

Proceedings of the Iowa Academy of Science

Volume 83 | Number

Article 4

1976

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Murtha, M. J. and Burnet, G. (1976) "Recovery of Alumina From Coal Fly Ash By High Temperature Chlorination," *Proceedings of the Iowa Academy of Science*, 83(4), 125-129.

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Recovery of Alumina From Coal Fly Ash By High Temperature Chlorination

M. J. MURTHA and G. BURNET¹

MURTHA, M. J. AND G. BURNET (Ames Laboratory-ERDA, Iowa State University, Ames, IA 50011). Recovery of Alumina from Coal Fly Ash by High Temperature Chlorination. Proc. Iowa Acad. Sci. 83(4):125-129. 1976. The recovery of metals from low value sources will help reduce our national demand for foreign resources. The ash from bituminous type coals contains about 20 percent aluminum oxide and 20 percent iron oxides by weight. Recovery of these metals would provide an alternate source to the ores now

used. The iron and aluminum materials in fly ash are recoverable by high temperature chlorination. Passing dry chlorine gas through a bed of nonmagnetic fly ash maintained at 850 to 900°C chlorinates the iron and aluminum constituents forming volatile compounds which are carried from the bed by the exit gas stream. In exploratory runs, 55 percent of the aluminum has been recovered as aluminum chloride in a nearly silica-free state.

Most of the coal used in power generation plants in this country is fired as pulverized material. The coal particles burn away as they pass through the furnace and the remains after burning are carried through the boiler and are collected as a fine powder known as fly ash. This is a waste material of which only about 15-20 percent is being commercially utilized. The remainder represents a very large disposal problem.

Pulverized coal usage in the United States now produces over 40 million tons of fly ash per year. Because of increasing capacity and problems with other power production methods, fly ash production is expected to be at least 75-80 million tons annually by 1980 (1, 2).

There have been many applications developed where fly ash can be used as an additive. Such diverse areas as soil conditioning, land reclamation, building materials, highways, water purification, fire control, and others have provided uses for some of the coal fly ash. This material contains metal components which if recovered would represent a much more valuable utilization of the ash. United States fly ash contains as an average 19 wt. percent iron oxides and 22 wt. percent aluminum oxide. Recovery of these materials from the ash will not totally eliminate the disposal problem, but will reduce the amount of waste material and will improve the economics of fly ash disposal.

Metal recovery from fly ash also represents a conservation of natural resources since, as an extreme, complete recovery would provide 90 percent of the nation's aluminum demand and 10 percent of the iron demand.

SEPARATION OF METAL COMPONENTS

There is variation in the composition of fly ash from different United States coals, but the range for each component is actually smaller than one might expect. Figure 1 shows data taken for a large number of coal fly ashes (3).

Size analysis of fly ash shows that the material is quite fine. About 75 wt. percent will pass through a 200 mesh screen (particle size less than 74 microns). The particles are also highly refractory, appearing microscopically as clear or black glassy spheres or craggy

