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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 plant fly ash. Definition and refinement of steps in the high-temperature (HiChlor) gas chlorination process and in the lime-soda sinter process are emphasized. Samples of chlorinated ash residues were analyzed to determine changes in physical structure and to measure compositions of individual particles. The results show that when ash particles are fractured by heat treatment the chlorination of contained alumina and iron is more complete. The use of $SiCl_4$ as a chlorination agent in addition to chlorine was studied as a method to reduce the amount of silica being chlorinated. Optimum conditions for $SiCl_4$ partial pressure and reaction temperature reduced the percentage of silica chlorinated from 20 percent without $SiCl_4$ to about 5 percent, with minimal reduction in the percentage of alumina reacted. Investigation of high-temperature prechlorination without carbon present resulted in the removal of about 65 percent of the iron and 5 to 7 percent of the alumina from carbon-free fly ash. Both high-temperature carbon-free chlorination, and low-temperature chlorination with carbon have now been investigated as ash pretreatments to remove iron from fly ash before HiChlor processing. Both pretreatment chlorinations remove only about 65 percent of the iron.

Evaluation of waste FGD sludges and FBC residues for use as lime resources in the lime-soda sinter process has begun, and further research was conducted on high-pressure desilication of sinter extraction filtrates. At optimum conditions, the concentration of dissolved silica was reduced by 60 percent, but this is still in excess of the silica specification for alumina used in metal production.

Chemical beneficiation of magnetically separated fly ash showed that the contained silica dissolves quickly during a high-pressure alkali extraction, and that most of the contained alumina is dissolved after one-half hour. Development of a two-stage process, first dissolving the silica and then the alumina in even less time, shows promise of further reducing the size and cost of the extraction equipment required.

## 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 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 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 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 processes for metal recovery are improved by the removal of as much iron possible from the feed mixtures before chemical processing. Bituminous coal fly ashes contain an average of about 18 weight percent 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 some coal washing plants. After this 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 - The reaction data for chlorination of mixtures of coal fly ash and carbon in horizontal fixed beds is now complete. Analytical results were determined using gas chromatography to analyze the noncondensible gases and atomic absorption spectrophotometry to analyze the condensed chloride products and partially reacted fly ash residues. Physical characterization of the solid residues included the determination of specific surface area and porosity and the electron microprobe examination of particles which were polished to expose the inner structure.

2. Preferential Chlorination of Metal Oxides - Experimentation using pure oxides, oxide mixtures, and fly ash samples determined the effects of temperature and amount of carbon added on the chlorination reactions. Samples with carbon added were chlorinated at moderate reaction temperatures of 500, 600, and 700°C. Comparative samples were then chlorinated without carbon at higher reaction temperatures; 800, 900, and 1000°C. Mixtures of pure oxides having the same bulk composition as the fly ash were reacted to determine the decrease in reactivity for oxides contained in the glassy fly ash structure.

3. Suppression of $SiO_2$ Chlorination with $SiCl_4$ - Research has also been conducted with $SiCl_4$ in the reactant gas to suppress the chlorination of $SiO_2$. Data were obtained with pure oxides and with coal fly ash. The effect of reaction temperature, $SiCl_4$ partial pressure, and carbon presence were determined.

## Results:

1. Reaction Kinetics - The specific surface areas and porosities of samples of reacted solid residues chlorinated for one-half hour at 750, 850, and 900°C, and for one hour at 800°C were determined by multi-point B. E. T. measurements using gas adsorption with nitrogen as the adsorbate. Adsorption isotherms were determined from equilibrium quantities of gas adsorbed at different relative pressures. These specific surface area data and the weight of oxide removed from the fly ash sample in the form of volatile metal chloride are given in Table 1. Sample surface area appears to be more dependent on the reaction temperature than on the

extent of oxide chlorination. Therefore, the increase in surface area as a function of reaction temperature may be caused by particle fracture rather than by increased particle porosity due to reaction.

