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DIRECT UTILIZATION - RECOVERY OF MINERALS FROM COAL FLY ASH

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DIRECT UTILIZATION - RECOVERY OF MINERALS FROM COAL FLY ASH

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Abstract

Research is focused on the development of methods for recovering minerals from power station fly ash, use of less costly reactants, improvement of energy efficiency, and development of uses for by-products. A research plan developed for collection of kinetic data for fly ash chlorination (HiChlor process) includes the use of different reactant gas mixtures contacting a small bed of fly ash in a new, vertical, down-flow reactor. In some runs, carbon monoxide gas will replace the solid carbon reductant used previously. Data collected to date in a horizontal bed system are being used in computerized thermodynamic calculations to validate possible reaction mechanisms and kinetics. Two proposed methods, one anhydrous and the other aqueous, for separation and purification of chlorination reaction products have been studied and critically reviewed.

In work on the lime-soda sinter process, research includes the common ion effect on the concentrations of dissolved alumina, silica, and calcium in the filtrates obtained from extraction of the sintered clinker. Experiments conducted to determine decomposition data for several samples of limestone scrubber sludge are reported. These experiments are the first step toward the possible use of the waste sludge as a replacement for limestone in the sintering process. A series of experiments conducted to evaluate the reactivity of commercial limestones showed that high grade limestone (97 wt. percent $CaCO_3$) gave alumina recoveries equivalent to those obtained using reagent-grade $CaCO_3$ for nine sinter mixtures which were tested.

Increased interest use of the iron-rich magnetic fly ash fraction as a heavy media material for coal beneficiation led to preparation of a research proposal to increase the scale of testing by use of commercial heavy media cyclones. The scope of the research is to be expanded to include a range of fly ashes and several commercial magnetite samples. Hydrochemical beneficiation tests of the iron-rich fraction to produce iron ore indicate that the limiteddissolution of alumina from the ash is probably due to secondary precipitation reactions during digestion.

X-ray diffraction methods and techniques developed to study the substructure of coal fly ash particles and to determine the mineralogical grouping of types of fly ash particles are described.

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 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 the HiChlor Process - Fly ash will react at about 800 C with chlorine gas in the presence of a carbon reducing agent to form volatile metal chlorides. The chlorides can be condensed and separated to give the products desired. Details of the process are being 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 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. Process conditions which may improve the filtrate desilication step are being investigated, as is the use of low quality, inexpensive limestone or waste limestone flue gas scrubber sludge in the sinter.

Task C - 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. A proposal based on bench-scale tests has been prepared for work to determine the coal washing potential of the magnetic fly ash fraction in commercial dense media cyclones. Work is continuing to increase the iron oxide concentration in the fraction by high-temperature caustic digestion to remove silicates and aluminates. Another coal waste containing significant quantities of iron is the refuse from some coal washing plants. After this coal refused is ashed, the residue is similar in composition to magnetically separated, iron-rich coal fly ash and is also being investigated as an iron ore source.

STATUS AND RESULTS

HiChlor Process Development

A schedule for the next phase of research has been developed and experimental apparatus assembled. Future experimentation will use higher chlorine rates per weight of solid to increase production rate and will be conducted in a vertical bed with gas flow downward. The range of operating conditions required for determination of the mass transfer and kinetically controlled regions of reaction have been investigated. Preliminary designs for two process product separation schemes, one aqueous and the other anhydrous, are presented.

1. Reaction Studies - Information needed to better parameterize the fly ash chlorine reaction system and experiments to collect the necessary data have been identified as follows:

Information to be obtained

1. That range of operating conditions (chlorine velocity, temperature, pressure, etc.) where the system is mass transfer controlled and kinetically controlled.
2. A kinetic model and parameters needed (activation energies, reaction rate constants, etc.) to fit into an overall reaction model.
3. The change in physical characteristics of fly ash, surface area, pore size distribution, and pore volumes as a function of conversion (reaction with chlorine).

Experiments to be conducted

A down flow reactor capable of high gas velocities has been assembled. Experiments will include incremental increases in the chlorine velocity while all other conditions are held constant. Fly ash conversion will be expected to increase with velocity up to a point where further increases in the chlorine velocity will not increase the conversion. At and above this velocity, the reaction rate will no longer be mass transfer dependent and the data needed for calculation of kinetic parameters can be collected.

The mass transfer limited section of the reaction will also need to be modeled. An important parameter is the effective gas diffusion coefficient. There are various methods outlined by Szekely (1) for determination of this parameter and these will be followed. The pore radii and volume must also be measured to determine whether Knudsen or normal molecular diffusion predominates.

In the new experimental apparatus, the reactor is in a down-flow configuration to allow for higher gas velocities. An integrator has been connected to the gas chromatograph output to give quick analysis of the exit stream. A gas sampling loop is designed and nearly assembled that will allow rapid collection of gas samples (one second intervals). The overall experimental system is reliable and should be easy to use.

There are other possible experimental systems and these are being studied. Cahn electrobalances have been used extensively in similar gas-solid reaction systems. In order to utilize the capabilities of such equipment, however, one needs to do pure component studies. Western fly ashes contain mostly lime, alumina, and silica and very little iron oxides. The calcium (lime) could be washed out with a weak acid solution to leave largely alumina and silica. There is a chance that a microbalance could yield useful data for such a two-component system. Chlorinations would be conducted for various time periods and the residues analyzed to determine how much of each component was removed. The microbalance would only indicate the total weight loss (silica and alumina) as a function of time.

The ideal reaction system would be one where the chlorine reacted with a bed of fly ash and the metal chloride products were analyzed at the exit. Several instrument company representatives have been contacted, but no on-line system that will do the desired analysis has been found. The search is being continued.

The use of graphite as the reductant in the chlorinations completed to date has to a degree complicated the reaction system. Two solids, fly ash and graphite, and two gases, chlorine and oxygen, must be considered in modeling the system and interpreting the data. To date this has been handled in the following manner. The gas chromatography data along with the graphite surface area data collected have been used to calculate the graphite reaction rate as a function of the amount of graphite remaining in the sample. Figure 1 is a plot of the reaction rate of graphite (grams/M^2 min.) versus grams of graphite remaining in the sample. Each data point represents the reaction rate for a given amount of graphite remaining at the end of a ten minute interval. The data points span a 120 minute period for each temperature.

The important feature of these data is the linear sections that follow the induction periods. If the total graphite surface area were being utilized the reaction rate (grams/M^2 min.) should be a linear function of the amount of graphite remaining. The linear sections of the curves indicate that this is the case. All of the graphite surface area is being utilized and, therefore, the kinetics of the oxygen-carbon reaction is limiting the total reaction rate of the fly ash-chlorine system. The induction period of each of the curves is not linear because the chlorine available was insufficient and, therefore, not enough oxygen was released to load the graphite surface. After about fifty minutes, excess chlorine was available and the linear relationship resulted.

Figure 2 is a plot of the graphite reaction rate versus the inverse absolute reaction temperature. An activation energy of 41.9 Kcal/G-mole was calculated from this plot. Arthur (2) reports an activation energy of 49 Kcal/G-mole for graphite which is reasonable agreement considering that the graphites could have been quite different.

Both the linear sections of the curves in Figure 1 and the reasonable activation energy in Figure 2 would indicate that fly ash chlorination is limited overall by the graphite-oxygen reaction. Because this limitation of rate is significant, future fly ash chlorinations will include use of a gaseous reductant, e.g., carbon monoxide. When this is done, the kinetics

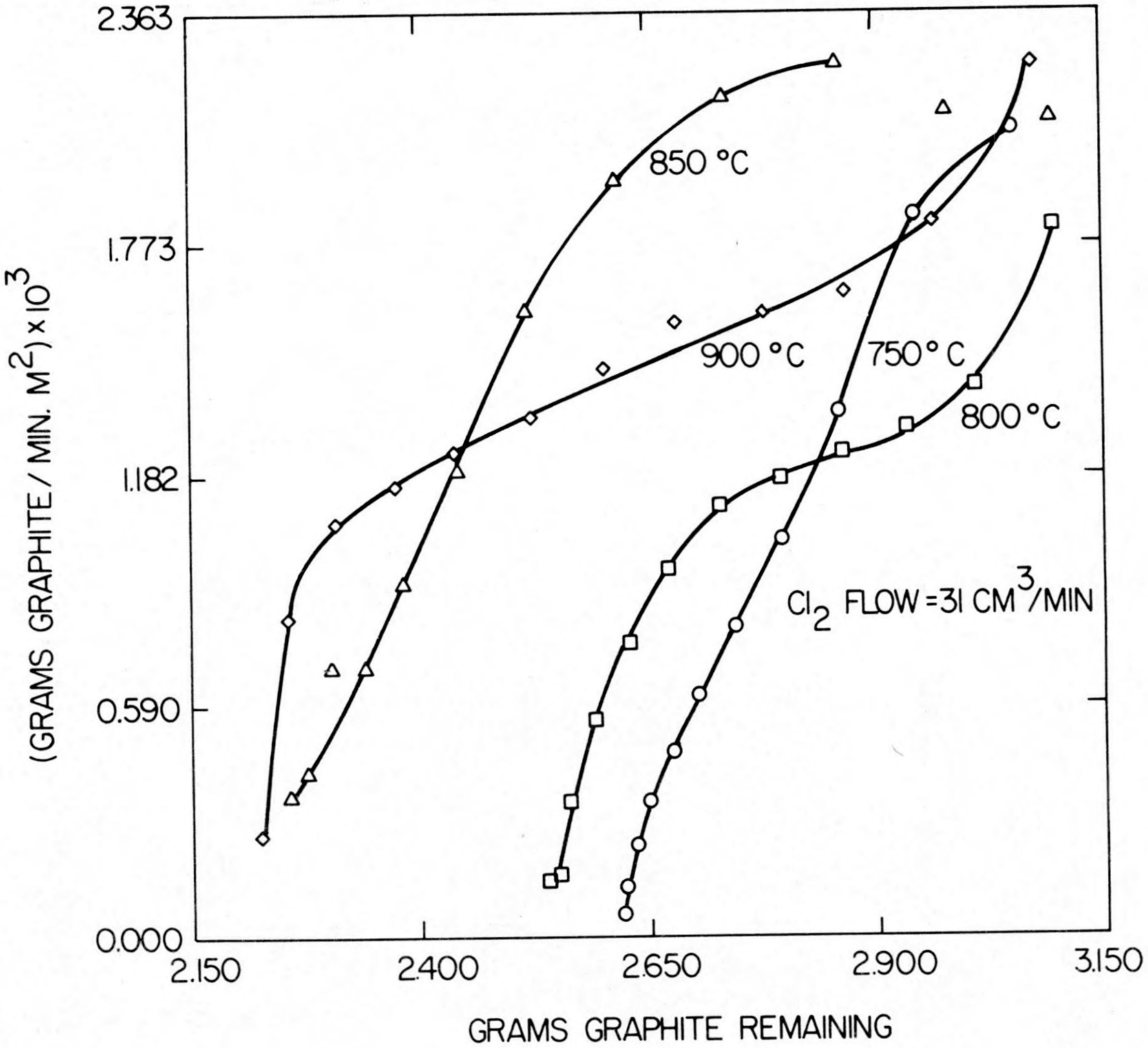

Figure 1. Reaction rate expressed as grams of graphite removed during chlorination vs. grams graphite remaining in sample, for four chlorination temperatures.