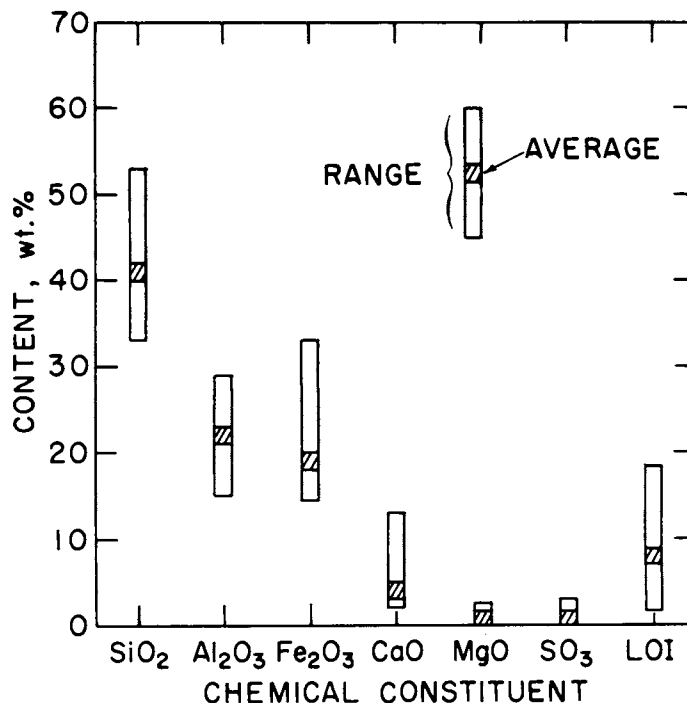


Fig. 1. Range and average content of different chemical constituents in United States fly ashes (3).

glass bits. The ash material is not crystalline; x-ray diffraction has shown fly ash to be 70 to 90 wt. percent amorphous glass (4) which requires severe chemical attack to break down its structure.

Most of the iron in fly ash is not chemically bonded with the aluminum or the silicon, an iron fraction containing 70 to 90 percent of the iron oxides in the ash can be separated magnetically. Table 1 contains chemical analyses of the whole fly ash and of the magnetically separated fractions for typical midwestern power plant fly ash. The fly ash used has been shown by earlier research (5) to contain about average mineral values for a midwestern fly ash, and is near the national average for bituminous-type ash. The bituminous-type ash contains more iron oxide than calcium oxide plus magnesium oxide. Lignite-type coal ash contains more calcium and magnesium oxides than iron oxide.

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³Work performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

Table 1. *Composition of C-1 Fly Ash and Fractions Obtained by Magnetic Separation^d*

Constituent	Chemical Composition, Wt. Percent		
	Whole Fly Ash	Magnetics ^c	Non-magnetics ^c
SiO ₂	39.1	14.4	46.9
Al ₂ O ₃	17.8	7.5	21.0
Fe ₂ O ₃	17.8	71.5	5.6
CaO	4.5	1.5	5.4
MgO	0.7	0.4	0.8
Na ₂ O	0.4	0.2	0.4
K ₂ O	1.7	0.8	1.8
SO ₃	1.9	1.1	1.9
LOD ^a	0.5	0.1	0.5
LOI ^b	10.6	0.6	13.0

^a LOD is loss on drying at 110°C

^b LOI is loss on ignition from 110-800°C

^c Whole fly ash separated as 24 wt. percent magnetics and 76 wt. percent non-magnetics.

^d C-1 fly ash was collected by mechanical precipitators from a dry bottom type boiler using coal from western Kentucky and southern Illinois. This particular sample was received from Lakeside Power Plant, Milwaukee, Wisconsin.

The magnetic separations were made using permanent magnets, not high-intensity high-gradient separation devices. Only the magnetic susceptibility of magnetite (Fe₃O₄) affects the separation. The magnetic particles contain much less alumina and silica than the nonmagnetic ores, which indicates that most of the iron is not in chemical combination or even fused into the alumina and silica particles. Because the magnetic particles contain low silica and alumina concentrations, the magnetic fraction, which represents about 25 weight percent of the fly ash, has potential as an iron ore substitute. Chemical processing to reduce alumina and silica levels will yield iron pellets similar in composition to taconite ore, about 65 weight percent iron. With no further processing the magnetic ash fraction has marketable value as a material which forms dense-media solutions for use in coal washing processes.

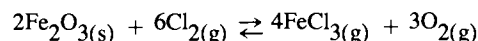
The nonmagnetic fraction is mostly silica and alumina, combined in a glassy amorphous structure. This material can be chemically attacked at high temperature by an aqueous alkali solution but the solubility of the resulting aluminate is quite low. Therefore, an alternate method of recovery was sought. It was found that several investigators had used chlorination to separate mixed oxides and ores (6-12). The glassy nature of the fly ash makes it less reactive than an ore material, but chlorination was investigated because of the possibility of selectively chlorinating the aluminum.