Table 1. Specific surface area of chlorinated fly ash residues as a function of reaction, temperature and time.

| Temp °C | Time, hr | Surface area, $M^2$/gram | Oxide Chlorination |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  | $Al_2O_3$ |  | $SiO_2$ |  | $Fe_2O_3$ |  |
|  |  |  | gm | % | gm | % | gm | % |
| 750 | 0.5 | 2.71 | 0.15 | 9.2 | 0.22 | 5.5 | 0.30 | 49.9 |
| 850 | 0.5 | 4.07 | 0.33 | 19.8 | 0.22 | 5.5 | 0.27 | 46.3 |
| 900 | 0.5 | 6.19 | 0.32 | 19.4 | 0.10 | 2.4 | 0.29 | 48.7 |
| 800 | 1.0 | 5.74 | 0.48 | 28.7 | 0.49 | 12.2 | 0.32 | 54.1 |

Examination of polished particles of each chlorinated ash residue using an electron microprobe revealed pieces which appear to be sections of fractured fly ash spheroids. These angular, jagged pieces contain very little alumina or iron, while the unbroken fly ash spheroids present are higher in alumina and iron content. This may indicate that the heat treatment which the particles receive during chlorination often fractures the ash particles and is beneficial for alumina and iron removal.

2. <u>Preferential Chlorination of Metal Oxides</u> - Preferential chlorination of iron and aluminum oxides as a function of reaction temperature was investigated to determine if a low temperature chlorination pretreatment could be used to separate iron from the ash which will then be used in the HiChlor process. The chlorination reactivities of pure oxides, mixtures of oxides, and coal fly ash, without carbon present, were determined at temperatures of 800, 900, and 1000°C. The chlorine flow rate was $6.12 \times 10^{-3}$ g mole $Cl_2$ per minute, and the time of each run was one hour. These data, shown in Table 2, indicate that pure iron oxide is easily chlorinated without carbon at a temperature of 900°C. However, the reactions using ignited fly ash (carbon burned out) only converted about 65 percent of the iron along with 5 percent of the alumina.

Table 2. Reaction of oxide, oxide mixtures, and coal fly ash with chlorine gas in the absence of carbon.

| Reaction Temperature | Percent Oxides Chlorinated** | | | | | | |
|---|---|---|---|---|---|---|---|
| | Pure Oxides | | Oxide Mixture* | | Ignited Coal Fly Ash | | |
| °C | $Fe_2O_3$ | $Al_2O_3$ | $Fe_2O_3$ | $Al_2O_3$ | $Fe_2O_3$ | $Al_2O_3$ | $SiO_2$ |
| 800 | 72.3 | 7.4 | 96.3 | 23.8 | 52.2 | 2.9 | 13.5 |
| 900 | 99.9 | 9.5 | 92.3 | 11.1 | 64.8 | 4.9 | 15.8 |
| 1000 | 99.9 | 12.3 | 61.9 | 10.0 | 69.8 | 3.2 | 15.4 |

* Oxide mixture; 76 weight percent $Fe_2O_3$, 24 weight percent $Al_2O_3$

** Values are the average of replicated runs.

These results are similar to the data presented previously for low temperature chlorination of oxide mixtures and coal fly ash with carbon present. At 700°C, with carbon added, about 90 percent of the iron oxide in a pure sample or in an oxide mixture will react at the above chlorine flow rate with a one-hour reaction time. Using a fly ash-carbon sample, 65 percent or the iron and 6.7 percent of the alumina were chlorinated.

Both low temperature chlorination with carbon and high temperature chlorination without carbon are effective methods for reducing the level of iron in the fly ash, but neither pretreatment removes sufficient iron that the HiChlor products will meet aluminum electrolytic cell product specifications without further iron separation.

3. Suppression of $SiO_2$ Chlorination with $SiCl_4$ - A series of experiments have been completed to measure the effect of the partial pressure of $SiCl_4$ in the chlorination reagent on the reactivities of pure oxides, oxide mixtures, and coal fly ash. The addition of $SiCl_4$ to the chlorine gas suppresses the chlorination of $SiO_2$. Experiments conducted for a range of $SiCl_4$ concentrations show that the optimal conditions for suppression of $SiO_2$ without appreciable effect on the chlorination of $Al_2O_3$ were a reaction temperature of 900°C and a 172 mm Hg partial pressure of $SiCl_4$. Because silica is the major constituent

in coal fly ash, a process extracting $AlCl_3$ by high temperature chlorination of the ash will benefit greatly from methods which suppress silica chlorination. Silica chlorination can consume large quantities of chlorine which must be recovered by oxidation or other treatment of the $SiCl_4$ so the chlorine can be recycled to the chlorination reactor. Recycle of $SiCl_4$ along with unreacted chlorine could reduce the amount of silicon in the reactor exit gases.

