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Direct Utilization-Recovery of Minerals from Coal Fly Ash

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Advanced Research and Technology

DIRECT UTILIZATION- RECOVERY OF MINERALS FROM COAL FLY ASH

G. Burnet and M. Murtha

Abstract:

Research focused on technical development of promising methods for recovering minerals from power plant fly ash. Development of the high-temperature (HiChlor) gas chlorination process and refinement and definition of the recovery steps of extraction and desilication for the lime-soda sinter process were emphasized. A preliminary design and cost estimate for commercialization of the HiChlor process and a proposal for a process development unit for scale-up of the lime-soda sinter process were prepared.

A comprehensive study of the fluidization of fly ashes, fly ash-carbon mixtures, and chlorination residues were conducted. Fluidization velocities, bed pressure drops, and particle size effects provide data for design of a continuous process fluidized bed fly ash chlorination reactor. Fly ashes and pure oxides have been reacted in fixed-bed chlorination reactors. The use of a gas chromatograph has provided on-line reaction data for CO, CO_2, Cl_2, and $SiCl_4$ during fly ash chlorinations. Pure oxides were chlorinated to investigate the potential for low-temperature preferential chlorination as a separation and purification technique. Chlorination without carbon was also studied as a iron separation method.

Several high-alumina content bituminous coal fly ashes were tested for alumina extraction by the lime-soda sinter method. With proper conditions, alumina recovery in excess of 90 percent was obtained for each fly ash. For further development of commercialization of this process, quarry limestones of various qualities were used in sinter preparations. Testings of extraction, filtrate carbonation, desilication, and filtration were conducted to obtain information required for specification of equipment for the process development unit. The diffusion mechanisms and kinetics for the sintering reactions were determined using electron microprobe and high-temperature x-ray methods for analytical measurements.

Both physical and chemical beneficiation techniques to upgrade the iron content of the magnetic fly ash were tested; chemical beneficiation using high-temperature NaOH leaching was found to be the most effective method. Pretreatment for each of the processes includes magnetic separation of coal fly ash.

Bituminous coal fly ashes contain magnetic iron oxide particles which can be removed by magnetic separation. The magnetic material consists primarily of iron oxides, with small amounts of silica and alumina. Removal of additional silica and alumina will give a product which can be used for steel production.

Physical investigations included careful study of internal structure of fly ash particles. Fly ash samples were separated for a range of electromagnetic power settings and the fractions were analyzed for size determinations, chemical compositions, and morphological contents. Nonmagnetic fly ash samples were also fractioned into size ranges by settling techniques and each of these fractions were analyzed in a similar manner. Chemical analyses showed that, for the nonmagnetic fly ash fractions, the silica and iron contents are independent of size, and that the alumina content is highest in the smaller particles.

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 titatium oxides 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 at about 800°C with chlorine gas in the presence of carbon as a reducing agent to form volatile metal chlorides. The chlorides can be condensed and separated to give the products desired. Details of the process remain to be developed, including an understanding of the reaction mechanism, a continuous fluidized bed reactor system, 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 well 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 components is proceeding.

Task C - Recovery of an Iron-Rich Fraction from Fly Ash by Magnetic Separation- The above 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% iron oxides, a significant portion 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. The amount of iron-rich material available exceeds the demand for heavy media applications so its purity must be increased to where it can be used as an iron ore. Another coal waste containing significant quantities of iron is the refuse from coal washing plants. After coal refuse is ashed, the residue is similar in composition to magnetically separated, iron-rich coal fly ash. Methods for increasing the purity of the fly ash iron-rich fraction should also be applicable to coal refuse.

Status:

HiChlor Process Development

1. Reaction Kinetics - To enable better understanding of the reactions occurring when mixtures of coal fly ash and carbon are chlorinated, a gas chromatograph has been installed to measure the composition of the noncondensible gases. The condensible products such as $FeCl_3$, $AlCl_3$, and $TiCl_4$ are removed from the effluent gases by a cold trap, then the carbon oxides and excess chlorine compositions are determined by the gas chromatograph. Although $SiCl_4$ is not detected by the chromatograph column, the volume of $SiCl_4$ in each gas sample can be calculated by difference because volume of the sample loop is precisely known. The results of these noncondensible gas analyses from fly ash chlorination runs indicate that the quantities of carbon monoxide and carbon dioxide formed are a function of the chlorination temperature. The data listed in Table 1 indicate that as the chlorination temperature increases the carbon oxide balance progressively favors the formation of carbon monoxide rather than carbon dioxide, as can be predicted by use of thermodynamic calculations. These data also indicate that $SiCl_4$ production is almost constant over this temperature range, and that chlorine utilization is nearly equal at 850°C and at 900°C.

These results for chlorine reactivity and $SiCl_4$ formation agree with previous data determined by analysis of the reacted solid residues.

Table 1. Cumulative Noncondensible Gas Compositions as a Function of Reaction Temperature for Two-Hour Fixed Bed Chlorination Runs.

Temperature °C	Mole Fraction			
	Cl_2	CO	CO_2	$SiCl_4$
750	0.426	0.141	0.214	0.218
800	0.384	0.230	0.162	0.223
850	0.288	0.329	0.148	0.235
900	0.271	0.376	0.129	0.224

This research shows that there are many significant reaction parameters. Some of the most important of which are the surface area and porosity of the solid reactants, the use of gaseous or solid reductants and the type of each (CO, H_2, HCL, $COCl_2$ or graphite, charcoal, coke, coal), and the type of chlorinating agent ($COCl_2$, $HClCl_2$, $SOCl_2$). Other variables shown to be important are the relative proportions of reductant and chlorinating agent to the fly ash, and the reaction temperature, pressure, and duration. Factors remaining to be studied are the geometry and type of reactor, the use of catalysts, and the recycle of chlorination products to influence the distribution of metal chlorides formed.

2. Preferential Chlorination of Metal Oxides - Preferential chlorination of iron and aluminum oxides as a function of reaction temperature was investigated to determine the potential of pretreatment of the ash for the HiChlor fly ash chlorination process. The chlorination reactivity of pure oxides of iron and aluminum, and of mixtures of the two oxides was determined for the temperature range 500°C to 700°C.

It was found that chlorine reacts primarily with iron oxide at these relatively low temperatures. At a reaction temperature of 700°C, seventy to eighty percent of the iron oxides are chlorinated for both the pure oxides and the fly ash. Less than twenty percent of the aluminum oxide reacted in the tests using mixtures of two oxides. The reactivity of the alumina in the fly ash was even lower with only four percent being chlorinated. This work indicates that lower temperature preferential iron chlorination may be used to separate most of the iron prior to alumina chlorination at a higher temperature.

Low-temperature Chlorination in the Presence of Carbon

Table 2 shows the results for the chlorination of pure oxides, oxide mixtures, and nonmagnetic fly ash. The effect of temperature on chlorination was substantially more significant for Fe_2O_3 than for Al_2O_3. The conversion of Fe_2O_3 was increased from about 62 percent to 90 percent, while that of Al_2O_3 remained at about 10 percent as the temperature was raised from 500°C to 700°C. The amount of chlorination of oxide mixtures was about 36 percent, 59 percent, and 85 percent for Fe_2O_3 and 13 percent, 13 percent, and 17 percent for Al_2O_3 at 500°C, 600°C and 700°C, respectively.

Little of the Al_2O_3 in the non-magnetic fraction of fly ash was chlorinated at temperatures less than 700°C, whereas the percentage of Fe_2O_3 chlorinated at 500°C, 600°C, and 700°C was about 15 percent, 39 percent, and 65 percent, respectively. By this preferential chlorination the Fe_2O_3 content in the fly ash can be decreased by as much as 65 percent with little loss of Al_2O_3.

The chlorination of Al_2O_3 in fly ash is less than that for pure oxide mixtures. This may be attributed to the presence of oxides such as SiO_2 in fly ash which physically isolate the Al_2O_3.