Table 2 contains information on chlorination affinity of some common metals and also boiling point information on the chlorides (10). The chloride-forming affinity of a metal at a given temperature is measured by the difference between the Gibbs free energy of its chloride and its oxide. As can be seen in Table 2, metals have an order in which they will chlorinate and also most metal chlorides are relatively volatile. In a mixture of metallic oxides, the metal of greatest affinity is the first to react with chlorine to form the chloride, provided that chlorine is present in a limited amount. Since the largest ash component, silica, is less reactive, gaseous aluminum and iron chlorides can be removed if the chlorine reacts with the glassy ash material.

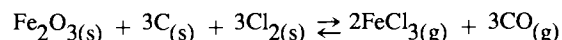
Table 2. *Chlorination Order and Boiling Point of Chlorides for Some Common Elements (10)*

Conventional electrochemical series (highest at bottom)	Chloride forming affinity from oxide (highest at top) at		Atmospheric Boiling point of chlorides, °C
	1300°C	800°C	
Cu	Cu	Pb	CuCl 1,690
Pb	Pb	Cu	PbCl ₂ 954
Sn	Zn	Zn	ZnCl ₂ 732
Ni	Co	Co	CoCl ₂ 1,050
Co	Ni	Sn	NiCl ₂ 973
Fe	Sn	Ni	SnCl ₄ 114
S	Fe	Fe	FeCl ₃ 319
V	Ti	Ti	TiCl ₄ 136
Ti	Ge	Ge	GeCl ₄ 84
Al	Al	Al	AlCl ₃ 183
	Si	Si	SiCl ₄ 58
	V	S	
	P	V	
	S	P	

The reaction of chlorine with metal oxides consists of oxidation-chlorination. Large quantities of energy are required for these reactions, and even at high temperature yields are low because the affinity of the resulting atomic oxygen from the iron is much higher than the affinity of the chlorine for the iron. The reaction will reverse until equilibrium is reached. As an example,

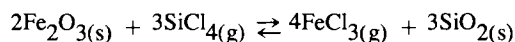


Reduction-chlorination is a method for increasing yield with no additional external energy required. If solid carbon is mixed with the solid ores, the oxygen from the oxides will react with the carbon forming CO and/or CO₂.



The combined reduction and chlorination reaction is exothermic. High yields can be obtained easily because the oxygen of the iron oxide is bound as CO and CO₂, and the reaction product gases can be withdrawn, forcing the reaction to the right. Because reduction-chlorination is exothermic, oxides of all the metals in a mixture will be chlorinated to some extent.

The high affinity metal chlorides can then be separated from the lower affinity ones by use of an oxidation-chlorination step. If the gaseous chlorides are brought in contact with additional metal oxides, the less reactive chlorides will react to reform oxides and convert more reactive metal oxides to chlorides, as follows:



From a mixture of metal oxides, the metal chloride of the highest affinity can be withdrawn as a gaseous product if the temperature is maintained above the boiling point of that chloride. When that chloride has been completely removed, the next highest affinity chloride becomes the product and temperature can be changed, if required, to withdraw it as a vapor.

EQUIPMENT

The equipment used for this research is shown schematically in

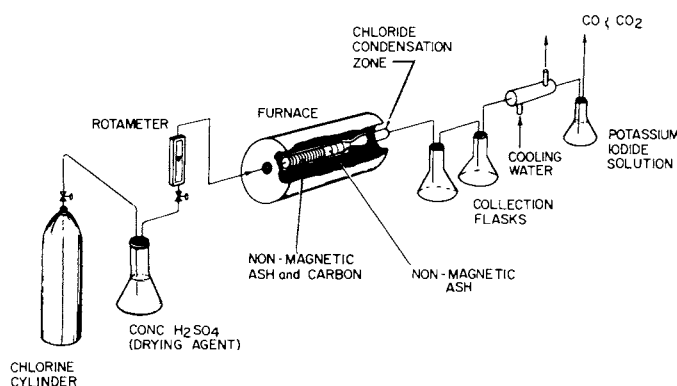
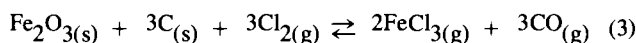
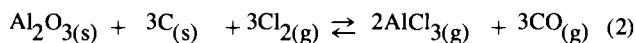
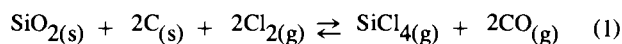


Fig. 2. Equipment used in fly ash chlorination.

