of coal ash produced presents a unique opportunity for the recovery of minerals. Using average values, the fly ash produced by a 1,000 megawatt power plant will contain mineral equivalents as listed in Table 1. The total amount of fly ash produced per day from this single plant will be about 1,500 tons.

A 1974 listing⁵ stated that there were 32 privately owned, coal burning steam power plants with capacities of 1,000 megawatts electricity generated, or greater. These plants are located nationwide but a large percentage are in the Eastern states. Figure 3 illustrates this distribution by showing the locations where coal ash is produced in the United States.⁶

Recovery of all of the alumina from the fly ash from one 1,000 megawatt facility would produce approximately 60,000 tons of aluminum metal per year. This would permit a reduction in imported bauxite ore of 250,000 tons. The iron oxide can also be

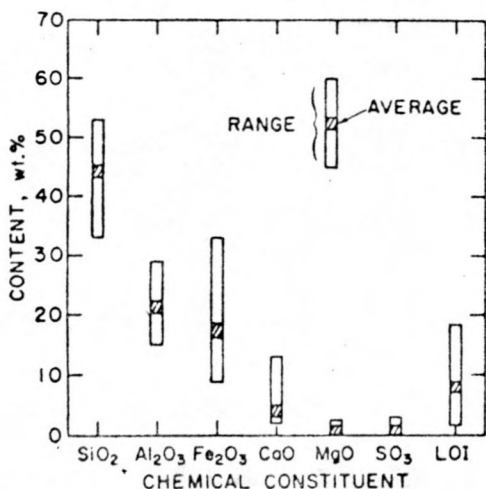


Figure 2. Range and Average Content of Different Chemical Constituents in United States Fly Ashes.^{3,4}

Table 1. Annual Equivalent Mineral Content of Fly Ash from a 1,000 Megawatt Power Plant

Mineral	Tons/yr
SiO_2	231,800
Al_2O_3	111,300
Fe_2O_3	90,700
CaO	20,100
SO_3	13,800
K_2O	8,000
TiO_2	6,400
MgO	6,400
Na_2O	3,200
P_2O_5	1,600
Total tons/yr	493,300



Figure 3. Locations of Privately Owned, Coal Burning Steam Power Plants with Capacities of 1,000 Megawatts Electricity Generated, or Greater.⁶

recovered and theoretically would produce 60,000 tons of steel per year.

A fly ash processing complex could be a central plant serving several power generation facilities. Such an installation could be built to serve each of our large cities and would recover 500 to 2,000 equivalent tons of aluminum per day. The amount of transportation required would be small. As few as 50 such installations could process as much as 75 percent of the total fly ash produced.

The development of processes for the recovery of valuable minerals from waste coal ash has great economic potential. The material is not being used now in any significant amount, is already mined and pulverized, and could be processed to produce 70 percent of our current aluminum requirement and 10 percent of the national iron demand. These processing facilities would provide jobs, reduce power generation costs through the sale of recovered minerals, and reduce our national deficit in the balance of trade for metals, which is now over two billion dollars annually.⁷ In 1975 only 10 percent of the fly ash produced in the United States was utilized; 37.8 million tons were trucked or sluiced to a disposal area.⁸

Requirements for aluminum metal are increasing at 5 to 7 percent each year and the demand by the year 2000 may be as high as 30 to 40 million tons per year.⁹

Magnetic Separation of Iron Oxide from Fly Ash

Since most of the iron oxide in fly ash is not chemically bonded to the aluminum or the silicon compounds, an iron fraction containing 70 to 90 percent of the iron oxides in the ash can be separated magnetically. Table 2 contains chemical analyses of the whole fly ash and of the magnetically separated fractions for a typical midwestern power plant fly ash. The fly ash used has been shown by earlier research¹⁰ to contain about average mineral values for a midwestern fly ash, and is near the national average for bituminous-type ash.