The equipment used for these experiments is shown in Figure 1. The reactor tube was made of Vycor, and the connecting lines of Tygon or Teflon. The products were collected in a vacuum trap immersed in liquid nitrogen. The line from the reactor to the vacuum trap was maintained at 350°C so that the volatile chlorides would not condense before reaching the vacuum trap. Dry chlorine gas passed through the reactor tube at a controlled rate, and the $SiCl_4$ was added by bubbling the chlorine through liquid $SiCl_4$. Adjustment of the gas flow rate and the temperature of the liquid $SiCl_4$ controlled the concentration of $SiCl_4$ in the chlorine stream.

The variables investigated were the reaction temperature and the initial partial pressure of $SiCl_4$. The chlorine flow rate ranged from 0.75 to $1.28 \times 10^{-3}$ g mole $Cl_2$ per minute. The time for each run was one hour. Pure alumina was reacted with mixtures of $SiCl_4$ and chlorine and the resultant data show that the reaction occuring is

$$3/2\ SiCl_{4(g)} + Al_2O_{3(s)} \rightleftarrows 3/2\ SiO_{2(s)} + 2\ AlCl_{3(g)} \qquad (1)$$

At 750°C, the chlorination rate was found to be independent of the $SiCl_4$ partial pressure, possibly due to adsorption of $SiCl_4$ on the alumina surface. At higher temperatures, the amount of adsorption of $SiCl_4$ was less and the reaction was observed to be a function of $SiCl_4$ partial pressure. For temperatures of 750 to 900°C, the reaction rate was slow, with conversions of 12 to 16 percent of the alumina occuring in one hour. The data show that $SiCl_4$ was the chlorinating agent rather than $Cl_2$ and that $SiO_2$ is being deposited in the bed. It appears that the chlorine gas acts only as a carrier in the reactant mixture of $SiCl_4$ and $Cl_2$ when carbon is not present.

Experiments were also conducted in which mixtures of alumina, silica, and carbon were reacted with $SiCl_4$ - $Cl_2$ gas mixtures at 900°C. These results, listed in Table 3, show a significant increase in alumina conversion as the partial pressure of $SiCl_4$ in the gas mixture increases, reaching a value of 64.5

