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DIRECT UTILIZATION - RECOVERY OF MINERALS FROM COAL FLY ASH

FOSSIL ENERGY PROGRAM

Technical Progress Report

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Advanced Research and Technology

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G. Burnet, M. Murtha and J. R. Frederick

Abstract

The purpose of this investigation is to develop methods to utilize coal fly ashes through processes for the extraction of alumina and titania, and for the separation and utilization of an iron-rich fraction. During this report period, research of the HiChlor process for the extraction of alumina and titania by high-temperature chlorination of a fly ash-reductant mixture has involved comparative calculations for several fly ashes, development of design restrictions for fly ash fluidization, and the design of a bench-scale fluidized chlorination system. In addition, work was begun on a computer calculation of the fly ash chlorination system. Computer evaluations will include: the simulation of fly ash chlorination data previously collected, calculations for chlorinations using several reductant schemes, and calculations for reactions at increased pressures. These results will be valuable for the design of further experiments and of a commercial HiChlor fly ash processing facility. The initial chlorination research of the high-volume fly ashes from western coals was begun. These high calcium, low iron fly ashes are reactive but the contained calcium reacts to form calcium chloride, consuming a substantial amount of chlorine.

Process development of the sinter process for alumina recovery has included the investigation of several variables for improving the quantity and quality of the alumina extracted from sintered materials. As a result of this work, it is clear that further optimization of the sintering and extraction variables is required for commercialization of the fly ash sinter process. In a new development significant improvement in the alumina recovery levels and a reduction in energy requirements has resulted from the addition of waste coal refuse to the sinter mixture. Testing has also included the use of inexpensive or waste materials in place of soda ash and/or limestone in the sinter feed.

Iron-rich, magnetically separated coal fly ash particles were beneficiated to a quality equal to high grade, naturally mined iron ore by a high-temperature pressurized caustic treatment. About 95 percent of the contained silica and 65 percent of the alumina was extracted. Particle examination of leached and unleached mate-

rials by electron microprobe indicated that alumina is uniformly distributed throughout the particles. Dot field images of individual elements in the particles showed element location and indicated the combination of elements in the magnetic ash particles.

Work was begun on the assembly of equipment for a detailed comparison of magnetically separated iron-rich fly ashes and commercial magnetites for use in heavy media coal beneficiation. Characterization of the particles, and stability and rheological properties of media solutions prepared with these mediums will provide data for further evaluating magnetic fly ash as a heavy media material. A circuit is also being built for long-term flow tests of the media suspensions for measurement of construction material erosion and solid medium particle friability.

OBJECTIVES AND SCOPE OF WORK

Background

The primary objective of this investigation is to develop and/or improve methods for the utilization of coal fly ash as a source of minerals. Processes are being studied for the recovery of alumina, iron oxides, and titanium oxide from fly ash and for utilization of the residue. Use of fly ash as a source of minerals will help the United States reduce its ash disposal problems and dependency upon imported ores and metals.

Objectives

Task A - Development of HiChlor Process - Fly ash will react with chlorine in the presence of a carbon reducing source at high temperatures to produce volatile metal chlorides. Practical constraints on the problem need to be further identified and studied. Details of the process are being developed including an understanding of the reaction mechanism, a reaction scheme and reactor design that is capable of handling the required ash volume (possibly a fluidized bed), a scheme for recycling excess reactants, and a method for recovering and separating the products.

Task B - Improvement of the Lime-Soda Sinter Process - Soluble sodium and calcium aluminates are formed when fly ash is mixed with the proper amount of limestone and soda ash and sintered at about 1100°C. The aluminates can be extracted from the clinker using a dilute soda ash solution. A commercial grade hydrate of alumina is recovered from the extract by precipitation. The sintering step is now well understood and work is underway on the remainder of the process. A proposal for construction and operation of a process development unit (PDU) as the first step toward commercialization of the process has been submitted for funding approval, and design of the equipment is proceeding. Process conditions which may improve the filtrate desilication step are being investigated, as is the use of low quality, inexpensive limestones, waste flue gas scrubber sludge, and other waste materials in the sinter. Methods to reduce the process energy requirements are also being studied.

Task C - Improvement of the Lime-Fly Ash Sinter Process - Research of the lime-fly ash sinter method was essentially discontinued about two years ago because of low recoveries and high energy requirements, but the use of new additives now makes this process appear economically feasible. The addition of a small amount of carbon and sulfur to the raw sinter mixtures has increased alumina recoveries to about 90 percent, with a sintering temperature of 1200°C. Waste materials such as flue gas scrubber sludge and cement kiln dust may replace limestone, providing a process to produce alumina and Portland cement entirely from high volume waste materials--fly ash, kiln dust or scrubber sludge, and coal refuse.

Task D - Recovery and Use of an Iron-Rich Fraction from Fly Ash by Magnetic Separation - The processes for metal recovery are improved by the removal of as much iron as possible from the feed mixtures before chemical processing. Bituminous coal fly ashes contain an average of about 18 weight percent iron oxides, about two-thirds of which can be separated magnetically. The magnetic fraction consists of high-density, finely-divided, spheroidal particles which can be used as heavy media material for coal and ore beneficiation, or as an iron ore. Coal beneficiation with magnetic fly ash heavy media has been demonstrated on a bench scale. The research is now being expanded to include larger scale comparisons of fly ash-derived magnetic heavy media and commercial magnetite media using dense media cyclones at the Iowa State University Coal Preparation Plant. Investigations of sample characterization, rheological properties, stabilities of media suspensions, and material abrasion and medium particle friability will be conducted for both magnetically separated fly ash samples and commercial magnetite samples. Fly ashes representative of the major United States coal fields and representative commercial magnetites will be used for these tests. This work is being carried out in collaboration with the Pittsburgh Energy Technology Center. Bench-scale research is nearly complete on the production of iron ore quality material from iron-rich fly ash by using pressurized caustic digestions to remove silicates and aluminates.

STATUS AND RESULTS

HiChlor Process Development

The physical and chemical restraints for large scale chlorination of fly ash were identified and analyzed. Working with these parameters, several reactor designs were proposed and the experimental questions that will differentiate between the practical applications of these schemes were identified. The economic effect of the choice of chlorination reactants was investigated. Preparations for integration of theoretical and experimental work was made. Chlorination of different types of ash was started. Design of an experimental apparatus for high temperature chlorination was completed which will allow for incremental analysis of products and reactants.

1. Theoretical Studies - The basis for the productive use of theoretical thermodynamic calculations to plan and supplement experimental work was accomplished. Dr. John Riter of University of Denver, who has experience with and computer programs for such theoretical calculations, visited Ames Laboratory and established an understanding of the relevant problems and goals. A brief summary of the potential and use of thermodynamic equilibrium calculations in this work follows.

A. K. Mehrotha, P. R. Bishol and W. Y. Svrcek published an equilibrium computer model of the chlorination of fly ash in 1979 (1). In addition to the multitude of chemical species which Dr. Svrcek incorporated, Dr. Riter's program also includes phase equilibrium data. While these calculations do not indicate kinetic activity terms, they do indicate whether a reaction is possible and what compounds should be expected during experimental analysis. Since the extraction of metal is not a very exothermic reaction, the intermediate actual concentrations of the products will not greatly deviate from the calculated equilibrium values.

During the calculations for a given set of reactants, the value of two intensive state functions are specified and the system is then allowed to computationally relax to the final condition of complete simultaneous heterogeneous phase and chemical equilibria. If temperature and pressure are the two intensive state functions, this means there is an assumption of an infinite heat sink or source at a specific temperature. The sum of Gibb's free energies (total enthalpy and entropy) is a dependent variable and is minimized by iterative calculations. For each product and reactant temperature, dependent enthalpy and entropy, standard heat of formation, a reference enthalpy, and a standard (1 atmosphere) entropy at some temperature value are needed. The end result of the calculations is the mole fraction (above a predetermined threshold) for each product compound in each phase at the specific temperature and pressure.

Preliminary calculations on the fly ash, carbon, and chlorine system indicate that SiC is a product in a chlorine starved reaction. The SiC appears to disappear with a slight excess of chlorine. While the formation of SiC suggests a solid-to-solid interaction which might be kinetically unfavorable, the theoretical work demands that an investigation be undertaken to determine if SiC is present in partially reacted ash.

2. Exploration of Restraints on Process Design - The choice of overall method for

recovery of metals from fly ash as influenced by pelletization is illustrated in Figure 1. The preferable choice of no treatment appears to mean that the chlorination reaction would have to be carried out by fast or light phase fluidization as depicted in Figure 2. If the time to reach the desired extent of conversion is limited by kinetics, and not by mass transfer, to more than 10 minutes, then the reaction would need to be conducted in a modified fluidized bed using a combination of techniques as suggested by Figure 3. If, on the other hand, mass transfer limits the reaction to say 15-20 minutes for the desired conversion, it could be difficult to design a fast fluidization reactor with the necessary residence time.

As will be discussed later, untreated fly ash cannot be economically treated by conventional fluidization techniques due to physical restraints. While it might be possible to react the unpelletized fly ash in a packed bed, the material handling and maintenance problems of keeping a porous support from plugging make it unlikely. On the other hand, if the fly ash were pelletized, then both conventional fluidization and packed bed technology could be applicable. One would then need to investigate the stability of the pellets and compare the effects on mass transfer, efficiency and conversion with nonpelletized ash.

As there is a wide variety of metal contents in ashes, Tables 1-4 give some calculated process design values based on the analysis of the fly ash and expected chemistry. The moles of chlorine required are calculated using the following percentage of conversions: 40% SiO_2, 76% TiO_2, 78% Al_2O_3 , 94% Fe_2O_3 and 100% of Na_2O, K_2O, MgO, and CaO. If CO or phosgene is the reductant, the CO_2 is the gas product. When carbon is the reductant, the calculations assume 100% production of CO. The quantity of moles in pretreatment is the sum of all the metal oxides potentially converted to chlorides excluding Si and Al.

In all the fly ashes, evaluated in Tables 1-4, as much chlorine is used by the Si as by the Al in the ash. Experimental results have indicated that effective Si chlorination can be suppressed by $SiCl_4$ recycle. Table 5 summarized the effect of fly ash composition on reactant demand and product yield with and without $SiCl_4$ recycle. The total demand for chlorine and amounts of products formed is not significantly affected by the fly ash composition. This indicates that if one reactor is used to treat the entire ash, the equipment design would not be affected and the plant could treat a wide variety of fly ashes. On the other hand, if one wanted to

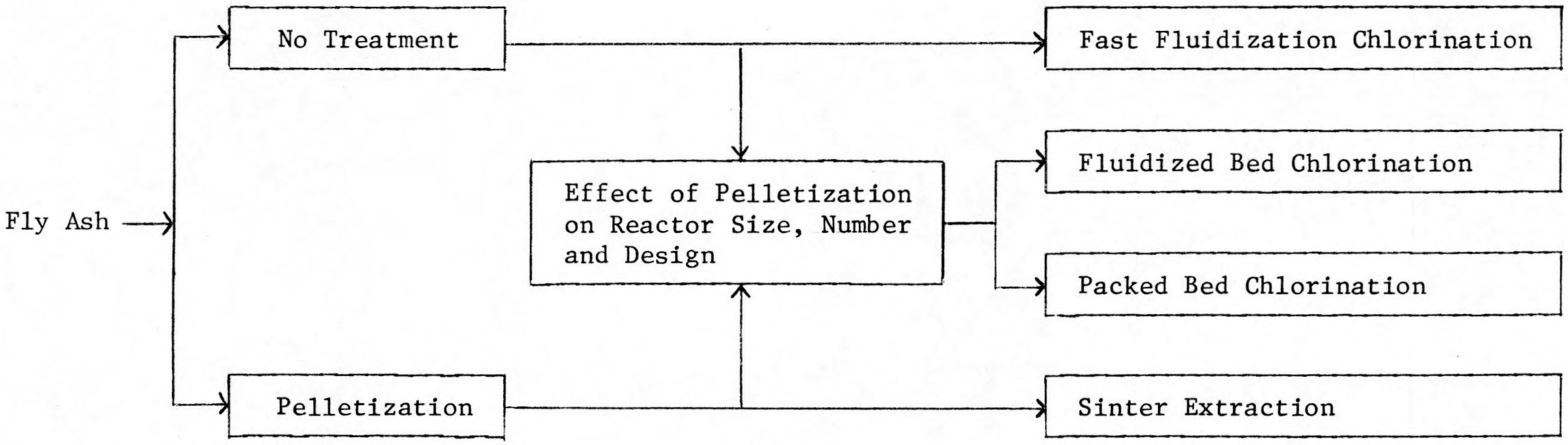

Figure 1. Factors affecting overall choice, size and design of treatment method to extract metals from power plant fly ash

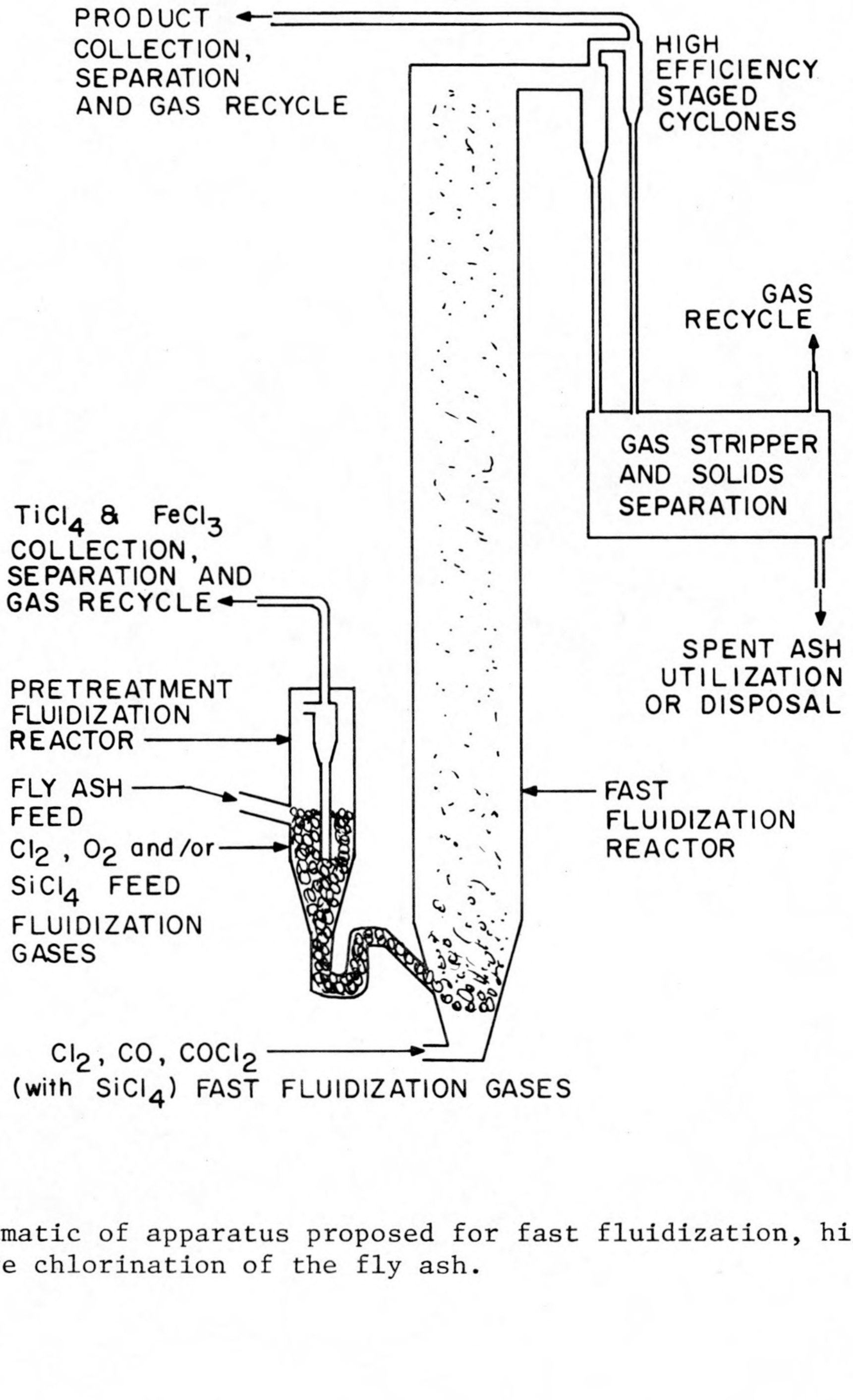

Figure 2. Schematic of apparatus proposed for fast fluidization, high-temperature chlorination of the fly ash.