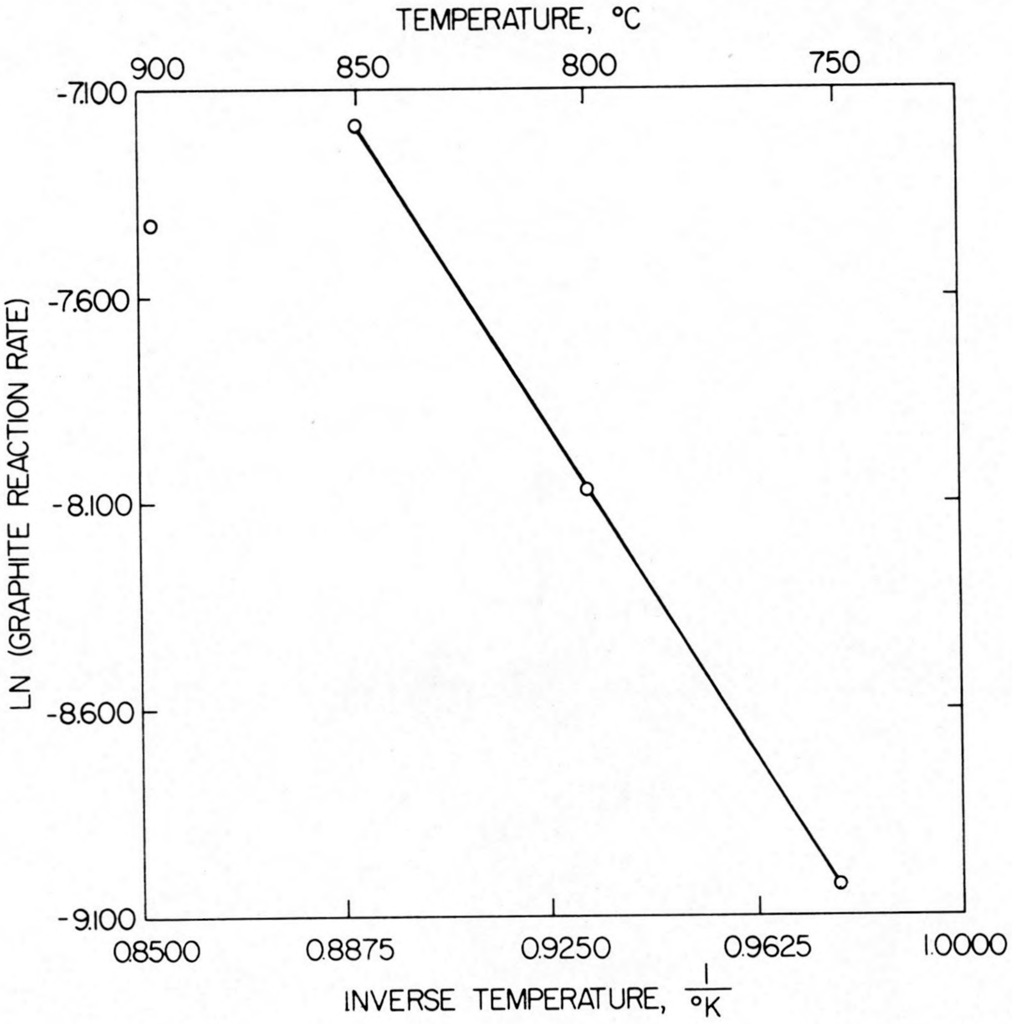

Figure 2. Arrhenius plot for the combustion of graphite in the presence of oxygen and carbon monoxide and carbon dioxide.

of the chlorine-carbon monoxide-fly ash reactions on the fly ash surface can be determined.

2. Product Separation - Recovery and separation of the metal chloride products is difficult. A thorough search of the literature has suggested several possible methods. Work to date is discussed under two general headings, Anhydrous Methods and Aqueous Methods. Results are included for $AlCl_3.6H_2O$ crystallization work completed during this report period.

Anhydrous Methods

Based on chlorination results previously reported, a flow diagram has been prepared for a possible anhydrous separation process. Material balances were determined on the assumption that certain process steps not previously demonstrated experimentally will prove successful.

The need to separate and recycle chlorine and silicon tetrachloride is of primary importance as is the recovery and separation of the metal chloride products.

Several alternatives were considered for many of the process steps before the flow plan shown in Figure 3 was chosen. Condensation of $TiCl_4$ with the less volatile products was ruled out due to the apparent difficulty of recovering the relatively small quantities of $TiCl_4$ from the condensed mixture. An alternative method of $TiCl_4$ recovery in a condensed phase employs liquid $TiCl_4$ as an absorbent for the less volatile chlorides in a packed column, A-2. As an alternative, $TiCl_4$, $AlCl_3$, and $FeCl_3$ can be condensed and/or absorbed, leaving only $SiCl_4$, Cl_2, CO, and CO_2 in the vapor. An evaporation unit would be used to recover $TiCl_4$.

An absorbent (for use in A-1) which will leave $TiCl_4$ in the vapor phase is described in a patent by Sebenik (3) which proposes the use of a fused salt mixture to quantitatively recover $AlCl_3$ and $FeCl_3$ from the chlorination product gases. The chlorination product mixture is first cooled to about 250 degrees to condense any chlorides of Na, K, Mg, and Ca which exit the chlorination reactor. The absorbent is a fused eutectic mixture composed mainly of 40 weight percent $FeCl_3$ and 60 percent molybdenum pentachloride ($MoCl_5$) used at about $88^{\circ}C$. The chlorination products enter the absorber as gases at $250^{\circ}C$. The absorption unit recovers virtually all of the alu-

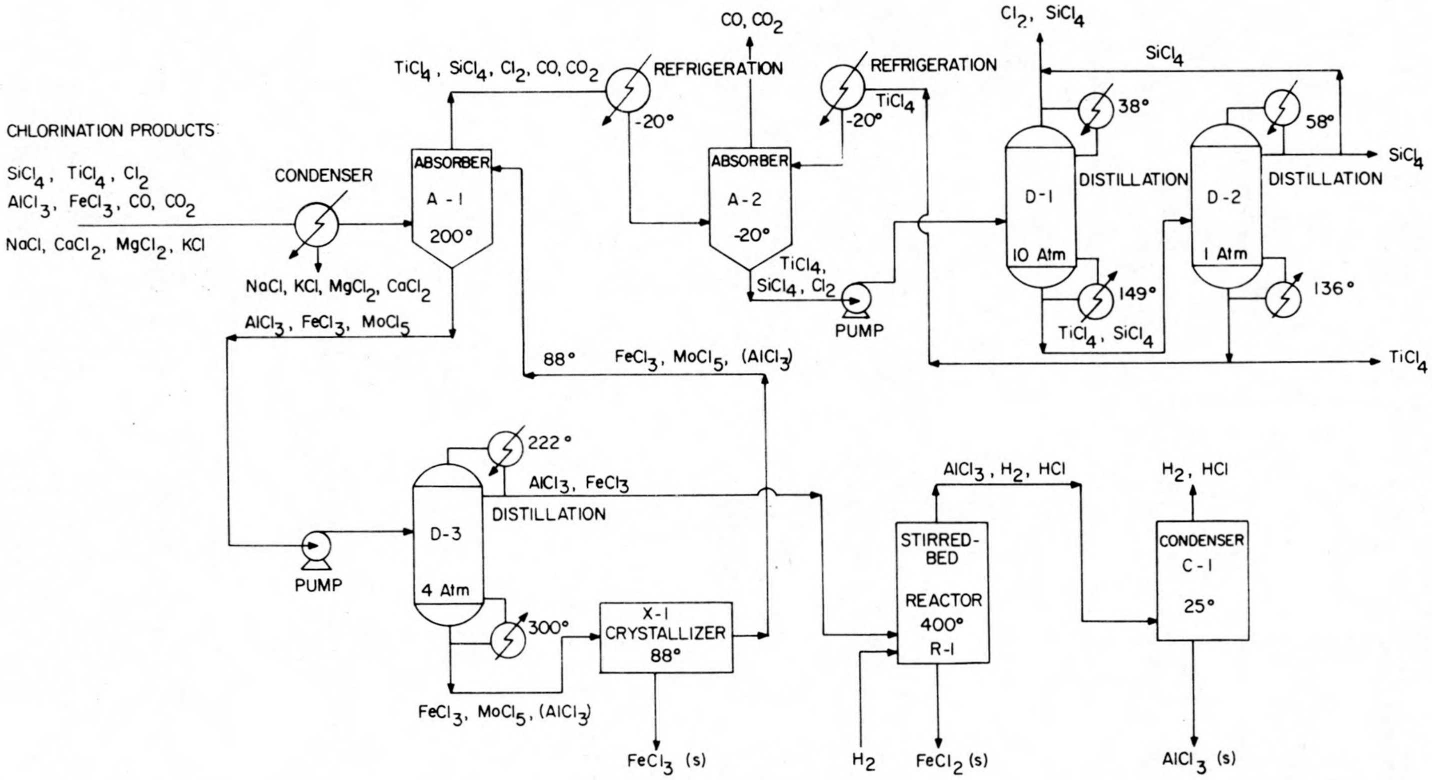

Figure 3. Anhydrous process for recovery and separation of HiChlor products.

minum and ferric chlorides, allowing $SiCl_4$, $TiCl_4$ and the remaining gases to leave as a gas mixture. The fused absorbent-product mixture is subsequently distilled (in D-3) at about 4 atmospheres pressure to yield a liquid mixture of $MoCl_5$ and $FeCl_3$, and gaseous $FeCl_3$ and $AlCl_3$ (mostly as Fe_2Cl_6 and Al_2Cl_6).