High-temperature Chlorination without the Addition of Carbon

High-temperature chlorination without the addition of carbon was conducted at 800°C, 900°C and 1000°C for pure oxides, oxide mixtures, and nonmagnetic fly ash (dry ash and ignited ash residue). The work was carried out to determine the degree to which carbon is required for chlorination of the individual metal oxides. Duplicate analyses of samples were performed. The results, listed in Table 3, show that more than 80 percent of the Fe_2O_3 is reacted for dry fly ash as is 40 percent of the Al_2O_3 in the ignited ash. The significant reaction of Al_2O_3 in the fly ash during chlorination occurs because of the residual carbon in the ash. The effect of carbon in the ash on chlorination is evident by the reduced amount of chlorination products for runs using ignited ash from which the carbon has been burned out.

The chlorination extents of pure oxide Fe_2O_3 - Al_2O_3 mixtures listed in

Table 3 show a trend opposite to those of pure oxides and ashes chlorinated with carbon where an increase in temperature generally results in an increase in the degree of chlorination. From Table 3, both oxides in the pure oxide mixtures show a decrease in reactivity as the temperature increases.

3. Fluidization Studies - A plexiglass fluidization column system was constructed for measurement of fluidization parameters for fly ashes and fly ash mixtures. Several bituminous and subbituminous coal fly ashes were tested, and large differences in fluidization properties were observed. Fly ashes having a mean particle size of 40 microns or larger fluidized uniformly at low gas flow rates. Most fly ashes, particularly those separated by electrostatic precipitation, have a smaller mean particle size of about 20 microns. These ashes are cohesive and do not fluidize uniformly. It has been discovered that fluidization properties of cohesive ashes improve when the finely divided carbon reductant is added to the mixture. Fluidization of very fine, electrostatically separated fly ash was found to be unsteady but uncontrollable: the fly ash would not fluidize until carbon was added and the addition of the larger size carbon particles was particularly helpful and expanded the range of types of fly ash that fluidized satisfactorily.

The effects of charcoal particle size and bed aspect ratio (bed height to diameter) on fluidization were examined. Also, several batches of fly ash and charcoal material were partially chlorinated and the solid residue used to investigate the fluidization characteristics of partially chlorinated fly ash.

Fluidization data were collected for a subbituminous western coal fly ash; this material which has a small mean particle diameter is cohesive and difficult to fluidize. Poor fluidization was observed because the fly ash tended to agglomerate which inhibited air flow and caused channeling through the bed.

Fluidization properties of fly ashes were found to improve when charcoal was added. Fluidization of a mixture of fly ash and charcoal with a narrow size distribution (53 to 147 μm) gave the appearance of good fluidization. However, the bed pressure drop data indicated that significant particle size segregation was occurring. Charcoal-fly ash mixtures for all the charcoal sizes used fluidized at higher air flow rates. Mixtures containing a wide range of charcoal particle sizes seemed to have the best fluidization characteristics, and the mixture with the smallest charcoal particles showed the

Table 2. Extent of Chlorination of Pure Oxides, Oxide Mixtures, and Nonmagnetic Fly Ash in the Presence of Carbon.

Temperature	Percent of Oxide Chlorinated*							
°C	Pure Oxide		Oxide Mixture		Nonmagnetic Fly Ash			
	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	SiO_2	TiO_2
500	62.4	11.1	35.7	12.9	15.3	2.6	6.4	5.2
600	74.4	10.5	58.8	13.1	38.9	3.8	10.5	7.2
700	90.0	10.1	85.4	17.1	65.1	6.7	11.8	6.2

* Average values for replicated runs and duplicated analyses.

Table 3. Extent of Chlorination of Pure Oxides, Oxide Mixtures, and Nonmagnetic Fly Ash without Carbon.

Temperature	Percent of Oxide Chlorinated*											
°C	Pure Oxide		Oxide Mixture		Nonmagnetic Fly Ash				Ignited Ash Residue			
	Fe_2O_3	Al_2O_3	Fe_2O_3-	Al_2O_3	Fe_2O_3-	Al_2O_3-	SiO_2-	TiO_2	Fe_2O_3-	Al_2O_3-	SiO_2-	TiO_2
800	72.3	7.4	97.1	30.0	57.5	18.7	20.0	23.0	54.6	4.0	5.7	--
900	99.9	9.5	94.6	12.7	79.4	20.5	15.1	38.0	63.9	2.5	4.5	21.4
1000	99.9	12.3	67.0	8.6	84.2	40.2	28.3	51.0	62.6	3.5	3.5	21.0

* Average for duplicate analyses.

poorest fluidization. Fly ash - charcoal mixtures in bed depths up to five times the bed diameter where found to fluidize without bed stratification, if a sufficiently high superficial velocity was maintained.

Fluidization of mixtures of cohesive fly ash and dried coal was similar to that of fly ash - charcoal mixtures, but mixtures using undried coal would not fluidize. The chlorinated bed residue of partially reacted fly ash and charcoal fluidized easily, which indicated that fluidization should be controllable in high-temperature, fluidized bed chlorination reactors.

Overall, the results obtained to date suggest that fly ash - charcoal mixtures that would be used in a continuous fluidized bed chlorination reactor can be adequately fluidized.

4. Product Recovery and Separation - Several methods have been examined for separating mixtures of the metal chlorides which are the products from the chlorination of fly ash. Information about both anhydrous and aqueous methods has been obtained from the literature. Fused salt extraction, solvent extraction, stagewise precipitation, and ion exchange processes are potential separation methods. A process design and an economic evaluation were completed for a commercial fly ash chlorination facility which uses extraction and distillation for product separation and purification.

5. Process Cost Estimation and Economic Evaluation. - A conceptual process for the chlorination of coal fly ash on a commercial scale is shown in Figure 1. Material balances, energy balances, and equipment sizes were calculated for a plant processing 6,000 tons of fly ash each day, which is equivalent to the fly ash from 2,500 to 3,000 MW of coal-fueled electricity generation capacity. The plant will produce about 2,000 tons/day of $AlCl_3$, 1000 tons/day of an iron-rich fraction for use in heavy media systems, 500 tons/day of $FeCl_3$ and 60 tons/day of $TiCl_4$. Process equipment for feed preparation, reaction, product separation and purification, recycle, and gas clean-up is provided. Refrigeration for the $SiCl_4$- $TiCl_4$ absorption-distillation separation is to be delivered by a propylene compression circuit.

Information was developed for process cost evaluation based on design estimates for the equipment and related accessories. The single largest equipment items are the fluidized bed chlorination reactors which must be sized to handle the very low fluidization velocities required. Future research on process improvements will include alternate reactor designs and product purification methods.