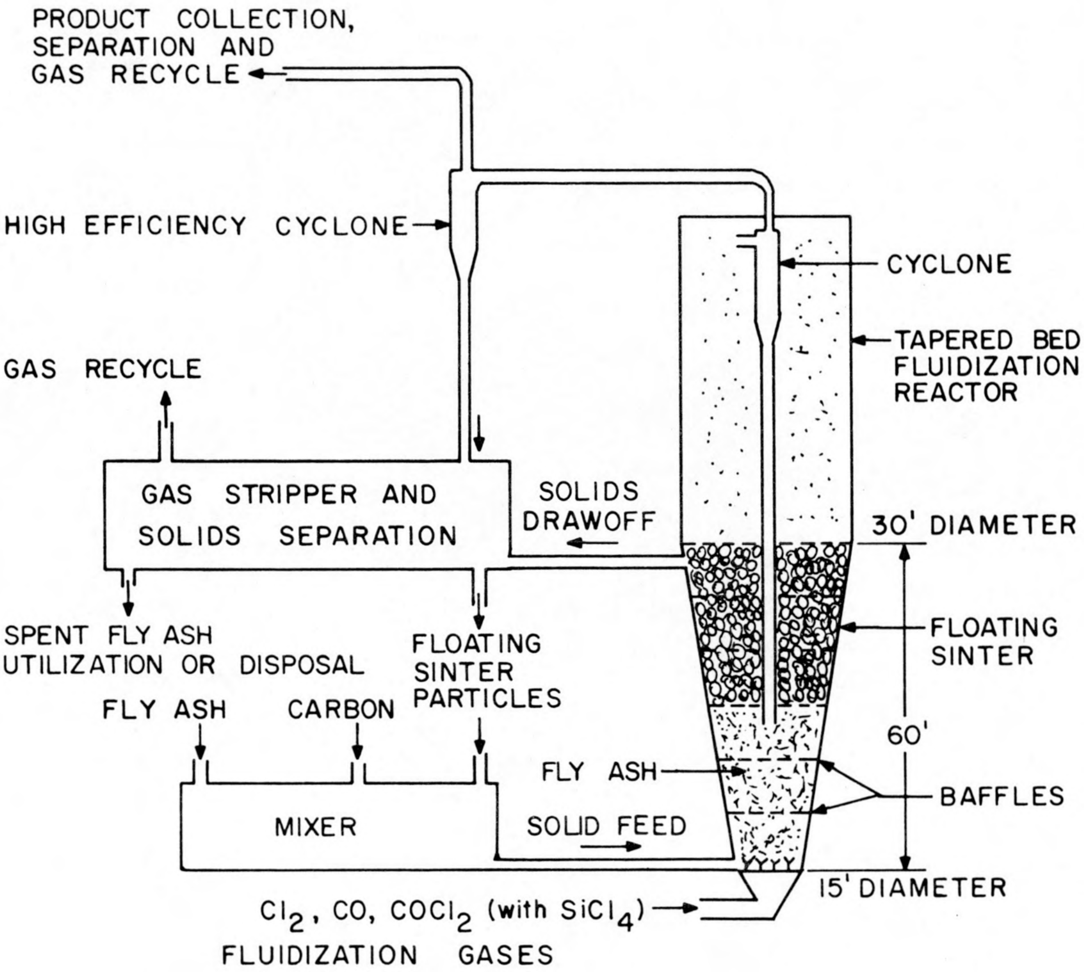

Figure 3. Schematic of apparatus proposed for modified fluidized bed, high temperature chlorination of fly ash.

Table 1. Moles of reactants and product gases as a function of components in fly ash[1]

Oxide	Composition wt. percent	Moles of oxide in 100 gm.	Moles Cl_2 used at est. conversion	Moles of gas products formed
SiO_2	30.2	0.503	0.402	0.603
Al_2O_3	19.8	0.194	0.454	0.757
Fe_2O_3	5.38	0.0336	0.095	0.158
CaO	28.8	0.514	0.154	0.514
MgO	4.47	0.111	0.111	0.111
TiO_2	1.51	0.0189	0.029	0.043
K_2O	0.32	0.0034	0.003	0.003
Na_2O	1.66	0.0268	0.027	0.027
Total moles			1.635	2.216
Total moles in pretreatment			0.779	0.862
Total moles after pretreatment			0.856	1.354

[1] Subbituminous whole fly ash electrostatically precipitated, Comanche Power Plant, Pueblo, Colorado, Wyoming Coal.

Table 2. Moles of reactants and product gases as a function of components in fly ash[1]

Oxide	Composition wt. percent	Moles of oxide in 100 gm.	Moles Cl_2 used at est. conversion	Moles of gas products formed
SiO_2	55.67	0.926	0.741	1.11
Al_2O_3	31.76	0.311	0.729	1.21
Fe_2O_3	2.70	0.0167	0.048	0.08
CaO	1.92	0.0342	0.034	0.03
MgO	0.42	0.010	0.010	0.01
TiO_2	0.63	0.0078	0.012	0.02
K_2O	0.36	0.0038	0.004	0.00
Na_2O	0.31	0.005	0.005	0.01
Totals			1.583	2.45
Total moles in pretreatment			0.113	0.15
Total moles after pretreatment			1.470	2.31

[1] Lignite whole fly ash electrostatically precipitated from Mexican-Texan coal.

Table 3. Moles of reactant and product gases as a function of components in fly ash[1]

Oxide	Composition, wt. percent	Moles of Oxide in 100 gm.	Moles of Cl_2 used at est. conversion	Moles of gas products formed
SiO_2	57.8	0.962	0.770	1.15
Al_2O_3	31.3	0.307	0.718	1.20
Fe_2O_3	3.6	0.0225	0.064	0.11
CaO	0.63	0.011	0.011	0.01
MgO	0.78	0.019	0.019	0.02
TiO_2	1.78	0.022	0.034	0.06
K_2O	2.47	0.026	0.026	0.03
Na_2O	0.21	0.003	0.003	0.00
Total moles			1.645	2.57
Total moles in pretreatment			0.157	0.22
Total moles after pretreatment			1.488	2.35

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[1] Bituminous whole fly ash electrostatically precipitated, Kanawha Power Station Glascow, W.Va., West Virginia Coal

Table 4. Moles of reactants and product gases as a function of components in fly ash[1]

Oxide	Composition wt. percent	Moles of Oxide in 100 gm.	Moles Cl_2 used at est. conversion	Moles of gas products formed
SiO_2	51.1	0.850	0.680	1.02
Al_2O_3	27.8	0.273	0.638	1.06
Fe_2O_3	12.3	0.077	0.218	0.36
CaO	2.3	0.041	0.041	0.04
MgO	1.5	0.037	0.037	0.04
TiO_2	1.3	0.016	0.025	0.04
K_2O	3.6	0.038	0.038	0.04
Na_2O	0.4	0.006	0.006	0.01
Total moles			1.683	2.61
Total moles in pretreatment			0.365	0.52
Total moles after pretreatment			1.318	2.08

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[1] Bituminous whole fly ash electrostatically precipitated, TVA Kingston Steam Plant, Kentucky coal.

use a multiple-stage chlorination and chlorinate the most reactive metals first to aid in product separation, then the composition of the fly ash would have major effects on equipment design making it unlikely that a plant could treat a wide variety of fly ashes. Besides the cost savings in chlorine, it is apparent that effective recycling of $SiCl_4$ can mean a 20% increase in production if C or $COCl_2$ is used as the reductant and 30% if CO is used.

3. Partial Economic Study - Figure 4 illustrates the effect of fly ash composition and other items on the economics of different ash processing methods. As calculated in Tables 1-4 the consumption of chlorine by Na and K is not a major factor. However in the high Ca fly ash (Table 1), Ca accounts for a major portion of the chlorine required. Conversely, if the ash is processed using a lime-sinter method, the Ca in the ash can be used for a credit. The moles of chlorine used per mole of desired primary products, Al and Ti, in a variety of fly ashes is presented in Table 6. The increase in cost of the recovery of aluminum in the high calcium ashes is apparent. However, when one includes the difference in monetary value of the titanium in the analysis, the high calcium ashes become a much better candidate for chlorination.

Another important factor is the cost of the reactants. As of May 1980, the cost of chlorine was $145/ton which converts to 1.4¢/mole. The cost of carbon from coke or coal is approximately 0.2-0.3¢/mole based on coke at $150/ton and coal at $40/ton with only 40% reactive carbon. Air Products quotes CO at $400-$700/ton which converts to 1.5 - 2.6¢/mole. Phosgene is quoted at 32¢/lb which converts to 8.7¢/mole. The volume of phosgene that would be needed would make it likely that phosgene would need to be made on site from Cl_2 and CO at 4-6¢/mole. From both an economic and equipment point of view, C is the preferred reductant, although the kinetic and chemical properties may make it unattractive. Phosgene might be preferrable to CO due to reduced equipment size and lower reaction temperatures resulting in reduced maintenance and perhaps less equipment cost. These generalizations need to be verified by experimentation.

4. Design Considerations - For an engineering comparison, it is assumed that 1000 tons/day of fly ash can be treated in five 20-foot diameter reactors. The other raw material requirements would be 1200 tons of chlorine, 450 tons of CO (or 250 tons of coke) per day. Alternatively, one could use 1650 tons of phosgene/day.

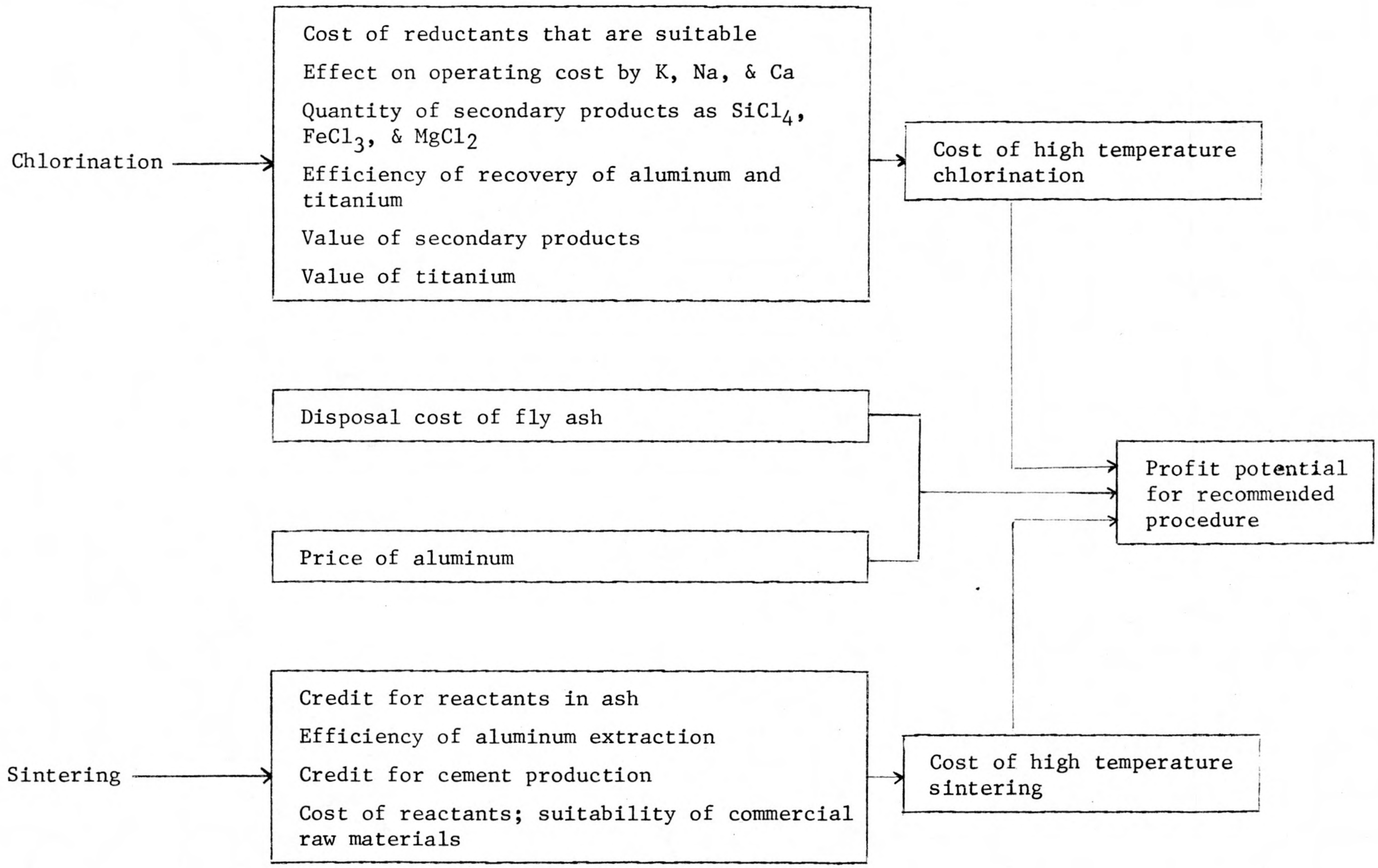

Figure 4. Items having an effect on economics and recommended metal extraction procedure

Table 5. Effects of fly ash composition on moles of reactants and products during high-temperature chlorination.

