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Advanced Research and Technology
DIRECT UTILIZATION—RECOVERY OF MINERALS FROM COAL FLY ASH
FOSSIL ENERGY PROGRAM
Technical Progress Report
1 October 1980 - 31 December 1980

G. Burnet
S. J. Weiss
M. J. Murtha

Date Transmitted: February 1981

Ames Laboratory
Iowa State University
Ames, Iowa 50011

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Contents

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DIRECT UTILIZATION - RECOVERY OF MINERALS FROM COAL FLY ASH

G. Burnet and M. J. Murtha

Summary

The purpose of this research is to develop methods to process fly ash for the separation and use of an iron-rich fraction, for the recovery of metals, primarily Al and Ti, and for use of the process residues. Research during this report period of the HiChlor process for the extraction of alumina and titania by high-temperature chlorination of a fly ash-reductant mixture included investigation of the simulation of the reactions as a design tool, the assembly of a unit to measure reaction kinetic rates and particle specific surface areas and porosities, and the design of equipment to measure necessary chloride product separation data. A pretreatment chlorination reaction using CO and Cl_2 was found to be capable of removing 80 percent of the iron with only minimal alumina and silica reaction.

Development of the lime-soda sinter process includes the collection of data on the phenomenon of auto-disintegration of lime-fly ash sinters. Results indicate that it is the presence of minor constituents having +5 or +6 valence cations of a size that can enter the lattice of the calcium silicate which prevent sinter auto-disintegration.

OBJECTIVES AND SCOPE OF WORK

Background

The primary objective of this investigation is to develop and/or improve methods for utilization of coal fly ash as a source of minerals. Processes are being studied for the recovery of aluminum oxide, iron oxides, and titanium oxide from fly ash and for utilization of the residues. Processing of fly ash as a source of metal oxides will reduce the quantity of coal ash for disposal and help decrease dependence on imported ores and metals.

Objectives

Task A - Development of the HiChlor Process - Fly ash will react with chlorine in the presence of carbon or other reductant at high temperatures to produce volatile metal chlorides. These chlorides are then condensed and separated to yield high purity metal chloride products. Details of the process are being developed including an understanding of the reaction mechanism, a reactor design (possibly fluidized bed) that is capable of handling the required ash volume, 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. Fundamentals of the sintering step are 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 development and commercialization of the process has been submitted for funding approval. An engineering cost estimate has been prepared for commercial application of this process to the fly ash from a coal-burning 1000 MWe power station. Process conditions which may improve the filtrate desilication step are being investigated, as is the use of low quality, inexpensive limestones and waste materials as feed to the sinter. Methods to reduce the process energy requirements and for use of the process residues are also being studied.

Task C - Improvement of the Lime-Fly Ash Sinter Process - Research of the lime-fly ash sinter method, discontinued about two years ago because of low recoveries and high energy requirements, has been reinitiated since the discovery of new additives that make the process appear economically and technically feasible. The addition of a small amount of carbon and sulfur, even that present in coal refuse, to the raw sinter mixtures increases alumina recoveries to about 90 percent when a sintering temperature of 1200°C is used. Waste materials such as cement kiln dust can replace limestone, providing a process which produces alumina and Portland cement entirely from high volume waste materials--fly ash, kiln dust, and coal refuse.

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

Bench scale research is nearly complete on a process to produce an iron ore that uses pressurized caustic digestion to dissolve silicates and aluminates from the iron-rich fly ash fraction. Control of the stability of the sodium aluminum silicate solutions and the precipitation of dissolved material has been shown to require additional work. A combination of caustic leaching with an acid wash shows promise as an economical magnetic ash beneficiation method.

STATUS AND RESULTS

HiChlor Process Development

Using a systematic combination of computer simulation, engineering design, and basic data collection, results are being compiled for development of the HiChlor process for high-temperature chlorination of coal fly ash as a method to extract contained metals.

1. Computer Simulation of Fly Ash Chlorination Reactions

Data collected by computer simulations of fly ash chlorination experiments were used to calculate expected chlorination product compositions. The ash composition used was for an ash produced by the burning of bituminous Kentucky and southern Illinois coals and collected by mechanical precipitators at Lakeside Power Plant, Milwaukee, WI. Theoretical equilibrium vapor, liquid, and solid compositions were determined for a range of fly ash chlorination temperatures, pressures, and compositions. This was followed by actual fixed bed chlorinations of fly ash-carbon mixtures carried out to determine the influences of bed dilution and/or increased particle-to-particle distance on reactivity. One purpose of these experiments was to simulate the change in particle-to-particle distances that occurs when going from a fixed bed to a fluidized bed reaction system.

As part of the simulation work, chlorination product data were calculated for a wide variety of anticipated chlorination reactions and mole fractions of the stoichiometric amount of Cl_2 required. The results, shown in Table 1, led to several important conclusions.

Table 1. Data Calculated for Computer Runs on Fly Ash Chlorination*

Chlorination Products	Mole Fraction Products in Vapor (excl. carbon oxides) Chlorine Provided, Percentage of Amount to React All Oxides				
	10	30	40	70	100
$AlCl_3$	0.3077	0.5392	0.6584	0.4111	0.2982
Cl_2	---	---	---	---	0.0023
$FeCl_2$	0.4934	0.2934	0.1157	0.0576	0.0050
Fe_2Cl_4	0.0201	0.0108	---	---	---
$FeCl_3$	---	0.0075	0.0245	0.0323	0.0568
KCl	0.0397	0.0284	0.0080	0.0056	---
$MgCl_2$	0.0610	0.0447	0.0116	0.0081	---
NaCl	0.0230	0.0167	---	---	---
$SiCl_4$	---	0.0165	0.1667	0.4758	0.6268
$TiCl_4$	0.0551	0.0429	0.0152	0.0095	0.0071
	1.0000	1.0000	1.0000	1.0000	1.0000
	Mole Percent Carbon Reacted**				
	69.86	76.56	79.63	71.19	77.06
Oxides	Mole Percent Chlorinated				
Al_2O_3	12.83	43.58	100.00	100.00	100.00
Fe_2O_3	100.00	100.00	100.00	100.00	100.00
SiO_2	0.20	1.07	12.40	56.85	100.00
TiO_2	100.00	100.00	100.00	100.00	100.00

---

*Temp 850°C, 100% Total Carbon, Equilibrium Concentrations.

**Temp not significant factor on product yield (850-950°C) but at higher temp C(s) converted to SiC(s).

First, significant advantages accrue when less than the stoichiometric amount of chlorine is present. For example, the amount of silica reacted is greatly reduced (see Figure 1). Second, at reduced chlorine conditions the iron products are predicted to be 80 to 90 percent $FeCl_2$, which is much more separable from other metal chlorides than is $FeCl_3$.

The above computed results appear to agree quite well with the experimental fly ash chlorination data collected to date. The computer results show very little difference in equilibrium yields for reactions using different reductants, e.g., C(s), CO(g), or $COCl_2$(g). Where differences do exist, they may be due to reaction rate, the effect of which would not be evident in equilibrium calculations. Good agreement between calculated and experimental results is found when solid carbon is the reductant. When C(s) is used, 97 percent of the reacted C is converted to CO which can theoretically be recycled to the reaction, further reducing coke requirements. Further experimental and computer work is required using other fly ash compositions, $SiCl_4$ recycle, and mixtures of C(s) and CO(g).