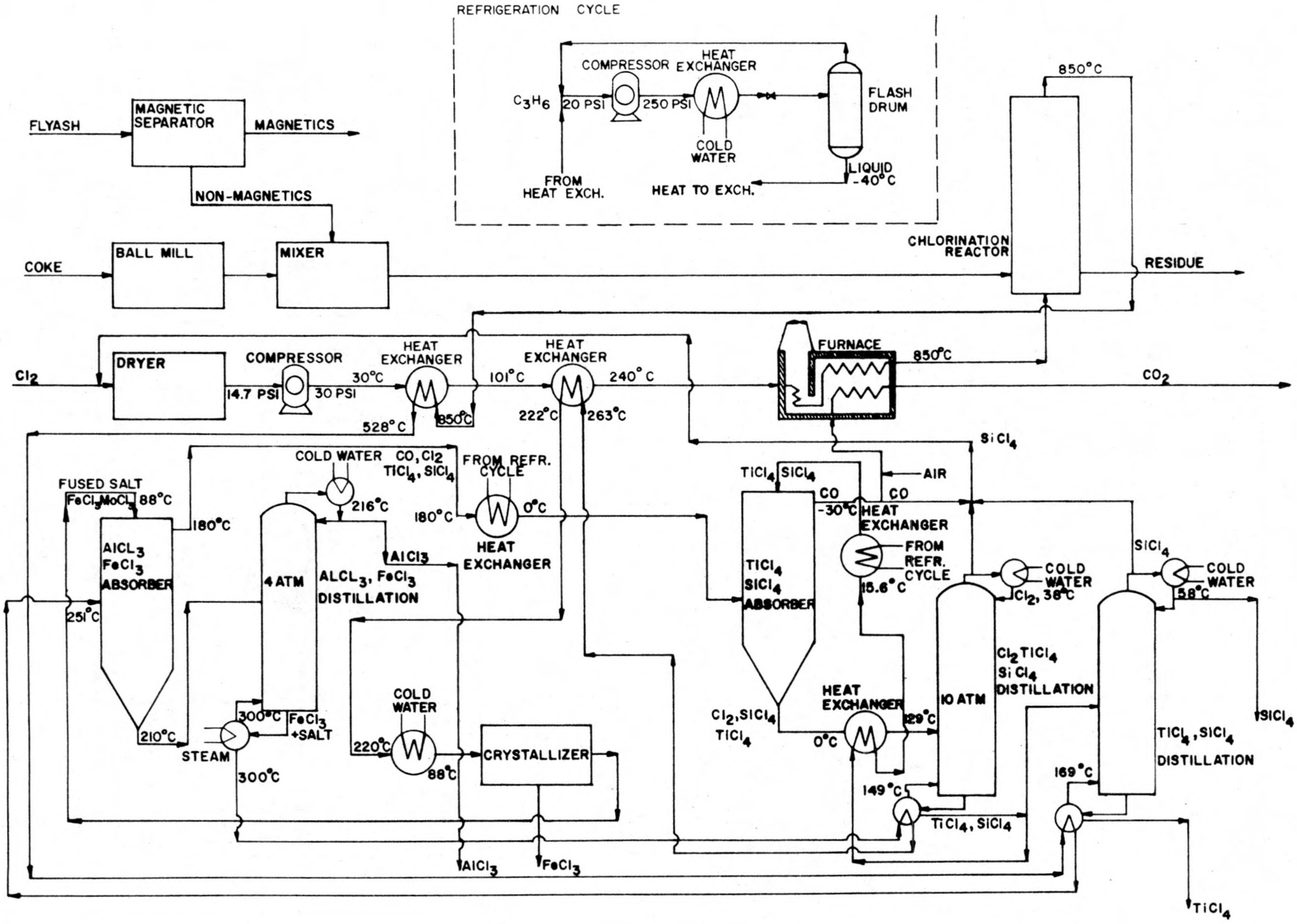

Fig. 1. Flow plan for proposed coal fly ash chlorination (HiChlor) process.

Lime-Soda Sinter Process Improvements.

1. Reaction Mechanism and Kinetics - Fundamental studies are being conducted to increase understanding of the sintering reactions. These investigations will determine the atomistic reaction mechanisms and kinetics for reaction of the calcium and sodium oxides with the alumina and silica in the fly ash and may suggest ways for improving yield and energy efficiency. Sintering runs at 1250°C and 1350°C showed evidence of liquid phase formation. The liquid forms amorphous material on cooling which makes it difficult to interpret the results of x-ray diffraction analysis of these powders. Limited success was encountered when x-ray diffraction measurements were used to determine the progression of compound formation until a method was developed to remove the amorphous calcium silicate. Samples were leached in a solution of maleic acid and methanol which dissolves calcium orthosilicate. The extracted residues were then analyzed by x-ray diffraction and, with the removal of the calcium orthosilicate, the peaks of the calcium aluminate compounds were easily identified.

Sinter products were also examined by electron microprobe (EM) to study the elemental distribution within the samples. These data indicate that the reactions are not complete after a 1-hour sinter at 1350°C. The product was found to be more completely reacted after a 2-hour sinter at 1350°C. After two hours, unreacted areas were small indicating the progress of the reaction with time.

Research to determine the reactions occurring during the sintering of mixtures of pure oxides of alumina, silicon, and calcium has resulted in the following conclusions concerning calcium aluminate and calcium silicate formation:

1. When a ternary mixture of CaO, Al_2O_3 and SiO_2 is heated to any temperature below the entectic temperature predicted from the equilibrium phase diagram, it will simply behave like two binary systems, CaO-Al_2O_3 and CaO-SiO_2. For the temperature range 1200°C-1350°C studied, only binary compounds formed.
2. The reactions between CaO and SiO_2 start at lower temperatures and proceed faster than those between CaO and Al_2O_3. As a result, some calcium oxide will enter the structure of dicalcium silicate.
3. The reactions between CaO and Al_2O_3 are carried out through the diffusion of Ca ion, accompanied by the diffusion of either oxygen ion or electrons with oxygen transported through the gas phase. Because of the nature of this process, layer-like products are formed. The C_3A, $C_{12}A_7$ or C_5A_3, CA

and CA_2 are all observed at one time or another during the sintering runs ($C = CaO$; $A = Al_2O_3$).

4. The first aluminate to be formed between CaO and Al_2O_3 is probably $C_{12}A_7$, which quickly reacts with Al_2O_3 to form CA as sintering temperature and time increase. When Ca ion diffuses through the CA layer to react with Al_2O_3, it forms the C_3A phase. As time progresses, at 1200°C, the C_5A_3 phase will be formed from the reactions between CA and C_3A. However, at higher temperature, the C_5A_3 phase is unstable and $C_{12}A_7$ will be formed instead.
5. The apparent activation energies for the formation of C_3A and CA have been determined to be 45.6 Kcal/mole and 89.8 Kcal/mole, respectively. These values are probably related to the diffusion processes in their respective phases.
6. The results of Na_2CO_3 leaching of pure compounds and sinters show that the total extractable alumina is the sum of the extractable alumina from each aluminate phase. Under the leaching conditions employed in this research, the solubility of CA in 3% $NaCO_3$ solution is 91%, while that for $C_{12}A_7$ is 89.1% and that for C_3A is 55.5%. The silica can enter the filtrate through reactions between C_2S and Na_2CO_3 or sodium aluminate.

2. <u>Sinter Composition</u> - Research on alternate sources of limestone with a range of sintering times, and an investigation of the desilication and the carbonation process steps is being conducted to provide information required for the complete design of a Process Development Unit (PDU) (500 lbs fly ash per 8 hr day) for the lime-soda sinter process. Additional information on the process steps is required for correct design and sizing of the items of process equipment. The time required for sintering, for example, will determine the size of the rotary kiln for a given throughput rate. The time and conditions for desilication will determine the capacity and pressure rating of the desilication vessel. Tests of the filtrate carbonation step will determine the degree of precipitation of dissolved constituents relative to one another as the pH of the solution decreases.

Sintering runs with mixtures of limestone and fly ash, plus mineralizer additives were carried out. Data on alumina solubilization were collected for sinters with the mineralizer CaF_2 added to the mixture. The alumina solubilization increased from 49.8 percent for the mix without CaF_2 to 72.7 percent when 20 weight percent CaF_2 was added. The addition of the mineralizer reduced the optimum sintering temperature from 1380°C to 1100°C.

Limestone-fly ash sinter runs were also made with pulverized coal refuse added to the mixture. The addition of 5 weight percent coal refuse to the sinters resulted in an alumina solubilization of 66.5 percent. This is a significant increase above the 45 percent alumina solubilization obtained for the same sinter composition without coal refuse. These runs were made at 1380°C and additional investigation is planned.

High Alumina Content Bituminous Fly Ash

Samples of fly ashes from West Virginia coals were used for sinter formulation as part of the program to apply the lime-soda sinter process to fly ashes of coals from all of the major coal producing states. A series of sintering-extraction experiments were conducted to investigate the effect of sinter mixture composition on the percentage of extractable alumina for a West Virginia coal fly ashes, which contained 30 wt. percent alumina. Several mixture compositions were sintered to determine (1) the composition yielding the maximum soluble alumina and (2) the required sintering temperature for optimum recovery. These tests showed that over 95 percent of the alumina can be extracted at a sintering temperature of 1100°C. These results for ash from a high-volume West Virginia coal are encouraging and speak well for the commercial viability of the lime-soda sinter process.

