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The Status and Potential of Metals Recovery from Coal Fly Ash by High-Temperature Chlorination

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Coal fly ash is a potential commercial source of aluminum, iron, and titanium. A high-temperature chlorination process (HiChlor) is under development at the Ames Laboratory to remove these metals and purify the products. A reduction-chlorination reaction is used to convert the metal oxides in the fly ash to volatile metal chlorides. Bench scale tests have been conducted by flowing chlorine gas through a horizontal fixed-bed composed of a fly ash-graphite mixture. The amounts of iron, aluminum, titanium, and silicon removed have been determined as a function of reaction time (0.5 to 2 hours) and temperature (750°C to 900°C). On-stream product gas analyses of CO, CO₂, and Cl₂ using a gas chromatograph have permitted calculation of chlorine balances and reaction rates in terms of the O₂ evolution rate. Reaction controls, surface area and particle size distributions as a function of fly ash conversion, and final conversion limitations also have been investigated.

INDEX DESCRIPTORS: Aluminum chloride, chlorination, coal ash, fly ash, waste utilization.

Coal contains both organic and inorganic constituents. When pulverized coal is combusted, the organic fraction is consumed and the inorganic portion is collected as boiler slag, bottom ash, or fly ash. Figure 1 pictures the amounts of each of these coal wastes collected and utilized (shaded areas) in the United States during 1978 (1). Present uses include road fill, cement admixtures, lightweight aggregate, and ice anti-skid materials. It is evident that most of the coal waste, particularly the fly ash, is not used.

The elemental composition of a typical western United States coal fly ash is given in Table 1(2). Using these data and the coal waste production data given in Figure 1, the amounts of aluminum, iron, and titanium available from coal wastes in 1978 were calculated and listed in Table 2. It was assumed that the elemental compositions of boiler slag and bottom ash are the same as that of fly ash, which is approximately true. Also, the amounts of metals derived from coal wastes are based on an 80 percent metals recovery rate. Research to date (3, 4) indicates that an 80 percent recovery rate is realistic, especially for aluminum.

The net amounts of aluminum, iron, and titanium imported during 1978 by the United States (5) are reported in Table 3 along with the totals from Table 2. The figures in Table 3 indicate that the recovery of 80 percent of the aluminum, iron, and titanium in coal combustion

Table 1. *Elemental weight percent composition of a whole fly ash from Comanche Power Plant, Pueblo, Colorado. Fly ash of coal from Gillette, Wyoming collected by electrostatic precipitators (2).*

Constituent	Weight Percent
Si	14.1
Al	10.4
Fe	3.8
Ca	20.6
Mg	2.7
Na	1.2
Ti	0.9
K	0.3

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Table 2. *Million tons of aluminum, iron, and titanium available for 1978 coal combustion wastes based on an 80 percent metals recovery rate.*

Coal Waste	Aluminum Iron Titanium			
	Million Tons	(Million Tons)	(Million Tons)	(Million Tons)
Fly Ash	48.3	4.02	1.47	0.35
Bottom Ash	14.7	1.22	0.45	0.11
Boiler Slag	5.1	0.42	0.16	0.04
Total Million Tons Metal		5.66	2.08	0.50

wastes could replace 90 percent of the aluminum imports, 10 percent of the iron imports, and all of the titanium imports. Therefore, if economical metal recovery processes are developed, coal wastes could be utilized as a significant source of aluminum, iron, and titanium.

Since fly ash comprises the greatest fraction of coal wastes, only fly ash utilization will be addressed in this paper. The recovery and separation of the aluminum, iron, and titanium in fly ash is difficult for two reasons. First, fly ash is an extremely heterogeneous substance composed largely of an alumina-silica glass. Some iron and titanium oxides are distributed throughout the glass (6). Primary ores such as bauxite and rutile are composed mostly (>90%) of the metal hydroxide or metal oxide of interest. Bauxite is mostly aluminum hydroxide trihydrate and rutile is largely titanium dioxide. Metal extraction in either case is not particularly difficult because the metals are not bound in a matrix such as the alumina-silica glass in fly ash. The second difficulty is the complex composition of the ash. Table 1 indicates that there are appreciable amounts of silicon, aluminum, iron, calcium, magnesium, sodium, and titanium.