The iron content in the magnetic fly ash fraction is about 70 wt. percent Fe_2O_3 . With further treatment to reduce the silica and alumina content this material should be usable in pelletized form as a blast furnace feed. No additional treatment is necessary to market the material as "magnetite" for use in the preparation of dense-media suspensions used in coal washing and ore beneficiation. There also may be applications for magnetic fly ash as a seed material in high-intensity, high-gradient magnetic processes for desulfurizing coals.¹¹

The magnetic separation is made using a specially designed electromagnetic device. A linear electromagnet attracts the ferromagnetic particles and transports them along the length of a magnetic surface thus separating the magnetic from the non-magnetic particles. The separation is made dry because the fractionation obtained is satisfactory and because dry material is used for the chlorination reaction. Magnetic separation can be conducted commercially either wet or dry, and ordinary magnetic drum or magnetic rotor equipment should be

Table 2. Composition of C-1 Fly Ash and Fractions Obtained by Magnetic Separation^{d,10}

Constituent	Chemical Composition, Wt. Percent		
	Whole Fly Ash	Magnetics ^c	Non-magnetics ^c
SiO_2	39.1	14.4	46.9
Al_2O_3	17.8	7.5	21.0
Fe_2O_3	17.8	71.5	5.6
CaO	4.5	1.5	5.4
MgO	0.7	0.4	0.8
Na_2O	0.4	0.2	0.4
K_2O	1.7	0.8	1.8
SO_3	1.9	1.1	1.9
LOD ^a	0.5	0.1	0.5
LOI ^b	10.6	0.6	13.0

^aLOD is loss on drying at 110°C

^bLOI is loss on ignition from 110-800°C

^cWhole fly ash separated as 24 wt. percent magnetics and 76 wt. percent non-magnetics

^dC-1 fly ash was collected by mechanical precipitators from a dry bottom type boiler using coal from western Kentucky and Southern Illinois. This sample was received from the Lakeside Power Plant, Milwaukee, Wisconsin.

satisfactory. Commercial size equipment of this type is readily available.

Chlorination of the Non-magnetic Fraction of Fly Ash

The objectives of our research are to demonstrate the feasibility of chlorination of coal fly ash as a method for recovering the aluminum, and to develop a process capable of being used for the large-scale recovery of aluminum and iron from fly ash. Figure 4 shows a schematic diagram for such a process based on the work to date.

The reaction of chlorine with metal oxides requires large quantities of energy and even at high temperatures the yields are low. If carbon is added, however, the yield is increased and the energy requirements are reduced. The carbon reacts with the oxygen released from the oxides when chlorination occurs. If the resultant gaseous carbon oxides are withdrawn as they form, the reactions proceed to completion. In addition the combined reduction and chlorination reaction is exothermic so the energy requirement is lower. Because the overall reaction is exothermic, oxides of all the metals in a mixture can be expected to be chlorinated to some extent.

The non-magnetic fraction of coal ash contains from 5 to 10 wt. percent iron oxides. Because iron has a high chlorine affinity, it is removed selectively from the fly ash by chlorination at 500 to 600 C. At this relatively low temperature, little aluminum or silicon reacts. After most of the iron is removed, the remaining fly ash is chlorinated at 850 to 950 C to produce a vapor mixture of AlCl_3 , SiCl_4 , and CO plus some remaining FeCl_3 . When this vapor is cooled, solid AlCl_3 contaminated with some FeCl_3 condenses at 120 to 150 C. Silicon tetrachloride does not condense because of its low partial pressure and the relatively high temperature

There are several possible methods for removing the FeCl_3 impurity from the AlCl_3 based on differences in vapor pressure and solubility. Some type of fused salt scrubbing of the mixed vapor to remove the FeCl_3 will probably be most adaptable to a commercial process. The AlCl_3 can then be condensed with very little SiCl_4 present.

Procedures are yet to be developed for separating the SiCl_4 and CO . Silicon tetrachloride is a valuable product used in making silicons, metal silicides, silanes, silicon organic compounds, and silicon ammoniates. It also has use in electronics for the preparation of transistor-grade, high-

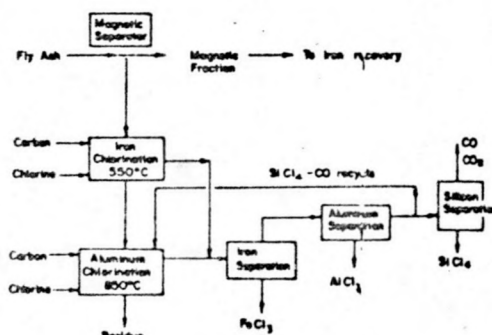


Figure 4. Schematic Diagram for Fly Ash Chlorination Process.

purity silicon metal, in the glass industry, for the manufacture of high-purity fused-silica, and in the petroleum industry for preparation of oil field drilling muds.¹² Recycle of SiCl_4 to the chlorination step will, however, reduce SiCl_4 formation and minimize chlorine consumption. Optimization of this part of the process may include recycle and could become quite complex.¹³

The byproduct FeCl_3 from the pretreatment step can be oxidized to Fe_2O_3 and used to upgrade the magnetic ash fraction if it is to be used as blast furnace feed.