A. Recovery of $SiCl_4$, Cl_2 and $TiCl_4$

Turning to Figure 3, the vapor mixture leaving the fused-salt absorber (A-1) must be separated into $TiCl_4$, $SiCl_4$, and Cl_2 as separate fractions. As a first step, a gas-liquid absorption system (in A-2) is used to separate the carbon oxides from the remaining components. The absorbant is liquid $TiCl_4$ at about $-20^{o}C$, a temperature well below the boiling point of $SiCl_4$ and near the melting point of $TiCl_4$. Chlorine is quite soluble in $TiCl_4$ at this low temperature while the carbon oxides are not. The liquid mixture exiting from this absorption unit is readily separated into its components.

The liquid mixture of $SiCl_4$, $TiCl_4$ and Cl_2 from A-2 is stripped of chlorine in a distillation unit (D-1) operating under pressure. The bottom product mixture is stripped in a second column (D-2) to yield pure $TiCl_4$ as a specification grade product.

In summary, the gas mixture leaving absorber A-1 at $200^{o}C$ is cooled to $-20^{o}C$ in heat exchanger E-3 before entering absorber A-2. The resulting solution of $TiCl_4$, $SiCl_4$, and Cl_2 is stripped of chlorine in column D-1 under a pressure of 10 atmospheres to yield a vapor composed of a small amount of $SiCl_4$ and a liquid composed of the remaining $SiCl_4$. This liquid stream is then separated by fractional distillation in column D-2 into pure $SiCl_4$ distillate and $TiCl_4$ bottom product. Silicon tetrachloride distillate from column D-2 is divided into fractions-one to be oxidized to SiO_2 to recover Cl_2 and the other to be recycled to the chlorination reactor. Titanium chloride is also divided - one fraction recycled to absorber A-2 and the other drawn off as specification grade $TiCl_4$ product.

B. Recovery and purification of aluminum chloride

Ferric and aluminum chlorides are absorbed from chlorination product gases in absorber A-1. The resulting fused mixture which exits the absorber is distilled in column D-3 under a pressure of 4 atmospheres to maintain the distillate as a liquid. Aluminum chloride exits column D-3 as distillate at about 220°C while the bottom product, rich in $FeCl_3$, is transferred to a crystallization unit from which solid FeCl is recovered from the melt at 88°C. The remaining fused eutectic is recycled to absorber A-1.

It may or may not be assumed that the aluminum chloride distillate leaving column D-3 is substantially free of iron impurities. If the $AlCl_3$ thus recovered is adequately pure, the separation process ends with a condensation unit at this point, to recover solid $AlCl_3$. If the complex $FeAlCl_6$ occurs in the vapor to a significant extent, there will be an objectionable quantity of iron remaining in the distillate from D-3. This iron would probably not be removable by anhydrous physical methods. One method for the further purification of $AlCl_3$ would be the reduction of iron (III) to iron (II), yielding less-volatile $FeCl_2$. The following reactions are employed in this process.

$$Fe_2Cl_6(g) + H_2(g) \xrightleftharpoons{400^\circ} 2FeCl_2(s) + 2HCl(g) \tag{1}$$

$$2FeAlCl_6(g) + H_2(g) \xrightleftharpoons[400^\circ]{} 2FeCl_2(s) + 2HCl(g) + Al_2Cl_6(g) \tag{2}$$

Equilibrium constants determined for these reactions by use of thermochemical tables (4) and the data obtained by Jorgenson (5) and by Shieh and Gregory (60) indicate that both reactions (1) and (2) proceed to completion at about 400°C and one atmosphere. High reaction rates were observed by McIntosh (7) in the removal of iron from $NbCl_5$ -$FeCl_3$ mixtures via reaction (1). Zirconium chloride ($ZrCl_4$) has also been purified by this method (8).

To accomplish the above, it is assumed that a five-fold excess of hydrogen is fed to a vertical stirred bed reactor (R-1) along with impure Al_2Cl_6 vapor at 400°C. It is further assumed to condense on an inert support such as quartz chips. The solid $FeCl_3$ is assumed to be freed from the quartz surfaces by constant agitation, and withdrawn from the bottom of the reactor as a fine powder. The purified aluminum chloride is condensed by conventional means and HCl and H_2 are recovered as gases.

It is felt that the anhydrous recovery and separation scheme described above is capable of achieving its objectives- the recovery of pure, anhydrous $AlCl_3$ and $TiCl_4$, with the accompanying recovery of chlorine and $SiCl_4$ necessary for recycle to a chlorination reactor. Although the proposed process is based entirely on assumptions and work of others at this time, it provides a sufficient means for determining economic feasibility.

Aqueous Methods

A mostly aqueous process for the recovery of alumina (and possibly TiO_2) is shown in Figure 4. Emphasis is placed on the use of conventional unit operations wherever possible. As in the anhydrous process previously discussed, silicon tetrachloride and chlorine are separated and recovered from the remaining products so that they may be recycled to the chlorination reactor.

In Figure 4, chlorination products from the HiChlor reactor are cooled to about 250°C in a fraction desublimation unit (C - 1) so that alkali earth chlorides may be removed from the product stream. The remaining chlorination products enter a separate condensation unit (C - 2) which operates at about zero°C to recover all of the $TiCl_4$ as a liquid, plus solid $FeCl_3$ and $AlCl_3$. This second condenser may also be a conventional desublimation unit or it may be a spray condenser in which a spray of cold $TiCl_4$ acts as a direct coolant for the metal chlorides. Titanium chloride, in the slurry of condensed products which would exit a spray condenser, would be recovered by evaporation. While a conventional solids condensation unit might operate less efficiently than a $TiCl_4$ spray condenser, the additional process steps required for $TiCl_4$ recovery render spray condensation or absorption by $TiCl_4$ less desirable for the proposed process.

From the second condensation unit all of the chlorine and carbon oxides, and most of the $SiCl_4$, exit as gases. This resulting mixture of $SiCl_4$, Cl_2, CO and CO_2 is separated by absorption. Solubility data for chlorine in $SiCl_4$ indicate that an absorber (A-1) operating at -40 to -30°C with $SiCl_4$ as the absorbing medium, can recover chlorine quantitatively. The gases exiting the absorber, essentially free of Cl_2 and $SiCl_4$, can be oxidized to CO_2 and vented. Alternatively, CO can be recovered for recycle to a HiChlor reactor.

Liquid $SiCl_4$ with dissolved chlorine exits the absorber and is pumped to a pressurized stripping column (S-1) from which a Cl_2-$SiCl_4$ distillate is recovered for recycle to a chlorination reactor. Excess $SiCl_4$ is oxidized to silica and recyclable chlorine.

Anhydrous metal chlorides, recovered from the chlorination product stream, are fed to and dissolved in a stirred tank (T-1) containing water or dilute aqueous HCl. The resulting solution may be filtered to remove any undissolved solids (such as SiO_2) that may form under the conditions of the dissolution.

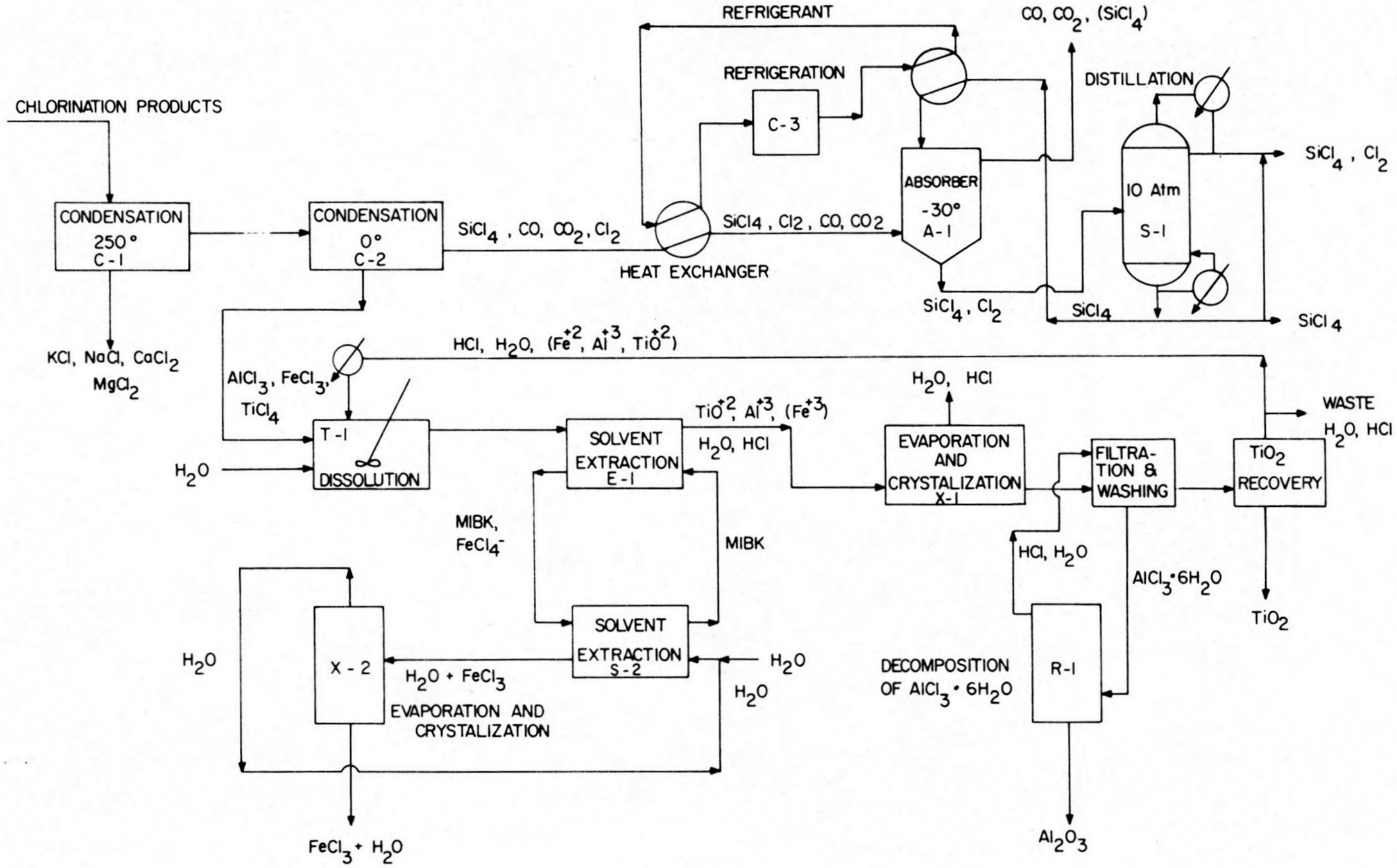

Figure 4. Aqueous process for recovery of Al_2O_3 from HiChlor process products.