Turning to the reaction step, the process must be designed so that undesirable metals (e.g., silicon) do not consume the reagents added. An alternative approach would be to react everything and then remove the desired products before recycling the remainder plus unconsumed reactants. In either case, unnecessary use of reactants will be uneconomical, especially if the reactants are lost and not recycled.

The product stream resulting from the fly ash reaction will contain many different constituents. An important part of the process will be the recovery and separation of the products of reaction. A review of possible separation schemes was the subject of a recent investigation (7).

In summary, any process to recover metals from fly ash must provide

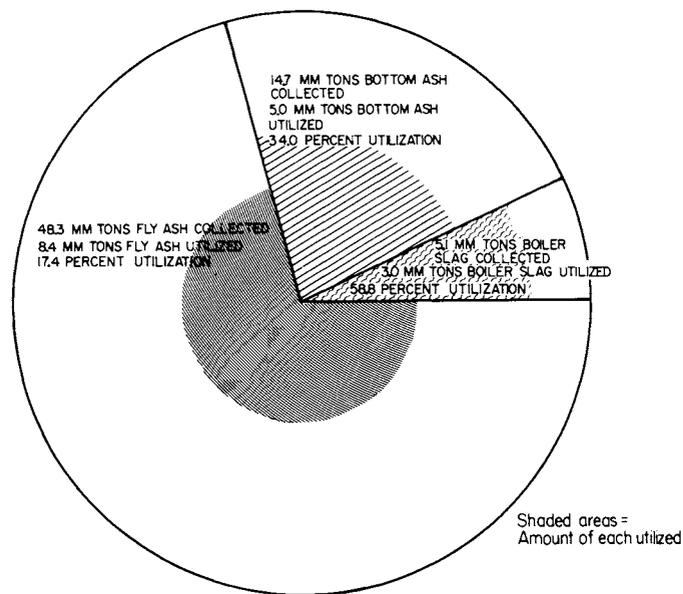


Figure 1. Million (MM) tons of coal combustion wastes produced and utilized in the U.S. during 1978.

for the following: 1) breakdown of the alumina-silica glass, 2) reaction of only the metals of interest with the supplied reactants or else easy recovery of reactants from undesirable products, and 3) separation of the metal compounds in the product stream.

The proposed Ames Laboratory HiChlor process (8) meets the above requirements and is presently undergoing development. Figure 2 is a schematic flow sheet of the process. A gas-solid reaction of fly ash and a reductant with chlorine is to be used to remove the metals from fly ash in the form of volatile metal chlorides. This reduction-chlorination reaction is the principal subject of this paper.

Experiments which employed such a reduction-chlorination reaction as the removal step were reviewed as part of a second recent investigation (3). The reaction was applied to such primary reactants as low-grade bauxite, aluminous clays, ilmenite, rutile, alumina, and iron oxides. The secondary reactants used were carbon and chlorine, carbon monoxide and chlorine, or phosgene (COCl₂). The reaction temperatures ranged from 600°C to 1150°C. Phosgene was found to be the most effective secondary reactant, followed by carbon monoxide and chlorine and then carbon and chlorine. Kinetic effects were determined to be the reason for the differences in the effectiveness of the secondary reactants.

Murtha et al. (2) examined a fly ash-chlorine-carbon reaction system. The possibility of preferential chlorination of the iron oxides present to remove the iron prior to the reaction of alumina or silica was explored. It was determined that only a portion of the iron could be removed using the conditions employed.