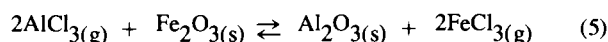
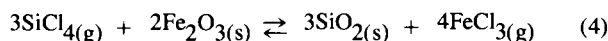
Figure 2. Dry chlorine gas flows through a nonmagnetic ash and carbon bed where nonselective chlorination occurs. Gaseous products then flow into a bed of nonmagnetic ash where the less reactive chlorides are oxidized. Both beds are maintained at a high temperature in the uniform temperature zone of a tube furnace. All of the connecting tubes, the reactor, and the collection equipment are glass. Vycor or quartz glass is used in the high temperature region. To improve bed porosity and gas flow distribution the reactor bed volumes are filled with small quartz cylinders and the ash materials occupy the voids in the packing. Unreacted chlorine is removed from the gas before venting by reaction with potassium iodide solution. There was no unreacted chlorine, however, until silicon chloride vapor reached the potassium iodide flask.

There are two separate ash beds because of the two successive chlorination operations, reduction and oxidation. The reaction sequence for the major components in the ash in the first bed is as follows:

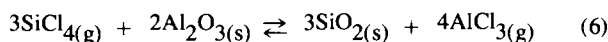


The chlorine flow is very low and the temperature must be at least 700°C for reaction to occur. At this temperature the oxide gas formed is carbon monoxide rather than carbon dioxide.

The hot gas containing the chloride compounds and carbon monoxide then flows through the second bed of nonmagnetic fly ash. The reactions occurring in this bed should be oxidations of the aluminum and silicon chlorides with formation of additional iron chlorides, as follows:



When all of the iron oxide has reacted the silicon chloride oxidation will produce aluminum chloride product.



RESULTS

The minimum operating temperature where chlorination products were recovered from the fly ash was 700°C. This agreed with previous work done using mixed ores. It had been expected that higher temperatures might be required because fly ash is in an amorphous vitreous form. A separate iron chloride product was not collected. A mixture of iron and aluminum chloride condensed as the exit gases left the furnace. Thermodynamic calculations had indicated that the yield of aluminum chloride would be increased at higher reaction temperatures, and the silicon chloride production would be reduced. Figure 3 shows this relationship with respect to reaction temperature. Data were obtained over the temperature range 700 to 1000°C. As indicated on Figure 3, the actual data do not correlate with the calculations. The calculated curves were determined from Gibbs free energy data (13) and simultaneous material balance solutions. Concentrations of the outlet gas at 725°C and 940°C were determined based on gravimetric analyses of each bed composition before and after chlorination, and of the condensed chloride products. These data do not agree with the thermodynamic calculations because selective reoxidation did not occur in the second bed. At the high temperature, additional amounts of all three chlorides formed in the oxide bed, but at the low temperature only the quantity of aluminum chloride increased.

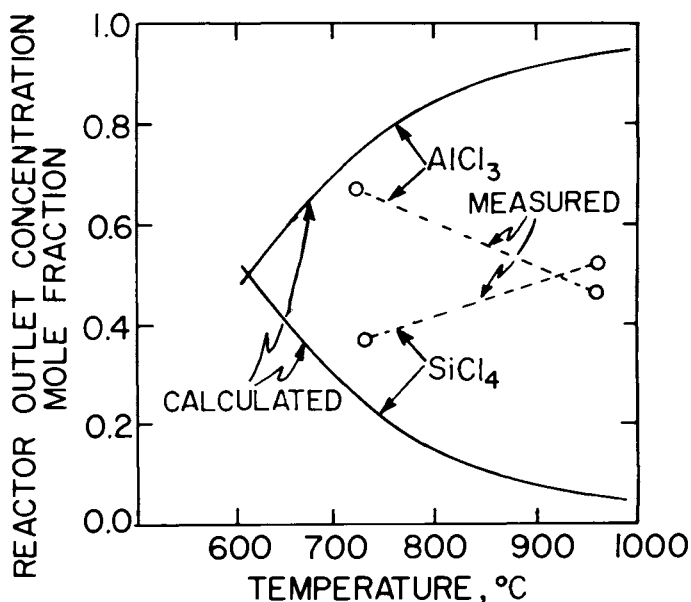
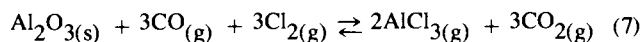