Fly ash	Wt. Percent		Moles Cl_2 in pretreatment	Moles gas products in pretreatment	Total Moles Cl_2 used	Total Moles gas products produced	Effect if $SiCl_4$ recycled (No Net SiO_2 converted)		
	CaO	Fe_2O_3					Total Moles gas using C or $COCl_2$	Total Moles gas using Cl_2 & CO	Total Moles gas products
Comanche subbituminous	28.80	5.38	0.779	0.86	1.635	2.22	1.434	2.667	1.82
Mexican lignite	1.92	2.70	0.113	0.15	1.583	2.46	1.212	2.054	1.71
Kanawha bituminous	0.63	3.60	0.157	0.22	1.645	2.57	1.26	2.135	1.81
Kingston bituminous	2.3	12.30	0.365	0.53	1.683	2.61	1.343	2.346	1.93

Table 6. Effect of fly ash composition on the number of moles of chlorine required to produce one mole of primary product, Al and Ti.*

Fly ash[1]	Wt. percent		Moles of chlorine/mole product without $SiCl_4$ recycle			Moles of chlorine/mole product with $SiCl_4$ recycle		
	Al_2O_3	TiO_2	Per Mole Al	Per Mole Ti	Per Mole Al & Ti, with Ti weighted 9 times[2]	Per Mole Al	Per Mole Ti	Per Mole Al & Ti, with Ti weighted 9 times[2]
Comanche subbituminous	19.8	1.51	5.40	114	3.78	4.07	56.5	2.85
Mexican lignite	31.76	0.63	3.26	267	2.94	1.73	142	1.56
Kanawha bituminous	31.3	1.78	3.44	98.4	2.61	1.83	52.3	1.39
Kingston bituminous	27.8	1.3	3.96	138	3.15	2.36	62.5	1.88

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[1] Note the amount of fly ash required to produce one mole of titanium is from 15 to 85 times that required for aluminum.

[2] Expresses the moles of titanium as equivalent to 9 moles of aluminium which is based on the price differential of the metal oxides corrected to a mole price differential.

If one were to use $SiCl_4$ recycle effectively, it would reduce the requirements to 800 tons of chlorine or 1100 tons of phosgene/day. This size of facility would produce about one-tenth of the needed volume to feed a small aluminum plant.

To treat the 1000 tons/day in the five reactors, one would be treating 8-10 ft of settled ash per day per reactor. The linear velocity of the product gases at 850°C would be about 18 cm/sec. If chlorine and CO are to be used, then the velocity of the feed gases would be about 20 cm/sec. At room temperature, the incipient fluidization velocity of fly ash is 0.1 to 0.3 cm/sec and an estimated maximum velocity of fluidization without excessive entrainment or elutriation is 4 cm/sec. If one assumes that the gas in the reactor is going to be similar to chlorine under operating conditions and assumes spherical particles, then one can calculate from chlorine density and viscosity a minimal fluidization and entrainment velocity for a given particle size. In non-magnetic fly ash, 45 micron diameter or smaller particles (90% of the fly ash) would be entrained by a gas velocity of 6 cm/sec. A linear velocity of 15cm/sec would entrain 70 micron diameter particles. Therefore dense phase fluidization in a standard bed is not going to be practical.

At the required linear flow rate of 18 cm/sec, the contact time of the gas in a packed bed would be < 10 seconds and in a fluidized bed < 20 seconds. In fast or light phase fluidization, depending on the linear velocity and the height of the reactor, the contact time of the gas could be as long as 3 to 10 minutes. Conversely, the particles in the packed and fluidized bed would probably have a residence time of up to 24 hours and those in fast fluidization would have a residence time of 3 - 10 minutes.

In fast fluidization the ash would be easily entrained at the required velocity. Two to ten 20-foot diameter fast fluidization reactors, as illustrated in Figure 2, depending on the time required to reach the desired amount of conversion, could process 1000 tons fly ash per day. From the required residence time, the volume or heights of the reactor would be determined. In a fast fluidization scheme, it would be possible to incorporate a pretreatment step to remove much of the Ti and Fe which could make it easier to separate products from the chlorination to recover aluminum. In the pretreatment, carbon would probably not be used as a reductant. Also in fast fluidization, it is unlikely that carbon would be a good reductant as the solid to solid distance would be at least 8000 times greater than in a packed bed. The efficiency of conversion might be hindered by not having the products swept away from the particles by the gas stream, thus driving the equilibrium in the direction desired. Finally one needs to remember that incorporating pretreatment in this scheme makes optimization of equipment and conditions highly dependent on fly ash composition.

If the reaction time to achieve a desired level of extraction is too long, the fluidization equipment and methods to fluidize unpelletized fly ash must be modified. Some modifications include using a tapered bed so there is a decrease in linear flow rate toward the top of the bed. A tapered bed design is more stable to variation in flow rates and could provide the agitation necessary to fluidize a cohesive powder such as fly ash. The smaller the angle of the tapered bed, the less back mixing will be obtained at a given flow rate of the fluidizing media and the efficiency and conversion of the fluidized bed will approach that of a staged fluidization or packed bed. Another approach to increase fluidization efficiency is to install baffles and/or diffusers in the bed to break up the large bubbles. Besides increasing the efficiency of gas to solid contact, there is also a decrease in entrainment characteristics. A third approach to reduce entrainment would be to have a low density layer of particles floating on top of the bed. While it is unlikely one or two of these techniques will allow sufficient fluidization velocities to be industrially practical, the combination of all three might. Depending on the success of these methods, three to nine of the reactors depicted in Figure 3 would be needed to process 1000 tons of fly ash per day.

As the bulk density of fly ash is approximately 2.3 - 2.6 gm/cc, porous vycor with a density of 1.5 gm/cc is suitable for a floating sinter. If one assumes chlorine is a representative gas under actual conditions, the theoretical particle size for the sinter would be 90 - 800 microns for a linear flow rate of 15 cm/sec. At a linear flow of 3 cm/sec, which might be present at the top of the tapered bed, the theoretical size range is from 40 - 370 microns. Since the porous vycor is not going to be perfect spheres and the bed is going to have fly ash particles in the range of 0.1 - 200 microns, the actual optimum size range will need to be experimentally determined.

Baffles help to maintain segregation so one would optimally be placed at the interface of the fly ash-floating sinter. Knowledge of the kinetics of the desired conversion as a function of fly ash size would be the ideal criteria of whether the combination of techniques had slowed particle elutriation sufficiently for it to entirely react. Unfortunately, due to the change in moles of reactants and products during chlorination (Table 5), room temperature studies are going to give inadequate prediction of high temperature operation.

If the above techniques prove to be inadequate, the variables of pressure and pelletization will need to be investigated. Pressure might increase the reaction rate enough so fast fluidization becomes practical if it is too slow at one atmosphere. Figure 5 provides a graphical presentation of important questions to be answered by long range work. The experimentation that can be done sequentially or concurrently is indicated. The items in parentheses are the important variables to be investigated.

5. High-Temperature Chlorination of Western Fly Ash - One experimental run was conducted chlorinating a sample of high calcium Comanche fly ash (Table 1) and carbon in a horizontal bed with a high flow rate of chlorine gas. The temperature was $850^{\circ}C$ and the duration of the run was 2 hours; the gas flow rate was $4.5(10)^{-3}$ g moles Cl_2 per minute. At this rate the stoichiometric quantity of Cl_2 was supplied in 45 min. The sublimed products were collected, dissolved, and analyzed; the soluble chlorination products remaining in the residue were dissolved and analyzed, and the insoluble silica precipitate in the collection flask was combusted and weighed. The results of this analytical sequence are given in Table 7, and the material balance for the reacted products is excellent. These data show that all of the Fe, Ca, Mg, and Ti were chlorinated, as were about 80 percent of the Al and 40 percent of the Si.

These data support the conclusion that calcium, by reacting with the chlorine may adversely affect the economics of the extraction of metals from western coal fly ashes by the HiChlor process as almost one-third of the reacted chlorine formed $CaCl_2$. Early theoretical studies (1) suggested that calcium would chlorinate more readily than aluminum.

6. Reaction System Designs - A reaction system for the study of chlorination has been designed and is presented in Figure 7. The system will be able to collect incremental samples of gases, products, and solid reactants. The system will be able to investigate all the variables of high temperature chlorination indicated in Figure 6 except for pressure and kinetics where the time of reactor

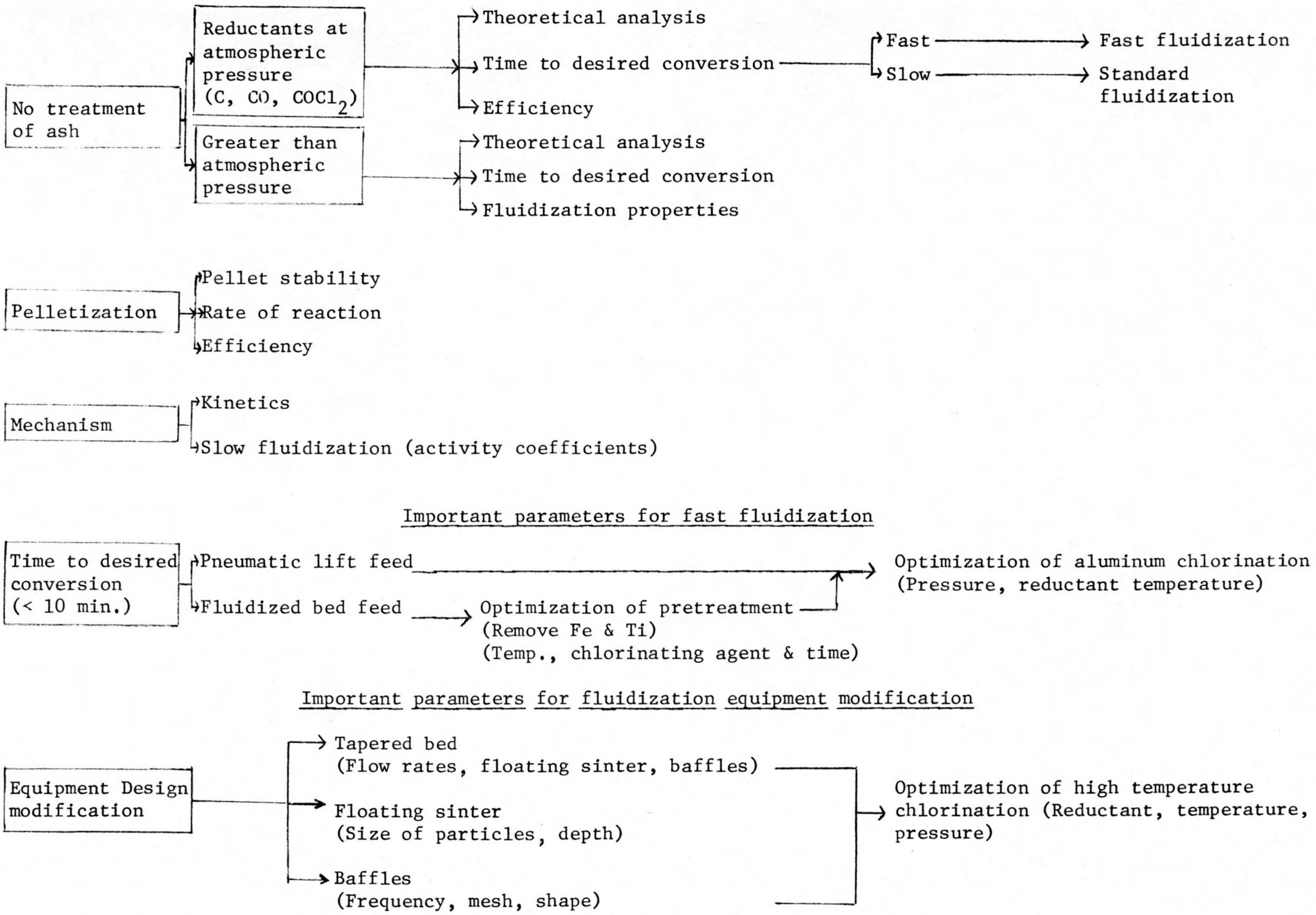

Figure 5. Parameters to be investigated to determine a feasible scheme for high-temperature chlorination

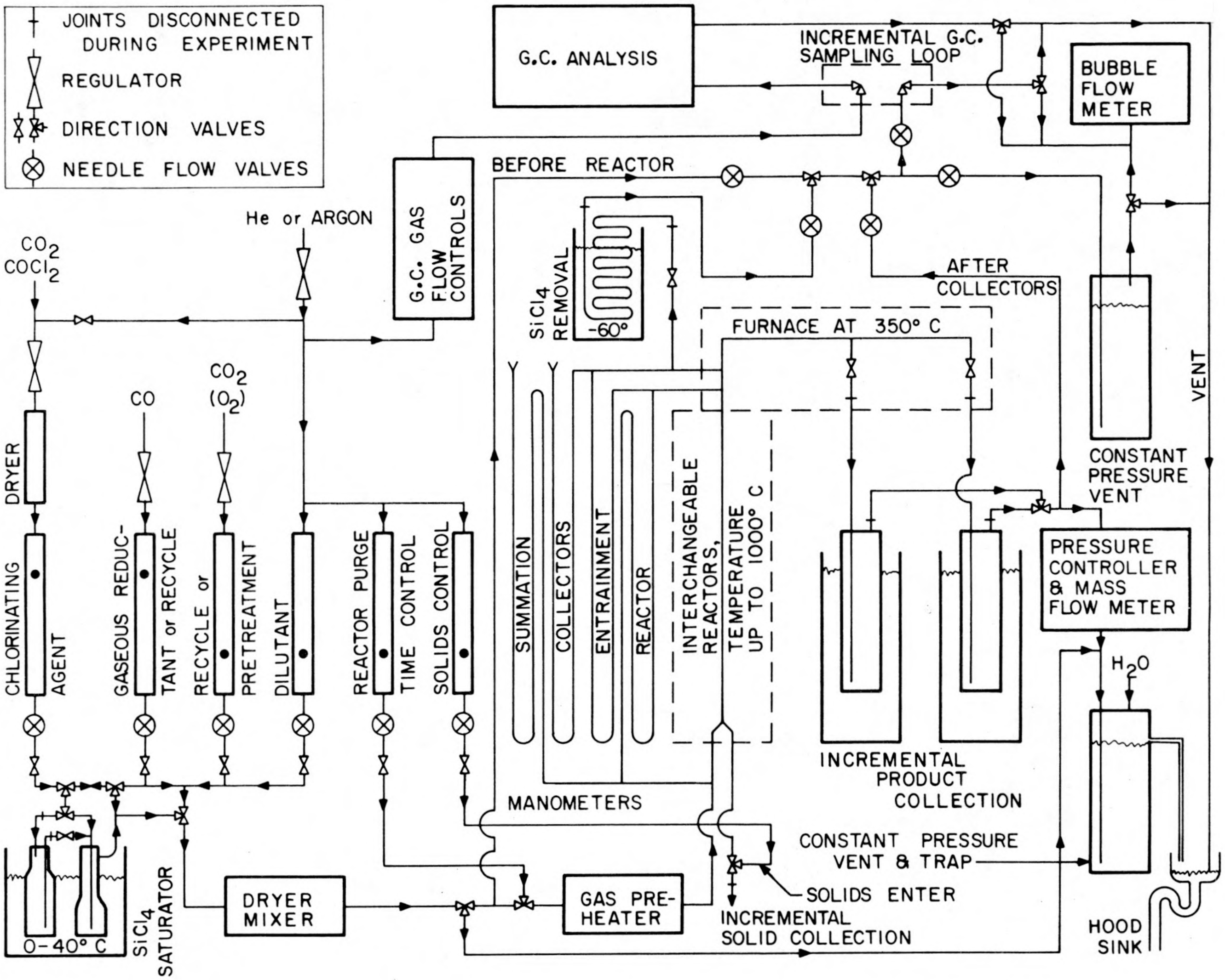

Figure 6. Schematic of experimental setup to investigate all variables of high temperature chlorination except pressure and kinetics.