2. Chlorination of Subbituminous Fly Ash in a Horizontal, Fixed Bed Reactor

Runs made to investigate the effect of using particles of inert fused quartz to increase the porosity of fixed beds of fly ash in a horizontal reactor showed very little change in reaction product yields with the amount of quartz added. The first run was made as a one-hour chlorination of a subbituminous ash-graphite mixture with no quartz

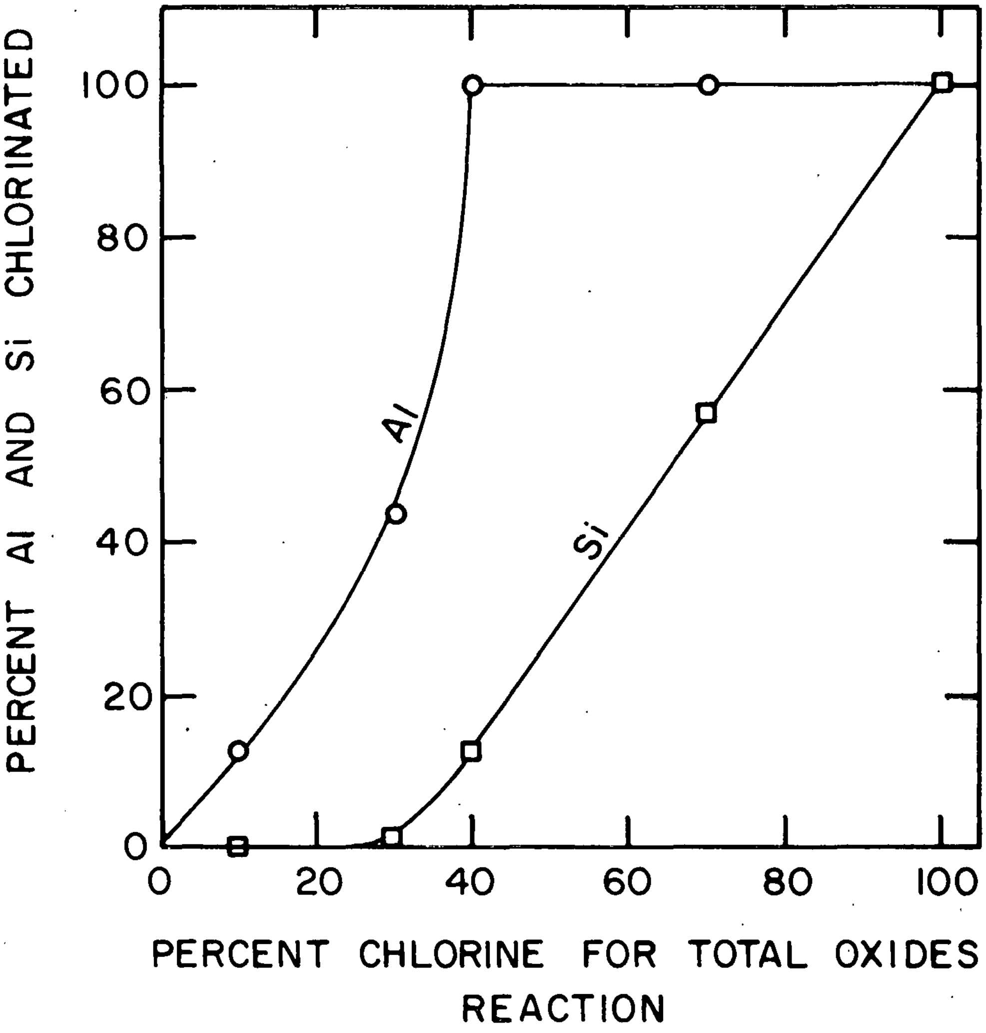

Fig. 1. Percentage of Alumina and Silica Chlorinated as a Function of the Amount of Chlorine Present, 100 percent Carbon Present, 850°C (Computer Results).

present. A mixture of the same composition was then chlorinated with the bed diluted by quartz particles at 4 and 8 parts of quartz to one part of ash. These data, shown on Table 2, indicate no reduction in reactivity with bed dilution. Bed dilution, however, may not actually increase the particle to particle distance because the fly ash-graphite mixture may be coating the quartz chips.

To further investigate ash-C interaction, a run was made with the graphite and ash completely separated. The chlorine first contacted the graphite then flowed through the fly ash bed. These results are also included in Table 2 and show conversions similar to those obtained when CO is used rather than graphite (first three runs). Over 80 percent of the iron was chlorinated with minimal reaction of alumina and silica.

Because of the potential importance of a method for removing iron from the fly ash by pretreatment, several experiments using CO were conducted. Previous data from exploratory fly ash chlorinations with a mixture of $CO-Cl_2$ indicated that about 80 percent of the iron reacted with minimal chlorination of alumina or silica. This experiment was repeated for 60 and 90 minutes at 850°C. Comparable results were again obtained--about 70 percent of the iron was chlorinated while less than 5 percent of the alumina or silica reacted. Further research will use shorter reaction times and lower temperatures to optimize this pretreatment step.

3. Measurement of Reaction Rates for the Chlorination of Fly Ash

A Cahn microbalance, obtained to generate data on the time-dependent kinetic rates of fly ash chlorination reactions, is being installed and auxiliary apparatus designed and tested. The system

Table 2. Chlorination results for fixed bed chlorinations of subbituminous fly ash(1).

Bed Material	Reactant Gases	Percent of Oxide Reacted Fe_2O_3	Al_2O_3	SiO_2	TiO_2
Fly ash	$CO\text{-}Cl_2$	78.9	1.8	1.1	23.4
Fly ash	$CO\text{-}Cl_2$	68.6	2.7	2.0	32.6
Fly ash(2)	$CO\text{-}Cl_2$	70.8	4.9	0.7	36.7
Fly ash-Graphite	Cl_2	100.0	54.3	25.7	100.0
Fly ash-Graphite-Quartz	Cl_2	82.8	70.6	35.4	85.0
Fly ash-Graphite-Quartz(4)	Cl_2	85.2	67.3	28.0	76.4
Fly ash-Graphite(5)	Cl_2	81.8	0.8	0.6	5.7

(1) Subbituminous western coal fly ash, wt. ratio of ash to graphite 10:3 when graphite present, 850°C, 60 min.

(2) 90 min. chlorination.

(3) Wt. ratio quartz chips to fly ash-graphite mixture 4:1.

(4) Wt. ratio quartz chips to fly ash-graphite mixture 8:1.

(5) Graphite and fly ash in separate beds separated by a bed of quartz chips.

will also be used in adsorption-desorption measurements to determine sample surface areas and porosity. In addition to the microbalance the system will include a vacuum system, miscellaneous gas connections, an on-line chromatograph, pressure and flow measurement devices, and the necessary valving.

To utilize the full capabilities of the microbalance for an extended period, two important features were designed into the unit glassware. Since the reaction gases (Cl_2 or $COCl_2$) would readily corrode the balance mechanism, precautions were taken to prevent contact between the corrosive gases and the balance mechanism. Figure 2 is a schematic diagram of the glassware to be used for fly ash reaction rate studies. A continuous helium purge entering the jar flows down through the venturi to prevent the back diffusion of corrosive gases which enter at the lower location as shown. Calculations indicate that for a 20 cc/min helium purge flow and an 80 cc/min chlorine flow, the ratio of the helium molar flux to the chlorine molar diffusive flux is 20:1 in the venturi section. Under these conditions, there should not be any back-diffusion of Cl_2 gases up into the balance. As a precaution, however, a gas leak detector will be part of the system. The detector operates on the same principle as a gas chromatograph and will be connected as shown in Figure 2. The right-hand connection will supply the reference gas (He) and the left-hand connection will sample the gas just above the venturi. An alarm will sound if a concentration of several PPM of a gas other than helium is detected.