Fig. 3. Equilibrium composition of mixed chloride vapor product on an iron, carbon dioxide, carbon monoxide free basis.

Figures 4 and 5 show the yields and compositions of condensed chloride products as a function of reaction temperature. Although more silicon chloride was formed at the high temperature, the concentration of silicon in the condensed product decreased. The actual chemical reactions occurring in the second bed were not those predicted by reactions 4, 5, and 6. Although the chlorine flow rate was very low, there still must have been excess chlorine so that the following type of reaction occurred in the second bed.



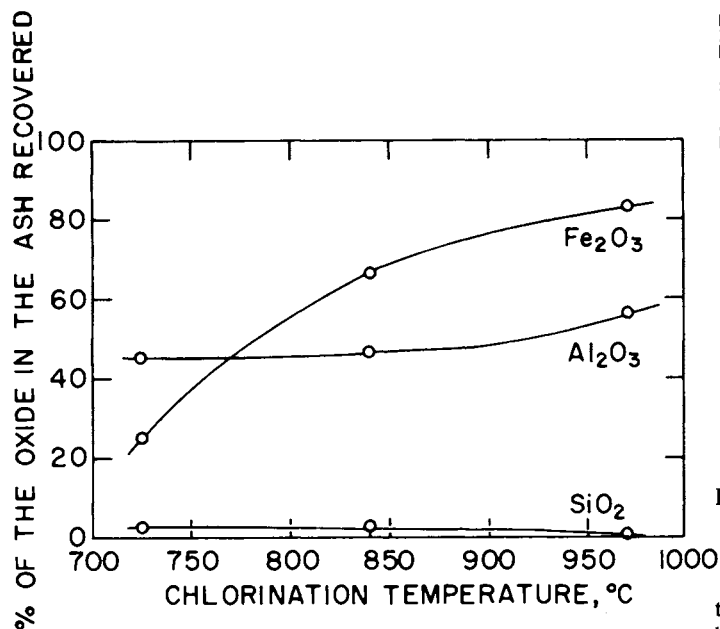


Fig. 4. Percentage of each metal oxide removed from the fly ash as a function of chlorination temperature.

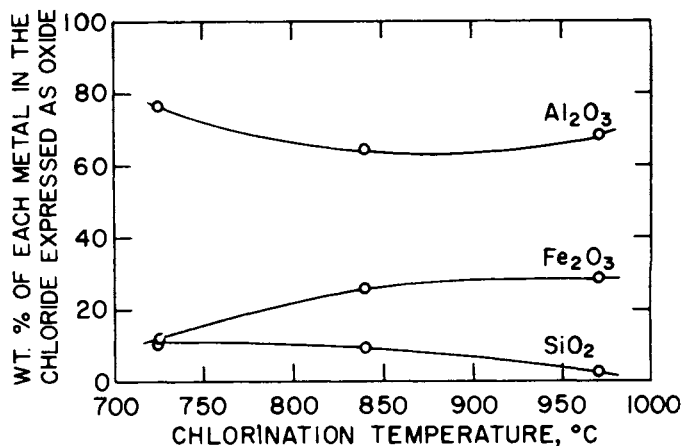


Fig. 5. Composition of the condensed chloride product as a function of chlorination temperature.

With chlorine and carbon monoxide present additional oxides of each metal will be chlorinated. A lower chemical reactivity of vitreous fly ash particles may also contribute to the deviation between calculated and actual results.