3. Commercial Limestone for the Lime-Soda Sinter Process - In the lime-soda sinter process, the fly ash, which is composed of silica, alumina, calcium, and iron, is first magnetically separated to remove part of the iron. Precalculated amounts of limestone and soda ash are next added to the nonmagnetic fraction of the fly ash and the mixture then pelleted and sintered at the desired temperature. During the sinter reaction, limestone reacts with silica in the ash to form dicalcium silicate. This frees the alumina that was combined with silica to react with either soda ash or limestone, forming sodium aluminate and calcium aluminates. Previous research on the lime-fly ash sinter process and the lime-soda-fly ash sinter process has been done using reagent-grade chemicals rather than commercial materials. Therefore, comparative tests were conducted using commercial limestones, as will be used in the process development unit. Limestone road rock from several quarries was analized and used in sintering-extraction experiments. The results showed that the impurities contained in quarry limestones require minor changes in the

previously determined optimum compositions, but equally high alumina recoveries were obtained. Measurements show that quarry limestone when crushed and ground is much less porous than reagent-grade calcium carbonate but any influence on the sinter reactions appears to be minor.

4. Process Development Unit Equipment Design - Data required for the specification of items of process equipment are being assembled. Figure 2 shows the equipment items which are required for the three sections of the process development unit. Tests have been conducted using several types of magnetic separation units for removal of the highly magnetic iron-rich fraction from bituminous coal fly ashes. Physical treatments influencing the sintering operation, such as mixing, wetting, pelletizing, and pellet drying, are being studied to better define the feed preparation equipment requirements and to determine the design values for the sintering kiln.

Desilication

Tests were conducted for the desilication of extracted filtrates. Desilication without aluminate precipitation is required if a metallurgical grade alumina product is to be economically produced. The equipment used for exploratory desilication tests did not correctly simulate the required closed system pressure treatment and this research will need to be repeated. New equipment has been obtained which will permit treatment of small-volume filtrate samples under pressure.

Extraction

Data collected by testing extracted sinter residues have been used to specify the extraction and filtration equipment for the process development unit. Because the grinding of sinter pellets to fine powder consumes a significant amount of energy, tests were conducted to determine the effect of powder fineness on alumina extraction. Sintered material was lightly crushed, then graded into three size fractions which were extracted. These results, given in Table 4, indicate that alumina and silica solubilization are related to particle size, with finely ground sinter powder being more soluble than lightly ground material. It appears that size reduction to <200 mesh (75 μm) will be necessary to obtain 90% or better recovery.

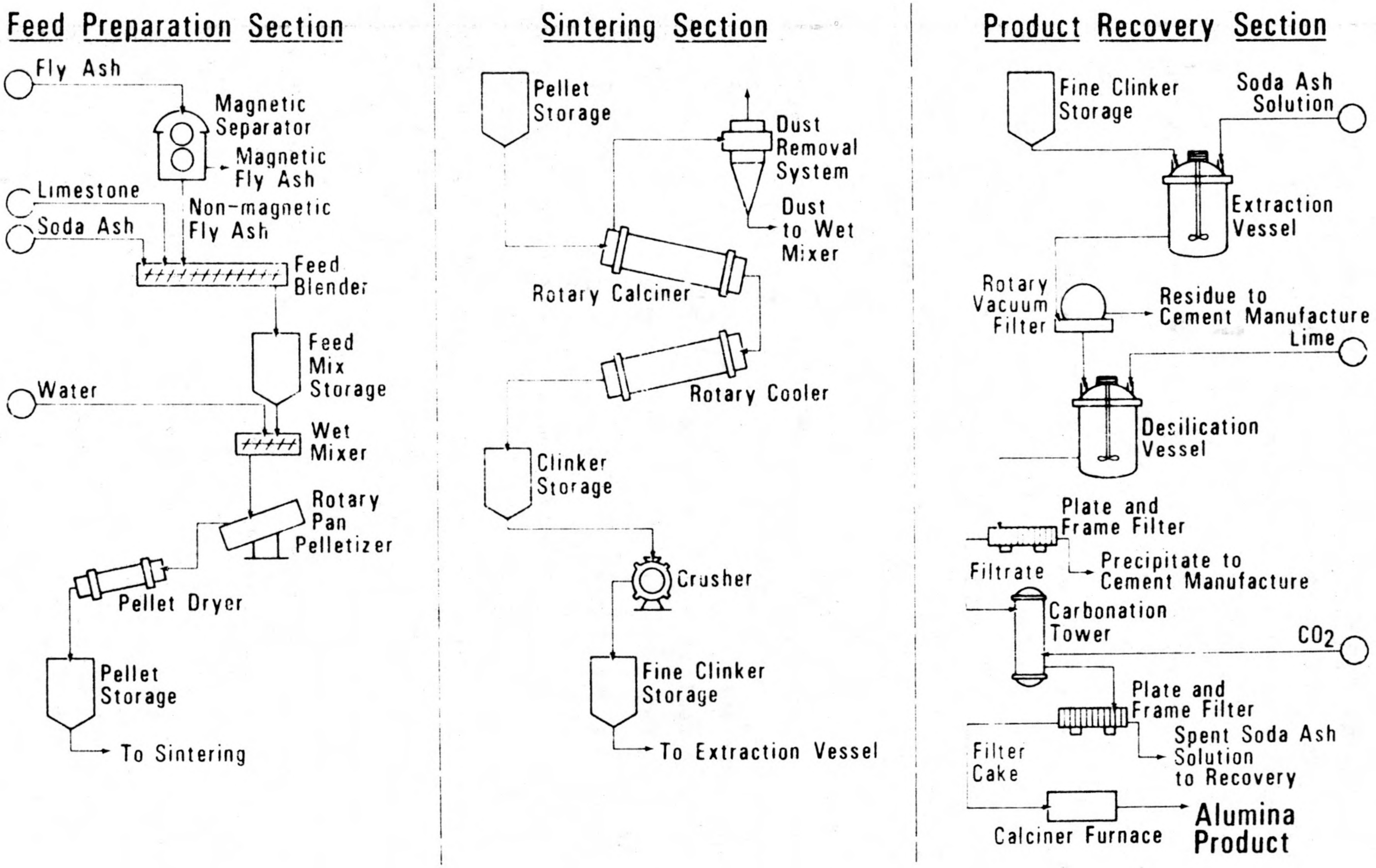

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Figure 2. Ames Lime-Soda Sinter Process for Alumina Recovery from Coal Fly Ash.

Table 4. Dissolution of Oxide Constituents from Lime-Soda-Fly Ash Sinters as a Function of Degree of Crushing of Sintered Material.

Sieve fraction (mesh)	Average particle size (μm)	% Alumina recovery	SiO_2 concentration (ppm)
60-100	200	74.3	24.4
150-200	90	84.7	28.5
270-325	48.5	100.0	43.8

Design of the Continuous Extraction Unit

As a method for design, optimization work on batch extraction was used. The following process variables were selected from previous work;

(i) Sinter feed to extraction 200 mesh.

(ii) A 3 (wt) % Na_2CO_3 solution.

(iii) Extraction at 65°C.

(iv) An extraction time of 10 minutes.

(5) A weight ratio of 3% Na_2CO_3 solution sinter product of 10 to 1.

Since the PDP unit is to process 500 lb fly ash in an 8 hr day, i.e. 62.5 lb/hr fly ash, the solids rate for extraction will be approximately 125 lb/hr sinter, with a liquid requirement of 1,250 lb/hr of 3 wt. percent Na_2CO_3 solution. If a residence time of 10 minutes is used, an extraction volume of about 25 gallons results.

Unless a perfect plug flow system can be attained a continuous reactor will have a distribution of residence times. This distribution will result in a reduction in alumina recovery when compared with the batch product. On a large scale a tubular reactor could be a used, giving a relatively small distribution of residence times. One or more stirred tank reactors is probably a better choice for a PDU because of greater flexibility of operation.