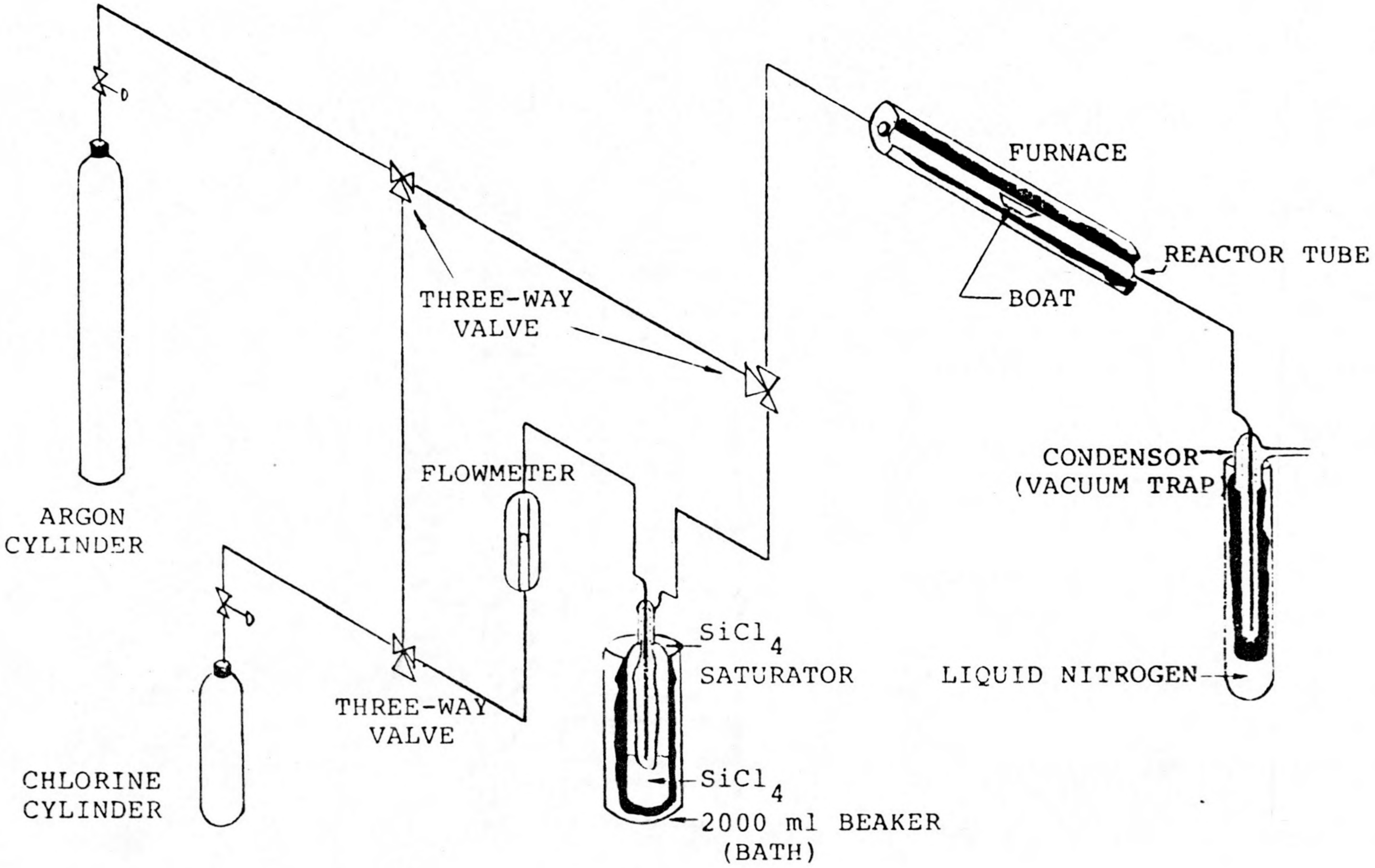

Figure 4. Equipment used in aluminous materials chlorination.

percent alumina reacted. The increased conversion of $Al_2O_3$ to $AlCl_3$ when carbon is present is due to the reaction

$$Al_2O_{3(s)} + 3\ C_{(s)} + 3\ Cl_{2(g)} \rightleftarrows 2\ AlCl_{3(g)} + 3\ CO_{(g)} \qquad (2)$$

Table 3. Reaction of a mixture of silica, alumina and carbon with $SiCl_4$-$Cl_2$ mixtures at 900°C.

| Composition $Al_2O_3/SiO_2/C$ gm | $SiCl_4$ Partial mm | Percent Alumina Reacted |
|---|---|---|
| 1.50/0.88/0.87 | 57 | 26.26 |
| 1.50/0.88/0.87 | 74 | 32.43 |
| 1.50/0.88/0.87 | 195 | 64.52 |

Comparative experiments were made using coal fly ash rather than pure oxides to determine the reactivity of the oxides in the structure of the fly ash. These data were obtained at temperatures of 750 and 900°C, with and without carbon added. Although carbon was not added to some of the runs, some carbon was present because the fly ash contains 10 weight percent unburned carbon. These results, for the chlorination of fly ash - carbon mixtures with $SiCl_4$ - $Cl_2$ gases, are given in Table 4.