Table 7. Results of Packed Bed Chlorination of a High-Calcium Comanche Fly Ash-Carbon Mixture[1]

Element	mg in fly ash	mg sublimed during reaction	mg reacted but not sublimed	Total mg reacted	Percent reacted
Fe	290	294	--	294	101
Ca	1582	28	1558	1586	100
Mg	206	27	190	217	105
Al	803	622	--	622	77
Si	1083	444	--	444	41
Ti	70	68	--	68	97

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[1] Two-hour chlorination at 850°C, $4.5(10)^{-3}$ g mole Cl_2 per minute, 7.7 gm of fly ash and 2.3 gm of graphite

Table 8. Concentrations of Dissolved Alumina and Silica in Lime-Soda Fly Ash (C-1) Sinters Extracted at Several Solid to Liquid Ratios.

Solid/Liquid ratio expressed as g sinter per ml solution[1]	Analyses of extraction filtrates at sinter compositions shown[2]			
	2.4 - 0.7		2.2 - 1.2	
	ppm Al[3]	ppm Si[4]	ppm Al[3]	ppm Si[3]
0.05	2,226	26		
0.10	4,389	49	4,874	51
0.10	4,185	48	4,900	36
0.10			4,900	44
0.15	6,482	59		
0.17			8,405	73
0.27	11,541	110		
0.30			14,918	264
0.44			20,700	319

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[1] Extraction with 3 wt. percent aqueous Na_2CO_3 solution, 65°C, 10 minutes.

[2] Composition of fly ash, soda ash, limestone mixture before sintering: molar ratio CaO/SiO_2 - Na_2O/Al_2O_3. C-1 is a bituminous coal fly ash of Illinois-Kentucky coal, mechanically separated.

[3] Atomic absorption measurements.

[4] Colorimetic spectronometer measurements.

component flushing must be minimal. A reactor system has also been designed for use in a kinetic study of fly ash chlorination. This design includes a provision for collecting up to three gas samples in the first 30 seconds of the reaction. If there appears to be a substantial change in the kinetics of reaction in the first few minutes, other experimental setups may need to be designed to determine the reactive species.

An on-line analysis system for the metal chlorides is still required. A high pressure liquid chromatography method has been developed for the anions and columns for the determination of cation metals are under development by Dionex of Sunnyvale, California. Workers at Iowa State University have a promising method for the electrochemical analysis of metals and the analysis of titanium and iron is possible, but silicon and aluminium as of yet cannot be determined. Gas chromatography by specially designed systems is a possibility; $SiCl_4$ have been separated using gas chromatography (3). Anvor and Dragon (4) reviewed the possibility of separating $AlCl_3$ and $FeCl_3$ by gas chromatography.

7. Product Separation - The experimental apparatus needed for the sublimation of an $AlCl_3$ and $FeCl_3$ mixtures was designed and constructed during this report period. This equipment will allow experimental determination of the feasibility of the anhydrous separation scheme presented in the last progress report (May 1980).

Lime-Soda Sinter Process Development

1. Solubility of the Lime-Soda Sinter - The recovery of alumina from fly ash by dissolution of aluminates from sintered fly ash - limestone - soda ash mixtures is influenced by reactions occurring during both the sintering and extraction steps. The lime-soda sinter process has been demonstrated to extract alumina from fly ashes but additional research is required to increase the purity of the dissolved aluminate, reduce the energy requirements, and demonstrate an ability to use other waste materials as process raw materials. To attain these objectives, concentrations of dissolved Al, Si and Ca in extraction filtrates were measured to determine the effects of extraction solution pH, solid to liquid ratio in the extraction step, and the times of sintering and of extraction. The results of the investigation of extraction solid to liquid ratio and the sintering and extraction times will assist in the design of process equipment and permit careful evaluation of energy requirements. Data were obtained for a range of pH values to ascertain whether pH will improve the ratio of the amount of alumina to silica which dissolves.

Ratio of Solid Material to Liquid Volume

Results for dissolved ion concentrations of several elements as a function of the grams of solid sinter extracted per unit volume of 3 wt. percent aqueous Na_2CO_3 solution are shown in Table 8 and on Figures 7 and 8. These data are the dissolved aluminate and silicate concentrations of extraction filtrates expressed as elemental wppm as determined by atomic absorption (AA). Over a five-fold change in the solid to liquid ratio these results indicate a uniform extraction of aluminum per gram of sinter. They also indicate that one part silicon dissolves per 50 to 100 parts aluminum. Data were obtained for two different lime-soda sinter compositions and the same linear relationship and ratio of dissolved alumina to silica resulted. Operation at a high solid to liquid ratio, in addition to reducing the size of extraction equipment and of solution volumes, gives more concentrated aluminate solutions which will facilitate filtrate desilication.

Sintering Time and Extraction Time

Further improvement of the desilication process may result if the sintering time and/or the extraction time are adjusted to improve the ratio of dissolved aluminum and silicon in the extraction filtrates. Previous research has indicated that increasing sintering time and shortening extraction time is effective for reducing silica dissolution. Therefore, sintering runs of 30, 60, 90, 120, and 150 minutes were made and the materials were extracted for times of 2, 5, and 10 minutes. Results of these experiments are shown in Table 9.

These extraction results indicate that there is very little difference in the soluble alumina and silica contents of the sinters as long as the materials are not extracted for longer than 10 minutes. All of the sinters show a tendency toward increased silica dissolution as the extraction time increases from 7 to 10 minutes, but the increase is very small. The data indicate that sinterings of 30 minutes and extractions of 2 minutes are adequate to solubilize the contained alumina, so there is potential for both equipment and energy cost reductions for the proposed lime-soda fly ash sinter processing facility.

pH of Extraction Solutions

The data in Table 10 represent the concentrations of dissolved Al, Si, and Ca for filtrates of sinter material extracted with dilute aqueous soda solutions of varying pH. Each solution contained equivalent amounts of Na_2O, with pH adjustment by using mixtures of NaOH, Na_2CO_3, and $NaHCO_3$. The use of higher pH solvents may reduce the dissolution of calcium and in this way inhibit the dissolution of silicon.

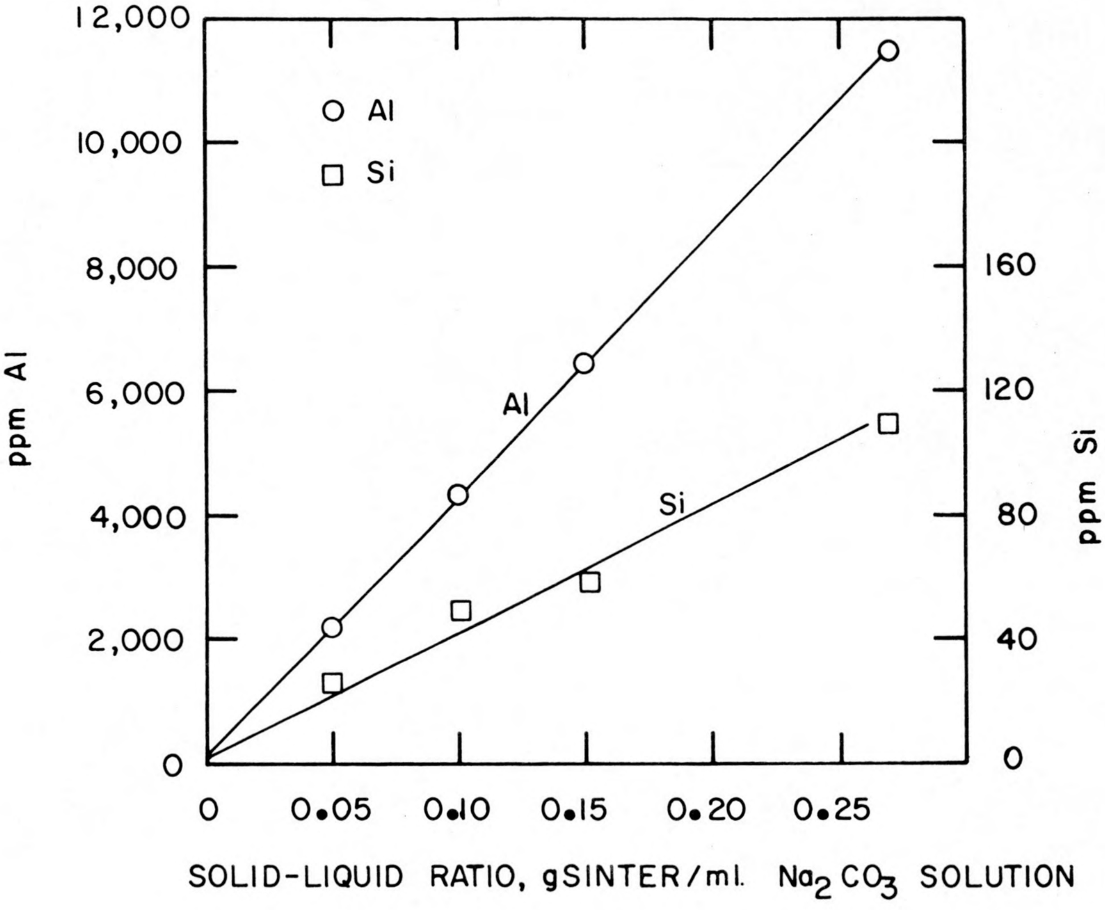

Figure 7. Effect of Solid-Liquid Ratio on the Amounts of Al and Si Extracted from a 2.4 - 0.7 C-1 Sinter by 3 wt. percent Na_2CO_3 Solution at 65°C and 10 Minutes.

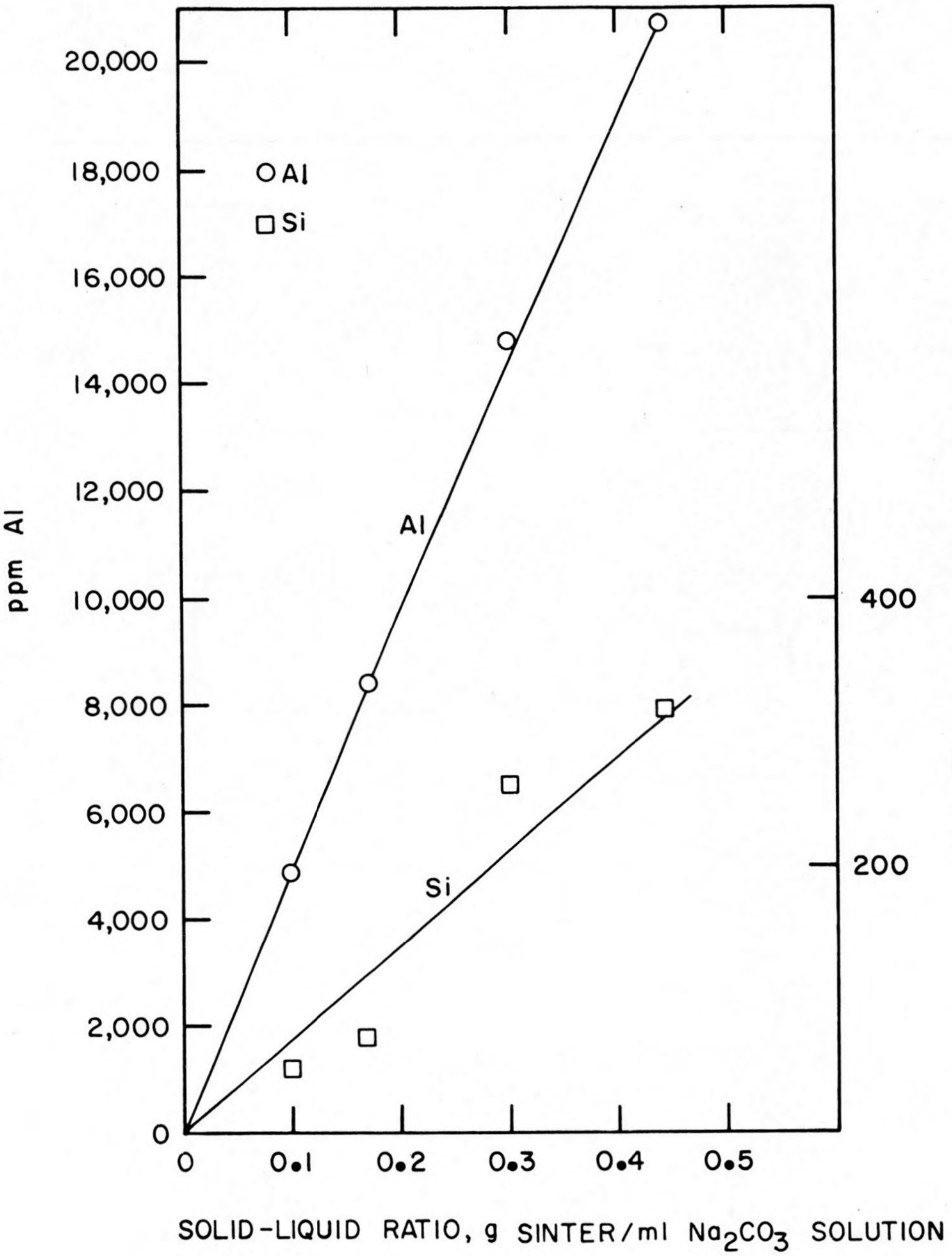

Figure 8. Effect of Solid-Liquid Ratio on the Amounts of Al and Si Extracted from a 2.2 - 1.2 C-1 Sinter by 3 wt. percent Na_2CO_3 Solution at 65°C and 10 Minutes.

Table 9. Concentrations of Dissolved Alumina, Silica, and Calcium for Extractions of Lime-Soda Sinters as a Function of Sintering Time and Extraction Time

Sintering Time Minutes[1]	Extraction Time Minutes	Analyses of Extraction Filtrates[2]		
		ppm Al	ppm Si	ppm Ca
30	2	4263	40.6	1.6
	5	4501	47.0	2.0
	10	4837	55.0	2.3
60	2	4595	42.3	3.7
	5	4785	46.0	2.3
	10	4792	52.0	2.4
90	2	4689	40.0	4.5
	5	4790	41.0	3.6
	10	4609	45.0	3.6
120	2	4916	41.0	3.0
	5	4648	42.0	4.4
	10	4749	44.0	2.7
150	2	4717	39.0	2.3
	5	4549	41.0	3.4
	10	4783	43.0	3.5

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[1] Time held at temperature, each run has heatup and cooldown from 800°C at 3.6°C/min.

[2] Extraction of 2.2-1.2C-1 mixture sintered at 1200°C, extracted at 65°C with 3 wt. percent aqueous Na_2CO_3 solution, 0.1 solid/liquid ratio. Analyses by AA.