The aluminum in the solution is then recovered by crystallization of aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$).

Iron removal by both solvent extraction and ion exchange are mentioned in the literature. For this process, solvent extraction of iron is carried out in a countercurrent extractor (E-1) by use of methyl isobutyl ketone (MIBK) as the organic phase in contact with aqueous $AlCl_3$ maintained at 7 normal with respect to HCl. It is assumed that no aluminum or titanium is extracted by the organic phase. Distribution coefficients of the chloroferrate ion ($FeCl_4$) in MIBK have been reported by Specker and Doll (9). The iron-rich extract from this extraction step is sent to a stripping unit (S-2) in which iron is removed from MIBK by water.

Experimental crystallization of $AlCl_3 \cdot 6H_2O$. Since little information regarding crystallization of $AlCl_3 \cdot 6H_2O$ in the presence of impurities appears in the literature, an experiment was designed and conducted to study the apparent effect of the presence of iron on the crystallization of pure aluminum chloride hexahydrate. This information was needed so that the tolerable concentration of iron in an $AlCl_3 \cdot 6H_2O$ crystallizer (X-1) could be determined. The results of this experiment allow the specification of necessary iron removal steps prior to the crystallization of $AlCl_3 \cdot 6H_2O$.

Standard stock solutions of aluminum and iron were prepared by dissolving known quantities of the metals in hydrochloric acid. From these stock solutions, two sets of six different solutions were prepared from which $AlCl_3 \cdot 6H_2O$ would be crystallized. Each solution was about 10 Normal in HCl and contained 2.133 parts per thousand Al. The iron contents of the solutions ranged from zero to 1.00 milligrams of iron added per 100 ml sample.

Each of the above solutions was evaporated at about 95 degrees until only traces of liquid water remained. The resulting solids, yellow in color due to the presence of iron, were transferred to and filtered in a fritted-disk beuchner funnel by addition of 10 ml of cold concentration HCl to the solids and pouring the resulting slurry onto the frit. One duplicate of each solution was washed with a total of 40 ml of cold HCl. The other sample of each solution was not washed.

The hydrated $AlCl_3$ crystals were then dissolved on the frit with a minimal amount of water. The $AlCl_3$ solution, now held in the beuchner funnel, was drawn into a second filtering flask. The frit was washed with water several times to insure complete recovery of $AlCl_3$. Finally, the $AlCl_3$ solution in the filtering flask was poured into a 50 ml volumetric flask and diluted to the mark with water.

The resulting 50 ml samples, consisting of concentated $AlCl_3$ solution with $FeCl_3$ as a contaminant (in varying amounts depending on the degree of cocrystallization or adsorption), were analyzed for iron and aluminum by use of a Perkin-Elmer model 373 atomic absorption spectrophotometer with the appropriate standard solutions. The yields of $AlCl_3 \cdot 6H_2O$ and the degrees of iron entrainment were thus determined.

The effect of iron concentration and washing on the purity of crystallized $AlCl_3 \cdot 6H_2O$ is shown in Table 1. An acceptable iron concentration is estimated to be 0.35 percent iron as Fe_2O_3 in Al_2O_3. The limit of iron removal appears to be controlled mainly by iron present in the washing liquor.

Table 1. Effect of Solution Iron Concentration on Degree of Cocrystallization and Purification of Crystals by Acid Washing.

Wt. Percent Fe in Solution	Wt. Percent Fe in $AlCl_3 \cdot 6H_2O$ Crystals		Percent of Al Crystallized	
	As Precipitated	Acid Washed	As Precipitated	Acid Washed
0.354	0.044	0.00833	90.2	87.3
0.177	0.034		91.3	
0.0355	0.0069	0.00444	82.0	75.9
0.0177	0.0053	0.00434	90.1	77.6
0.00355	0.0041	0.00361	91.4	83.4
--	0.0036	0.00332	89.5	85.5

The presence of iron during crystallization has a lesser effect. When no iron is added, iron impurity present in the evaporation step because the reagent HCl contained 0.05 ppm iron is recovered quantitatively with the aluminum chloride. With adequate washing, purities of products obtained in this experiment met established specification (12) with respect to iron for all initial iron concentrations used.

Alumina Recovery. Returning to the flowsheet in Figure 4, aluminum chloride hexahydrate, recovered from a crystallizer (X-1) under the conditions described in the above experiment, will be pure enough to be decomposed to specification grade alumina following filtration and washing. This is accomplished by heating the $AlCl_3 \cdot 6H_2O$ to about 110 degrees. The decomposition of $AlCl_3 \cdot 6H_2O$ takes place in a reactor (R-1) as follows:

$$2AlCl_3 \cdot 6H_2O\ (s) \rightleftharpoons Al_2O_3\ (s) + 6HCl(g) + 9H_2O\ (g). \qquad (3)$$

Water and HCl, liberated by the decomposition reaction, are recycled to the crystallizer and provide ample chloride to force the crystallization of the aluminum chloride hydrate.

Titanium Recovery. Separating titanium from dilute solutions in the presence of concentrated HCl is arduous, and is probably not a practical endeavor from the standpoint of cost or efficiency. The separation is necessary, however, to prevent accumulation of titanium in the separation process. Solvent extraction of titanium from an aqueous phase was reported by Seeley et al. (13) and Kiss (14). In the process described by Seeley, titanium was extracted from nitric acid solutions with di (2-ethylhexyl) phosphoric acid in diethylbenzene. An acid pH of at least 1.4 was required. Kiss reported quantitative extraction of a titanium cupferron chelate from dilute acid into chloroform. Either extraction method necessitates the restoration of a higher HCl concentration later in the process.

There is also the possibility of evaporating the Ti-containing liquors or treating those liquors with a strong base to produce a hydrated TiO_2 precipitate. Another procedure would be ion exchange recovery of Ti, though the elution of Ti generally requires highly corrosive acids such as concentrated hydrofluoric acid or HF-HCl mixtures.

Given the possibilities for titanium recovery outlined above, the titanium purge step in the aqueous separation scheme (Figure 4) is left unspecified at this time.

Lime-Soda Fly Ash Sinter Process Development

1. Solubility of the Lime-Soda Sinter - The recovery of alumina from coal fly ash using the lime-soda sinter process is the result of reactions which occur when a mixture of fly ash, limestone, and soda ash is sintered at a temperature of about 1200 C, and then extracted with a dilute soda ash solution. Extraction of the sintered material produces a complex solution of calcium and sodium aluminates and silicates. At the pH (about 13) of the solution, both aluminate ions and silicate ions are highly soluble.

The data of Table 2, calculated from solubility product values (1), indicate the individual solubility limits of different ions of calcium, aluminum, and silicon in solution as a function of solution pH. At each pH, several ionic forms of each element may exhibit some solubility, but at each pH one ionic form for each element will be more soluble. For example, at pH 6 soluble calcium will be Ca^{+2}, soluble aluminum will be the aluminate AlO_2^- , and soluble silica will be as $HSiO_3^-$; at pH 14, dissolved calcium will be Ca^{+2} and the solubility limit will be very low, aluminum will be soluble as AlO_2^- and much more soluble than at pH 6, and dissolved silicon will be in the form of the silicate ion SiO_3^{-2} and highly soluble.

In the course of experimentation, extracted sinter filtrate samples at several pH values have been analyzed and the amounts of dissolved calcium, aluminum, and silicon determined. These data are shown in Table 2 for comparison between the actual ion solubilities in extracted filtrates and the levels attainable if each ion were in solution individually. The values are presented as elemental ppm of Ca, Al, and Si, although it is understood that the elements are in solution as aluminate and silicate ions. Expressing the solubility limits as elemental ppm facilitates comparison with measured values from atomic absorption (AA).

The values measured for filtrates containing mixtures of these ions are presented for pH of 9, 10, 11, and 13. These concentrations indicate that common ion effects with calcium are limiting the solubilization. Aluminum solubility is limited for all filtrates with pH 11 and above (note the correspondence of values at pH 9, 10, and 11), and the silicon solubility is limited

Table 2. Solubilities for Calcium, Silicon, and Aluminum in Aqueous Solution as a Function of Solution pH(1).

Solution	Ion Form (Values are ppm Ca, Al, or Si)				
pH	Ca^{+2}	Al^{+3}	AlO_2^-	$HSiO_3^-$	SiO_3^{-2}
1	5.2×10^{24}	1.4×10^{10}			
2	5.2×10^{22}	1.4×10^{7}			
3	5.2×10^{20}	1.4×10^{4}			
4	5.2×10^{18}	1.4×10		2.8×10^{-2}	
5	5.2×10^{16}	1.4×10^{-2}		2.8×10^{-1}	
6	5.2×10^{14}	1.4×10^{-6}	2.4×10^{-2}	2.8×10^{0}	
7	5.2×10^{12}	1.4×10^{-9}	2.4×10^{-1}	2.8×10^{1}	2.8×10^{-4}
8	5.2×10^{10}	1.4×10^{-12}	2.4×10^{0} (50)*	2.8×10^{0} (4)*	2.8×10^{-2}
9	5.2×10^{8}		2.4×10^{1} (190)*	2.8×10^{3} (2.3)*	2.8×10^{0}
10	5.2×10^{6}		2.4×10^{2} (2400)*	2.8×10^{4} (9)*	2.8×10^{2}
11	5.2×10^{4}		2.4×10^{3}	2.8×10^{5}	2.8×10^{4}
12	5.2×10^{2}		2.4×10^{4} (5000)*	2.8×10^{6} (50)*	2.8×10^{6}
13	5.2×10^{0}**		2.4×10^{5}	2.8×10^{7}	2.8×10^{8}
14	5.2×10^{-2}		2.4×10^{6}	2.8×10^{8}	2.8×10^{10}

* PPM solubilities of Al and Si for actual fly ash sinter extract filtrates, (values in parentheses).