Table 4. Reaction of coal fly ash with and without added carbon with $SiCl_4$ - $Cl_2$ mixtures at 750 and 900°C.

| Reaction Temperature °C | $SiCl_4$ Partial Pressure mm | Without Added Carbon Percent Oxide Reacted | | | With Added Carbon Percent Oxide Reacted | | |
|---|---|---|---|---|---|---|---|
| | | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ |
| 750 | 57 | 61.60 | 21.33 | 66.16 | 63.77 | 45.05 | 67.28 |
| | 74 | 60.47 | 17.07 | 63.49 | 61.94 | 42.91 | 56.36 |
| | 195 | 40.26 | 13.63 | 62.25 | 50.57 | 35.60 | 57.13 |
| 900 | 55 | 58.32 | 17.24 | 64.74 | 59.70 | 56.50 | 80.35 |
| | 74 | 58.39 | 10.80 | 57.73 | 55.80 | 53.79 | 81.39 |
| | 172 | 59.90 | 4.01 | 68.25 | 68.27 | 33.33 | 85.00 |

These results indicate that the reactivity of alumina in fly ash is equal to that of the reagent grade alumina. As shown in Tables 3 and 4, about 65 percent of the alumina reacts during a one-hour chlorination in the presence of $SiCl_4$. However, the effects of temperature and $SiCl_4$ partial pressure are significant. At 750°C, the $SiCl_4$ is not effective at suppressing $SiO_2$ chlorination, but at 900°C an increasing $SiCl_4$ partial pressure reduces the extent of $SiO_2$ reaction to 4 percent. This beneficial effect requires that the quantity of carbon be limited. Reaction (1) is favored over reaction (2) when carbon is limited. The chlorination of alumina with $SiCl_4$, depositing silica, reduces the amount of $SiCl_4$ exiting the reactor to a value nearly equal to that in the gas entering. The reacted silica percentage listed in Table 4 is actually the difference between the amount of silica reacted in the fly ash and the amount of $SiCl_4$ in the gas which is deposited as $SiO_2$as a result of reaction (1) and reaction (3).

$$SiO_{2(s)} + 2\ C_{(s)} + 2\ Cl_{2(g)} \rightleftharpoons SiCl_{4(g)} + 2\ CO_{(g)} \qquad (3)$$

Suppression of the amount of $SiO_2$ chlorinated by the recycling of $SiCl_4$ and by use of limited carbon, could reduce the quantity of process chlorine required by 30 percent, resulting in a significant improvement in process economics and feasibility.

## Lime-Soda Fly Ash Sinter Process

1. Waste Materials as Alternative Lime Resources - Samples of waste residue materials containing substantial quantities of calcium are being evaluated for use in the lime-soda fly ash sinter process. The use of a waste material as the lime resource will improve the economic feasibility of fly ash sintering processes.

Three samples of flue gas desulfurization (FGD) residues and one sample of fluidized bed coal combustion (FBC) residue were analyzed and tested. Two scrubber sludges are from wet limestone flue gas scrubber systems and one residue is from a dry flue gas desulfurization process. The fluidized bed combustion residue is from a process under development at the Argonne National Laboratory. Composition data for these materials are given in Table 5. These results show that the wet process sludge No. 1 and the dry FGD residue contain substantial quantities of calcium carbonate and calcium sulfite. The wet process sludge No. 2 and and the FBC residue appear to contain calcium in the form of calcium sulfate. The power station producing sludge No. 2 uses a forced oxidation stage to convert the calcium sulfite in the sludge to calcium sulfate. Oxidation of the sulfite gives a sludge of earth-like consistency which can be disposed of as landfill. The sludge No. 2 and the dry FDG residue also contain coal fly ash. The high silica contents of these two materials limit their value as lime sources for the lime-soda sinter process.