The data given in Table 5 represent calculated estimates of the effects on extraction when a batch extractor is replaced by one or more continuous tank reactors (CSTR). It is evident that an appreciable alumina loss occurs if a single continuous stirred tank reactor replaces the batch reactor. The loss is reduced considerably by using two stirred tanks in series. Increasing the number of CSTR's would improve alumina recovery but looks like an investment of diminishing returns.

Table 5. Estimated Effect on Sinter Oxide Extraction as a Result of the Conversion from a Batch to a Continuous Extraction Process

Mixing system	Alumina Recovery (%)	SiO_2 concentration (ppm)
Batch mixer	87.5	44
One continuous stirred tank reactor	79.1	28.1
Two continuous stirred tank reactors in series	84.4	34.5

In practice, some of the required reactor volume will be provided by the solid/liquid separation device. If it is assumed that a rotary vacuum filter is to be used, then the volume of filtrate in the filter sump will be of the same order as the reactor volume. This requires that the filter sump consist of a well mixed solid/liquid system. If, on the other hand, a centrifugal separation was adopted, residence time within the centrifuge would be small and reaction would proceed almost entirely within the stirred tank reactor system.

The precise volumetric requirements for the extracting vessel cannot be determined until the hold-up volume within the solid/liquid separation device is known. At this point, a two-stage extraction is assumed with a stage volumetric capacity of 2 ft^3 and a normal operating volume of 1.7 ft^3. The design is structured so that the working volume can be varied to optimize performance during operation of the pilot plant. A basic requirement of the agitation is that a homogeneous suspension of the sinter within the Na_2CO_3 solution can be achieved. To do this there will need to be a strong vertical component of circulation within the vessel.

Filtration Equipment

The separation unit must be capable of handling approximately 0.34 ft^3/min.

(2.6 U.S. gal/min), of slurry containing approximately 10 (wt) % solids. An appreciable alumina loss can result if a gravity filtration is used without washing the precipitated cake. On the other hand, wash water has a deleterious effect on the final alumina product because additional calcium as a contaminant will be dissolved from the sinter. For this reason, washing should be avoided if possible and replaced by vacuum, pressure or centrifugal dewatering of the cake. Filtering has proved satisfactory in the laboratory but its commercial use will depend on the effect of washing, the residence time, and the porosity and stability of the cake formed. Centrifuging would have low residence time but would probably involve alumina loss as the solids would be removed as a thick slurry. An optimization study is in order to resolve this question.

Filtration Characteristics

A series of filtration tests were conducted to determine the filter characteristics of the extract-sinter residue system. These tests were conducted using a bench-scale leaf filter apparatus and measured the filterability (mass of filtrate per unit volume per unit time), the cake compressibility and the cake thickness. The results indicated that a rotary vacuum filter capable of a vacuum of at least 3×10^4 N/m^2 with a filtration area of about one square foot will be required for the process development unit.

Cake dewatering tests were also conducted which showed that dewatering is rapid, with little water removed after 20 seconds. Dewatering is a function of vacuum, and it was found that the vacuums typical of commercial filters (on the order of 1×10^5 N/m^2) can reduce the moisture content to 20 percent of the cake weight. This represents an overall liquid loss of about 2 weight percent which is preferable to the risk of product contamination by cake washing.

Commercially available rotary vacuum filters

The smallest available rotary vacuum filter from the Eimco Corporation is a 3 dt. dia, 1 ft. wide model with bottom feed. It has a vat 2 ft. wide which is contoured to give a 7-inch clearance between the vat base and the rotating drum surface. The vat is equipped with a blade agitator. A vacuum of 22-24 inch Hg, $(7.45 - 8.13) \times 10^4$ N/m^2 is pulled and this probably could be reduced if necessary. The speed of rotation of the drum can be varied between 1 min per revolution and 10 min/revolution. For a firm filter cake, a belt arrangement is recommended for the removal of the cake. With this system 35% of the drum would be immersed, about 50% available for dewatering and/or drying and the remaining area taken up with cake removal.

Summary of First Stage Product Recovery Design Recommendations

It was shown that more efficient extraction took place when the sinter was reduced to a particle size no greater than 50 μ. A qualitative assessment would be that the lime-soda sinter clinker is a tough material and that it will probably require the energy input of a machine such as the pin-mill rather than a simple ball mill. A two-stage CSTR system will be required to obtain the desired recovery of alumina from the ground clinker.

The rotary vacuum filter investigated is the smallest commercially available filter of its type and it can probably handle twice the design throughput of the PDU. It is felt, however, that a rotary vacuum filter will be the logical choice for larger scale operation and that valuable operating experience can be obtained on this unit for subsequent scale-up.

A proposed layout for the first stages of the product recovery unit of the Process Development Unit is given in Figure 3.

Recovery and Beneficiation of Iron-Rich Fractions

Magnetic separation has been shown to be an effective physical method for removing an iron-rich fraction from fly ash. The iron content of the ash is thus reduced making recovery of a highly pure alumina easier. However, not all fly ashes contain enough magnetic material to make recovery of an iron-rich fraction feasible. An iron oxide content in the fly ash of less than 6 to 8 percent ordinarily means that no significant fraction will be separated.

1. Physical Beneficiation - Tests were conducted to determine the effect of electromagnetic separator power setting on the separation of fly ash. A high-iron-content Missouri coal fly ash was used, and the magnetic ash fraction was separated, weighed, and analyzed for six power settings. These data indicate that with increasing power to the magnet, the magnetic fraction contains progressively higher concentrations of silica and alumina.

Some preliminary work has been done to determine the possibility of removing the residual magnetism in the magnetic ash to make subsequent processing easier. A roasting method was tested and found to at least partially destroy residual magnetism.

Other possible methods, physical as well as chemical for beneficiation of the iron-rich fraction,are being investigated. A sample was sent to the Sturtevant Mill Company for ultrafine grinding. Fine grinding of the magnetic ash may liberate the impurity particles from the magnetic particles. Sturtevant