** Low Ca^{++} solubility is limiting the SiO_3^{-2} and AlO_2^- concentrations.

at all measured pH values, 9 to 13. In high alumina solubility sinter mixtures, calcium and silica are combined and the calcium silicate compound is not soluble at pH 13 even though the silicate ion is highly soluble because calcium is insoluble. If any aluminum is combined with calcium it also is insoluble, but the aluminum combined with sodium will be highly soluble. It is not evident from these data but there are also common ion effects between dissolved silicates and aluminates. If sufficient silica dissolves it will precipitate sodium aluminum silicates from solution.

Table 2 also shows an increased solubility for calcium as the solution becomes less basic. Increased calcium dissolution permits higher dissolved silicon concentrations which explains observed increased silicate concentrations in the water used to wash extracted sinter residues. Desilication of the extraction filtrates may result if pH is increased. The dissolved silicon concentration must be decreased from the 50 ppm level shown on Table 2 (pH 13) to about 2 ppm before the contained aluminum can be precipitated as aluminum trihydroxide and calcined to specification grade alumina for production of aluminum metal. At increased pH, calcium will precipitate removing some aluminum and silicon with it, but lowering the silicate concentration.

Table 3. Dissolution of Lime-Soda Fly Ash Sinters as a Function of Solid to Liquid Extraction Ratio

Solid/Liquid Ratio $MlNa_2CO_3$/2.5 g Sinter	Sinter Composition *					
	2.4 - 0.7			2.2 - 1.2		
	% Al_2O_3 Dissolved	g Al_2O_3 Dissolved	mg SiO_2 Dissolved	% Al_2O_3 Dissolved	g Al_2O_3 Dissolved	mg SiO_2 Dissolved
50	81	0.210				
25	79	0.208	2.7	95	0.240	1.8
17	77	0.203	2.2			
15				95	0.239	2.3
9	77	0.204				

* Composition of fly ash, soda ash, limestone mixture before sintering, moles CaO/mole SiO_2 - moles Na_2O/mole Al_2O_3. The fly ash used (C-1) is from an Illinois--Kentucky bituminous coal and was mechanically separated.

Sinter extraction compositions for a range of solid to liquid extraction ratios are given in Table 3. Dissolved alumina and silica concentrations for two different lime-soda fly ash sinter compositions and for a range of solid to liquid extraction ratios are listed. At the extraction conditions used (3 wt. percent Na_2CO_3, 65 C, and 10 minutes) the dissolutions of alumina and silica are dependent on the composition of the sinters, not on the solid to liquid ratio. The amounts of alumina and silica dissolved over a range of solid to liquid ratios are nearly equal. The solubilities may be controlled by the calcium and if so, the calcium in calcium silicate and calcium aluminate does not dissolve nor does the alumina and silica combined with it. The 2.4 - 0.7 sinter, which contains more calcium aluminate than the 2.2 - 1.2 sinter, shows a lower alumina recovery, 80 percent vs. 95 percent.

The effects of the sinter and extraction times were also investigated to determine the relative rates for solubilization of alumina and silica. Samples of the 2.2 - 1.2 lime-soda fly ash mixture were sintered for times of 18, 30, and 60 minutes and then leached for 10 minutes. Another sample was sintered 60 minutes and then leached for times of 2, 5, 15, and 20 minutes. As shown on Table 4, the concentration of both Ca and Si decreased with longer sintering times and shorter extraction times. The alumina dissolved quickly from the sinter and, as the extraction time decreased, less silica dissolved.

Table 4. Solubility of Sinter Ions as a Function of Sintering Times and Extraction Times

Sintering Time, Min.	Extraction Time, Min.	2.2 - 1.2 Sinter*		
		PPM Dissolved Material		
		Ca	Al	Si
18	10	2.6	4600	60
30	10	1.9	4800	50
60	10	0.1	4875	36
60	2	3.4	4320	21
60	5		4680	38
60	15		4430	44
60	20	5	3530	26

* C-1 fly ash

2. Decomposition of Calcium Sulfates - The results of a literature search showed that thermal decomposition of calcium sulfate requires a temperature of about 1400C. It can be decomposed in reducing atmospheres at about 1100°C, however, and the kinetics of the reductive decomposition are increased by use of a gas flow to remove reaction products from the reacting surfaces.

Tests were conducted for reductive decomposition of the calcium sulfate and sulfite in flue gas scrubber sludge (FGSS) and in fluidized bed combustion (FBC) residue. As an alternative to providing a reducing gas, mixtures of samples containing powdered graphite were roasted in muffle and tube furnaces. Loose powder mixtures were first roasted but gave limited conversions. The experiments were then changed to the use of mixtures in pelleted form. The results for the reductive decomposition tests are shown in Table 5. The FGSS sample has a L.O.I. of over 20 wt. percent, which is due to the decomposition of $CaCO_3$.

Table 5. Reductive Decomposition of Flue Gas Scrubber Sludge and Fluidized Bed Combustion Residue Mixtures Containing Graphite*

Sample	Form	Percent Weight Loss from the Sludge or Residue	
		1000°C	1100°C
FGSS	Powder	20.4 (L.O.I.)	
FBC	Powder	0.2 (L.O.I.)	
FGSS-20 wt % Graphite	Powder	21.5	
FGSS-20 wt % Graphite	Pellet	21.5	24.2
FGSS-20 wt % Graphite	Pellet w/N_2 flow		32.4**
FBC-20 wt % Graphite	Powder	3.4	
FBC-20 wt % Graphite	Pellet	6.8	8.0
FBC-20 wt % Graphite	Pellet w/N_2 flow		27.1**

* Runs for one hour duration. ** FGSS contains 35.06 wt. percent CO_2 plus SO_2. FBC contains 25.48 wt. percent CO_2 plus SO_2.

The FBC residue contains no $CaCO_3$, and the L.O.I. is negligible.

These data for sample decompositions show that calcium sulfate and sulfite can be decomposed in admixture with graphite powder so that the contained lime can react in the lime-soda sintering reactions. Decomposition is increased significantly by pelleting the material and using a gas flow to sweep away the reaction products. The weight percent loss for the sludge (FGSS) and residue (FBC) pellets, heated one hour at 1100°C with a N_2 gas flow, agree well with the weight percent CO_2 and SO_2 contained in each sample.

Mixtures of fly ash, FGSS sludge, soda ash, and graphite have been prepared for sinter testing. Mixtures have been prepared for investigation of both lime-soda-fly ash and lime-fly ash sintering reactions using waste scrubber sludge as the lime resource.

3. <u>Sinters with Commercial Limestones</u> - Experiments were conducted to investigate the maximum yield of aluminum from the sub-bituminous western coal fly ash by sintering at different ratios of CaO/SiO_2 and Na_2O/Al_2O_3 using commercial limestone. Results of the experimental work are summarized in Tables 6 and 7. The experiments were conducted at 1100°C with 9 different sinter compositions, using both reagent grade $CaCO_3$ and high grade limestone as quarried.

The data in Table 6 show that there is no significant difference in alumina recovery when commercial limestone is used in place of reagent grade $CaCO_3$. A comparison between these results and data collected by a different researcher (15) using reagent grade $CaCO_3$ is shown in Table 7. The values are very similar and when they are plotted on Figure 5 they agree with the predicted recovery curves. These results obtained by different researchers over two years apart demonstrate the reproducibility which can be obtained with the lime-soda sinter process.

Table 6. Comparison of Alumina Recovery from Lime-Soda Sinters Prepared using Reagent Grade $CaCO_3$ and Commercial Limestone.

Sinter Mixture Composition, Mole Ratios		Percent Alumina Solubilized*	
$\frac{CaO}{SiO_2}$	$\frac{Na_2O}{Al_2O_3}$	Reagent $CaCO_3$	Commercial Limestone
2.6	0.8	91.71	84.47
2.4	0.8	84.4	83.6
2.2	0.8	62.5	65.02
2.6	1.0	79.2	81.05
2.6	1.2	74.10	78.5
2.4	1.2	90.77	98.44
2.4	1.0	90.18	88.95
2.2	1.2	92.02	95.38
2.2	1.0	82.40	85.55

* 1 hr. sinter at 1100°C, 10 min. extraction at 65°C using 3 wt. percent Na_2CO_3 solution. Subbituminous fly ash used.

Table 7. Comparison of Extraction Data for Reagent $CaCO_3$ Sinters with Results Obtained in Previous Research.

Sinter Mixture Composition, Mole Ratios		Percent Alumina Solubilized*	
$\frac{CaO}{SiO_2}$	$\frac{Na_2O}{Al_2O_3}$	Paper (IS-M- 177)(15)	This Work
2.6	0.8	91.55	91.71
2.4	0.8	84.23	84.4
2.2	0.8	65.95	62.5
2.6	1.0	--	79.2
2.6	1.2	84.67	74.10
2.4	1.2	91.87	90.77
2.4	1.0	91.75	90.18
2.2	1.2	92.89	92.02
2.2	1.0	---	82.40

* 1 hr. sinter at 1100°C, 10 min. extraction at 65°C using 3 wt. percent Na_2CO_3 solution. Subbituminous fly ash used.