Table 3 contains composition data for the major constituents for the separate reaction beds. It was only when data on the individual beds was obtained that it was realized that selective chlorination was not occurring. The chlorine flow had been assumed to be correct because no unreacted chlorine entered the potassium iodide solution. But reaction (7) shows that unreacted chlorine will be used up in the second bed. Each run was terminated after about two hours when silicon chloride vapor entered the potassium iodide solution.

Compositions of the condensed chloride products were determined using a gravimetric procedure which separated the different metal constituents. Each was precipitated as a hydroxide, then calcined to

the respective oxide before being weighed. The solid ash materials both before and after chlorination were also analyzed. The ash samples were fused with sodium carbonate which caused the breaking of the silica-alumina-iron bonds. The sample is then soluble in a dilute acid solution and gravimetric separations can be made. The procedure which has developed for analyses of coal ash is similar to methods used in the portland cement industry. The materials are reported as mixtures of oxide constituents, but the samples actually consist of glasslike oxides and silicates, not crystalline oxides.

The concentrations of iron and aluminum in the condensed chloride product were also determined by a volumetric procedure. A method which complexes dissolved aluminum with 1, 2 — diaminocyclohexane tetra-acetic acid (CDTA) has proved to yield reliable aluminum measurements (14). The values obtained using the volumetric and the gravimetric procedures agreed within 5 percent.

The composition of the chlorination-oxidation bed for 970°C chlorination is of interest because the color of the material was changed from grey-black to almost white. As indicated in Table III, the composition after chlorination is primarily aluminum and silicon compounds. Photomicrographs of this material before and after chlorination are shown as Figures 6 (a) and 6 (b). The chlorinated residue is white even when examined microscopically. Crushing of the particles revealed that they were white throughout.

Table 3. Composition Data for the Chlorinated Reaction Beds

	Temp, 725°C				Temp, 970°C			
	Chlorination-Reduction Bed		Chlorination-Oxidation Bed		Chlorination-Reduction Bed		Chlorination-Oxidation Bed	
	Start	End	Start	End	Start	End	Start	End
Total Wt., grams	9.4	6.7	9.4	9.1	9.6	5.5	8.6	4.8
Constituent, wt. %								
SiO ₂	36.2	36.5	49.0	49.7	36.2	37.2	49.0	60.0
Al ₂ O ₃	15.5	9.6	21.1	13.6	15.5	6.8	21.1	17.3
Fe ₂ O ₃	4.1	0.9	5.6	5.7	4.1	0.4	5.6	0.4
LOI ^a	36.0	43.0	14.0	17.6	36.0	40.1	14.0	7.9