Reynolds and Williams included both fly ash-chlorine-carbon and fly-ash-chlorine carbon monoxide experimental data in a recently filed United States patent (4). The fly ash-chlorine-carbon data are very similar to those reported by Burnet et al. (2). However, the fly ash-chlorine-carbon monoxide data presented in the patent showed an advantage over the fly ash-chlorine-carbon data. The fly ash alumina conversions were comparable but the silica conversion was much lower in the system where carbon monoxide was used as the reductant. No

explanation was given for the difference in silica conversion because of reductant.

In neither of the above studies was an attempt made to explain the chlorination mechanism. The data presented allow one only to predict the fly ash conversion for a very specific set of reaction conditions. The first step toward understanding such a complex reaction system is to determine what is limiting the reaction rate. Several effects could be involved. For example, the kinetics of the reactions on, or mass transfer of reactants to or from, either the fly ash or carbon surface could limit the system reaction rate.

EXPERIMENTAL INVESTIGATION

Two sets of experiments were conducted in an effort to determine what limited the reaction rate of the fly ash-chlorine-graphite system. In the first, fly ash-graphite samples were chlorinated for 0.5, 1, and 2 hour periods over a temperature range of 750-900°C. The unreacted residue was analyzed for alumina, silica, iron oxide, and titania losses. This set of experiments gave information about the removal of elements from the fly ash as a function of reaction time and temperature.

In the second set of experiments, the same temperature range was investigated but all runs were for a two-hour period. A gas chromatograph was connected downstream from the reactor and used for on-line analysis of carbon monoxide and dioxide, and excess chlorine during the experiments. A schematic of the experimental system is pictured in Figure 3 and the system is described in detail elsewhere (3). This set of experiments supplied information about the graphite conversion rate while the first set supplied data about the conversion of fly ash.

Table 3. Net million tons of aluminum, iron, and titanium ores and metals imported by the United States during 1978 (5).

Ore or Metal	Net Million Tons	Conversion ^a Factor	Amount of Metal	Total Metal ^b from Coal Ash
Bauxite	16.0	0.25	4.0	
Alumina	3.4	0.53	1.8	
Aluminum	0.56	1.00	0.6	
Total of aluminum imported			6.4	5.66
Iron ore	32.4	0.62	20.1	
Pig iron and steel	0		0	
Total of iron imported			20.1	2.08
Ilmenite	0.46	0.32	0.15	
Rutile	0.29	0.58	0.17	
Titanium dioxide	0.12	0.60	0.07	
Titanium metal	0		0	
Total of titanium imported			0.39	0.50

^a Multiplication factors that convert ores to an equivalent amount of metal.

^b Million tons of metals available from 1978 coal combustion wastes based on an 80 percent metals recovery rate.