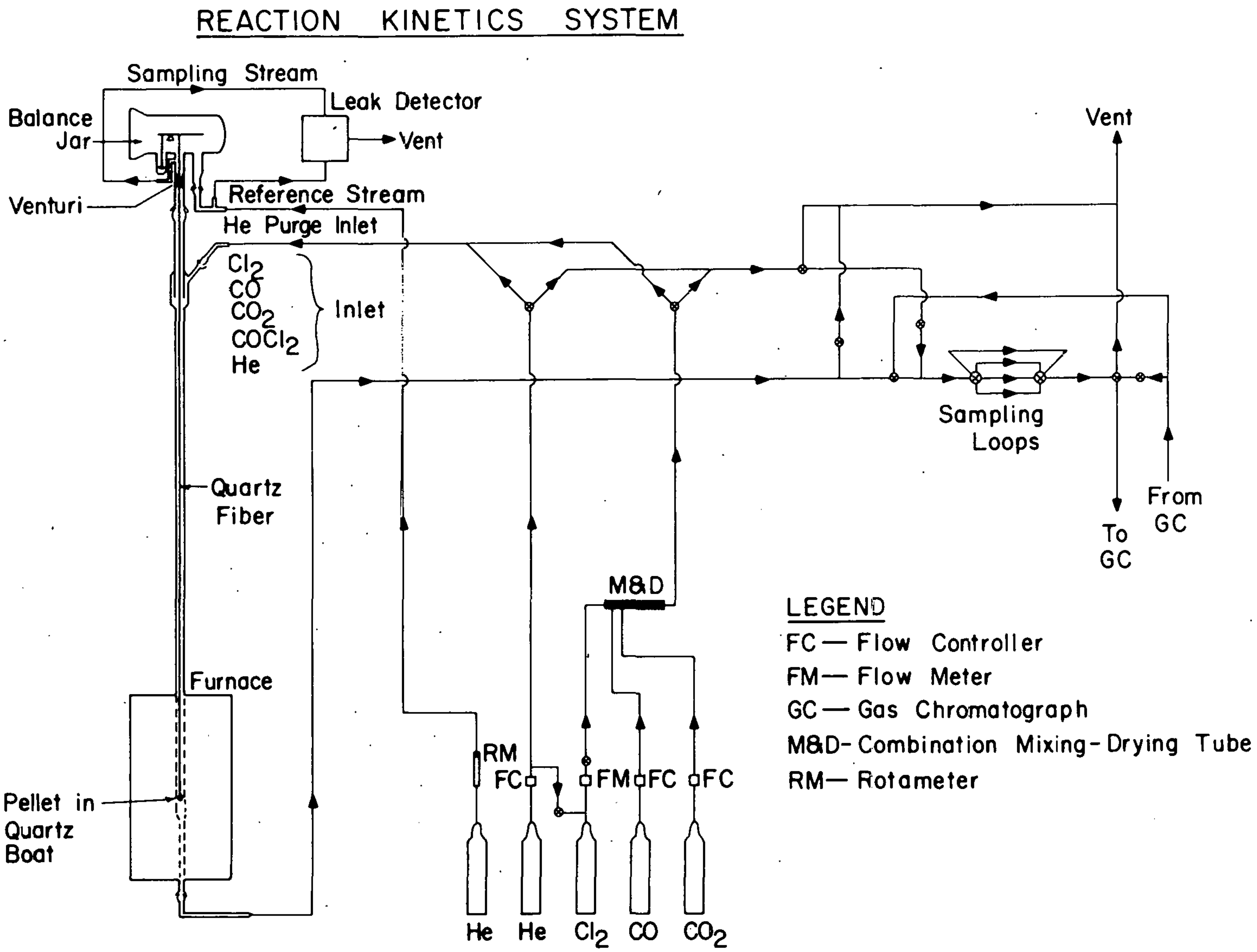

Fig. 2. Schematic diagram of equipment used in the kinetic study of the fly ash reduction-chlorination reaction.

For optimum balance stability, it will be necessary to operate with the balance at a constant temperature. Therefore, as shown in Figure 2, the overall system has been designed with the furnace located far below the balance jar. The heat emitted by the furnace will be dissipated before it reaches the balance. Also, due to the corrosive nature of the gases used in the experiments, the sample pellets will be supported using an inert material. The pellets will be held in a quartz boat and the boat will be suspended from the balance using a quartz fiber. Most metal supports would react with the chlorine to give false pellet weight change measurements.

Figure 2 also shows the tubing and valving to be used in the system. The center section is primarily for the delivery of gases to the reactor and the right-hand section is the gas sampling loop system for the chromatograph. The sampling loop system allows for rapid collection of three gas samples. The gas samples will be delivered to the gas chromatograph for analysis of CO, CO_2, and Cl_2.

For fly ash surface area measurements, it is necessary to precisely measure the volume of a gas adsorbed on the solid sample at a given system pressure, thus making accurate pressure measurements a necessity. The pressure sensors and supplementary components schematically shown in Figure 3 will permit continuous digital output over a pressure range of 10^{-5}/1000 torr.

The capability also will exist for the connection of a strip chart recorder to the sensor output to provide a permanent record of the pressure readings. The Cahn balance will measure the weight of gas adsorbed as a function of system pressure, and the weight change can then be converted to a volume change using an appropriate equation of state.