Table 5. Compositions of FGD sludges and FBC residue

| | Wt. Percent Constituent | | | |
|---|---|---|---|---|
| Constituent | Sludge No. 1 | Sludge No. 2 | Dry Residue | FBC Residue |
| Total $SO_3^{-2}$ | 28.30 | 14.90 | 13.82 | 30.90 |
| Free $SO_3^{-2}$ | 19.90 | 0.05 | 12.60 | 0.10 |
| $CO_3^{-2}$ | 17.50 | 4.04 | 17.40 | 1.03 |
| $SiO_2$ | 7.81 | 25.22 | 24.40 | 2.29 |
| $Al_2O_3$ | 2.04 | 11.59 | 8.71 | 0.85 |
| $Fe_2O_3$ | 2.35 | 14.70 | 5.04 | 1.37 |
| MgO | 0.32 | 2.37 | 3.47 | 0.65 |
| CaO | 41.71 | 19.28 | 25.44 | 58.21 |
| $Na_2O$ | | 0.37 | 8.15 | 0.03 |
| Moisture | | 1.31 | 1.17 | 0.02 |
| L. O. I. | 16.91 | 5.63 | 4.62 | 0.48 |

2. Desilication of Extracted Sinter Filtrate - Desilication of lime-soda sinter extract filtrate is required if the final alumina product is to meet specification on maximum silica content. The filtrate, as extracted, contains 1 to 2 weight percent silica with respect to alumina. For use in the production of aluminum metal, alumina must contain 0.05 weight percent or less silica. Filtrates of lime-soda sinter extractions can be desilicated by high-temperature, high-pressure digestion with lime. Agitated pressure treatments were conducted

using a teflon container within a small pressure vessel. Agitation was provided by positioning the pressure vessel in a rocking furnace which rocked at a rate of three times per minute.

The filtrate for desilication was obtained by extracting lime-soda fly ash sinter in a 3 weight percent aqueous solution of sodium carbonate at 65°C for 10 minutes. Samples were treated at a range of temperatures (pressures) and rates of lime addition to give the results shown in Table 6. The silica content was reduced, but not enough to meet commercial alumina specifications.

Table 6. Results of Desilication tests for lime-soda fly ash sinter filtrate

| | | PPM in Filtrate After Treatment | | Percent Precipitated | |
|---|---|---|---|---|---|
| Pressure Psig | CaO, mg per 20 ml filtrate | Si | Al | Si | Al |
| -- | -- | 52.0 | 5200 | -- | -- |
| 225 | 9 | 29.7 | 4860 | 42.5 | 6.5 |
| | 12 | 28.1 | 5020 | 45.7 | 3.5 |
| | 15 | 30.9 | 4955 | 40.0 | 4.7 |
| 450 | 12 | 35.6 | 5044 | 31.2 | 3.0 |
| 225* | 12 | 20.8 | 4810 | 60.0 | 7.5 |

* Treatment of 2 hours duration, others were for 1 hour.

The results of the filtrate desilication tests agree with previous research conducted on the dissolution of fly ash fractions in alkali solvents. The alumina and silica in the glass-like structure of fly ash do not follow the solubility limits for silica and alumina materials which have not been fired. The solubility results, together with the observed instability of the filtrates and the viscous nature of the desilicated solutions, indicate that complex polymerized aluminate-silicate ions may be forming. Polymerization may explain the limited solubility of the lime-soda-fly ash sinters as well as the difficulty in desilicating the filtrates.

## Beneficiation of the Iron-Rich Fraction of Coal Fly Ash

Experiments were conducted to measure the effect of extraction time on the leaching of alumina and silica from the magnetically separated fraction of coal fly ash. These extractions used hold times from 0 to 2.0 hours after the extraction temperature was reached. Data for the percentage of the contained alumina and silica solubilized at each hold time are listed in Table 7.

Table 7. Percentage of contained alumina and silica dissolved from magnetic fly ash by alkali extractions as a function of extraction time.

| Time hrs | Percent of Oxide Solubilized $Al_2O_3$ | $SiO_2$ |
|---|---|---|
| 0 | 24.80 | 73.38 |
| 0.5 | 31.80 | 73.76 |
| 1.0 | 31.20 | 74.50 |
| 2.0 | 27.83 | 73.76 |

Conditions: solid/liquid - 100 gm/liter
$200^oC$, 30 wt. percent NaOH

The results of these runs indicate that the alumina and silica solubilization reaches a maximum after an extraction time of 30 minutes at temperature. The solubilization level attained with a zero hold time run shows that part of the material dissolves during the heat-up period. The data in Table 7 indicate the relative ease with which silica dissolves from the magnetic fly ash structure. The silica which dissolves during the two hour extraction is in solution by the time the reaction mixture reaches the extraction temperature. Separation of the liquid and solid at that point, with a second extraction of the desilicated solid with fresh alkali solution may increase the percentage of alumina which can be dissolved. Such a two-stage process may also reduce the size of the reaction vessels required for a commercial-scale process.