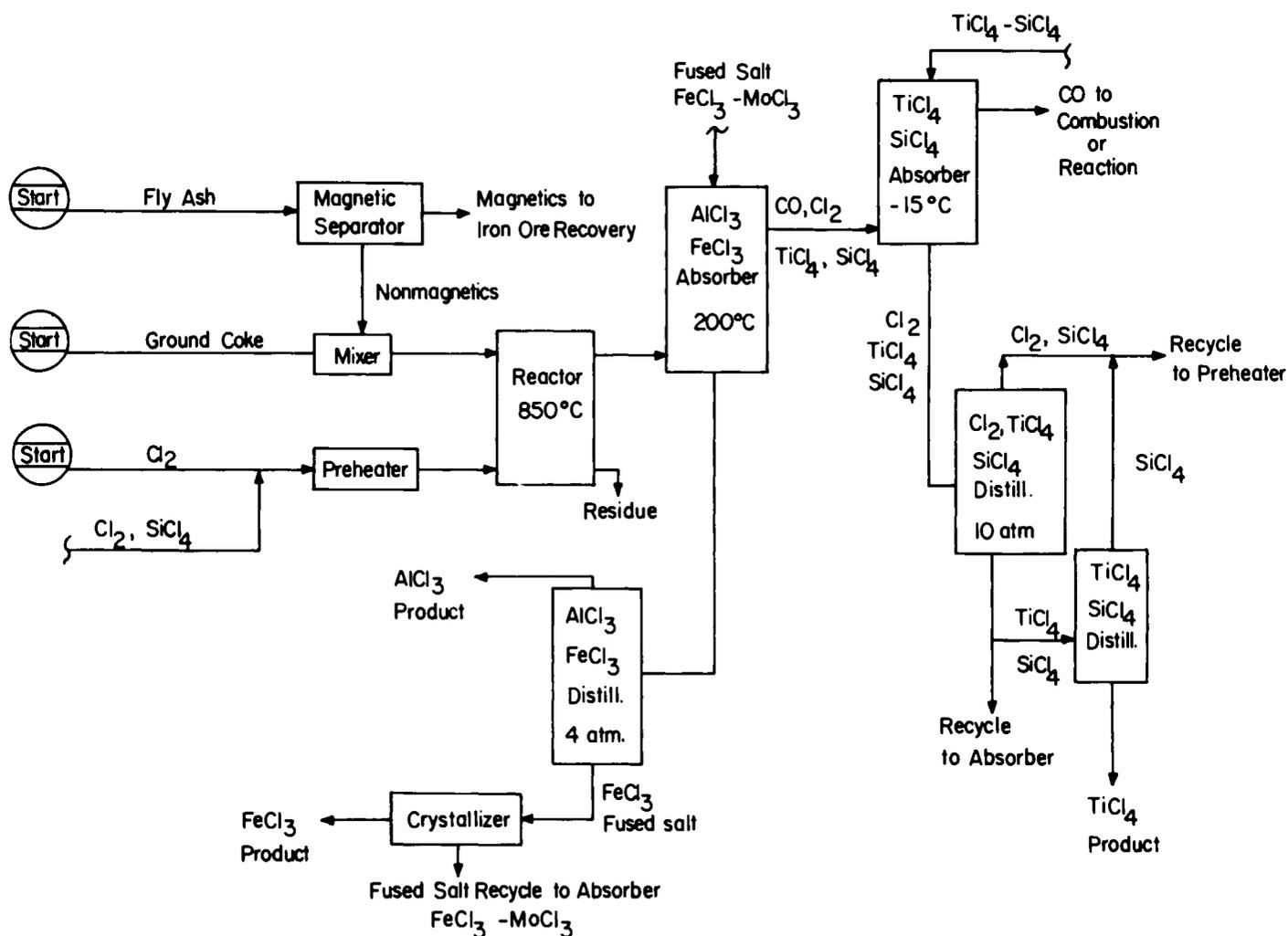


Figure 2. Schematic flowsheet of Ames Laboratory HiChlor process.

RESULTS AND DISCUSSION

The experimental data were used to make plots of the weight loss rate versus the mass of graphite or fly ash remaining in the samples. The rates were calculated as grams of graphite or fly ash removed per minute per square meter of surface area. The fly ash specific surface area as a function of conversion is shown in Figure 4. The graphite specific surface area at zero conversion was measured as 5.64 meters²/gram and was assumed constant for conversions up to twenty weight percent. This was shown to be a valid assumption by Tien and Turkdogan (9). All surface areas were measured using a Micromeritics Accu-Sorb BET instrument.

The graphite weight loss rate versus mass remaining is shown in Figure 5. There are 12 data points plotted for each temperature at 10 minute intervals. Time increases when moving from right to left. After an induction-type period (first 5 points), the relationship between the weight loss rate and grams remaining becomes nearly linear. The linearity indicates that the total graphite surface area available in the

sample is being utilized for reaction. All of the surface area being utilized, in turn, indicates that reaction kinetics are limiting the graphite reaction rate rather than any form of mass transfer.

The induction period is possibly due to an initial lack of exposure of the sample to chlorine. During the first 40-50 minutes, little excess chlorine was detected in the reactor exit stream. If a deficiency of chlorine was limiting the reaction, then not enough oxygen was produced from the metal oxide/chlorine reactions at the graphite surface to result in total surface utilization. However, as the graphite was consumed, the total surface area decreased to a point where oxygen was reaching the surface faster than it could react, resulting in kinetic control.