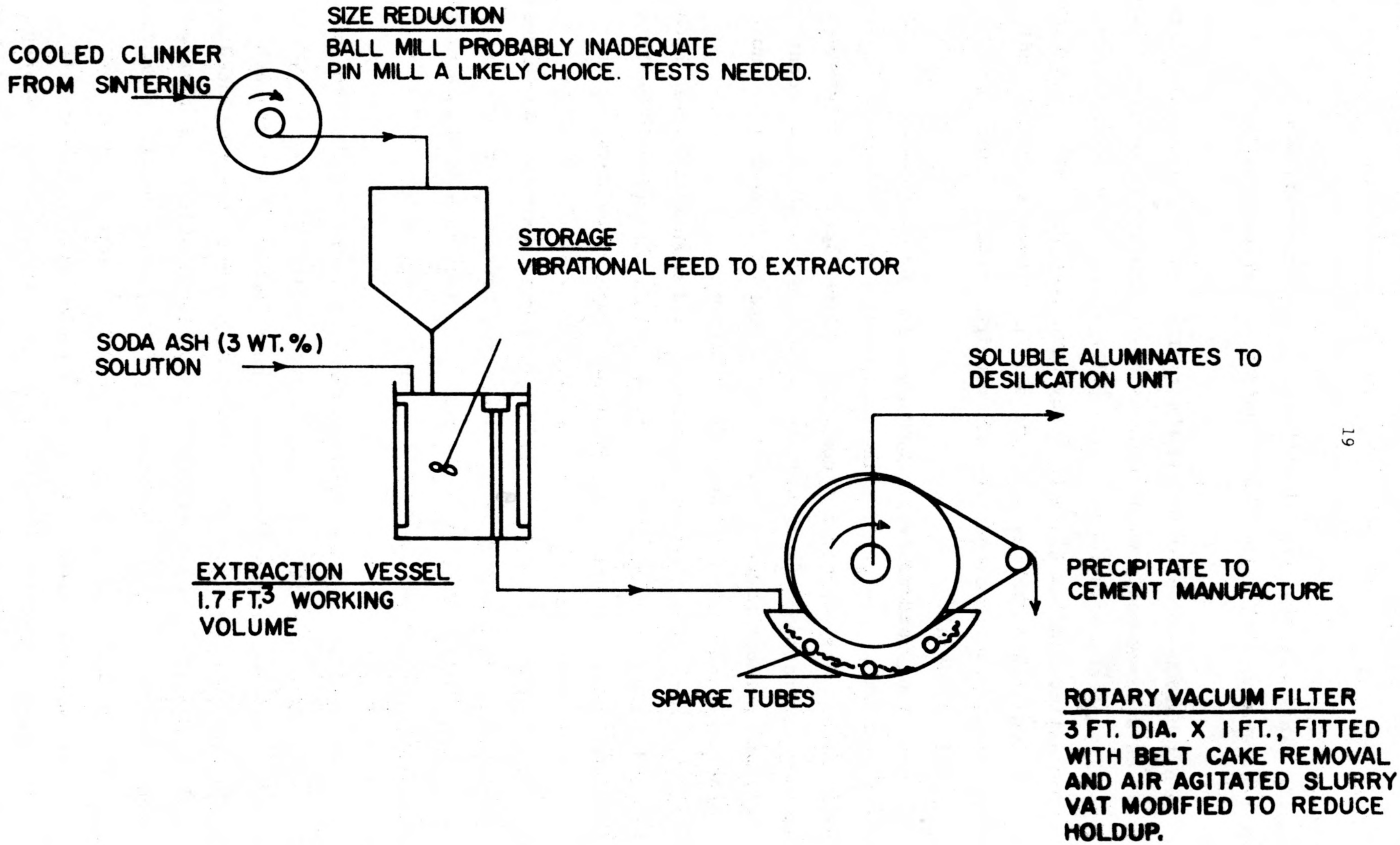

Figure 3. Layout for the first stage of product recovery for the lime-soda sinter process.

reported that the final material contained 96 percent - 325 mesh (-44 μm). Coulter counter data showed that the median particle diameter was reduced from 35μm to 12μm.

Two experiments have been performed on the microground fly ash. The first experiment involved a heavy media separation using a bromoethane-acetone mixture. The specific gravity of the solution was 2.86 which should have been enough to float any free silica-alumina glass that may have been present. From the experiment it was found that there was essentially no free glass, which indicates that microgrinding while effective for reducing particle size did not liberate nonmagnetic material.

The second experiment used magnetic separation of the micro-ground ash at lower power settings. The results of this separation have not been fully explained since chemical analyses are not complete. Three large fractions were obtained from this separation: 21 wt. percent nonmagnetic, 40 wt. percent middling, and 33 wt. percent magnetic, with 6 wt. percent losses. The inordinately large middling fraction is difficult to explain.

In general, the magnetic separation of microground magnetic fly ash does not appear to hold promise as a beneficiation method at this time. The fractions obtained from this experiment do not appear to have any apparent physical differences such as color or general appearance. Also, the magnetic fraction was relatively small though it may be possible to include the middling fraction as magnetic product. More work is required before a final decision can be made about the feasibility of this approach. Improvement may be possible using a higher power for the second magnetic separation or a wet magnetic separation.

2. Chemical Beneficiation - Work has continued on chemical beneficiation of the iron-rich fraction to permit its use as an iron ore. Experiments were conducted to determine general conditions and the response of the fly ash to high temperature NaOH extractions. Fly ash and NaOH solution were placed in a pressure vessel; the fly ash was suspended above the liquid so that it would not be in contact with the leach solution until the desired operating conditions were obtained. Initiation of a stirring action dropped the fly ash into the NaOH solution. Agitation was then maintained for one hour after which the reactor was cooled and the solid filtered from the leach liquor and washed. The leach and wash solutions, and dried solid samples were analyzed using AAS

methods.

These experiments included two solid-liquid ratios, two NaOH concentrations, and two temperatures. Table 6 references the experiment number to the experimental conditions used.

Table 6. Experimental Conditions for NaOH Extraction of Fly Ash

Exp. No.	Solid-Liquid Ratio: g/l	NaOH Concentration wt. %	Temperature ^{o}C
1	70	20	150
2	50	20	150
3	70	30	150
4	50	30	150
5	70	20	200
6	50	20	200
7	70	30	200
8	50	30	200

The results of these experiments are shown in Table 7 and indicate that NaOH concentration and temperature, when increased will result in an overall increase in both silicate and aluminate concentrations in the leach liquor. Increasing the solid-liquid ratio increases the silicate concentration at the expense of the aluminate concentration.

The data from these experiments will help determine optimum operating conditions but the important fact resulting from this work is that NaOH extractions can reduce the silica and alumina levels in magnetic fly ash significantly. Caustic extraction of magnetic fly ash can remove from 75 to 90 wt. percent of the contained silica and 15 to 55 wt. percent of the alumina, producing a product containing 77 to 92 wt. percent iron oxide (Fe_2O_3).

Analysis for trace materials such as calcium, sodium, sulphur and phosphorus are pending, but previous work as well as results reported in the literature indicate that phosphorus and sulphur will be reduced below the minimum tolerance limits for use of the beneficiated residue as iron ore. There was no qualitative evidence of significant sodium contamination based on AAS analysis, and calcium is expected to be an inert in this process based on results reported in the literature.

A second series of experiments was run to help determine if the extraction system is solubility limited and to help locate the solubility limits, if they exist. The conditions for these experiments were 30 wt. percent NaOH, 200°C, with 1 hour at temperature. The heat up time averaged 30 minutes; the solid-liquid ratios investigated were 70 g/l, 100 g/l and 140 g/l. The results are shown in Figure 4 where the three solution concentration values fall on a straight line, which may indicate a solubility limit due to a common ion effect. If this line is taken to be a solubility limit, then a relationship results by which the composition of the ash and the solubility limit can be used to calculate the solid-liquid extraction ratio. For this fly ash the critical extraction value, as shown in Figure 4, occurs at a solid-liquid ratio of 50 g/l. The critical solid-liquid ratio, based on one hundred percent removal of both components, will be a function of the composition of each fly ash. Because some of the material to be extracted is trapped within particles, however, one hundred percent removal is not possible. Therefore, the actual optimum solid-liquid ratio will be somewhat greater than that predicted from the composition of the fly ash.

Table 7. Solid Compositions for the Original Fly Ash and the Solid Residues from NaOH Extraction Runs Shown in Table 6.

Exp. No.	% Fe_2O_3	% SiO_2	% Al_2O_3
Original Mat.	66.0	22.0	9.4
1	77.4	8.0	7.4
2	77.6	8.0	7.9
3	79.6	4.5	6.5
4	84.8	3.8	5.2
5	77.8	7.5	7.7
6	77.9	6.3	7.1
7	83.4	4.2	5.1
8	91.8	2.5	4.2