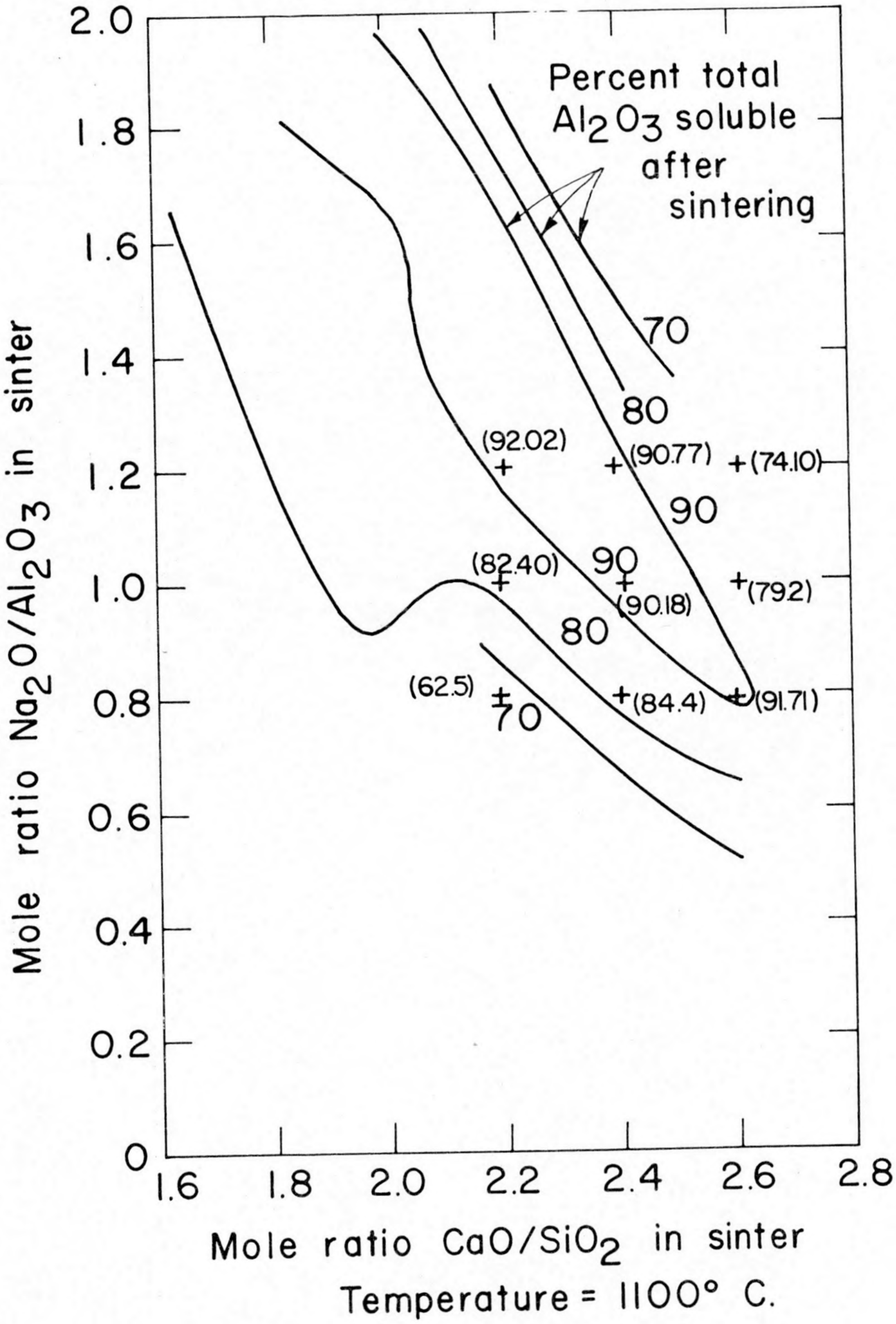

Figure 5. Lines of constant alumina recovery as a function of sinter feed composition for reagent grade $CaCO_3$ at 1100°C (Figure from paper (15)). Alumina recovery percentages for this research are shown in parentheses.

Iron-Rich Fraction of Coal Fly Ash

1. Heavy Medium Material for Coal Beneficiation - During this report period, interest has been expressed in expanding the scale of work completed earlier comparing magnetically separated coal fly ash and natural magnetite as heavy media for coal washing. In the earlier work, results from bench scale tests with 200 gram batch samples of Iowa coal showed that heavy media suspensions prepared from the iron-rich fraction of fly ash did beneficiate the coal satisfactorily.

An industrial company, Halomet, Incorporated, Manlius, NY, has developed a process for magnetically separating commercial quantities of fly ash, and has proposed that the D.O.E. conduct larger scale coal washing tests to demonstrate the value of its product in the preparation of heavy media. On February 12, 1980, a meeting was held at the Bruceton Research Center, Pittsburgh, PA, to discuss research which will demonstrate the feasibility of using magnetically separated iron-rich coal fly ash in coal washing.

Participants at this meeting were three representatives of the DOE/PETC Preparation Group, Al Deurbrouck, Richard Killmeyer, and Richard Hucko; two individuals from Penelec's Homer City coal preparation plant, James Tice and Richard Bosold; two individuals from Halomet, Dr. Robert Aldrich, president and Stanley Vankatesen, consultant; and M. J. Murtha representing Ames Laboratory. Dr. Aldrich proposed that a set of tests using the Halomet product as the heavy medium in commercial coal beneficiation equipment be conducted. Halomet has equipment to produce 2 to 5 tons of magnetic fly ash in a 24 hr. period. Prior tests of this type have been mentioned in some publications but no data have been given. The Consolidated Coal Company was associated with some of the reports. Inquiries by Mr. Killmeyer produced a report which showed that, although full scale coal beneficiation tests using the iron-rich fraction of fly ash were scheduled at Consolidated Coal, the tests were canceled because sufficient magnetic fly ash was not available. Some smaller scale jig tests were run though, and these were reported to be highly successful.

A proposal has been submitted since the Bruceton meeting for tests comparing commercial magnetite media and magnetic fly ash media suspensions in a heavy media cyclone circuit at the Iowa State University Coal preparation plant. In addition, characterization determinations and rheology studies will be conducted for magnetic fractions of fly ashes obtained from different parts of the country.

In addition to demonstrating the quality and stability of magnetic fly ash media suspensions, it is necessary to show long-term servicability of the solid particles. A test loop will be built to determine ash and magnetite particle long term attrition, and the erosion of a range of construction materials. Because of the spheroidal ash particle shape it is assumed that fly ash will be less abrasive but this must be demonstrated. The degree to which fly ash particles will fracture during extended use in a washing circuit must also be investigated.

2. Chemical Treatment of Magnetic Fly Ash - This work is directed toward reduction of the silicate and aluminate contents of the iron-rich fraction of fly ash so the residue can be used as iron ore. Experimental work to date (caustic digestions) has resulted in low dissolutions of alumina from the ash particles. These data, together with information obtained from the literature indicate that either the higher content of silica in the leach solution inhibits alumina dissolution or insoluble calcium or sodium aluminosilicates form and precipitate. There is also the possibility that some alumina is not assessible and hence does not react. It may be dissolved in the vitreous iron oxide structure.

To determine where the unreacted alumina and silica are in the leached ash, samples of leached and unleached ash are currently being subjected to electron microprobe examination. The major elements present are calcium, alumina, silica and sodium. These tests may also show if insoluble compounds are being formed during the leaching operation.

Figure 6 is a plot of time versus aluminate concentration in the leach solution. The alumina concentration goes through a maximum very quickly and then decreases. This would suggest that a secondary reaction is precipitating alumina to some degree.

Figure 7 shows the molar concentration of aluminate versus silicate in the leach liquor for several digestions. At 100 and 140 g/l, alumina is precipitated during the time span between fifteen minutes and 1 hour. The precipitation is more pronounced at the 140 g/l level. At 70 g/l, no change takes place between fifteen minutes and one hour. The 100 g/l and 140 g/l runs are in the region of silica saturation. At 70 g/l almost all the silica is removed yet the silica content is below saturation. Therefore, an excess of silica appears to cause the precipitation of alumina.

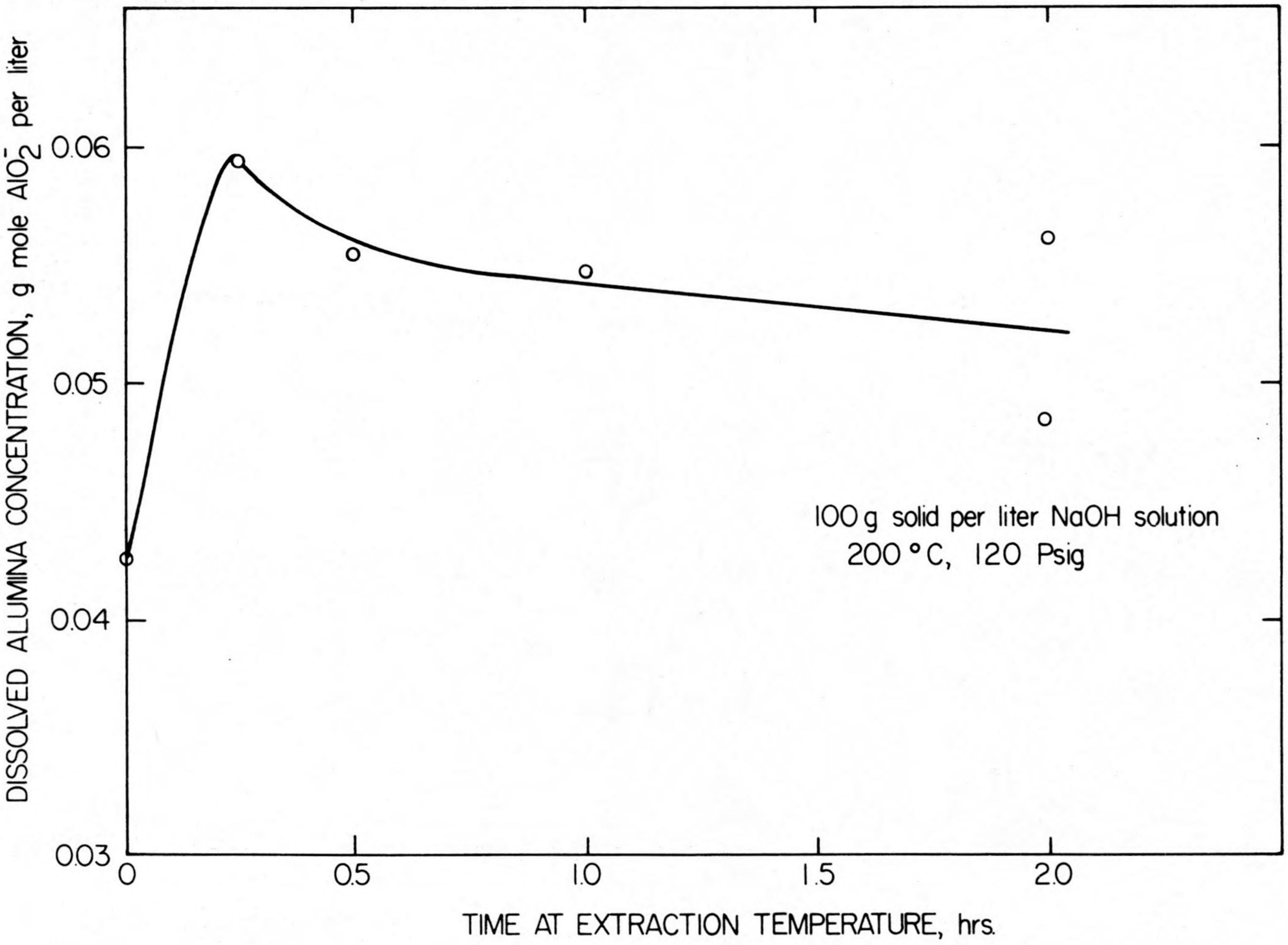

Figure 6. Effect of extraction time on the concentration of dissolved alumina in the solution on completion of extraction.