Table 10. Concentration of Dissolved Aluminum, Silicon, and Calcium in Extraction Filtrates of Lime-Soda Sinters as a Function of Solution pH.[1]

Solution pH	Filtrate pH	Analysis of Extraction Filtrates		
		ppm Al	ppm Si	ppm Ca
10.4	11.7	1599	13.4	2.9
11.4	12.4	5209	44.1	1.5
12.4	12.5	5085	53.7	1.6
13.4	13.3	5209	57.8	1.4
13.45	13.4	5053	54.3	1.3

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[1] Extraction solutions were mixtures of $NaHCO_3$, Na_2CO_3, and NaOH having the same soda content as 3 wt. percent Na_2CO_3. Extractions were at 65°C, 0.1 solid/liquid ratio, for 10 minutes using sinter 2.2 - 1.2 C-1.

These data show a small drop in Ca content at high pH but this did not significantly limit the Si dissolution. The most evident result of these experiments is the very sharp change in solubility between solutions of pH 11.7 and pH 12.4. The solution mixture of Na_2CO_3 and $NaHCO_3$ with an initial pH of 10.4 and a final pH of 11.7 permitted the precipitation of about 80 percent of the dissolved Al and Si, and about 50 percent of the dissolved Ca. The 3 wt. percent aqueous Na_2CO_3 solution appears to be the optimum pH for alumina dissolution, attaining a final pH value of 12.4 when soluble compounds in the sinter disssolve.

MgO and K_2O in Lime-Soda Sinters

As an extension of the research evaluating commercial limestones for use in the lime-soda sinter process, tests were made using dolomitic limestone. Initially, pure magnesium carbonate was used as a replacement for limestone, alumina solubilization for these sinters was negligible. In a second set of experiments dolomitic limestone, 46 wt. percent $MgCO_3$ 54 wt. percent $CaCO_3$, was used. When only the $CaCO_3$ portion of this material is included in the calculation of the sinter mixtures, the resultant alumina recoveries were high, greater than 90 percent; but when the magnesium content in the dolomite was calculated to replace part of the limestone, alumina recovery decreased. This work indicates the magnesium oxide is an inert material in the sinter reactions. Dolomitic limestones can be used but only the $CaCO_3$ portion of the rock is reactive.

In a third set of experiments, reagent potassium carbonate was used as a replacement for soda ash. These results show that K_2CO_3 is reactive and can replace soda, therefore, it is expected that credit can be taken for both Na_2O and K_2O contained in fly ashes, limestones, kiln dusts, etc., to decrease the amount of soda ash which must be added to sinter mixtures.

Lime-Soda Sinters Containing Mineralizers

Lime-soda sinters were prepared using mineralizers, additives, and flue gas scrubber sludge as a replacement for the limestone. The results for mixtures containing mineralizers are listed in Table 11. The value of such additives is to lower the required sintering temperature and/or reduce the required sintering time. Fluxing materials appear to form liquid layers on the particle surfaces which promote solid-to-solid diffusional mass transfer. For the lime-soda sinters, mineralizers are detrimental resulting in reduced alumina solubilization. The soda in the mixture provides sufficient flux action for liquid formation and in the course of our research excess liquid formation has been shown to reduce alumina recovery probably due to phase dilution.

The sintering and extraction experiments conducted using flue gas scrubber sludge as a limestone resource again resulted in very low alumina extraction levels. This result requires further investigation. Other less expensive lime and soda materials such as waste cement kiln dust, trona, nahcolite, salt, and spent oil shale residue are scheduled for testing in standard sinter mixtures.

2. Economic Analysis of the Lime-Soda Sinter Process - A paper on the economics of processing of fly ash as a means of disposal was prepared for presentation at the national meeting of the A.I.Ch.E. to be held in Portland,Ore. in August, 1980. An improved, updated process cost evaluation was made for a plant to process the fly ash from a 1000 MWe bituminous coal-fueled power station. The equipment cost estimate was based on the assumptions and design bases used in reports from the U.S. Bureau of Mines (5). Inflationary increases in raw material, utility, equipment, procurement, and labor charges have made fly ash processing for alumina production alone uneconomic under present conditions. If the residue from the alumina recovery process is used to manufacture Portland cement, the combined operation will show about a 15 percent return on investment. The total energy utilization for the processes is also quite encouraging. Tables 12 and 13 are production cost estimates for the alumina and cement processes respectively, and Table 14 is a discounted cash flow sheet for the combined facility.

Table 11. Concentration of Dissolved Aluminum, Silicon, and Calcium in Extraction Filtrates of Lime-Soda Sinters with Mineralizers Added.[1]

Mineralizer Added	Sintering Temperature, °C	Analyses of Extraction Filtrates ppm Al	 ppm Si	 ppm Ca
--	1200	5209	44.1	1.5
5 wt. % NaCl	1000	4584	60.0	1.0
	1200	4433	40.2	2.6
5 wt. % NaF	1000	4049	62.4	2.8
	1200	4607	50.7	4.3
5 wt. % Coal	1000	2875	52.2	1.3
Refuse	1200	2340	26.6	3.5

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[1] Sinter was from a 2.2 - 1.2 C - 1 mixture with additives, sintered one hour, extracted with 3 wt. percent aqueous Na_2CO_3 at 65°C, 0.1 solid/liquid ratio, for 10 minutes.

Table 12. Estimated Production Cost for a Lime-Soda Sinter Process Facility[1] for a 1000 MWe Power Station

	Mg per Year	Production Cost $ per Mg Alumina[2]		
Direct Cost:				
Raw Materials:				
Limestone, $6.60/Mg	460,000	66		
Coal fly ash, $6.60/Mg	275,000	39		(--)[3]
Soda ash, $82/Mg	8,200	14		
Coal, $33/Mg	109,000	78		
Total		197		(158)[3]
Utilities:				
Electric power, 4¢/Kwhr		24		
Steam, recovered at 55¢/Mg		8		
Water		5		
Total		37		
Direct Labor:				
Labor, $20 K/man-yr		13		
Supervision, 15 percent of labor		2		
Total		15		
Plant Maintenance, 5 percent of installed equipment cost		19		
Operating supplies, 15 percent of plant maintenance		3		
Total Direct Cost			271	(232)[3]
Indirect Cost, 50 percent of direct labor and maintenance			17	
Fixed Cost:				
Taxes and insurance, 2 percent of total plant cost		13		
Depreciation, 5 percent of fixed capital cost		36		
Total Fixed Cost			49	
Total Operating Cost			337	(298)[3]

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[1] Process facility produces 45,500 Mg alumina per year.

[2] Operating year of 350 days and recovery of 80 percent of the alumina in the ash from the coal used to fuel the kiln in addition to 80 percent of the alumina in the fly ash.

[3] Costs if fly ash is provided at no cost.

Table 13. Estimated Production Cost for Portland Cement from Lime-Soda Sinter Process Residue[1]

	Mg per Year	Production Cost $ per Mg Cement[1]	
Direct Costs			
Limestone, $6.60/Mg	114,000	1.35	
Sinter residue, no cost	455,000	--	(0.90)[2]
Gypsum, $22/Mg	27,000	1.09	
Coal, $33/Mg	243,000	14.56	
Electric power, 4¢/Kwhr		1.20	
Water, 10¢/m^3		0.10	
Operating labor		1.85	
Supervision and benefits		1.85	
Maintenance and supplies		2.65	
Total Direct Costs		21.80	(22.70)[2]
Indirect Costs			
Depreciation, 20-year life		3.25	
Interest, 7 percent for 20 percent debt		0.90	
Insurance and local taxes		1.85	
Overhead		1.85	
Total Indirect Costs		7.85	
Total Production Cost		29.65	(30.55)[2]

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[1] Wet process plant, 350 day operating year, producing 550,000 Mg cement per year, installed capital cost $36 million

[2] Sinter residue is purchased at $1.10 per Mg.

Table 14. Discounted Cash Flow for the Production of Alumina and Cement from Fly Ash for a 1000 MWe Power Station.

	$ per Year
Total Sales	
Alumina at $209 per Mg (45,500 Mg per Year)	$ 9,510,000
Cement at $66 per Mg (550,000 Mg per Year)	36,300,000
	45,810,000
Production Cost	
Alumina, $337 per Mg[1]	15,335,000
Cement, $30 per Mg[1]	16,500,000
	31,835,000
Profit before taxes	13,975,000
Federal income tax, 50 percent	6,987,000
Net profit after taxes	6,988,000
Depreciation, 5 percent of fixed capital cost	3,640,000
Cash flow	10,628,000

Payout time[2] = $\frac{\$68{,}780{,}000}{\$10{,}628{,}000}$ = 6.5 years

Discounted cash flow rate of return (20-year life of plant) = 14.4 percent

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[1] Limestone and fly ash purchased at $6.60 per Mg, sinter residue provided at no cost.

[2] Payout time= Total capital cost/Cash flow

Lime-Fly Ash Sinter Process Development

In this work, the research with mineralizers and additives was extended to include sinters prepared without soda ash. Work on lime-fly ash sinters was discontinued some time ago because the lime-soda sinter method produced much higher alumina extraction levels. Previous data with lime-fly ash sinters yielded about 55 percent soluble alumina when a sintering temperature of 1380°C was used.

Mineralizer additives were tested as a method for reducing energy requirements and lower sintering temperature. Data on extractions of lime-fly ash sinters prepared with additives are given in Table 15. The results for the addition of fluxes such as NaCl and NaF gave quite low alumina recoveries, although the sinter with NaCl added did yield 53.9 percent soluble alumina at the reduced sintering temperature of 1200°C. The other additive used in this study was pulverized coal refuse from the Iowa State University Coal Preparation Plant. This material is approximately 63.3 wt. percent FeS_2 and 36.7 wt. percent C. It was not effective in the lime-soda sinters but when added to the lime-fly ash mixtures, the alumina recovery level increased significantly. Alumina solubilization levels of about 85 percent were obtained when 3.75 percent coal refuse was added to the lime-fly ash mixture.

There is a definite relationship between the alumina recovered and the amount of coal refuse added to the sinter mixture. Data at 1200°C and 1380°C sintering temperatures are shown on Figure 9. Data on Table 15 indicate that both the carbon and the sulfur contained in the refuse are required to give this improved alumina solubilization. The mechanism which provides the increased alumina recovery has not been determined, but at the peak extraction (3.75 wt. percent coal refuse) each mole of S added results in a mole increase in soluble Al_2O_3. In addition to greatly increasing the alumina recovery, the coal refuse lowers the sintering temperature to 1200°C. These two factors provide new economic incentive for development of the lime-fly ash sinter process.

Table 15. Concentration of Dissolved Aluminum, Silicon, and Calcium for Extraction Filtrates of Lime-Fly Ash Sinters containing Additives[1]

Additive	ppm Al		ppm Si		ppm Ca	
	Analyses of Extraction Filtrates					
	1200°C	1380°C	1200°C	1380°C	1200°C	1380°C
None	2256	3275	70.0	48.2	3.9	1.4
5 wt. % NaCl	3377	2653	44.6	42.1	0.8	2.4
5 wt. % NaF	3238	240	84.8	114.8	7.3	5.8
2.5 wt. % Coal Refuse	3939	3855	51.0	55.0	2.6	2.7
3.75 wt. % Coal Refuse	4490	4024	54.0	49.8	4.4	1.0
5 wt. % Coal Refuse	3854	2640	45.0	48.0	5.1	1.6
7.5 wt. % Coal Refuse	1727	2553	51.0	37.0	1.5	2.9
FeS_2 equiv. to 4.75 wt. % Coal Refuse	2410	3115	37.0	41.0	3.8	5.0
FeS_2 and C equiv. to 4.75 wt. % Coal Refuse	3730	3878	41.0	50.0	2.5	10.0
S and C equiv. to 4.75 wt. % Coal Refuse	4740	4345	53.5	49.0	3.1	2.5

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[1] Mixture of 1.9 parts $CaCO_3$ to 1 part non-magnetic C-1 fly ash by wt. with additives, sintered one hr at temp. indicated, extracted with 3 wt. percent aqueous Na_2CO_3 at 65°C, 0.1 solid/liquid ratio, for 10 minutes.

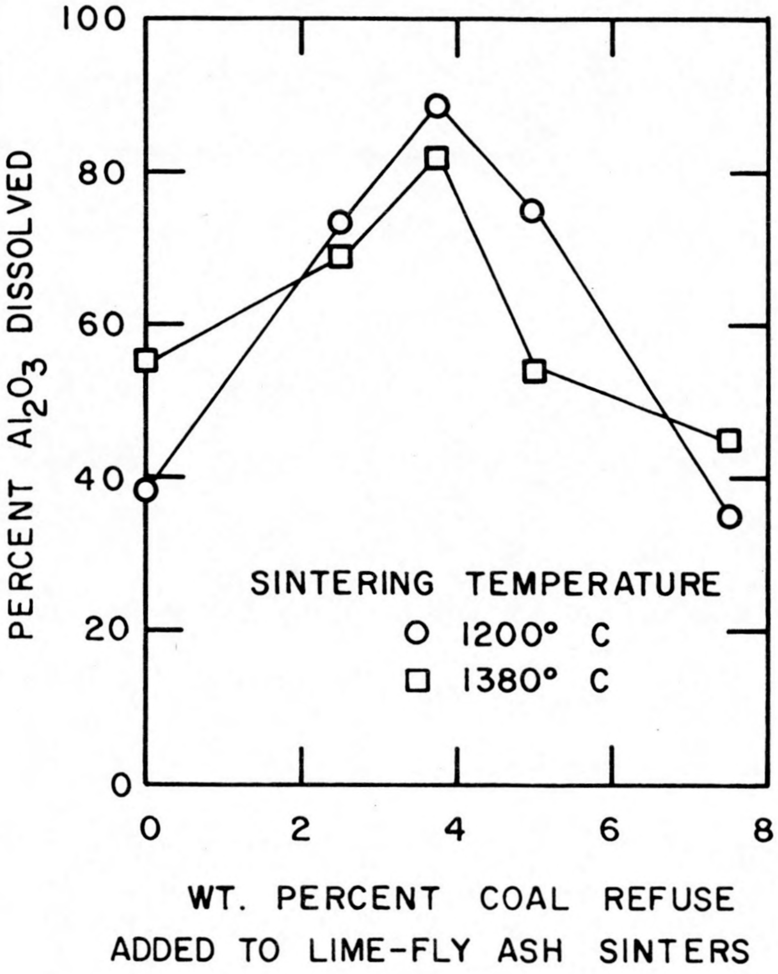


Figure 9. Effect of the addition of coal refuse to lime-fly ash sinters on the percent of contained alumina extracted (data from Table 15).

Iron-Rich Fraction of Coal Fly Ash

1. Magnetic Fly Ash as a Source of Iron - High iron content coal fly ash particles magnetically separated from fly ashes represent a potential iron resource. With a reduction of the silicate and aluminate contents the iron-rich fraction of fly ash will be equivalent to high quality iron ore. Particle characterization has indicated that chemical treatment is required to separate out the silicates and aluminates, but research of the size and composition of particles separated at different magnet field strengths has also been conducted.