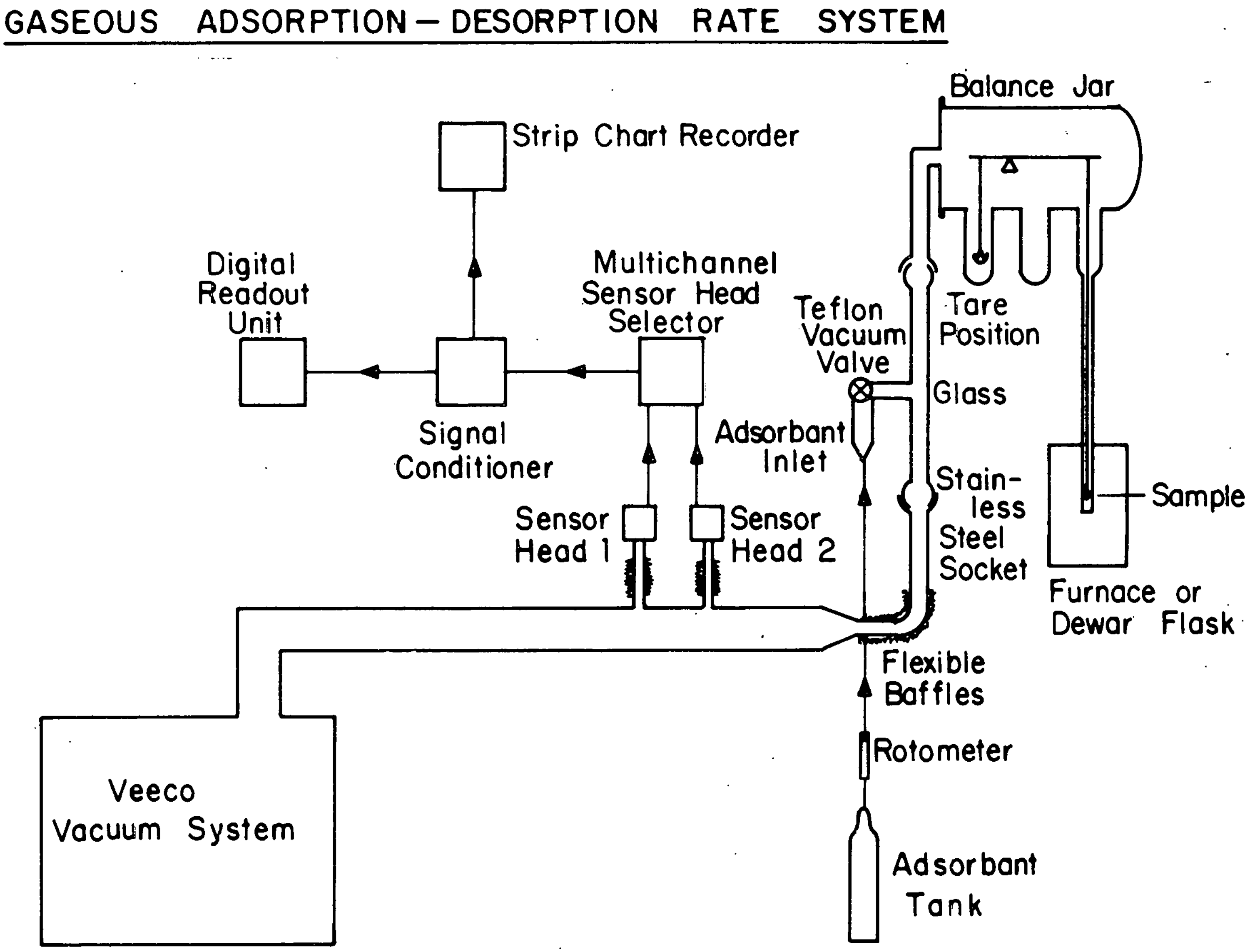

Fig. 3. Schematic diagram of equipment used for adsorption-desorption rate measurements on fly ash and ash-reductant mixtures.

4. Measurement of Gas Diffusion Rates in Ash-Reductant Pellets

Many factors affect gas diffusion rates through pellets: temperature, pressure, gas velocity, solid conversion, characteristics of diffusing gas, and pellet thickness. A cell has been fabricated to measure the effect of these variables on gas diffusion rates through pellets consisting of mixtures of fly ash and solid reductants. Figure 4 is a scale drawing showing several views of the cell. One inch diameter pellets are pressed directly in the cell. Spacers permit the pressing of pellets 1, ½, and ¼ cm in thickness. Copper o-rings are used to seal the joints between the stainless steel lids and center section of the cell. Due to its metallic construction, the cell can be operated at temperatures up to 500°C or even higher in an inert atmosphere. The cell will fit into a gas chromatograph oven in which the heating can be carried out.

Figure 5 shows the whole steady-state diffusion measurement system. A vent valve is used to vary the total cell pressure as desired. Any two gases exhibiting a variety of characteristics can be fed to the cell, the only limitation being that the gases must not react with stainless steel or copper. The flow meters used are capable of measuring a wide range of gas flow rates. In addition, the effects of pellet conversion can be simulated either directly or indirectly. Because the fly ash reaction system employs chlorine, it is necessary to use a simulated method. For example, known amounts of graphite can be introduced into a fly ash pellet and then reacted at temperatures up to 500°C with O_2 to simulate fly ash conversion. The cell can be weighed to determine the amount of conversion.

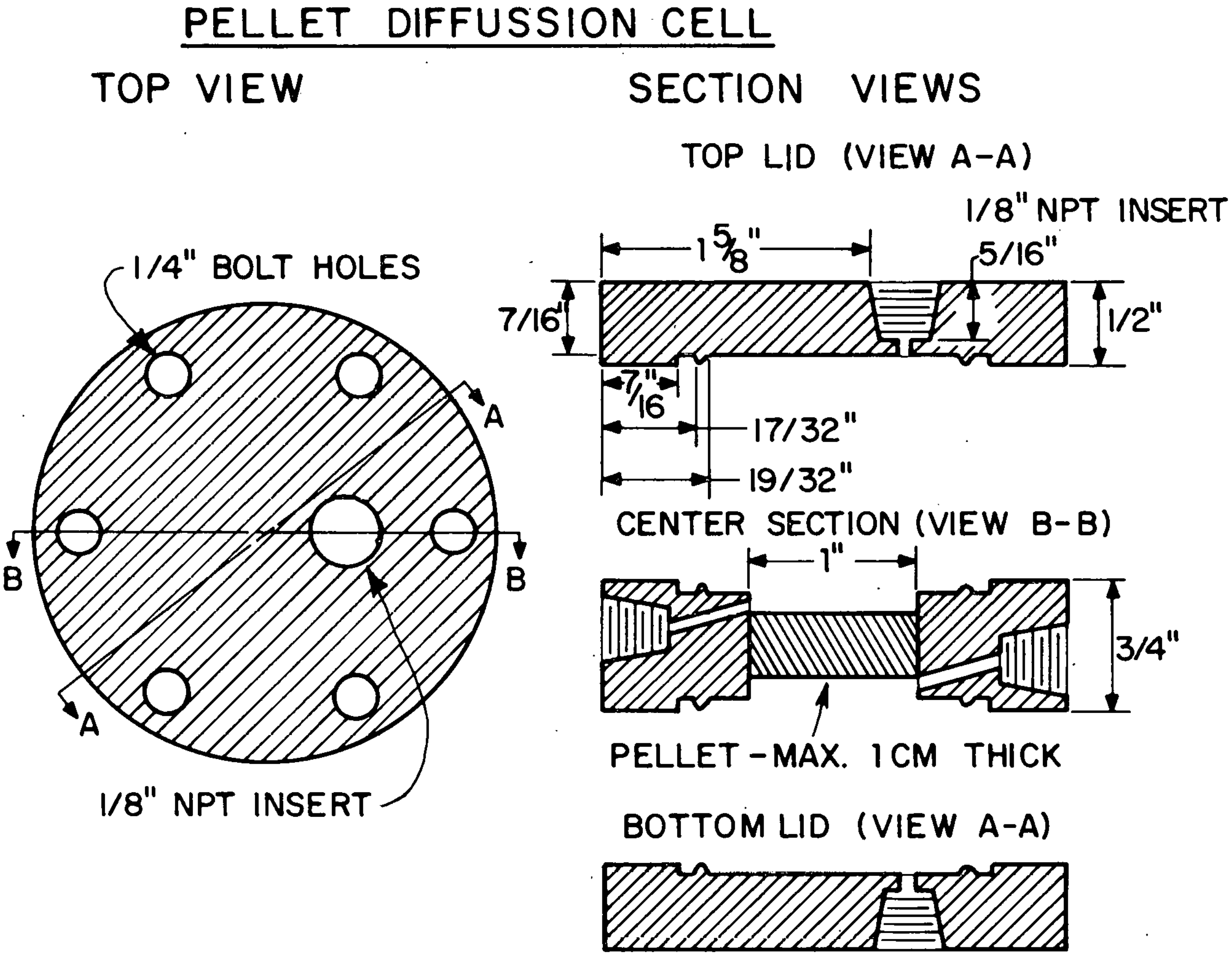

Fig. 4. Full-scale schematic diagram of pellet diffusion cell used in the measurement of gaseous diffusion rates through ash-reductant pellets.