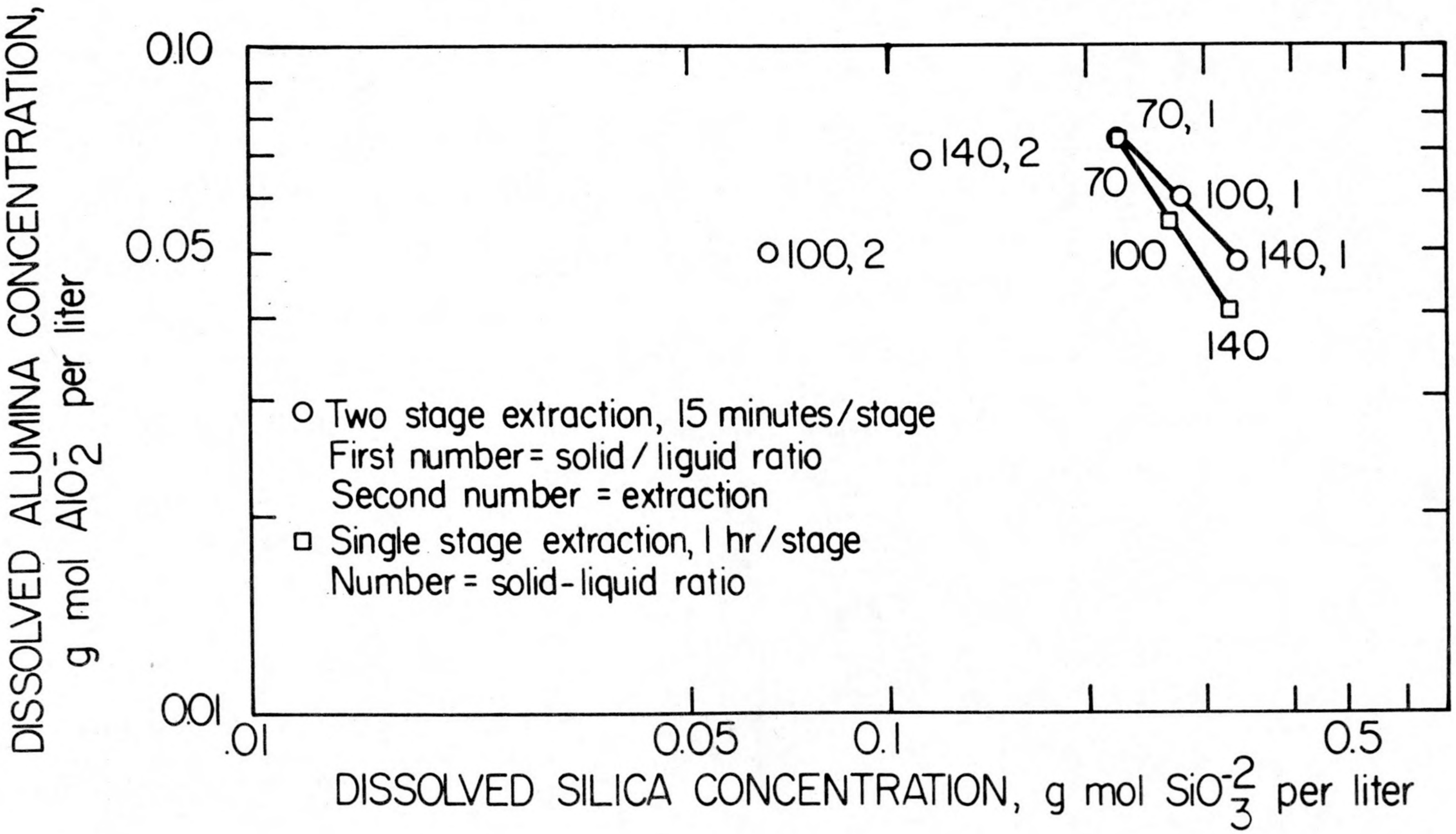

Figure 7. Relationship of the concentrations of dissolved alumina and silica for caustic extractions of magnetic fly ash, a comparison of single and two-stage extraction stages.

Also of interest are the results when a second stage leaching was used. The digestions were carried out with fresh 30% NaOH solutions so there should have been a minimal amount of silica present to interfere with alumina dissolution. In spite of this, the remaining alumina was still not solubilized, indicating that a fraction of the ash is either present as, or is converted to, a form that is insoluble in aqueous sodium hydroxide. A calcium aluminosilicate may be formed as the aluminosilicate glass is broken down, or sodium aluminosilicates may precipitate as the aluminate concentration increases. A combination of these two actions may also be taking place. A certain amount of sodium contamination has been noted in the solid residues. This could be due to the presence of sodium aluminosilicates. The electron microprobe work should help determine if other elements are combined with the aluminum.

Two series of experiments to determine the chemical content of magnetic ash fractions separated at different magnet power settings has been completed. The first was a series of magnetic separations of the Missouri magnetic ash that had first been microground. Table 8 gives the results of these tests. The iron contents are incomplete because of difficulties in the chemical analysis.

Table 8. Chemical Analyses of Magnetically Separated Fractions of a Microground Missouri Magnetic Ash Sample when Reseparated at Different Magnet Power Settings.

Magnetic Power Percent Maximum Voltage	Wt. Percent Magnetics Collect.	Chemical Composition of Magnetics, Fe_2O_3	Al_2O_3	SiO_2
30	32.8	69.8	7.6	17.2
37	81.2	N.A.	7.8	20.9
45	93.2	N.A.	7.6	20.7
Feed	--	65.5	8.6	19.8

Examination of these results indicates that very little glass material is liberated from the magnetic fraction. This work along with the work on chemical beneficiation of the microground material leads to the conclusion that there is little to be gained by microgrinding the magnetic fraction.

The second experiment dealt with the effect of magnetic separator setting on the composition of the iron-rich fraction obtained. Table 9 gives the results for this experiment.

Table 9. Chemical Analyses of Magnetic Fractions Separated From Missouri Fly Ash at Differential Magnet Field Strengths.

Magnet Power Range, Percent Max. Voltage	Magnetic Fraction Percent of Feed	Chemical Composition of Magnetics, Wt. %		
		Fe_2O_3	SiO_2	Al_2O_3
0 - 30	2.0	78.7	12.1[x]	6.5[x]
30 - 45	16.3	74.1	15.8[x]	7.9[x]
45 - 60	4.8	56.0	34.6	10.8
60 - 75	2.4	46.5	38.0	11.8

[x] These compositions need to be checked because of potential errors in the chemical analysis.

From Table 9 it is apparent that the bulk of the magnetic material is obtained in the 30 - 45 percent of maximum voltage range. Percent voltage refers to the fraction of maximum available voltage that is applied across the coils of the separator. The voltage range is from 0 to 108 volts while the current varies from 8 to 25 amperes and is a function of the voltage. It also appears that the magnetic fraction drops off in quality significantly at field strengths above the 45 percent voltage level.

3. Magnetic Separation of Coal Fly Ashes - Data from the magnetic separation of dry coal fly ash using commercial rotary drum magnetic separators (carried out in the laboratories of several separator manufacturers) indicate that the quality of the separations is quite poor. Agitation in the feed stream and on the magnet surfaces is required to physically separate the magnetic and nonmagnetic particles of electrostatically precipitated fly ashes. The Ames Laboratory-built moving-field magnetic separator used for the work to date produces an expanded-bed phase at the magnet surface as a result of cycling field strengths

and gradients. For some fly ashes, even this agitation level has not been sufficient to break the attractive forces of the very small, charges particles.

Finely divided charged particles can normally be separated more satisfactorily by wet magnetic separation. Mixing the fly ash with water to form a dilute suspension should dissipate the charges so the magnetic separation can be made. The magnetic susceptibilities of fly ash particles are quite high and high intensity magnets will recover most of the iron-rich fly ash as a magnetic fraction. By using a low field strength (100 to 300 G,) and wet separation, a low-volume magnetic fraction containing mostly iron oxide should be recoverable.

The above concept was tested by sending a large fly ash sample to Carpco, Inc., Jacksonville, FL, where a high quality magnetic separation was made by passing a fly ash-water slurry through a canister matrix of steel spheres using a field intensity of 500 G. Consideration was given to purchasing this Carpco unit but it was learned that results obtained are not suitable for scale up to commercial slurry application. The unit was intended as a polishing filter for filtrates containg a small amount of solids.

Discussions of scale-up data required for design of a carousel-type continuous magnetic separator with manufacturers resulted in the purchase of a canister-type unit: a Frantz Ferrofilter equipped with a 3-amp D.C. power supply. Laboratory scale magnetic separations can now be conducted to determine optimum slurry flow rates per unit of canister cross-sectional area, optimum solids content, and optimum magnetic field and gradient. These results will be compared to the data obtained for dry separations and used to specify the PDU magnetic separation equipment.

Investigation of the Substructure of Coal Fly Ash Particles

To determine the mineralogical composition and distribution of crystalline phases in high-iron Missouri and Kentucky ashes, x-ray diffraction patterns of ash fractions were studied. A theta-theta diffractometer with copper radiations was used. The slit was 1^o and the step scanning rate was 0.05^o per 5 seconds. The diffractometer was equipped with a graphite crystal monochronometer.

Samples were spread on a sample holder and properly aligned. All samples were scanned from 15^o to 70^o. Beam intensities were recorded on a strip chart recorder and a computer printout. The 2-theta values were read from the computer printout. Crystalline phases were identified from diffraction patterns. The diffraction patterns provided a means for determining the crystalline composition as well as qualitatively allowing comparison of crystalline component distribution in the size fractions of each fly ash.

The diffraction patterns from the coarsest fractions of the non-magnetic component of the ashes made it possible to identify the major crystalline phases found in each fly ash. Positive identification of a crystalline phase requires the presence of at least three peaks of correct relative intensity and 2-theta value in the x-ray diffraction pattern. The identification procedure was complicated by the occurrence of peaks which were broad and asymmetrical. This made it difficult to determine a single value for 2-theta.