Physical Beneficiation of Iron-Rich Fly Ash

Research of the dry magnetic separation of fly ash fractions using a moving field electromagnet has included comparisons of magnetic ash separated as a function of magnetic field strength. Data were obtained for size distributions of magnetic fractions cumulatively separated as the magnet field strength increased and also for the differential magnetic fractions which separated as the field strength increased. Size distribution is important because earlier work has shown some variation in composition with particle size.

Coulter Counter size determination data for these separated materials are shown in Figure 10 for the differentially separated materials, and in Figure 12 for the cumulative magnetic samples. The differential magnetic fractions were obtained by running the nonmagnetic fraction through the magnetic separator using successively higher magnetic field strengths; 30, 45, and 60 percent rheostat settings.

The size distributions of the various fractions appear to contradict the size distribution data for the separations made at various power levels. The material separated at 30 percent of maximum power has the largest size distribution which is in agreement with the cumulative data for a 30 percent rheostat setting. However, unlike the cumulative data, the differential material shows a dramatic shift towards smaller particle sizes for the 30-45 percent material; the mean diameter of the 0-30 percent material is 19 μm, the mean diameter of 30-45 percent material is 8 μm. Material collected at field strengths greater than 45 percent maximum voltage shows a small increase in the mean diameter to 10.5 μm. At low magnetic field strengths only large particles with high magnetite concentrations have sufficient interaction with the field to be recovered as magnetics. Smaller particles which are high in iron do not appear to be as numerous or are not attracted to the magnetic field

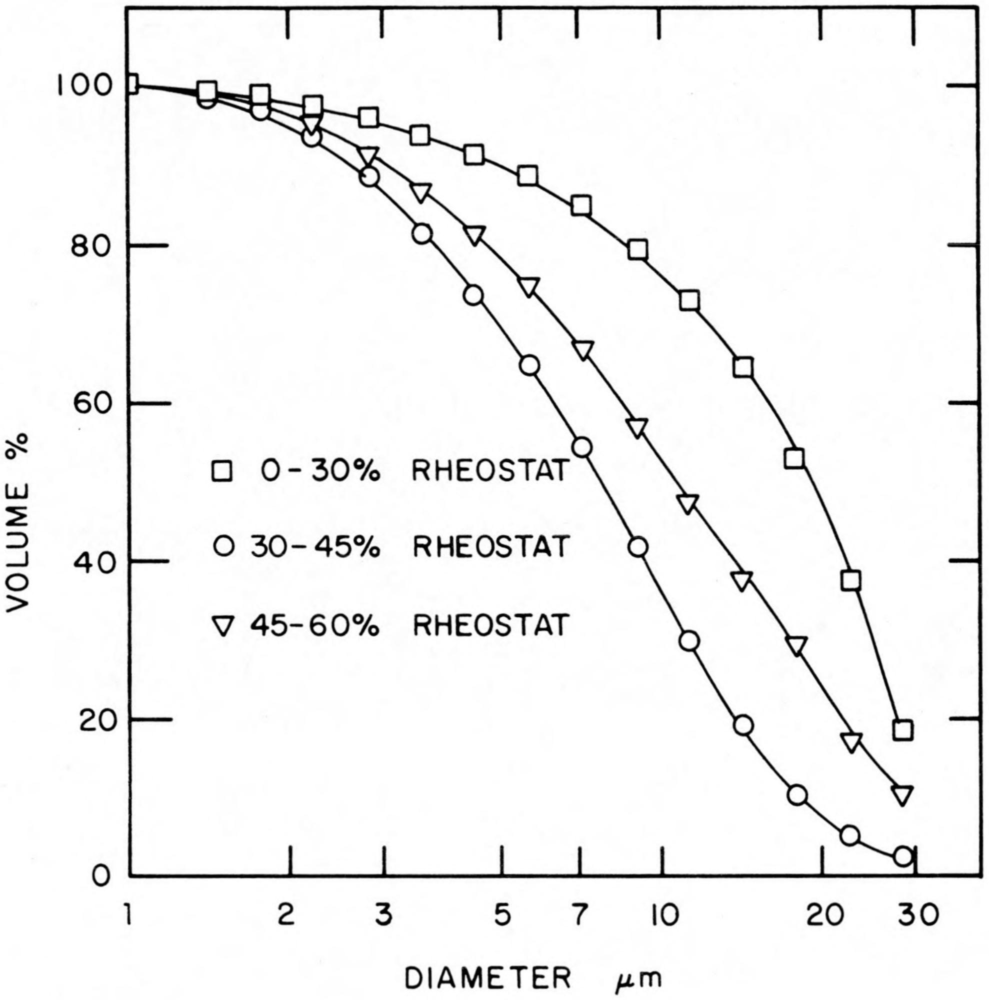


Figure 10. Size Distribution of Differential Magnetic Ash Samples Collected as Magnet Power is Increased.

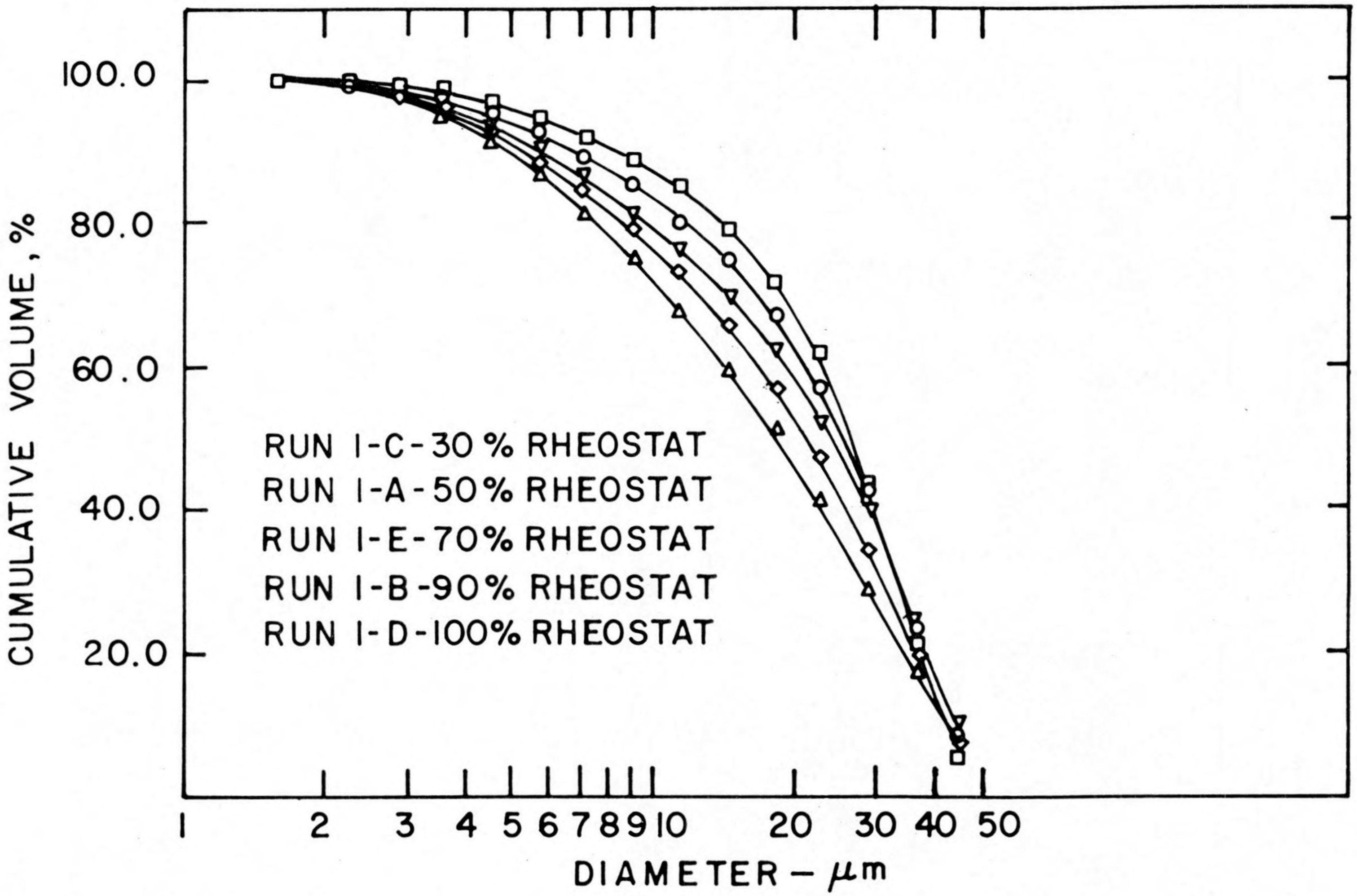


Figure 11. Size Distribution of Differential Magnetic Ash Samples Collected as Magnet Power is Increased.

strongly enough to be captured. The 30-45 percent fraction contains smaller particles because in the stronger field smaller particles are captured. At even higher power levels the size distribution increases slightly as less magnetic particles are captured in the field.

Chemical Beneficiation of the Magnetic Particles

Experimental data on chemical beneficiation of magnetic fly ash using pressurized caustic digestions show quite low dissolutions of alumina from the ash particles and, with proper conditions, removal of most of the contained silica. As a test of the reproducibility of the chemical beneficiation data, several caustic extraction experiments were replicated. The results of the replicated experiments are given in Table 16. These data indicate that the experiments replicate well. A statistical estimate of the error limits of the data was not made because of the limited number of replications, however, a conservative estimate of the error limits would be ± 10 percent for the total percent silica and alumina removed.

Electron Microscopy of Beneficiated Magnetic Ash Particles

SEM photographs of the treated materials were used to determine the reason the chemical extraction of alumina is limited at about 65 percent of the sample content. If the silica and alumina in each particle are randomly distributed, as has been assumed, then the percent removal should be identical for both oxides. Since equal removal is not occurring, a skewed distribution of some sort must exist. The results of the electron microscopy and microprobe analyses did not provide complete answers to these questions, but did give some results.

A point which this work did resolve was the question of precipitation during extraction. As reported previously, there were indications that dissolved silica and alumina were precipitating during the caustic treatment at the higher solid-liquid ratios. SEM pictures of treated material confirmed that precipitation was indeed occuring.

The microprobe work utilized a technique new to our research, but which may be of great value in the future. The analysis used is dot field imaging which is based on the microprobe detector being tuned to a particular element. When a specimen is scanned by the microprobe, characteristic X-rays for the element are detected and a dot appears on a polaroid picture corresponding to the position of the beam on

Table 16. Pressurized Caustic Extractions for Iron-Rich Fly Ash -- Demonstration of Reproducibility of Oxide Dissolutions.[1]

Time, Hrs	Solid-Liquid Ratio, gm/l	Percent Oxide Dissolved SiO_2	 Al_2O_3
2.0	100	76.4	28.2
2.0	100	75.4	32.4
2.0	100	74.2	31.3
1.0	70	91.3	61.5
1.0	70	91.7	60.9
1.0	100[2]	86.9	33.6
1.0	100[2]	82.9	33.3
0.5	100[3]	93.5	60.4
0.5	100[3]	90.5	64.9
1.0	140	68.3	16.7
1.0	140	65.4	16.7

[1] Solution used was 30 wt. percent aqueous NaOH at 200°C.

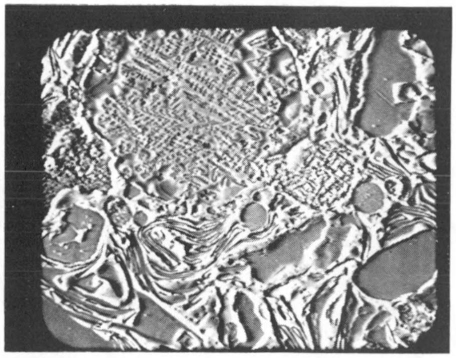
[2] Magnetic fly ash microground in 4-inch Sturtevant air mill.

[3] Two-stage extraction, 0.25 hr. per stage.

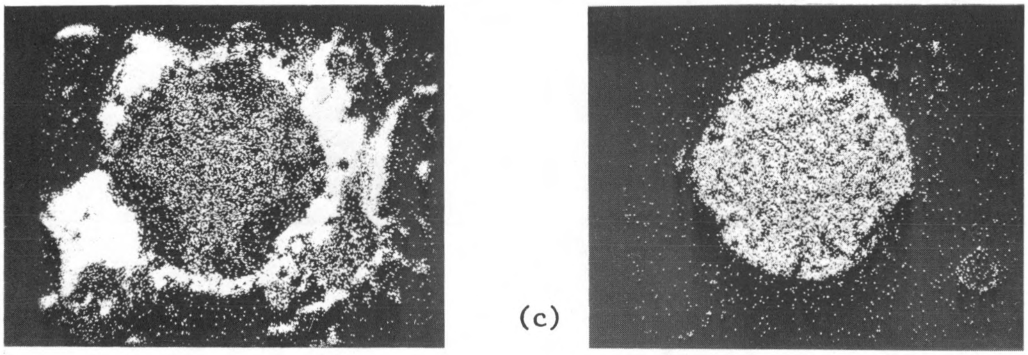
the sample. When enough X-ray counts are recorded by the machine (roughly 20,000) an image is produced that maps the location of the element of interest on the scanned particle surface. Image examples are seen in figures 12b-e. This technique is strictly qualitative and intensities of element images cannot be compared quantitatively. Dot field imaging provides information on the grouping of elements as well, which is of importance in chemical extraction because it helps in the understanding of the relationships between the elements and the compounds present.

Both treated and untreated material were examined with the microprobe. The specimen in Figures 12a-e was untreated; Figure 12a is the specimen current image which is similar to a normal SEM image. The particle is visible in the upper left hand corner and is distinguished by the characteristic structure of dendrites. Figures 12b-e are dot field images for aluminum, calcium, silicon, and iron respectively. The large areas of aluminum surrounding the particle are from polishing compound and are not associated with the fly ash structure.

Figure 12. (a)

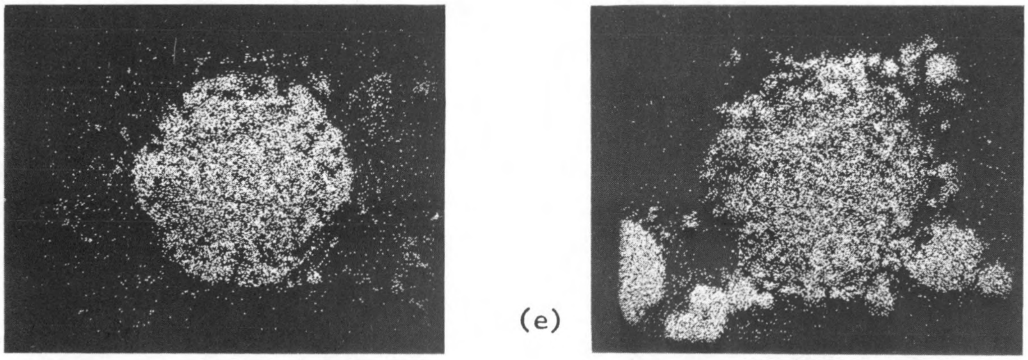


Specimen current image of untreated KCPL magnetic ash particle. (690X)



(b) Aluminum dot field image. The large areas surrounding the particle are polishing compound.

(c) Calcium dot field image. Note the dispersion throughout the particle interior.