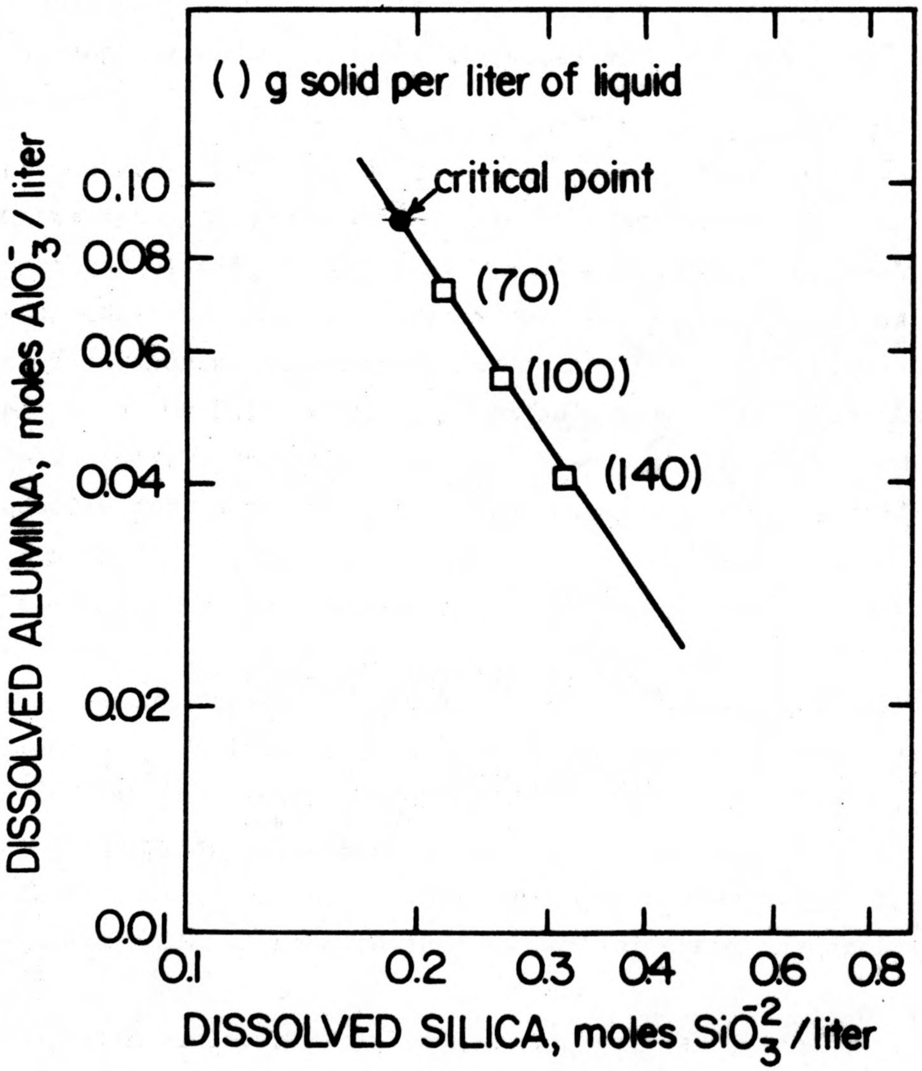

Figure 4. Concentrations of dissolved silica and alumina in 30% NaOH Leach Solutions after One Hour at 200°C as a function of Solid-Liquid Ratio.

3. Coal Refuse - Another coal waste material containing iron is the refuse removed when coal is beneficiated by washing. Coal refuse consists primarily of iron pyrite and coal. Ashing of coal refuse produces a residue with an iron content equivalent to magnetically separated fly ash and often containing less alumina and silica. Samples of coal washing plant refuse were roasted at low temperature to determine the energy requirements for the removal of carbon and sulfur. These results show that a two hour roasting at 600°C will remove as much coal as 96 percent of the carbon and 89 percent of the sulfur from the coal refuse. Additional work is required to determine optimum roasting conditions and the potential for sulfur recovery from the combustion gases.

Investigation of the Substructure of Coal Fly Ash

A study of the internal structure of fly ash particles is being conducted to determine how to best attack the structure and recover the metal constituents. Photomicrographs show that fly ash particles, particularly the magnetic fraction, are spheroidal in shape and have an internal structure that consists of aggregates of crystalline material. Cross-sections of magnetic fly ash particles were examined by scanning electron microscopy (SEM) with an analytical capability (Edax). The results indicate that there is a high iron concentration in the dendritic magnetite substructure. The interdendritic glass phase shows a decrease in iron concentration and an increase in silicon concentration. Titanium was found to concentrate within the magnetite dendrites rather than within the interdendritic glass phase.

SEM observations also revealed the occurrence of pleurospheres, hollow spheres packed with smaller spheres, in the magnetic fraction. The shell of the large sphere was found to consist of magnetite but the compositions of the smaller spheres were not determined. If the small spheres are high in silica, the iron content of fly ashes that contain many pleurospheres will be lowered which may help explain the range in iron content of magnetically separated fly ash fractions.

Nonmagnetic fractions of several fly ashes from midwestern bituminous coals were each separated into five size fractions by a specially developed settling technique. These separated fractions were then chemically analyzed and the actual size distribution of each was determined by Coulter counter measurement.

Before the ash samples could be separated by settling, it was necessary to find a method to prevent particle agglomeration since the nonmagnetic ashes tended to coagulate in water. By trial and error it was found that a sodium oxalate solution prevented coagulation. This type of anti-coagulant, an electrolytic peptizer, is thought to surround each particle with a like charged barrier. A sodium oxalate solution of less than one weight percent was found to prevent coagulation for over 12 hours. This solution was then used for the settling separations.

The size determinations, as measured by the Coulter counter, showed that the coarser fractions of the ashes consist of particles of smaller diameter than was indicated by settling. This discrepancy may be caused by the presence of a large number of small particles with densities higher than average of the whole nonmagnetic ash fraction.

The alumina and calcium contents of the coal fly ashes were found to vary inversely with particle size. Alumina was highest in the finest size fraction and lime highest in the coarse fractions. The silica and iron oxide contents were more independent of particle size.

X-ray analyses of the ash fractions showed that all fractions contained a major amount of SiO_2 in the form of quartz. Major intensity peaks of magnetite and hematite were found in the coarse fractions. Lime (CaO) was also identified in these fractions.

Microscopic particle observations revealed that many of the nonmagnetic particles had beads of magnetic material imbedded within them. Even with full magnetic power the magnetic force was insufficient to lift some of these magnetic particles because of the nonmagnetic mass.

Magnetic ash fractions were next x-rayed and then sized using dry sieving techniques. A sieved fraction from each magnetic ash was also x-rayed. Magnetic ash fractions separated at 100 and 50 percent of the power of the magnetic separator were characterized by x-ray diffraction for comparison purposes which should help to gain a better understanding of the magnetic separation process. The coarser fractions of the magnetic ash were observed microscopically.

1. X-ray Diffraction

All ashes were x-rayed using a monochromatic filter with copper radiation. The monochromatic filter was used to eliminate the high background present when white radiation is used. The results for one ash are given in Table 8. X-ray data from all nonmagnetic size fractions are not presented because the same minerals were found in all size fractions. The concentration of all minerals decreased as size decreased and as amorphous material increased. In the magnetic fractions, only magnetite and hematite were readily detectable. Quartz may have been present in very minute amounts.

Table 8. X-ray Diffraction Results from Various Fractions of a Kentucky Coal Fly Ash Separated at 50% of Magnet Power.

Minerals	Nonmagnetic	Magnetic	Magnetic (--150, +200 mesh)
Quarz	X	*	*
Lime	X		
Mullite	X		
Magnetite	X	X	X
Hematite	X	X	X

* Nearly undetectable by x-ray methods used.

In ash separated at 100 percent of magnet power, quartz, magnetite, and hematite are readily detectable. Coarse fractions from magnetic ash separated at 100 percent power were x-rayed to see if a relation existed between the occurrence of quartz and particle size. A slight increase in quartz was found in the coarse ash fraction.

2. Sieve Analysis

Fractions of magnetic ash separated at full power and at 50 percent of magnet power were sieved into six fractions. The purpose was to determine if the increase in SiO_2 and Al_2O_3 in the magnetic fraction with magnetic power is caused by an increase of SiO_2- Al_2O_3 rich particles in a particular size fraction.

3. Microscopic analysis

Particles from the coarser fractions of magnetic and nonmagnetic ash fractions were microscopically observed. Nonmagnetic particles were observed in thin section with transmitted light and as whole unpolished particles by attaching a dissecting lens to a Zeiss binocular scope and using side illumination from two high intensity lamps. Coarse particles from the magnetic fraction were observed under a dissecting lens as well as in reflected light samples.

The following is a list of the major crystalline constituents found in fly ashes and various properties of occurrence, structure and morphology which allow their optical identification. Glasses are the major constituent of most fly ashes and thus will be briefly discussed.