^a LOI is loss on ignition to 800°C

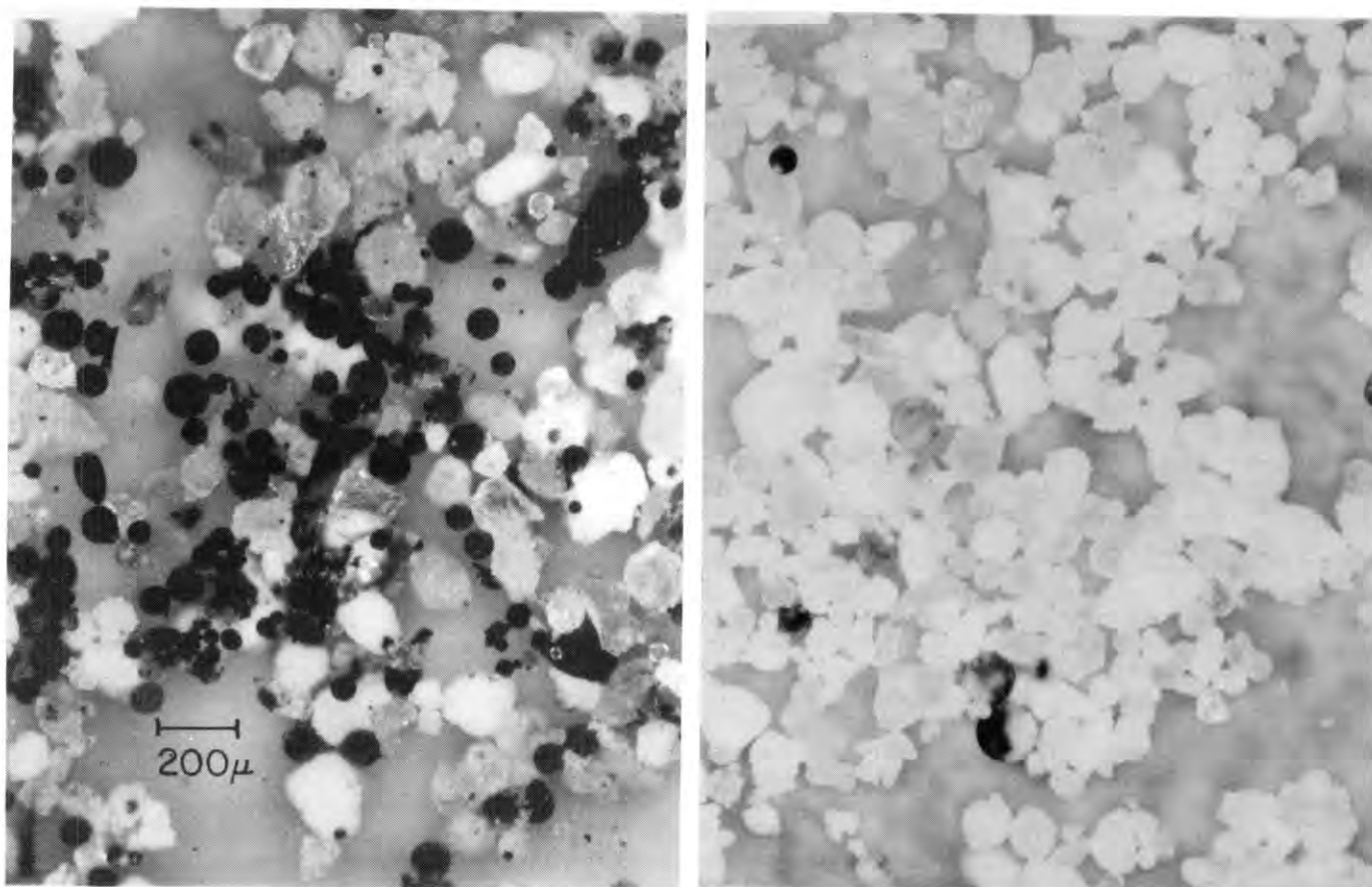


Fig. 6. Nonmagnetic fly ash (a) before chlorination, (b) after 970°C chlorination reaction. (50X)

CONCLUSIONS

1. A high iron content ash fraction can be recovered from fly ash by magnetic separation. The magnetic fraction will average about 25 weight percent of the total ash and will contain 70 to 90 percent of the total iron oxides.
2. The magnetic ash fraction can be marketed as an artificial magnetite which is used in coal washing processes. There is also potential for converting this material to an artificial iron ore, similar to taconite.
3. Iron and aluminum constituents can be recovered from vitreous fly ash by a high temperature chlorination process. The volatile metal chlorides then condense as a mixture of iron and aluminum chloride.
4. For the simple fixed bed reactor system which was used 55 percent of the aluminum in the ash was recovered as aluminum chloride.
5. Aluminum chloride can either be converted to aluminum oxide or used directly for aluminum metal production by a recently developed process (15, 16). The production of aluminum metal from the chloride requires only two-thirds of the energy for production from aluminum oxide.
6. Recovery of the metal constituents from power plant fly ash would reduce our dependence on foreign resources, and improve our balance of trade for metals. The U.S. deficit in the balance of trade for metals is now over two billion dollars annually.
7. Other low value sources from which metals could be recovered

by chlorination are spent oil shale, mine tailings, and nonbauxite alumina bearing rock and clay.

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