The crystalline phases identified were quartz, mullite, lime, hematite and magnetite. The broad peaks were characteristic for 2-theta values corresponding to those of mullite, hematite and magnetite. The breadth of these peaks, especially for mullite, is thought to result from the scattering of x-rays by poorly ordered crystals. Variations in the values of 2-theta for hematite and magnetite are thought to be due to ionic substitutions in the crystal structure which cause cell dimension variations. The 2-theta values used to identify hematite and magnetite, were determined from chemical end member minerals (16). Cations such as titanium, magnesium, manganese and chromium can replace iron in the magnetite structure. Replacement of iron by any of these cations can result in cell dimension changes (17). In Table 10, 2-theta values for magnetite and hematite in the magnetic fractions of fly ash are compared to those of magnetite and hematite whose composition approaches that of a chemical end member.

In nonmagnetic fractions of the fly ashes, all crystalline phases decrease in concentration with respect to amorphous material as particle size decreases. This determination was made by comparing the relative intensity and number of peaks for each crystalline phase in each size fraction to analogous 2-theta values in the other size fractions. A comparison of the two nonmagnetic ashes shows a similar suite of crystalline phases in each. The main difference is the higher concentration of magnetite in the coarser fractions of the Kentucky

Table 10. Comparison of 2-theta Values of Magnetite and Hematite Found in Magnetic Ash Fractions with Those of Chemical Member Minerals

Mineral in Magnetic Ash		End Member Minerals		Minerals	
2θ	d	2θ	d	hkl	
24.15	3.682	24.32	3.660	012	hematite
30.15	2.962	30.12	2.967	220	magnetite
33.15	2.700	33.31	2.690	104	hematite
35.57	2.522	35.46	2.532	311	magnetite
43.17	2.094	43.10	2.099	400	magnetite
49.45	1.841	49.60	1.838	024	hematite
53.60	1.708	53.43	1.715	422	magnetite
56.98	1.615	56.99	1.616	511	magnetite
54.06	1.697	54.29	1.690	116	hematite
62.63	1.482	62.56	1.485	440	magnetite
62.63	1.482	62.60	1.484	214	hematite
64.04	1.453	64.15	1.452	300	hematite

coal nonmagnetic ash. This is thought to result from the lower power used to magnetically separate this fly ash. A greater amount of magnetite was removed from Missouri coal nonmagnetic ash separated at 100 percent power; thus Missouri nonmagnetic ash has a lower concentration of magnetite.

Some lime was dissolved from the ashes during a sedimentation fractionation process where water was used to make the suspensions. This loss was more noticeable in the finer size fractions because their small size increased the rate of solution. Lime was determined to be the soluble phase by crushing 1 gram of ash, which had been previously x-rayed, stirring it in 100 ml. of cold water for several minutes, drying the recovered ash, and again subjecting it to x-ray analysis. The x-ray diffraction patterns no longer had 2-theta values corresponding to those of lime.

It was thought that nonmagnetic ash contained other minerals which could be identified from x-ray diffraction patterns if they could be concentrated enough to provide a good x-ray pattern. Using undiluted bromoform (s.g. 2.88) suspensions and a centrifuge, nonmagnetic ash fractions were separated into light and heavy fractions. The samples were centrifuged at 2000 rpm for 30 seconds, 2 minutes and 5 minutes respectively. The light particles were removed from the centrifuge tubes by freezing the bromoform containing the heavy particles at the bottom of the tube and pouring the unfrozen bromoform and light particles off.

X-ray diffraction patterns were then made of these light and heavy fractions. A small amount of quartz was detected in the heavy fraction along with, in order of abundance, lime, mullite, magnetite and hematite. The light fractions contained a high concentration of quartz; however, mullite, magnetite, hematite and lime were also present. The inability of the centrifuge to cleanly separate crystalline phases of variable density, as verified by x-ray data, showed that the phases were intergrown or fused together. Because quartz and mullite can be concentrated in the light and heavy fractions respectively, it is thought that these crystalline phases occur predominantly as discrete particles. Mullite, magnetite, and hematite are more commonly intergrown or fused to other phases which alter their effective density. Similar results were reported in a study by Simons and Jeffery (17).

In the magnetic fly ashes fractions separated at a percent voltage setting of 60, magnetite and hematite are the only detectable crystalline phases. Hematite is weakly magnetic and was therefore thought to be intergrown with magnetite. Simons and Jeffery (18) reported that x-ray photographs of magnetically separated ash derived from pulverized coal showed that it contained most of the magnetite as well as a high proportion of weakly magnetic hematite and a considerable proportion of the non-ferrous minerals. They concluded that the poor separation was due to the intimate intergrowth of magnetite and hematite, the mixture of iron and other minerals in the same particle, the sintering together of several particles to form clumps, and the combination of iron with alumina and silica in glass like phases.

In addition to magnetite and hematite, quartz was detected in Missouri coal magnetic ash separated at 100 percent voltage. To determine if quartz content was related to particle size, coarse size fractions of magnetic-60 ashes, separated at 60 percent voltage, and a similar size fraction from Kentucky coal magnetic fraction, separated at 100 percent voltage, were x-rayed. No quartz was detected in the size fractions of the ashes separated at 60 percent voltage. Only a slight increase in quartz, over that detected in the Missouri magnetic ash fraction separated at 100 percent voltage was detected in the coarse fraction extracted from it. The occurence of quartz in the magnetic fraction appears to have little relation to particle size. The magnetic separation power used to separate the ash is thought to control the phase composition of the ash to some extent.

This finding coupled with the conclusion drawn from the Missouri magnetic ash size distribution study (size distribution of magnetic ash fraction does not change as magnetic separation power is increased), is thought to show that magnetic susceptibility is related to the ratio of magnetic to nonmagnetic material and somewhat to particle mass. Because of the small mass of most fly ash particles, the magnetic to nonmagnetic relationship is thought to have the greater influence with respect to magnetic susceptibility. The particle size distribution shows only a slight change as magnetic separation power is increased because there is a random distribution of particles with a wide range in magnetic to nonmagnetic composition in fly ash. As magnetic separation power is applied, particles with a mass and magnetic nonmagnetic relationship determined by the intensity of the magnetic field will be drawn into the magnetic fraction. As the magnetic power is increased, particles of lower magnetic to nonmagnetic ratio will be drawn into the magnetic fraction. The bulk chemistry of the magnetic fraction will reflect the high-proportion of nonmagnetic material being carried along with the magnetic material. Mass becomes an important parameter when trying to attract large particles (+30 μ) of high magnetic to nonmagnetic composition. It is thought the magnetic power required to attract these particles, which make up a very small portion of the ash, will also attract many smaller particles of lower magnetic to nonmagnetic composition which make up the bulk of most fly ashes.

In summary, the crystalline phases identified in nonmagnetic ash were quartz, mullite, lime, hematite and magnetite. Lime and quartz were found to occur as discrete particles. Magnetite and hematite were the predominant phases in the magnetic fractions. Hematite was considered to be intimately intergrown with the magnetite. It was found that the magnetic susceptibility of particles is related to the magnetic to nonmagnetic material composition of particles and to particle mass for the larger particles.

FUTURE WORK

HiChlor Process Development

The data collected by chlorination of fly ash - carbon mixtures will be used in computerized thermodynamic calculations to develop methods for simulating the combination of reactions occurring during fly ash chlorination. A list of objectives to be determined by this thermodynamic study are being prepared.

Work will begin on the design and fabrication of a fluidized bed reaction system for chlorination of fly ash samples, and the recovery of the metal chloride products. Emphasis will focus on a capability to collect differential product samples during the course of the chlorination experiment. The capability to use mixtures of feed gases to the reactor will also be considered.

In the chloride product separation section of the process, the leaching of ferric chloride from solid $AlCl_3$ in an anhydrous system will be carried out. Since the solubility of the chloroferrate ion ($FeCl_4^-$) in several organic solvents is well documented, there is reason to believe that such a leaching process may successfully purify $AlCl_3$.

Anhydrous $AlCl_3$, prepared by sublimation of reagent $AlCl_3$ in an inert atmosphere, will be contaminated to a known degree with $FeCl_3$. The solid mixture will be leached with isopropyl ether saturated with HCl, dried, and then analyzed for iron by using the atomic absorption spectrophotometer.

Lime-Soda Sinter Process Development

Mixtures of both lime-fly ash and lime-soda-fly ash prepared with FGSS sludge or FBC residue as the source of the Ca ion, and graphite will be sintered at 1200°C and 1380°C, respectively. The percentages of contained alumina and silica which can be extracted will be determined. The effects of SO_2 and graphite on the extraction, desilication, and precipitation steps will also be investigated.

Extraction experiments using lime-soda sinter materials will be conducted for a range of solution pH to determine the effect of pH on the extract concentrations of Ca^{+2}, AlO_2^-, and SiO_3^{-2}.

Research will be conducted for sinter mixtures containing additive mineralizers. Additives which promote formation of a layer of molten material on the particle surfaces are expected to increase the rates of the diffusional sintering reactions. Initial mineralizers to be tested are NaF and NaCl. In previous work in this Laboratory, increased alumina recovery resulted when coal refuse containing pyrites was added, so FeS_2 will also be tested as a sinter mineralizer additive. These additives will be used with both lime-soda sinter and lime-sinter mixtures.

Lime-soda material will be sintered for longer times, 90, 120, and 150 minutes, and solutions extracted for 2, 5, and 10 minutes will be analyzed for Ca, Si, and Al to investigate a wider range of these variables.

Research using commercial limestones in the lime-soda sinter process will continue. Low-grade dolamitic limestones will be tested to determine the effect of magnesia on the sinter and extraction reactions. Other low-grade, impure limestones will also be obtained for testing. The objective of this work is to determine whether less expensive limestones can be used in the sinter process.

Recovery of Magnetic Fly Ash and Chemical Beneficiation of the Magnetic Fraction

On receipt of the new Ferrofilter and power supply, the equipment will be assembled and used to examine wet magnetic separation of fly ashes. Data will be collected for comparison with that collected using dry magnetic separation. The effects of percent solids in the slurry, feed rate, and magnet field strength will be examined.

Beneficiation research for the magnetic, iron-rich fly ash fraction will include the collection of size distribution analyses for the samples collected by differential magnetic separation. Several experimental runs, determined at random, will be replicated to measure the experimental error limits for the hydrochemical process used. Extracted residue material will be acid-leached as a final step in trying to further reduce the alumina content.

Scanning electron microscope (SEM) data and electron microprobe analyses will be completed for several of the extracted residue samples. Very low amount of solid will be used in extractions to further determine whether the limited alumina removal is due to an ion solubility limit or results because the alumina is encased in iron oxide, which is insoluble at high pH.

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