The principal product is AlCl_3 which has numerous uses including the manufacture of catalysts for many Friedel-Crafts reactions. Because of the large quantity potentially available, however, it would be expected that most of the AlCl_3 would be converted to aluminum metal. The process for doing this is well developed and is nearing commercialization.^{14,15}

Production of aluminum metal from AlCl_3 results in a large energy saving. The present commercial process from alumina consumes about 40 percent of all the electrical energy used in the metal producing industries of the United States. About 7 to 8 kwh of power is required per pound of aluminum metal produced. Aluminum metal production from the chloride is about 30 percent more efficient. For production of 4 million tons of aluminum metal per year, this process would reduce power usage by 1.8×10^{10} kwh which is equivalent to the power generated by a 2,000 megawatt power plant.

Experimental Work

Previous research has demonstrated that metal oxides can be removed from the non-magnetic fraction of fly ash by chlorination.¹⁶ The present work deals with the effects of reaction conditions such as temperature, time, chlorine flow rate, and the amount of solid carbon added. Using equipment made of glass and vycor and assembled as shown in Figure 5, a series of experiments was conducted in which dry chlorine gas was introduced into a fixed bed of ash and carbon. The major components in the ash react with the chlorine as follows:

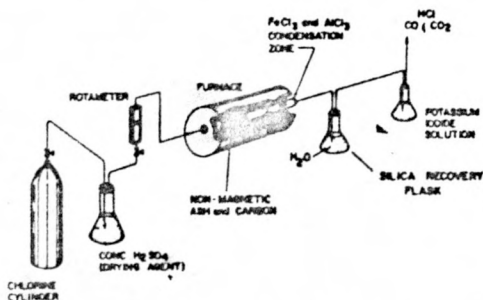
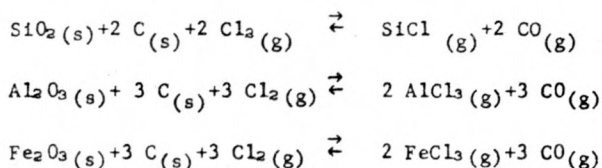


Figure 5. Equipment Used in Fly Ash Chlorination Process.

The gaseous chlorides formed in the high temperature section of the fixed bed reactor condensed in the cooler section at their respective dew points. Ferrous chloride condensed first just where the reactor tube left the furnace. A mixture of FeCl_3 and AlCl_3 then condensed in the tube downstream. The remaining mixture of SiCl_4 and CO did not condense but the silica and chlorine were recovered by hydrolyzing the SiCl_4 to silicic acid and HCl .

Figure 6 (a and b) shows the extent to which the metal oxides in the fly ash are chlorinated as a function of reaction temperature and chlorine flow rate. The chlorination reaction is very rapid. No chlorine was detected in the gases leaving the reactor until a significant amount of the ash had reacted. At the lower chlorine flow rate, the reactions involving alumina and silica do not appear to be temperature dependent. The iron oxide data are erratic, but iron is a minor component and sample inhomogeneity may be a factor. The higher chlorine flow data show a distinct temperature dependence for alumina but none for silica until the reaction temperature is increased to 900°C where the amount reacted increases.

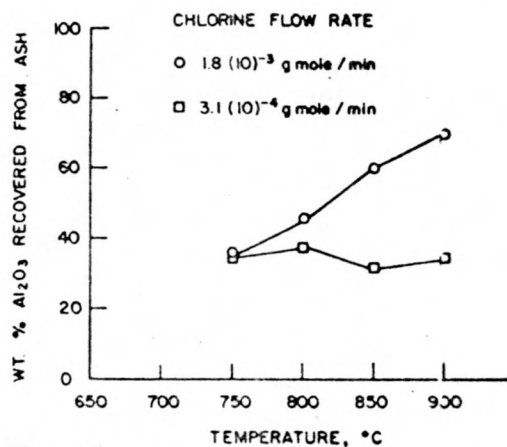


Figure 6a.