Figure 6 is an Arrhenius plot for the graphite reaction. It was assumed that neither the reaction rate constant nor the graphite specific surface area changed over the region that follows the induction period and continues up to a graphite conversion of about 20 percent (Figure 5). An activation energy of 42 Kcal/g-mole was calculated for the temperature range of 750-850°C. An activation energy of 49 Kcal/g-

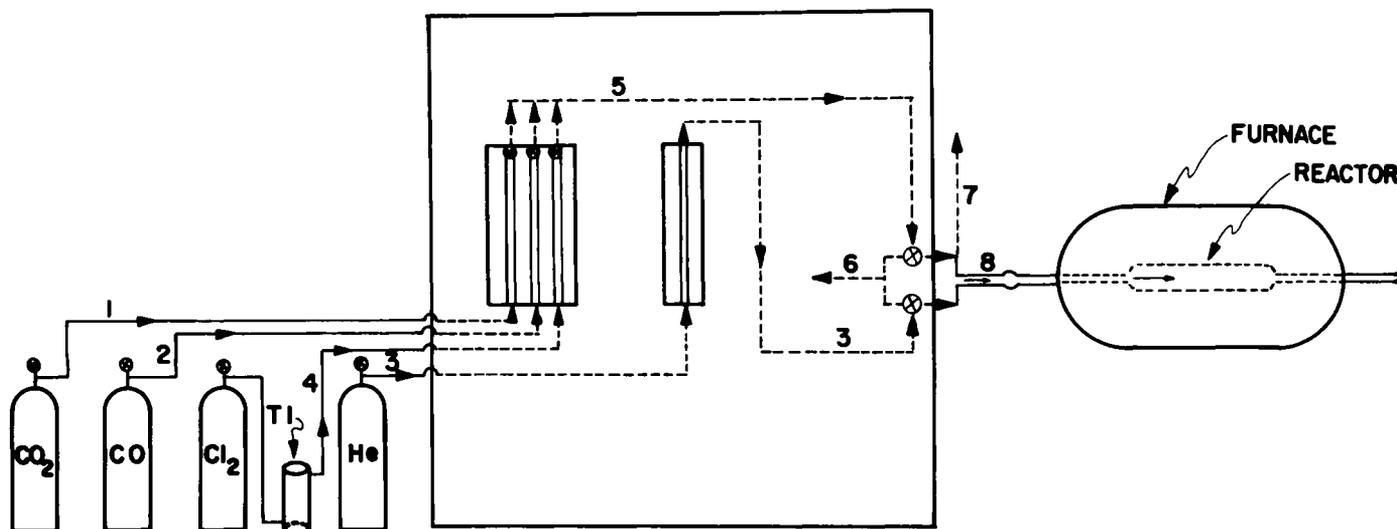


Figure 3. Schematic diagram of fly ash chlorination experimental equipment

1. Carbon dioxide supply stream used to calibrate GC.
 2. Carbon monoxide supply stream used to calibrate GC.
 3. Helium supply stream used for reactor purge.
 4. Chlorine feed stream to reactor and to GC for calibration.
 5. Connecting line between rotameter bank and reactor.
 6. Vent line to allow for purging gas lines up to reactor.
 7. Manometer line.
 8. Line through reactor.
- T1. Calcium chloride trap used to dry chlorine.