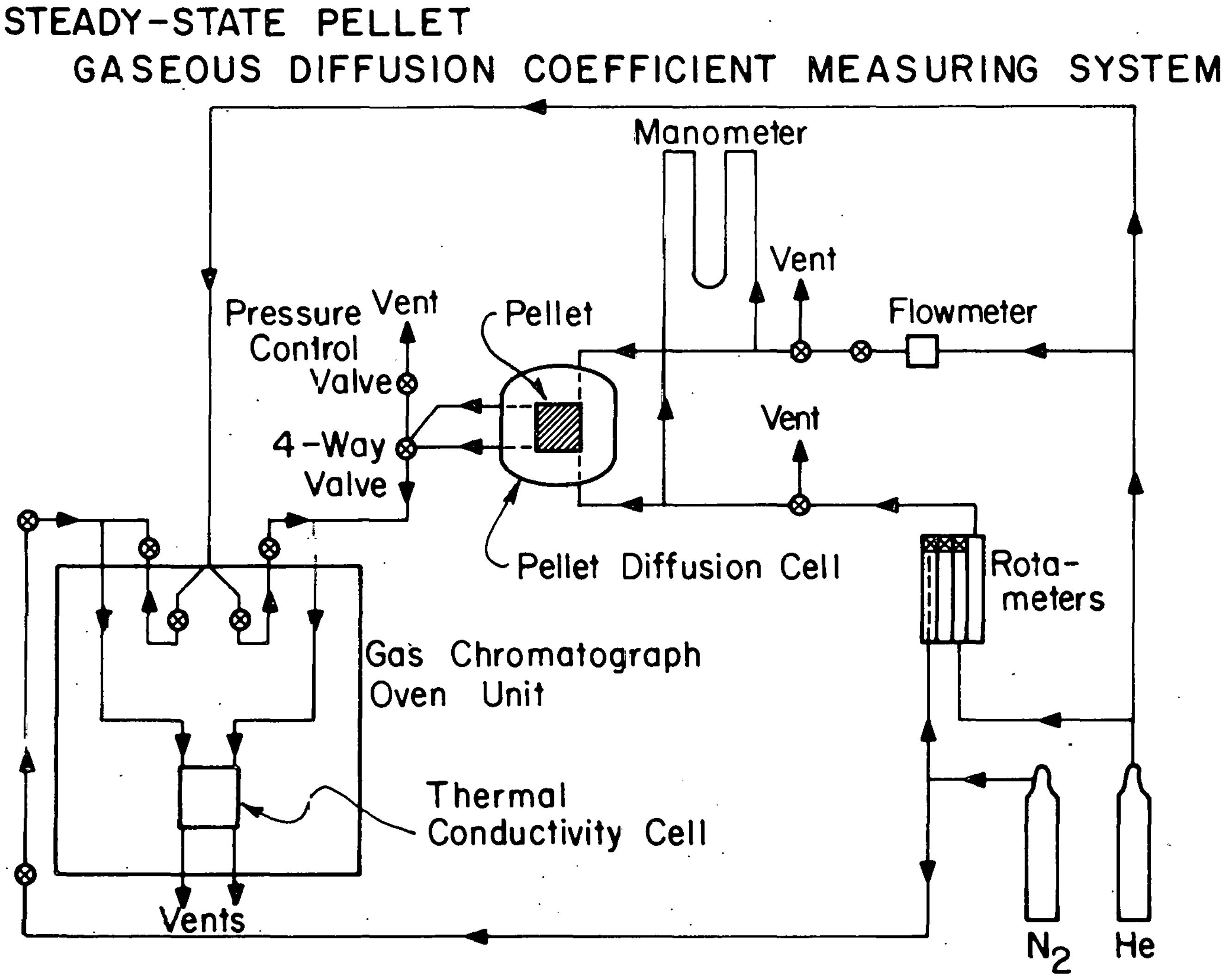

Fig. 5. Schematic diagram of system used for the measurement of steady-state gaseous diffusion rates through ash-reductant pellets.

The initial diffusion cell experiments used He and N_2 as the gases. As is shown in Figure 5, one gas enters on each side of the pellet. Normally the thermal conductivity cell is used to measure the concentration of helium in the nitrogen-rich stream exiting the diffusion cell. Then, based on this concentration measurement and the total flows entering and exiting the cell, an empirical relationship is used to predict the concentration of nitrogen in the helium-rich stream exiting the cell. The two concentrations along with the pellet thickness and cross-sectional area are used to calculate an effective diffusion coefficient. It was decided, however, to design the system so the concentration of helium in the nitrogen-rich stream and the concentration of nitrogen in the helium-rich stream could be measured directly by the thermal conductivity cell thus giving greater precision in measuring the gas compositions. The four-way valve shown allows for routing either stream into the detector. Also, the gas chromatograph carrier gas circuit was designed so either helium or nitrogen could be used as the reference gas.

In preliminary runs, the diffusion cell system was used to determine the effective diffusion coefficients for helium and nitrogen diffusion through a 0.6 cm-thick fly ash-graphite pellet. Subbituminous fly ash (Darold Tabor) was mixed with graphite in a 10:3 weight ratio and pressed into a pellet. The data collected and used to calculate the effective diffusion coefficients ($D_{e\ N_2}$ and $D_{e\ He}$) are listed in Table 3. The equation,

$$N_A = -D_{e\ A} \frac{dX_A}{dz} ,$$

was used to calculate $D_{e\,N_2}$ and $D_{e\,He}$. The values calculated for each gas in the two separate runs are in close agreement. Several other variables such as gas velocity and pellet thickness will have to be tested before the accuracy of any of the effective diffusion coefficients can be verified.

The determination of effective diffusion coefficients is important to the overall understanding of fly ash chlorination. The magnitude of the effective diffusion coefficients and kinetic rate constants (determined using the Cahn electrobalance system) will be compared to decide which step, diffusion or reaction, limits the overall fly ash conversion rate. The information thus obtained is essential in the design of pilot or commercial plant reactors.

Table 3. Data and results from two steady-state effective diffusion coefficient measurements.*

	RUN 1	RUN 2
N_2 Flow to Cell (cc/min)	108.71	105.26
He Flow to Cell (cc/min)	105.27	114.29
Net N_2 Flow Exiting Cell (cc/min)	92.77	88.40
Net He Flow Exiting Cell (cc/min)	71.88	82.55
N_2 Total Flow through Pellet (cc/min)	15.94	16.86
He Total Flow through Pellet (cc/min)	33.39	31.74
Mole Fraction N_2 on Helium-rich Side	0.18	0.17
Mole Fraction He on Helium-rich Side	0.82	0.83
Mole Fraction N_2 on Nitrogen-rich Side	0.74	0.74
Mole Fraction He on Nitrogen-rich Side	0.26	0.26
$D_{e\,N_2}$ (cm^2/sec)	0.055	0.057
$D_{e\,He}$ (cm^2/sec)	0.115	0.107

*The pellets were 0.6 cm thick and pressed from a 10:3 weight ratio mixture of a subbituminous fly ash and graphite.