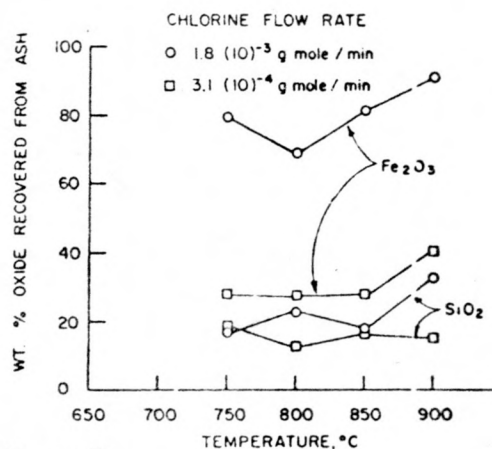


Figure 6b.

Figure 6. (a) Alumina Chlorination of (coal Fly Ash (3:10 Carbon Ratio) as a Function of Chlorine Flow Rate, (b) Silica and Iron Oxide Chlorination.

A series of experiments were made next using different carbon to ash ratios. Data were collected over a temperature range of 750 to 900 C, and the quantity of carbon used was varied from one-half the stoichiometric amount required for complete reaction to twice that amount.

The stoichiometric ratio is 3 grams of solid carbon to 10 grams of non-magnetic fly ash. The results of these runs are shown on Figure 7. It appears that the amount of carbon present is not a controlling variable, within the range of composition investigated. When less than the stoichiometric amount of carbon is present, it is possible that the CO formed enters into the reaction as a substitute for C and forms CO_2 .

Each of the runs conducted to investigate carbon to ash ratio was continued until chlorine gas was detected in the product vapor. Consequently, the runs were of different lengths of time. Figure 8 shows the same data given in Figure 7 but in a form which takes into account both time and the amount of reactant initially present. The kinetic reaction rate appears to be almost constant and independent of temperature and of carbon to ash ratio. The runs at higher temperature and lower carbon to ash ratios can be maintained for a longer period of time before any chlorine leaves the reactor unreacted. These runs therefore have higher recoveries of alumina from the ash. The results from the experiments conducted to investigate the effect of chlorine flow rate are treated in the same manner in Figure 9. The average reaction rate is about three times greater for the higher chlorine rate than for the lower one. This would suggest that the overall rate is controlled by gas phase diffusion at the gas-solid interface.

Conclusion

It has been estimated that by 1985 or 1990 the annual coal consumption by U.S. electric utilities will be about one billion tons. If this takes place, about 100 million tons per year of coal fly ash will be produced from which 10 million tons of iron and 10 million tons of aluminum can be recovered. Since most of the iron in fly ash is in magnetically susceptible particles, magnetic separation can be used to recover 70 to 80 percent of the iron.

Under proper conditions, 70 to 80 percent of the alumina in the non-magnetic fraction of the ash can be recovered as aluminum trichloride by high-temperature chlorination in a fixed bed. The reaction rates are sufficiently high that it appears a fluidized reaction bed could be used. Additional research is needed to investigate the use of a fluidized bed reactor and the recycle of silicon tetrachloride and carbon monoxide. Reactivity improvement through the addition of reaction catalysts should also be investigated. It is planned to develop the process to where a small pilot plant can be designed and operated which will incorporate recycles, product purification, and residue and off-gas cleanup.

Acknowledgement

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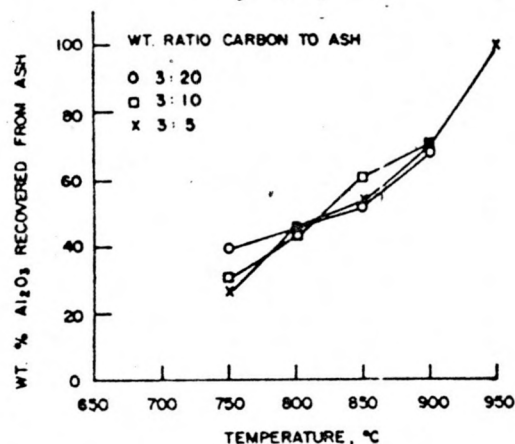


Figure 7. Alumina Chlorination of Coal Fly Ash (3.1×10^{-3} g mole Cl_2 /min flow rate) as a Function of Carbon to Ash Ratio.