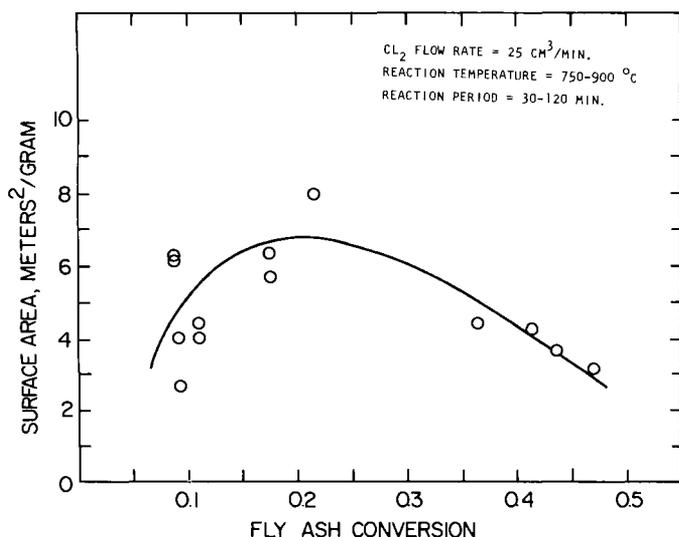


Figure 4. The effect of fly ash conversion on sample surface area.

mole was reported for graphite by Arthur (10). This is reasonable agreement for activation energies of two different graphites. The 900°C data point is not in line with the others. This discrepancy could be due to a difference in the reaction mechanism at 900°C. Some evidence of this can be seen in Figure 5. The straight line portions of the 750, 800, and 850°C curves roughly parallel each other but the 900°C slope is markedly different.

The plot of fly ash weight loss rate versus mass remaining exhibited no obvious linearity. The lack of linearity for fly ash and the presence thereof for graphite indicates that the fly ash part of the total reaction scheme did not limit the overall system reaction rate during the latter half of the experimental runs. The lack of chlorine limited the reaction rate during the first half.

ECONOMIC ANALYSIS

Although some questions concerning optimization of the fly ash reaction conditions remain unanswered, a detailed economic analysis has been made by Weiss, et. al. (11) to determine the feasibility of the HiChlor process. Assumptions concerning fly ash component conversions and the reductant used are based almost exclusively on the results of this investigation. The component conversions used for fly ash from bituminous coal and carbon as the reductant at 700-900°C were 80% for Al₂O₃, 80% for Fe₂O₃, 70% for TiO₂, and 1% for SiO₂. The silica conversion is suppressed and held to 1% by recycling silicon tetrachloride. Effectiveness of the recycle has been verified experimentally (12). An anhydrous product recovery and separation scheme was used to produce iron, aluminum and titanium chlorides. Oxidation of the metal oxides was used to free the chlorine for reuse.

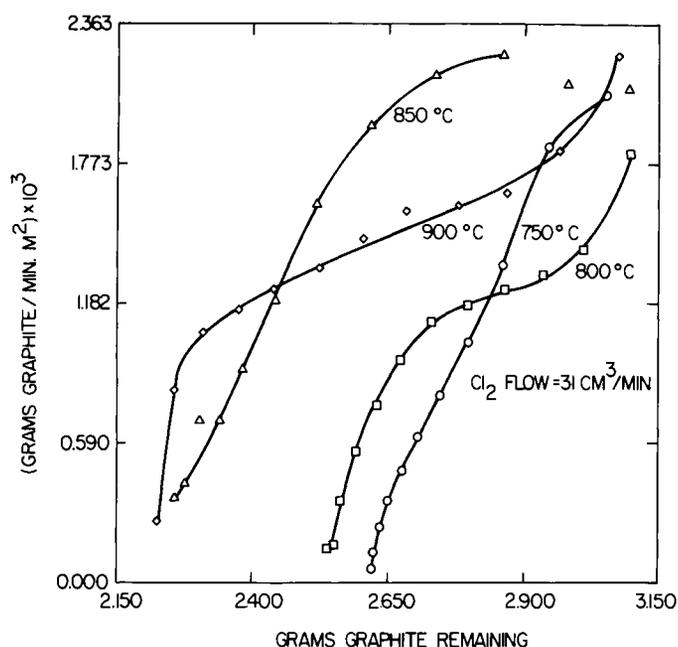


Figure 5. Grams graphite per minute per square meter surface area $\times 10^3$ versus grams graphite remaining in fly ash-graphite samples. The fly ash is from a western Kentucky and southern Illinois coal burned in a dry bottom type boiler at the Lakeside Power Plant in Milwaukee, Wisconsin and was collected by mechanical precipitators.