(d) Silicon dot field image. The silicon is dispersed over the interior of the particle.

(e) Iron dot field image. Iron is dispersed throughout the particle close examination shows a complementary effect with respect to other elements.

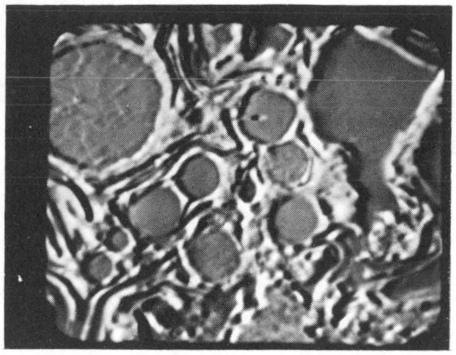
These images indicate that all four of the components are dispersed throughout the ash particle, and that calcium, aluminum, and silicon are not associated with the iron. This is as expected from the theory of formation of fly ash particles.

Treated ash particles were also examined, Figures 13.a-e are images of a particle that was treated for two hours at 200°C with a 30 percent caustic solution at a solid-liquid ratio of 100 g/1. This particular sample was selected because the data indicated possible precipitation of dissolved silica and alumina. Figure 1 a is current image of the specimen which shows the presence of several particles. Figures 13b-e are dot field images for aluminum, calcium, silicon, and iron respectively. The important point shown by these images is the apparent ringing of the particles by calcium, aluminum and silicon, as would be expected if material was precipitating from solution. The two large blotches of aluminum in the lower center of Figure 13b are Al_2O_3 polishing compound. Silicon and calcium tend to be very closely associated, i.e., the presence of one indicates the presence of the other. Aluminum is not as closely associated--it tends to be with silica and calcium. The presence of the latter elements does not necessitate the presence of alumina. All the particles in this sample show a certain amount of "coating", so it is concluded that precipitation was occurring.

Figures 14a-e are images of another particle from the same treated ash shown in Figures 13a-e. The specimen current image, Figure 14a, shows a large glass inclusion as well as several fractures. The aluminum dot field image, Figure 14b, shows a slight concentration of aluminum in the inclusion; however, aluminum also appears to be distributed throughout the particle. The calcium and silicon dot field images are very similar to each other but, unlike the aluminum image, they seem to follow the network fractures shown in the scanning current image. Also present is the layer of calcium and silicon on the surface of the particle, again evidence of precipitation.

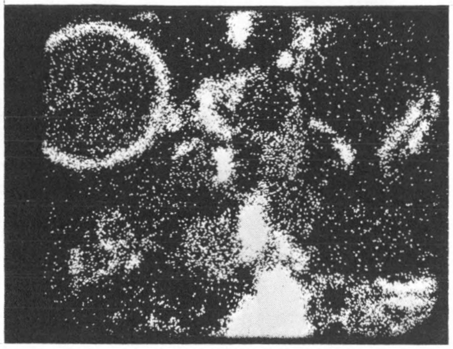
These photographs show the precipitation of silicon and alumina from the higher solid-liquid ratio extractions but they do not provide an answer for why only 65 percent of the alumina can be extracted compared to 95 percent of the silica. To help answer this question and to determine how extensively the particles were being attacked, standard SEM pictures were taken of the treated samples. Figure 15 is a SEM image of untreated ash particles that show the characteristic spherical shape

Figure 13. (a)



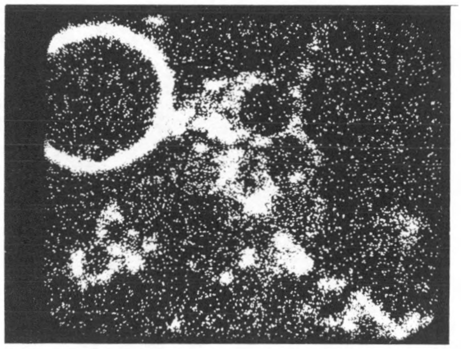
Specimen current image of treated ash particles. Treatment conditions: 30% caustic, 200°C, 2 hours and 100 g/l. (1500X)

(b)



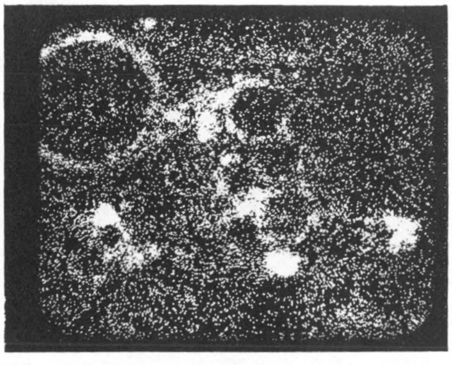
Aluminum dot field image. All particles show evidence of precipitation of alumina. Large areas in lower center are polishing compound.

(c)



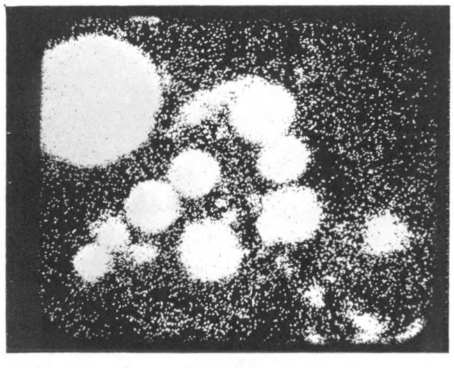
Calcium dot field image. Note the similarity between this image and the silicon dot field image. All particles show a rim of calcium.

(d)



Silicon dot field image. Silicon is present on the surface of all the particles. Silicon also tends to associate with calcium.

(e)



Iron dot field image. This image defines the particles for comparison with the other dot field images.

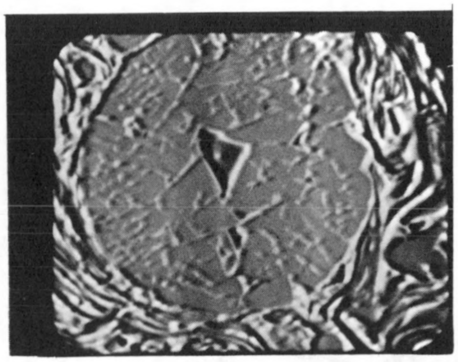
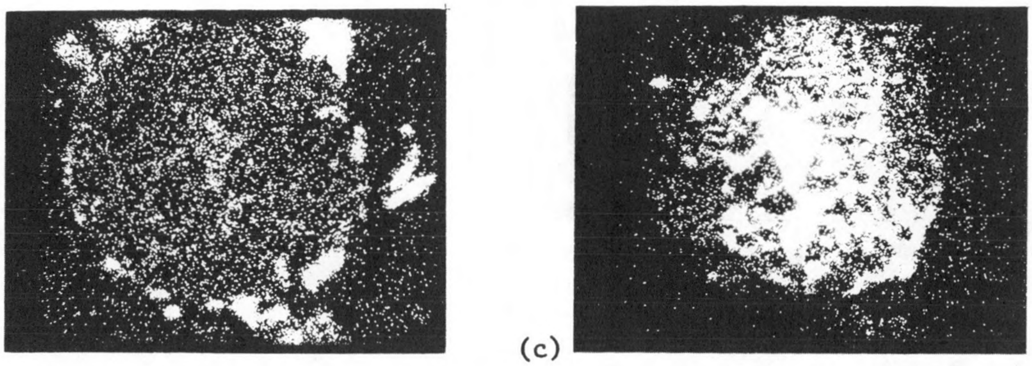


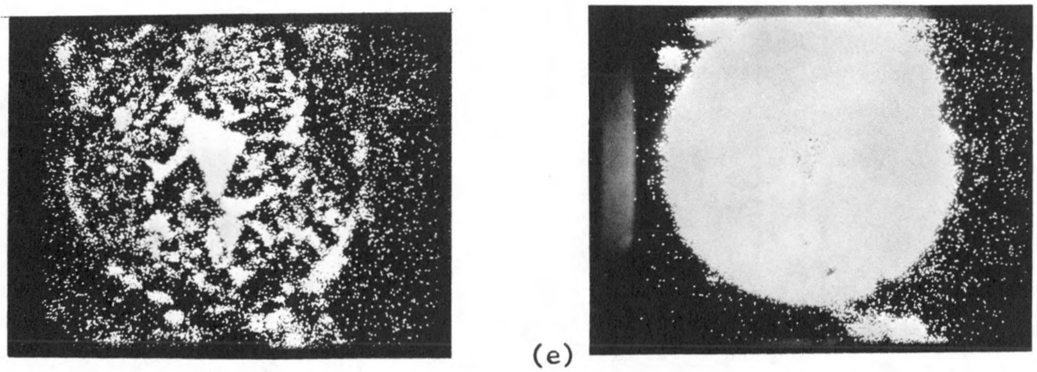
Figure 14. (a)

Specimen current image of treated ash particle. Treatment conditions: 30% caustic, 200°C, 2 hours and 100 g/l. The center area is a large glass inclusion. (900X)



(b) Aluminum dot field image. Aluminum is present in the glass inclusion as well as being dispersed throughout the particle. Also observable are precipitates on surface of particle.

(c) Calcium dot field image. Calcium tends to follow the glass inclusion and the network of fractures visible in the specimen current image.



(d) Silicon dot field image. Note similarity to calcium dot field image. Silicon presence on the surface of the particle is also observable.

(e) Iron dot field image. The particle appears to be all iron; however, a darker area is observed at the glass inclusion.

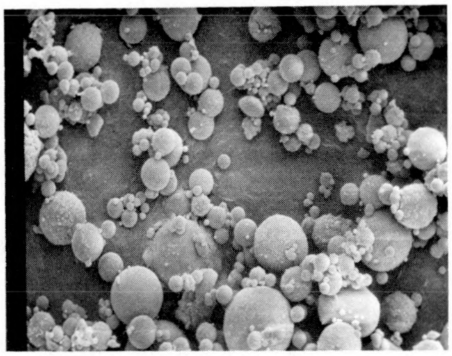


Figure 15. Untreated magnetic fly ash particles. This sample is typical of magnetic ash. (1,000X)

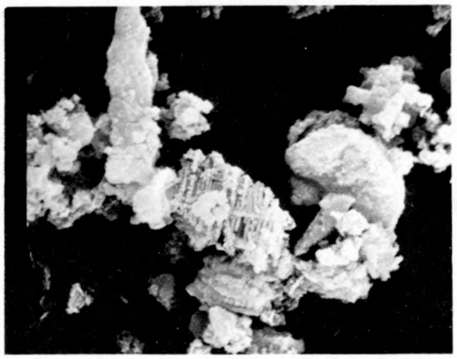


Figure 16. Magnetic ash treated with 30 percent NaOH for 1 hour at 200°C with a solid-liquid ratio of 70 g/l. The tree-like particle is dendrite. (5,000X)

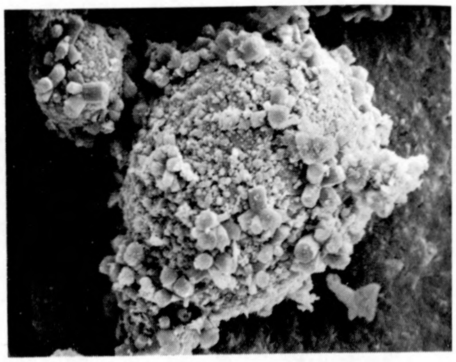


Figure 17. Magnetic ash treated with 30 percent NaOH for 2 hours at 200°C with a solid-liquid ratio of 100 g/l. Note the small crystals covering the sample; EDS analysis showed the presence of sodium aluminosilicates indicating precipitation of dissolved material. (3,000X)

of magnetic fly ash particles. Figure 16 is an image of material treated at 200°C with 30 percent caustic for one hour and at a solid - liquid ratio of 70 g/l, conditions that provide effective leaching (90 percent of the silica and 60 percent of the alumina were removed). The treated particles show extensive damage and evidence of attack from the caustic. The large tree-like structure in the center of the picture is the remains of an iron dendrite. Before treatment, silica and alumina filled the volume between the branches to form a spherical particle. The overall sample shows extensive attack and the almost complete absence of spherical particles. It is apparent that caustic treatment is capable of comminuting the fly ash particles.

EDAX analysis of the dendrite tree showed the presence of a slight amount of alumina and silica which was probably trapped in the dendrite thus limiting the available area for caustic attack. This appears to be the problem with removing alumina. The EDS and EDAX results indicate that alumina is evenly dispersed throughout the ash structure, whereas silica tends to form in inclusions which can be more readily attacked by the leach liquor.

Figure 17 is a SEM image of a particle from a sample which was leached for two hours at 200°C with 30 percent caustic at a solid - liquid ratio of 100 g/l. This particular sample was chosen because the chemical analysis suggested that precipitation had occurred so that precipitated material should be observable on the sample. The image shows small (1-3μm) tetrahedral crystals covering the surface of the leached particles. The crystals contain sodium, aluminum, and silica, the materials precipitating for the leach liquor. This SEM thus provides visual proof of the precipitation of dissolved material.

Since the SEM work provided conclusive evidence of precipitation, a review of the analyses of various leached samples was made to determine the approximate chemical composition of the precipitates. Figure 18 is a plot of the sodium content of the solid residue versus percent alumina removed. The samples show an increase in sodium content with decreasing alumina extraction. The sodium content increases with solid-liquid ratio, and all the samples show an increase in sodium content over the untreated ash. There is a definite trend of increasing sodium content with decreasing alumina removal, an increase which is much greater than can be accounted for by the possibility of incomplete washing of the sample. Acid extraction experiments for the treated ash materials may help determine the composition of the precipitates by solubilizing the sodium and alumina components.