5. Separation of Aluminum Chloride and Iron Chlorides in the Product Recovery System

It has been well established that the principal difficulty in purifying aluminum chloride contaminated with iron chlorides is a result of the formation of the mixed metal complex, $FeAlCl_6$, which is analogous to the pure metal chloride dimers Al_2Cl_6 and Fe_2Cl_6. In the presence of $FeCl_3$ and $AlCl_3$, the following equilibria are found to occur in the gas phase in the temperature range 200 to 700°C:

$$2FeCl_3(g) \rightleftharpoons Fe_2Cl_6(g)$$

$$FeCl_3(g) \rightleftharpoons FeCl_2(s) + \tfrac{1}{2}Cl_2(g)$$

$$2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g)$$

$$Fe_2Cl_6(g) + Al_2Cl_6(g) \rightleftharpoons 2FeAlCl_6(g)$$

Formation of the mixed dimer molecule occurs when gaseous Al_2Cl_6 contacts solid $FeCl_3$.

While formation of the mixed dimer limits the applicability of purely physical means for the purification of aluminum chloride, the extent to which $AlCl_3$ can be purified by fractional distillation, sublimation, or condensation is not well established. It is apparent, however, that reduction of ferric chloride to non-volatile iron by use of iron metal, aluminum metal, hydrogen gas, or come other reducing agent is a necessary step in $AlCl_3$ purification.

Research reported in the literature offers a basis for work on aluminum chloride-iron chloride separation. A solid-liquid phase diagram for $AlCl_3$-$FeCl_3$ has been discussed by Semenko, et al (1964).

In the phase diagram (Figure 6), a two-phase region separates to terminal solid solutions containing about 5 and 45 mole percent $FeCl_3$ respectively. The equilibria between solid solutions and the two-phase region were identified by use of x-ray diffraction analyses. The solid-liquid equilibria lines were found by use of DTA. A mass spectrophotometric analysis of the vapors above melts composed of 30 percent and 50 percent $FeCl_3$ established the presence of the mixed-metal dimer $FeAlCl_6$.

In characterization of the $AlCl_3$-$FeCl_3$ gas-solid system, Jorgenson and Moyle (1979) used a "pseudo-static" method for studying solid-vapor equilibria. Vapor in equilibrium with a given solid mixture was isolated from the solid, quenched, and then analyzed for Fe and Al. Under conditions in which a vanishingly small fraction of the gas phase contained free Fe_2Cl_6 (i.e., below 200°C), essentially all of the vapor-phase contained free Fe_2Cl_6. It was assumed, in accordance with Semenko's data, that a solid solution of $FeCl_3$ and $AlCl_3$ was present for solid compositions of between 45 and 100 mole percent $FeCl_3$. The activity coefficient of $AlCl_3$ in the solid was determined by the relationship

$$AlCl_3 = \frac{PY_{AlCl_3}}{P^o_{AlCl_3} \, X_{AlCl_3}}$$

where P is the total pressure of the system, $P^o_{AlCl_3}$ is the equilibrium vapor pressure of $AlCl_3$ at the temperature of the system, X_{AlCl_3} is the fraction of free $AlCl_3$ (Al_2Cl_6) in the vapor. The activity coefficient of $FeCl_3$ was then determined by the integration of the Gibbs-Duhem equation for the system.

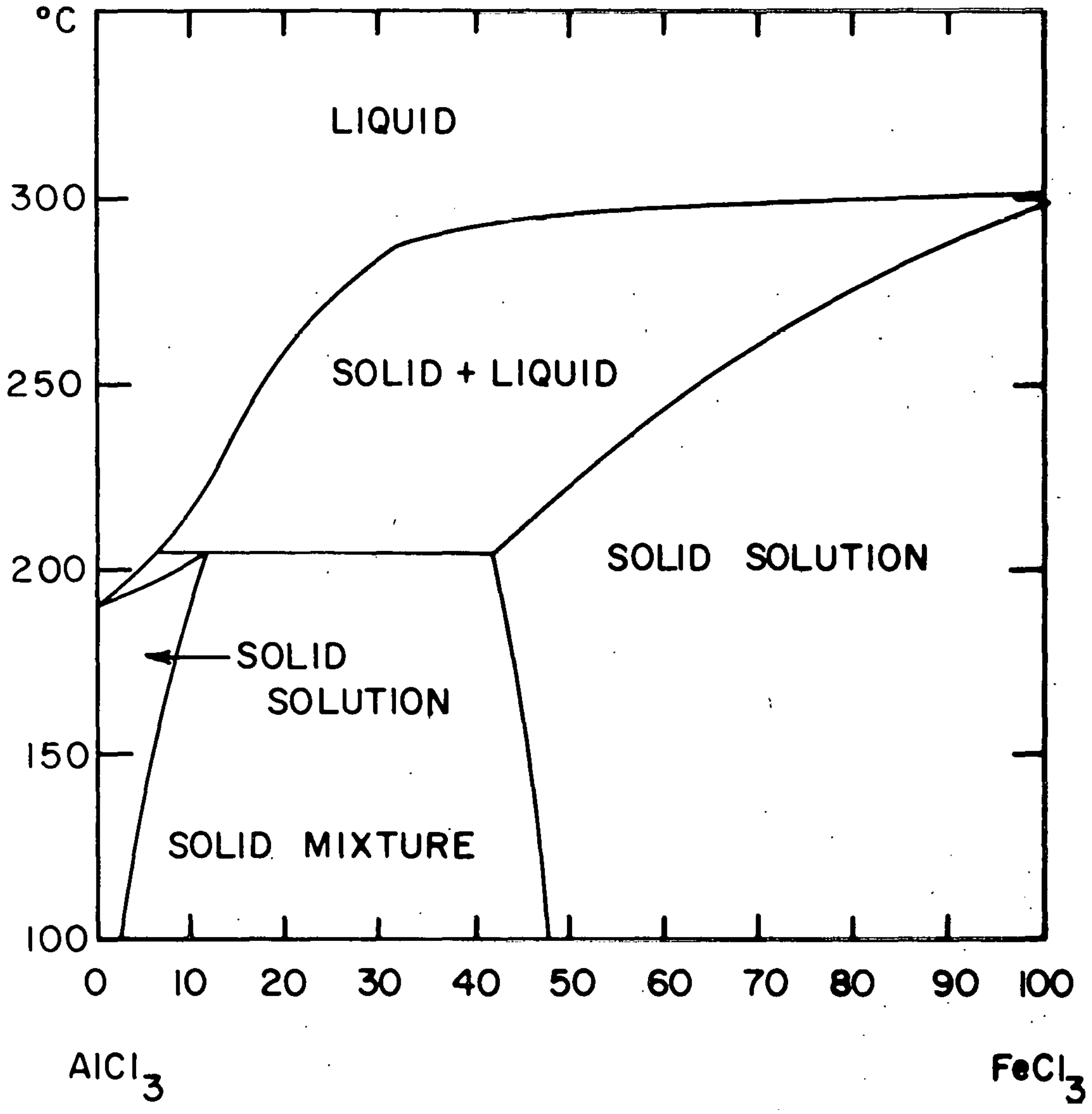

Fig. 6. Solid-liquid phase diagram of the $AlCl_3$-$FeCl_3$ two-component system. (Semenenko, et al., 1964).

$$-\frac{X_{AlCl_3}}{X_{FeCl_3}} d \ln \gamma_{AlCl_3} = d \ln \gamma_{FeCl_3}$$

The pressure contributions of free Al_2Cl_6, Fe_2Cl_6, and $FeAlCl_6$ permitted determination of the equilibrium constant

$$K_1 = \frac{P^2_{FeAlCl_6}}{P_{Fe_2Cl_6} P_{Al_2Cl_6}}$$

In the two-phase solid composition region the vapor pressure of Al_2Cl_6 was found to be independent of solid composition at a fixed temperature and pressure, in agreement with phase rule considerations. The dependence of $P_{Al_2Cl_6}$ on solid composition was significant in the $FeCl_3$-$AlCl_3$ solid solution region, in agreement with the phase rule for a 3-component 2-phase system at fixed temperature and pressure.