These solubility data further indicate the instability of dissolved aluminates in alkali solutions. Separation of the extraction process into two phases may stabilize the ion solubilities in the separated liquids. Although alumina precipitates from solution as the extraction time increases from one-half hour to two hours, the solubilities of the aluminates after the solids and liquids are separated will be more stable. As has been evident in previous hydrochemical alkali leachings of coal fly ash, the solubility limits of the dissolved aluminates are much lower than the concentrations attained for similar extractions from clays and bauxites. Either the silicates or other impurities dissolving from fly ashes may be limiting the aluminate solubilities by participating in parasitic reactions which remove dissolved aluminates from solution.

## Iron Recovery from Coal Washing Refuse

Chemical analyses of the fractions separated when Iowa coal was beneficiated by dense media flotation have shown that the refuse fraction contains substantial iron. For mineral analyses, these refuse samples are pulverized and ashed at 900°C for four hours. The ash then contains about 50 weight percent Fe in the form of $Fe_2O_3$. The analyses also showed that the refuse as separated, has a heating value of about 6,000 Btu per pound.

Tests were conducted to determine the minimum energy requirements for removal of the contained carbon and sulfur from the coal refuse. Roasting tests of one hour duration were conducted with temperatures from 500 to 900°C. Because these runs did not remove sufficient amounts of carbon and sulfur, longer runs were made. Data for all of the roasting tests are listed in Table 8. The roastings of four hours at 500°C and two hours at 600°C gave the maximum removal of carbon and sulfur. Chemical analyses of the coal refuse and of these two roasted samples are listed in Table 9. Roasting increased the Fe content from 30.9 weight percent in the refuse to 46 to 48 weight percent in the ash.

Little energy will be required to roast the pulverized coal refuse because the oxidation of the iron pyrite and fixed carbon in the coal refuse is highly exothermic. Preliminary design indicates that a rotary kiln 10 ft. in dia. and 150 ft. long can be used to roast 12 to 15 ton per hour of pulverized Iowa coal refuse. Six tons per hour of $SO_2$ would need to be scrubbed from the exit gases. The roasted refuse material can then be leached in an alkali extraction to remove the remaining sulfur and part of the alumina and silica. With roasting and alkali leaching, pulverized Iowa coal refuse should meet all specifications for use as iron ore for steel production.

Table 8. Results of roasting tests for pulverized coal refuse from ISU Coal Washing Plant.

| Temperature, °C | Time, Hr | Wt. Percent in Residue after Roasting C | S |
|---|---|---|---|
| | - | 30.0 | 32.5 |
| 500 | 1 | 19.6 | 14.3 |
| | 2 | 10.6 | 7.5 |
| | 4 | 2.5 | 3.1 |
| | 6 | 2.5 | 3.1 |
| 600 | 1 | 14.7 | 11.6 |
| | 2 | 2.5 | 3.6 |
| | 4 | 2.5 | 4.5 |
| 700 | 1 | 11.4 | 14.6 |
| 800 | 1 | 9.3 | 15.6 |
| 900 | 1 | 10.3 | 18.2 |

Table 9. Chemical analyses of coal refuse and roasted samples

| | Wt. Percent Constituent | | |
|---|---|---|---|
| Constituent | ISU Coal Plant Refuse | Pulverized Roasted Coal Refuse 500°C, 4 Hr. | 600°C, 2 Hr. |
| $SiO_2$ | 3.63 | 7.12 | 6.44 |
| $Al_2O_3$ | 1.19 | 2.00 | 2.49 |
| Fe | 30.90 | 48.60 | 46.10 |
| CaO | 4.50 | 7.00 | |
| C | 30.0 | 2.5 | 2.5 |
| S | 32.5 | 3.1 | 3.6 |
| L.O.I. | 41.5 | 2.4 | 6.0 |

## Investigation of the Substructure of Coal Fly Ash

A reflectivity study of magnetic ash particle was undertaken to provide a means for characterizing magnetic ash based upon a mean reflectivity. From previous optical studies, it was noted that magnetic particles consisted of magnetite, hematite, and glass in varying proportions. Because glass has a low reflectivity as compared to magnetite or hematite it was thought that mean reflectivity would represent the magnetite-hematite to glass ratio within a magnetic ash. Because SEM data had indicated that glass in magnetic particles was lower in iron and higher in silica, the mean reflectivity may indicate the iron content of a fly ash sample.