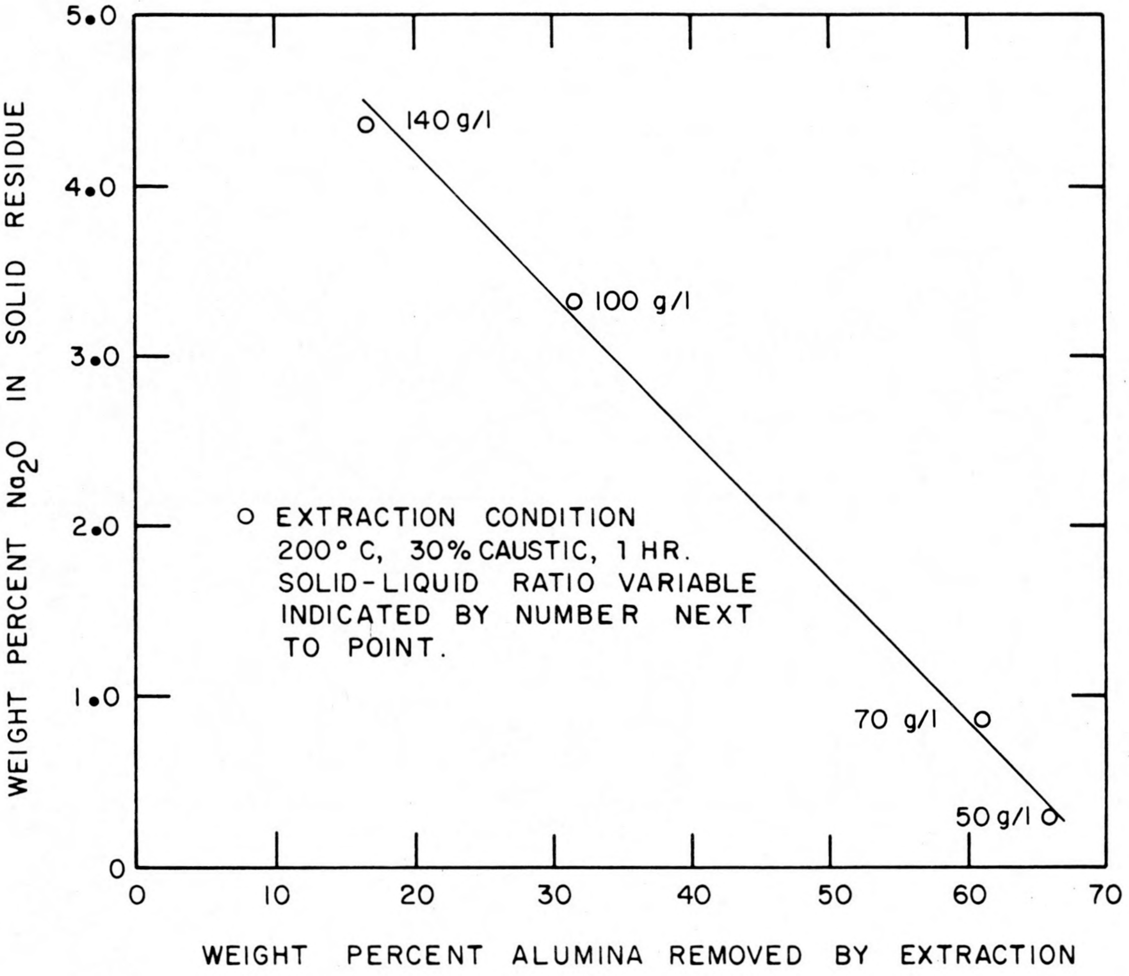


Figure 18. The amount of soda in the magnetic ash residue after caustic extraction as a function of alumina removal, indicating the precipitation of sodium aluminate from solution.

2. Heavy Medium Material for Coal Beneficiation - Data from bench-scale tests of coal washing by heavy media mixtures of magnetic coal fly ash and water have resulted in the scale up for larger tests. The actual coal beneficiation work will use dense media cyclones at the Iowa State University Coal Preparation Plant, but additional bench-scale tests for material characterization, media settling rates, suspension viscosities, and erosion, abrasion, and friability of the solid particles must be conducted.

Test Circuit for Material Abrasion and Particle Friability Determinations

Two samples of commercial magnetite of a particle size appropriate for use in heavy media cyclones (97 wt. % - 325 mesh) have been obtained. Design of a closed circuit pipe loop to test different heavy media solutions in long-term service and to measure the erosion of a range of construction materials has been completed and quotations have been obtained for the media slurry circulation pump. In the loop, characterization determinations and rheology studies will be made using magnetic fractions of fly ashes obtained from different parts of the country and a representative distribution of commercial magnetite materials.

The circuit will contain a surge volume considerably larger than the volume of the loop which will serve as an access for sampling and which will insure a more homogeneous suspension. The tank will be positioned above the pump to provide a flooded pump feed. A 3/4-inch ID tube size was selected for the test loop circuit which will require flow rates of 15 to 30 gal/min to simulate the velocities in a coal washing facility. The piping in the test loop will most probably be plastic (PVC) due to the abrasion resistance nature of this material.

Heavy Media Slurry Circulation Pump

The specifications for the slurry circulation pump are as follows:

Item	Specification
Material Description	Magnetite and water slurry, specific gravity from 1.3 to 2.0, maximum viscosity of 10 cps, very abrasive.
Capacity	15 to 30 gal/min.
Suction Pressure	Flooded.
Discharge Pressure	40 psi.
Operating Temperature	Ambient.
Materials of Construction	Tool steel.
Pump Drive	Variable speed with controller.
Fittings	Standard suction and discharge fittings.

Bids have been received from four companies providing specifications and costs for positive displacement and centrifugal pumps. No decision has been reached on the pump purchase at this time.

3. Magnetic Separation of Fly Ash - Water Slurries - A Frantz ferrofilter unit and power supply has been purchased so that the potential of wet magnetic fly ash separation can be evaluated. Preliminary tests of the separation of fly ash - water slurries indicate that little power is needed for the magnetic separation. The results shown in Figure 19 were collected by pouring 200 ml of a 25 wt. percent slurry slowly through the magnetic grid of the ferrofilter. The grid was then flushed with water to wash through the nonmagnetic particles, after turning off the power the magnetic material was washed through. These results show that a low power setting of 10 volts yields almost 25 wt. percent of the ash as a magnetic fraction.

The wet magnetic separator will be used for larger scale magnetic separations. Using pumps, stirrers, feeders, valves, and relays, the unit will operate in a semicontinuous mode. Figure 20 is a schematic of the design of the test system.

FUTURE WORK

HiChlor Process Development

Theoretical calculations will be made on some fly ash compositions to compare the effectiveness of chlorination with Cl and C or CO as the reductant, and with phosgene. Due to the constraints of gas volume (flow) on reactor design, theoretical work on the effect of pressure on chlorination will also be done to determine the importance of designing a pressurized, high-temperature chlorination experimental apparatus. Since in a practical application there is likely to be recycle of CO gas if C is used and/or of $SiCl_4$, some theoretical calculations delineating the potential changes will be conducted.

Using the reactor system for study of kinetics, research to determine the minimum time required for extraction of metals by chlorination will be conducted. This work will allow determination of reaction mechanisms for various fly ashes and whether they will need to be modeled using pure components. Experimental results will be compared with theoretical predictions. Specifically the presence of SiC will be analyzed for by X-ray diffraction analysis of fly ashes reacted under various conditions.

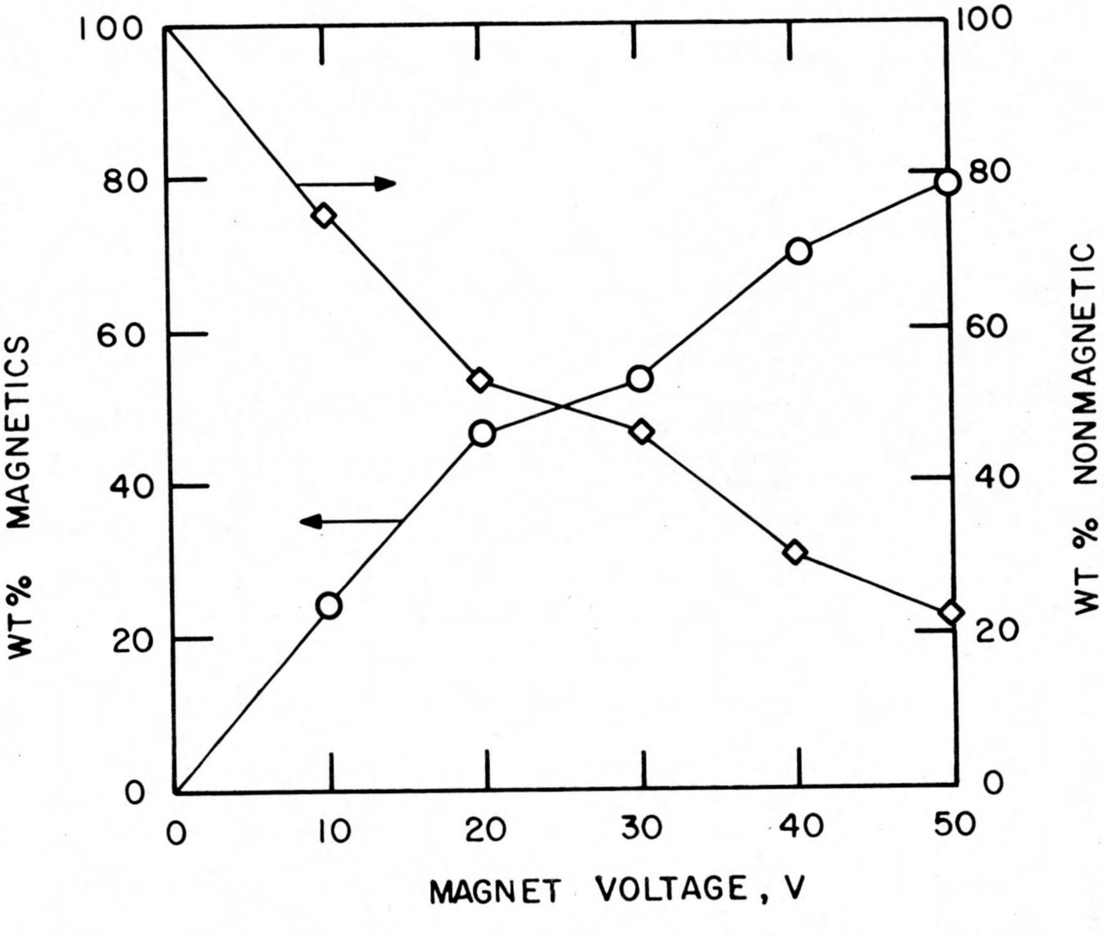


Figure 19. Effect of magnet voltage on the magnetic separations of fly ash fractions from fly ash-water slurries.

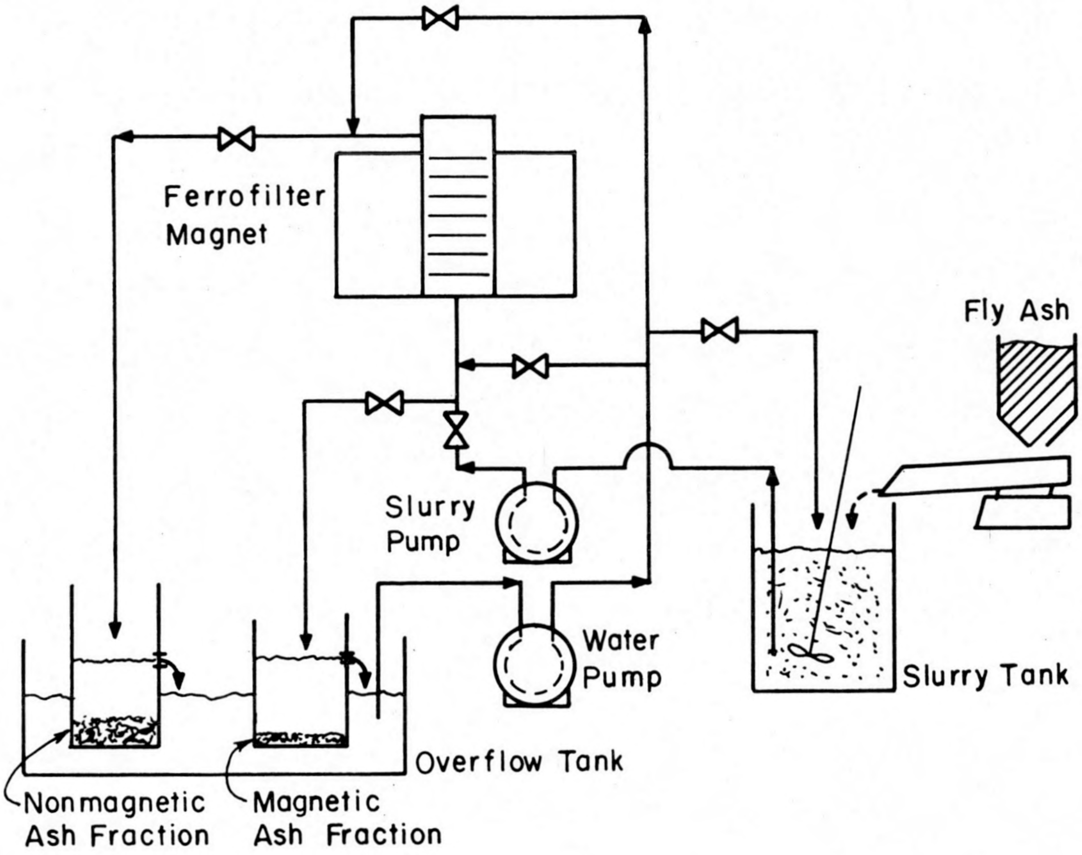


Figure 20. Schematic diagram of Franz Ferrofilter test system for magnetic separations of fly ash-water slurries.

The experimental apparatus for the study of room temperature fluidization of fly-ash in a tapered bed and with a floating sinter will be assembled for evaluation of the industrial practicality of this scheme. Depending on the experimental results of the above work, the new high-temperature chlorination experimental system will be refined and plans made for its assembly. Experimental studies should indicate the feasibility and design criteria for anhydrous collection and separation of the products.

The experimental studies will also be expected to indicate which reactor configurations are the most likely for industrial application. With this information and an experimental evaluation of potential separation schemes, a more complete economic analysis of the process will be prepared.

Fly Ash Sinter Process Development

Mixtures of lime, fly ash, and coal refuse, will be sintered at 1100°C and 1200°C. Experimental runs, sinter analyses, and a literature search will be conducted to determine the role of carbon and sulfur in the reactions. Sintered material will be examined by x-ray diffraction to define the compound differences of the more extractable sinter mixtures. DTA and TGA measurements will also be used in this work.

Alternate lime sources will be tested in both the lime-soda sinter process and the lime-fly ash sinter process with coal refuse. Conversations with limestone producers indicate that for large scale usage such as fly ash processing, limestone will not be inexpensive. Independent of grade, chemical content, etc, there is a substantial cost for quarrying and crushing. Cement kiln dust is a high-volume waste material containing about 45 wt. percent CaO in a reactive form. This waste dust represents about 20 percent of the throughput of a cement kiln and is usually disposed of by dumping back in the quarry rather than by recycling. The kiln dust from one 1,000,000 ton per year cement plant would supply the lime to process the fly ash of a 1,000 MWe power station, effectively disposing of two waste materials. Experiments will be conducted using samples of kiln dust on hand and data will be collected on the magnitude of cement kiln dust waste disposal, availability, and composition range.

Recovery of Magnetic Fly Ash

The unit which has been assembled for magnetic separation of fly ash-water slurries will be tested, a procedure for semi-continuous operation developed, and data will be collected for comparison with dry fly ash separations made previously. These results will indicate the method of magnetic separation most suitable for the proposed process demonstration unit (PDU).

The accumulated data on magnetic ash beneficiation will be assembled to provide comparative information on characterization and chemical analyses for the different ash samples separated to demonstrate the potential for physical beneficiation of the iron-rich ash fraction. Caustic leached samples will be extracted with acid to determine the composition of precipitated material, and an economic evaluation of the chemical beneficiation process will be developed.

Investigative studies of the rheological properties of the fly ash and magnetite samples will be begun. Chemical and physical analyses will include chemical composition, Coulter Counter size determinations, porosity, void volume, specific gravity. hardness, and SEM data. Settling characteristics of suspensions of water and magnetite or magnetic fly ash samples will be examined at several bed densities. Equipment will be assembled for measurement of suspension viscosities, and for a pipe circuit and circulation pump to investigate material erosion and medium particle friability during long-term flow tests.

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