The equilibrium constant K_1 determined by the use of the pseudo-static apparatus is in reasonable agreement with that determined by Shieh and Gregory (1975). Shieh and Gregory conducted a spectrophotometric study of the Al_2Cl_6-Fe_2Cl_6-Cl_2 gas system to obtain chemical equilibrium data.

Ultraviolet absorption properties of many Al_2Cl_6-metal chloride gas systems allow precise measurement of metal chloride partial pressures in the presence of aluminum chloride. Both Fe_2Cl_6 and $FeAlCl_6$ absorb ultraviolet radiation at about 245 and 360 nm, while Al_2Cl_6 does not absorb in that wavelength region. Therefore, total iron concentration in a vapor phase containing Fe_2Cl_6, $FeAlCl_6$, and Al_2Cl_6 can be determined directly by use of spectrophotometric analysis. In Shieh and Gregory's study, solid samples of $AlCl_3$-$FeCl_3$ mixtures were sealed in quartz absorption cells. The cells were heated until the samples were completely vaporized, and then the absorbances at both 245 and 360 nm were measured at various temperatures.

In general, the absorbance of chemical species in any homogeneous phase can be represented by the linear relationship,

$$A/b = \sum_i \varepsilon_i c_i$$

at a fixed temperature, pressure, and wavelength. A is the absorbance, b is the cell path length, ε_i is the specific absorptivity of component i at the temperature and pressure of the system and at a specified wavelength. The concentration of species i is represented by c_i. Specific absorptivities of the species of interest are found in the literature or measured experimentally before the multicomponent systems are studied. Shieh and Gregory were able to measure the specific absorptivity of $FeAlCl_6$ by using conditions similar to those used by Jorgenson and Moyle. Absorptivities for Cl_2 were summarized by Gibson and Bayless (1933).

If known quantities of $FeCl_3$, $AlCl_3$, and Cl_2 are charged to an absorption cell and the solids then completely vaporized, the following relationships are valid at pressures near one atmosphere:

$$A/b = \varepsilon_{Fe} c_{Fe} + \varepsilon_M c_M + \varepsilon_{Cl_2} c_{Cl_2}$$

$$c_{Al}(\text{total}) = 2c_{Al} + c_M$$

$$c_{Fe}(\text{total}) = 2c_{Fe} + c_M$$

where subscript "M" refers to the mixed metal dimer. Since the path length, specific absorptivities and initial concentrations of $AlCl_3$, $FeCl_3$, and Cl_2 are known, there is sufficient information to specify the system and to determine the equilibrium constant

$$K_1 = \frac{c_M^2}{c_{Fe}\,c_{Al}}$$

Corrections for dissociation of the Al_2Cl_6 and Fe_2Cl_6 dimers must be included in these computations.

A combination of the methods of Jorgenson and Moyle and Shieh and Gregory might allow further characterization of the $AlCl_3$-$FeCl_3$-Cl_2 system. The apparatus in Figure 7 consists of two chambers, A and B, separated by a narrow channel and valve. Chamber B has provision for charging a solid sample and for monitoring the total pressure. Chamber A has parallel quartz windows with path length b.

Chamber B is charged with a solid sample of known $AlCl_3$-$FeCl_3$ mixture. The entire system is then purged with chlorine at a known temperature and pressure so that the chlorine concentration is determinate. The system is heated to a uniform temperature (with the window temperatures slightly hotter to prevent condensation of gaseous species on the glass), and the total pressure is monitored or controlled. Once equilibrium is attained, the absorbance of the gas phase is measured at the appropriate wavelengths. Chamber A is then sealed and cooled to room temperature, and its contents are analyzed for Fe and Al. If the volume of chamber A is known and the appropriate phase diagram is known, the activities of $AlCl_3$ and $FeCl_3$ in all phases are determinable. This equipment will provide extensive vapor-condensed phase equilibrium data for the $FeCl_3$-$AlCl_3$-Cl_2 system under most conditions of interest and is presently in the design stage.