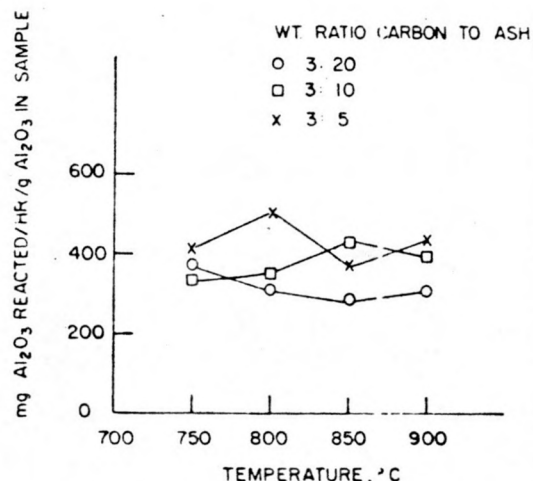


Figure 8. Reaction Data for the Chlorination of Alumina in Fly Ash (3.1×10^{-3} g mole Cl_2 /min flow rate) as a Function of Carbon to Ash Ratio.

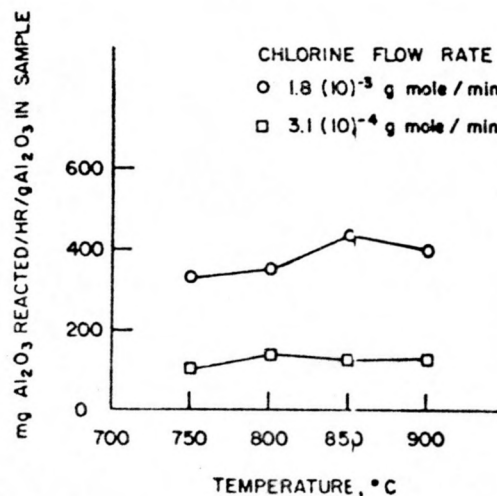


Figure 9. Reaction Data for the Chlorination of Alumina in Fly Ash (3:10 Carbon Ratio) as a Function of Chlorine Flow Rate.

References

1. Faber, J. H., "U.S. Overview of Ash Production and Utilization," Proceedings, 4th International Ash Utilization Symposium, St. Louis, 1976, Energy Research and Development Administration MERC/SP-7614 (CONF-760322), 5 (1976).
2. Abernathy, R. F., M. J. Peterson, and J. F. Gibson, "Major Ash Constituents in U.S. Coals," Bur. of Mines Rep. of Invest. No. 7240 (1969).
3. Kokubu, M., "Fly Ash and Fly Ash Cement," Proceedings, 5th International Symposium of Cement, Tokyo, Japan, v. 4, pt. 4, Oct. 7-11, 75 (1968).
4. Capp, J. P. and J. D. Spencer, "Fly Ash Utilization. A Summary of Applications and Technology," Bur. of Mines Inf. Circ. No. 8483 (1970).
5. Statistics of Privately Owned Electrical Utilities in the United States. Federal Power Commission (1974).
6. Collins, R. J., "Waste Products as a Potential Replacement for Aggregates," Proceedings 4th International Ash Utilization Symposium, St. Louis, 1976, Energy Research and Development Administration MERC/SP-76/4 (CONF-760322), 93 (1976).
7. Carlson, O. N. and M. McKimpson, "Environmental Problems in the Production of Steel and Aluminum," Unpublished paper. Iowa State University, Ames, Iowa (1974).
8. Ash at Work, National Ash Assoc. Vol. III, No. 2 (1976).
9. Mineral Facts. Bur. of Mines Bulletin No. 667 (1976).
10. Cavin, D. C., W. A. Klemm, and G. Burnet, "Analytical Methods for Characterization of Fly Ash," Proceedings, Iowa Acad. Sci. 81, 130 (1974).
11. "Assessment of Sulfur and Ash Removal from Coals by Magnetic Separation," Technical Progress Report. Magnetic Separation Laboratory. Auburn University, Auburn, Ala. (1976).
12. de Beauchamp, R. L., "Preparation of Anhydrous Aluminum Chloride," Bur. of Mines Inf. Circ. 8412. 19 pp. (1969).
13. Staib, K., "Process for Producing Anhydrous Aluminum Chloride," U.S. Pat. 1,866,731. July 12 (1932).
14. "New Processes Promise Lower Cost Aluminum," Chem. and Engr. News, 11, Feb. 26 (1973).
15. "Digging for Alumina Processes," Chem. Week, 40, March 6 (1974).
16. Murtha, M. J. and G. Burnet, "Recovery of Alumina from Coal Fly Ash by High Temperature Chlorination," Proceedings Iowa Acad. Sci. 83, 125 (1976).
17. White, Harry J., "Electrostatic Precipitation of Fly Ash," J. Air Pollution Control Assn. 27(1), 15 (1977).