Reflectivity readings of magnetic ash particles from C-1, Illinois, Missouri, and Kentucky magnetic ashes were taken using a Zeiss binocular research microscope and photometer. A monochronometer set at a wavelength of 546A was used. The mean reflectivity was determined by averaging the reflectivities of 100 to 150 particles for each ash. Only spherical particles with a diameter larger than 20 microns were measured and the reflectivity readings were taken at the center of each of the particles.

The mean reflectivity determined for each magnetic fly ash sample appeared to be directly related to the $Fe_2O_3$ weight percent in the sample. As shown on Table 10, the Illinois magnetic ash has the lowest mean reflectivity and the lowest $Fe_2O_3$ content. Reflectivity data show that the Illinois ash consists of a high percentage of magnetic particles with a low reflectivity. C-1 magnetic ash has a high mean reflectivity and a high $Fe_2O_3$ content. A high percentage of particles in C-1 magnetic ash have a high ratio of magnetite to glass, as indicated by the percentage of particles with relatively high reflectivities.

Particles of a wide range in reflectivity and chemistry comprise each of the magnetic fly ashes. These particles, all magnetically susceptible at normal separation power, show that magnetic field strength as well as the concentration of particles, rich or poor in magnetite with respect to glass, influences the bulk chemistry of the magnetically separated fraction. The fact that particles containing a high proportion of glass to magnetite contain less $Fe_2O_3$ and more $SiO_2$ may indicate that the crystallization of magnetite in a liquid droplet containing iron oxide and silica reaches a near equilibrium with the liquid phase prior to quenching.

Table 10. Mean reflectivity and chemical composition for the magnetic fraction of several fly ashes.

| Mag. Ash | Mean Reflectivity | Oxide Wt. Percent $Fe_2O_3$ | $SiO_2$ | $Al_2O_3$ |
|---|---|---|---|---|
| C-1 | 58.200 | 76.87 | 12.32 | 6.75 |
| Illinois | 28.025 | 49.09 | 24.59 | 9.73 |
| Missouri | 47.012 | 62.60 | 22.15 | 9.35 |
| Kentucky | 51.766 | 65.90 | 19.90 | 8.25 |

## 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 mechanisms and the reaction kinetics.

Developmental research of the HiChlor process remaining to be done includes the use of various reductants and chlorinating agents, the addition of catalytic additives, and further study of the recycle of $SiCl_4$ to suppress silica chlorination. Work on the recovery and separation of the metal chloride product mixtures will require determination of basic data such as vapor pressures and solubilities. The results obtained 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 of pure oxides more like fly ash, the effect 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 studies will be made to further reduce the level of dissolved silica in the filtrates. 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 continue on the use of different types of lime scrubber sludges and FBC residues 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 with additives such as coal refuse or mineralizers in the sinters.

### Recovery and Beneficiation of the Iron-Rich Ash Fraction

Evaluation studies will continue on beneficiation methods for producing a low-alumina, low-silica product for use in the steel industry. 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. Research will be conducted using two-stage extraction processes and several ash pretreatments prior to leaching. Work will continue on the development of coal refuse as iron resource.

Distribution List

| | |
|---|---|
| USDOE - CORO | 2 |
| USDOE - TIC | 27 |
| USDOE - Washington | 6 |
| (A. Dietz) | |
| (R. Wujkowski) | |
| George Burnet | 10 |
| M. J. Murtha | 10 |
| R. W. Fisher | 5 |
| L. E. Burkhart | 1 |
| Ames Laboratory Library | 9 |
| Total | 70 |