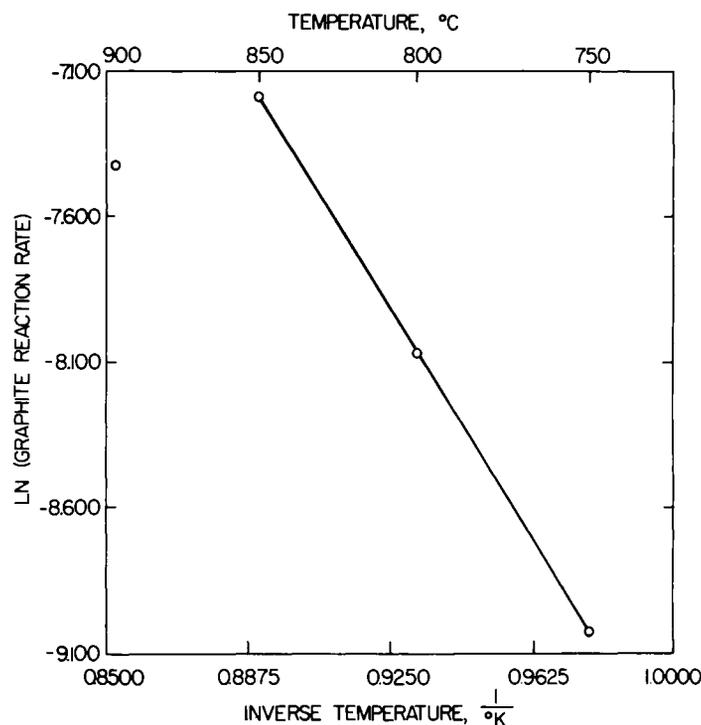


Figure 6. Arrhenius plot for the burning of graphite in the presence of oxygen and carbon monoxide and dioxide.

The economic analysis was for a plant capable of processing 6000 tons of fly ash per day. Raw material, equipment, labor, energy, engineering, and product entries were based on July 1980 values. A discounted cash flow rate of return (DCFRR) on investment of 9.8% was obtained using a fly ash cost of \$6.60 per ton, a 20 year plant life, continuous compounding, and a zero plant salvage value. When the fly ash was supplied at no cost, the DCFRR increased to 15.3%.

The HiChlor plant upon which the analysis was based is capable of processing the fly ash resulting from the generation of 7000 MW of electric power. The construction cost of a 7000 MW generating system, at a rate of \$500 per kilowatt, is \$3.5 billion. The corresponding HiChlor plant costs \$129 million or less than 4% of the power plant capital investment.

CONCLUSIONS

1. If coal combustion wastes in the U.S. were utilized at a metals recovery rate of 80 percent, 90 percent of the aluminum, 10 percent of the iron and all of the titanium ore or metal imports could be replaced by this source.
2. A fly ash metals recovery system must provide for the following: 1) breakdown of the alumina-silica glass, 2) reaction of only the metals of interest with the supplied reactants or else easy recovery of the reactants from reacted, undesirable products, and 3) separation of the metals in the product stream. The Ames HiChlor process satisfies all of these requirements.
3. Data from the literature indicate that the use of gaseous secondary reactants such as carbon monoxide-chlorine or phosgene in the HiChlor process would result in improved reaction kinetics when

compared to carbon-chlorine. Experiments reported here for carbon-chlorine indicate that reaction of the graphite limits the total system reaction rate and support use of gaseous reactants.

4. A preliminary design and cost analysis indicates that, under reasonable conditions, high-temperature chlorination of fly ash to recover metal values is a potentially profitable alternative to fly ash disposal.

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