Magnetite (Fe_3O_4) - This mineral can be concentrated into a magnetic because of its inverse spinel structure which creates its magnetic structure. Beneath the dissecting lens, magnetite may appear as opaque spheres, cenospheres, cenosphere fragments or irregular vesicular particles. Many times magnetite particles are attached to nonmagnetic material.

In reflected light the internal structure of magnetic particles can be observed. It is readily apparent that magnetite seldom appears as the only phase in a magnetic particle. Using oil immersion microscopy, magnetite appears to be of low to medium reflectivity and slightly grey in color. The magnetite crystals appear within magnetic particles as dendrites or octahedra. In many particles it appears that dendrites converge to form octahedra. Size range is extremely variable, ranging from sub-micron crystallites to crystals as large as 50 μm. Magnetite occurs with glass and hematite. Magnetite is isotropic which means that it will be extinct when observed in polarized light with crossed nichols.

Hematite (Fe_2O_3) - Hematite is a trigonal mineral. It is concentrated in the magnetic fraction because of its close association with magnetite rather than its own magnetic susceptibility. Optical investigations of magnetic particles in reflected light and oil immersion show that hematite occurs as lamallae or as pseudomorphs of magnetite. The lamallae commonly occur as parallel sets which outline cross-sections of magnetite octahedra. Hematite rims commonly surround magnetic particles and are pseudomorphs after magnetite.

In reflected light hematite has medium reflectivity. It is grey with a bluish tinge in color. It may be bireflectant. It is most easily differentiated from magnetite by its strong anisotropism. With the nichols crossed, hematite will appear bluish-grey in one 45^{o} position and brownish-grey in the other 45^{o} position.

Hematite is sometimes seen as independent particles and can be identified by a blood-red internal reflection.

Lime (CaO) - Under a dissecting lens lime appears as solid white spheres, cenospheres and cenosphere fragments. Lime has only been detected in the nonmagnetic fraction. Lime is an isometric mineral which makes it nearly impossible to locate in thin section. X-ray studies show that the concentration of lime in fly ashes probably accounts for a major portion of the CaO as determined by chemical analysis.

Mullite ($3Al_2O_3 \cdot 2SiO_2$) - Mullite is a mineral belonging to the orthorhombic system. To date it has only been observed in thin sections of nonmagnetic ash as rims surrounding glossy particles. These rims can only be seen in polarized light with crossed nichols. Alternate extinction occurs along the rim as the stage is rotated. Mullite may also occur as finely crystalline aggregates in the nonmagnetic ash. Only very low concentrations of mullite have been detected in fly ash.

Quartz (SiO_2) - Quartz is the most commonly occurring crystalline phase in fly ash. It is distributed throughout the nonmagnetic ash but it is slightly more highly concentrated in coarser particle fractions. If the power of magnetic separation is high, quartz may be included in the magnetic fraction. Quartz may readily be identified in thin section or under a dissecting lens. The quartz particles are commonly clear or white and irregular shaped. Some particles show slight rounding and corrosion when viewed in this section. Large quartz aggregates are also common. In thin section with nichols crossed, these aggregates are seen to consist of fine quartz grains which exhibit alternating extinction upon rotation of the stage. Many particles are independent yet others can be seen with imbedded or fused particles of magnetite or other ash constituents. Some quartz may occur as coatings on other particles and thus appear as rims under crossed nichols.

Coal - Coal particles are most commonly seen in the coarser nonmagnetic fly ash fractions. They are best observed under the dissecting lens. They are characterized by their irregular shape, darkness and layered appearance. Coal particles observed in reflected light are sometimes surrounded by a zone of more reflective, high rank coal created during the burning process.

Glass (Fe, Si, Al)- Glass comprises the largest percent of fly ash. Under a dissecting lens most glass particles are sphericals, but irregular shaped ones are not uncommon. Glasses may be clear, white, yellow, grey or varying degrees of red. They range from transparent to nearly opaque. Many glassy particles contain inclusions of, or consist partly of, magnetite.

Discussion of Results

Work to date has enabled the identification of nearly all mineral phases found in coal fly ashes. The tracing of these mineral phases in various size and magnetic fractions and their microscopic observation should present an accurate picture of ash chemistry as related to the magnetic separation process.

Investigations of the internal structure of magnetic particles reveal that SiO_2 and Al_2O_3 can occur in association with magnetite and hematite. Magnetic particles may be attached to or imbedded within other mineral or glassy particles. Because the size distribution of magnetic fractions separated at various magnet strengths did not vary significantly, it can be concluded that magnetic susceptibility is a function of the mass of combined magnetite and nonmagnetic material which creates particles in all size ranges. Thus, the particle size distribution changes very little with an increase in magnetic separation power. With an increase in separation power, particles with a higher ratio of SiO_2 and Al_2O_3 to Fe_2O_3 will be pulled into the magnetic fraction.

Optical analysis of magnetic ash reveals that SiO_2/Al_2O_3 -rich magnetic particles can be created in a number of ways. Many particles conclusively demonstrate collision or fusion of material in a somewhat molten state while others indicate an intimate relation between iron and silica or alumina-rich minerals prior to burning. Minerals also may melt with a composition which, upon cooling, will crystalize out magnetite within a glassy particle.

Future Work:

HiChlor Process Development

A vertical, downflow fixed-bed reactor will be connected directly to a gas chromatograph and chlorinations will be conducted with large chlorine excess to provide data required for the determination of the chlorination mechanism and of the reaction kinetics. Preferential chlorination as a method of beneficiation of fly ash will be continued using moderate reaction temperatures.

Chlorination reaction research remaining to be conducted includes the use of various reductants and chlorinating agents, the addition of catalytic additives, and the recycle of excess chlorine and of some chlorination products. Work on the recovery and separation of the metal chlorides produced will require determination of basic data such as vapor pressures and solubilities. The data accumulated for the fluidization characteristics of fly ash-carbon mixtures will be used in developing a high-temperature fluidized bed chlorination micro-reaction system. The use of fast fluidization will be investigated as a method to reduce reactor size.

Lime-Soda Sinter Process Development

Research will continue on the fundamental studies of the reaction mechanisms of sintering reactions. To make the test systems used more similar to fly ash, the effects of Fe_2O_3 will be included. Calcium aluminum ferrite forms during the sintering reactions and the effects of this compound will be included in subsequent research on alumina solubilization.

Other fly ashes will be treated by the lime-soda sinter method, and investigation of the precipitation and purification steps of the process will be continued. High pressure desilication experiments for silica removal from extraction filtrates will be performed for a range of pressures and rates of lime addition. Investigation of the extraction and filtration steps of the lime-soda sinter process will be conducted as continuous rather than batch processes.

The work will include verification of the stirred tank extractor design calculations.

Work will begin on the use of different types of lime flue gas scrubber sludges as calcium resources for the sintering reactions, and on the development and utilization of extracted lime-soda-fly ash sinter residue. Further research will be conducted using limestones of varying qualities and additives such as coal refuse or mineralizers.

Recovery and Beneficiation of the Iron Rich Ash Fraction

Evaluation studies will continue on beneficiation methods, physical and chemical, for producting a low-alumina, low-silica product for use in the steel industry. Microground magnetic ash samples will be subjected to chemical beneficiation in an effort to reduce silica and alumina impurity levels. Further experimental data will be collected on high-pressure caustic leaching of magnetic fly ash samples, optimizing the reaction temperature, NaOH concentration and reaction time. Consideration will be given to the potential of two-stage extraction and to ash pretreatments. Research will continue on the development of coal refuse as an iron resource.

Fly Ash Substructure

Chemical composition, mineral morphology, and structure are now identifiable for most particles in both magnetic and nonmagnetic fly ash fractions. Several bituminous and subbituminous fly ashes have been studied. Further work will be completed for identification of the internal structure of the fly ash particles, and on using this accumulated substructure data to improve the developing fly ash processes for metal constituent recovery.

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