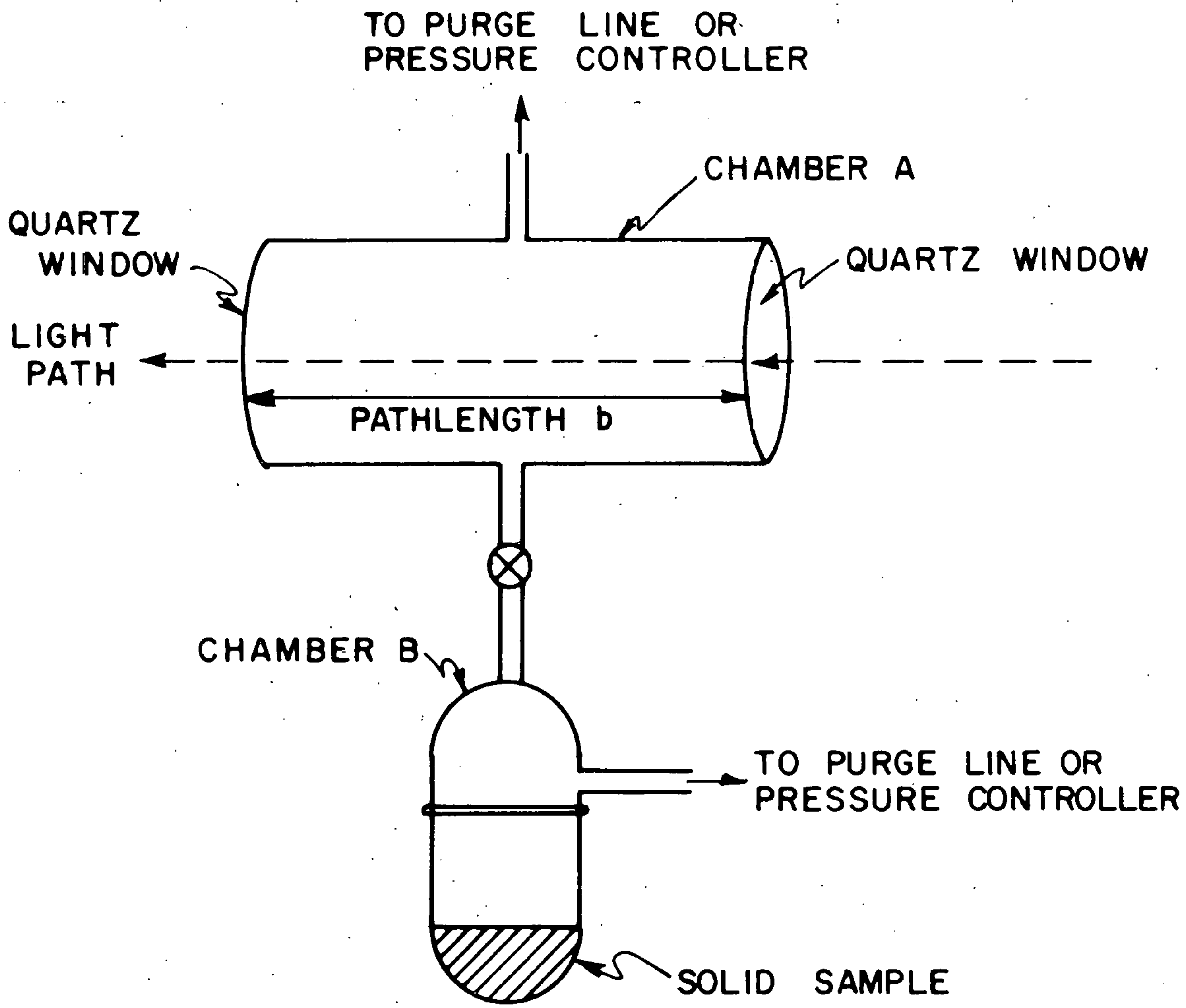

Fig. 7. Equilibrium absorption cell for use in spectrophotometer.

Lime-Soda Sinter Process Development

Research of the sinter processes consisted of a series of experiments investigating the auto-disintegration of sintered pellets. Sinters were prepared to determine the influence of small quantities of additives to the fly ash-$CaCO_3$ mixtures. Fly ash and limestone were combined in ratios which would form the compounds $2.3CaO \cdot SiO_2$ and $12CaO \cdot 7Al_2O_3$. Pelleted mixtures were sintered for one hour at 1380°C. The results obtained showed that the addition of small amounts of specific oxides have a pronounced effect on the auto-disintegration of the sintered pellets. Table 4 indicates the influence of the addition of several oxides on the rate of disintegration. Because the purpose of this work was to determine which minor components influence disintegration, rather than to determine a concentration for each additive which would inhibit disintegration, the oxide additives were limited to a maximum of 2 wt. percent added. As shown on Table 4, P_2O_5 and V_2O_5 are minor constituent additives which totally stop sinter disintegration. The oxides of Na, K, and Mn slow the rate of disintegration.

These limited data suggest that small radii ions having +5 and +6 valence charges probably enter the lattice structure of the calcium orthosilicate and prevent the lattice phase transformation from β-C_2S to γ-C_2S that cause the auto-disintegration to occur. The phase transformation increases the volume of the crystal lattice and results in the auto-disintegration of the sinters. Additional work is required to investigate amount of additive used, cooling pattern, temperature, and particle size of the product.

Table 4. Effect of the addition of trace constituents on the auto-disintegration of lime-fly ash sinters.

Additive, wt% added	Auto-disintegrate		Time for disintegration, Minutes
	Yes	No	
Fe_2O_3, 4	X		2
$CaSO_4$, 4	X		2
, 8	X		2
$CaSO_3$, 4	X		2
, 8	X		2
$CaHPO_4$, 4		X	-
, 1		X	-
, 0.2	X		5
Na_2CO_3, 0.2	X		1
, 1	X		5
K_2CO_3, 2	X		5
TiO_2, 1	X		2
$MgCO_3$, 2	X		1
V_2O_5, 2		X	-
MnO_2, 2	X		10

*Subbituminous fly ash-limestone mixtures sintered 1 hr. at 1380°C, 3.6°C/min heat-up from 800°C, 8 C/min cool-down.

Beneficiation of Magnetic Fly Ash

Results indicate that a combination alkali-acid extraction sequence will remove most of the alumina and silica from the magnetically separated fly ash, leaving a high iron content material. This beneficiated ash is of a high quality and can probably be used in either blast furnaces or electric furnace smelters.

The results of alkali and acid leachings indicate that less severe conditions than previously investigated may yield high levels of extraction. Tests were conducted to determine if recycled caustic leach liquor can extract material from fly ash or if fresh alkali solution is required. An alkali extraction was made for 30 minutes at 200°C with 30 wt. percent NaOH and 140 grams magnetic fly ash per liter of solution. The filtrate from this extraction was then used to extract another ash sample under the same extraction conditions. The solid residue from that extraction was then leached with 2N HCl for 10 minutes at 60°C and 100 grams solid per liter of acid.

The results for solid analyses from these extractions are given in Table 5. The compositions of the solid residues from the two alkali extractions are quite different, the residue from the second extraction is higher in alumina and silica, and much higher in soda content. The soda concentration indicates the precipitation of dissolved material on the ash particle surfaces. After acid extraction, however, most of the alumina, silica, and soda are removed and the residue meets specifications for iron ore use. Further work will include making three or four caustic extractions using the same leach liquor. Less severe acid and alkali conditions will also be investigated. The economics of processing would be improved substantially if the leachings can be made at atmospheric pressure.

Table 5. Composition of Solids From Multiple Caustic Extractions

Component	Caustic Extraction #1	Caustic Extraction #2	Acid Extraction
Fe, wt. %	53.7	50.1	65.2
SiO_2, wt. %	7.79	9.92	2.65
Al_2O_3, wt. %	7.43	8.23	3.61
Na_2O, wt. %	3.83	4.92	0.01

FUTURE WORK

HiChlor Process Research

The experimental plan for the measurement of kinetic rate data for chlorination of the mixed oxide glasses of which fly ash consists is being developed. The microbalance will provide sample weights versus reaction time data but no direct indication of which oxide in a mixture is reacting. For mixed oxides, however, a linear weight versus time relationship at low fly ash conversions will permit determination of overall rate constants and activation energies. The reactivity of different fly ashes can then be compared, and the effects of temperature and reductant source can be evaluated. The kinetics of individual pure components will also be studied, followed by work with component mixtures in concentrations similar to those found in fly ash. The kinetic studies of pure components and mixtures will help explain the weight versus time relationships which result for fly ash reaction studies.

Fly Ash Sinter Process Development

More definitive research will be initiated to investigate the influence of coal refuse on the high-temperature sinter reactions. Data show very substantial increases in soluble alumina yield when a small amount of coal refuse is added to sinter mixtures. X-ray diffraction will be used to identify the compounds formed. The distribution of the iron and sulfur added in the coal residue among the leachates, precipitated product, etc., will be determined.

Investigation of process conditions and lime requirements for desilication of the extract leachate is required. The dissolved silica must be removed from solution before aluminum trihydroxide is precipitated. At high pressure, with lime addition, insoluble calcium aluminum silicates are formed and precipitate. Alternate means of removal such as selective adsorption will also be investigated.

Recovery of Magnetic Fly Ash Fraction

The wet magnetic separation unit will be used for separation of the iron-rich fraction from fly ash-water slurries. A procedure is being developed for semi-continuous operation. Separation data for the fly ash-water slurries will be compared to dry ash separation results to determine the most feasible method.

In the preparation of an iron ore concentrate from the iron-rich fly ash fraction, the residue after caustic extraction is coated with a layer of precipitated sodium aluminum silicates. The precipitated material is easily dissolved in an acid solution, and research will identify the acid strength, temperature, and time required to most effectively remove this material from the ash residue particles. Additional caustic leaching studies will show the optimum conditions for operation of the combination alkali-acid extractions to yield high iron content beneficiated magnetic fly ash. Methods will also be sought for carrying out the initial caustic extraction without the precipitation occurring.

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