

VALUABLE PRODUCTS FROM UTILITY FLY ASH

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INTRODUCTION

Fly ash is a potentially important engineering raw material that has yet to be extensively utilized. Of the 48 million short tons of fly ash produced in 1993 from burning coal in power stations in the U.S., only 22% was utilized, with the major use occurring in cement and concrete products [1]. Utilization of fly ash represents a potential for utilities to both reduce costs and increase revenues. A major barrier to fly ash use is its variable nature, both chemical and physical, due to differences in source coals, boiler design and stack removal processes.

Because the variability of fly ash is manifested in the diversity of its chemical and mineral components, a novel way of exploiting the variability would be to physically separate these components and use them as raw materials for the manufacture of various value-added materials. Figure 1 shows components that may be separated from fly ash, and some of their potential uses. For example, the reactive aluminosilicate glass could be reacted to microengineer zeolites or other high surface area phases, or to prepare structural and insulation components. Unburned carbon can be converted to activated carbons or carbon black, or used as a supplementary fuel. Iron oxides (magnetite) can be used as a raw material for making ferrites (magnetic ceramics), in heavy media coal cleaning equipment to provide a high specific gravity suspension, and as cement additives. Cenospheres, hollow spheres composed mostly of silica, alumina and iron oxides, can be used as polymer fillers, in light-weight ceramics and as low dielectric constant substrates.

Recovery of useful components from fly ash can improve the economics of fly ash utilization and can offset costs associated with disposal. The Illinois State Geological Survey (ISGS) has a program to find new uses for fly ash. One objective of this work is to investigate the potential of recovering adsorbent carbon, magnetite and cenospheres from fly ash. Removing these components may improve the quality of the remaining fly ash so that it can be used in cement and concrete products. In this paper, results of preliminary efforts to recover adsorbent carbons and magnetite from fly ash are described.

EXPERIMENTAL

Fly ash was obtained from an Illinois utility burning high sulfur Illinois coal. The fly ash was sieved into plus 90- μm and minus 90- μm fractions. Only the plus 90- μm fraction was used in this work. Ash composition (major and minor oxides) was determined by X-ray fluorescence (XRF) spectrometry. Samples were dried overnight at 110°C, then ignited at 1000°C for one hour to determine loss-on-ignition (LOI). The ignited sample was fused at 1000°C for 15 minutes with 50% lithium tetraborate/50% lithium metaborate flux and formed into a 30-mm diameter disk. The specimen was analyzed with a Rigaku model 3371 wavelength dispersive X-ray fluorescence spectrometer with an end-window rhodium X-ray tube.

Magnetic components were recovered by dispersing 500 grams of fly ash in one liter of water and stirring by hand to wet the sample fully. A plunger type hand magnet was used to recover magnetic components that were transferred to another vessel. The procedure was repeated until very little magnetic component was collected by the magnet. The concentrate was dried and weighed to determine the amount of sample obtained.

The unburned carbon in fly ash was concentrated in a two-step process involving sieving through a 170-mesh screen and cleaning the -170 mesh particles by oil agglomeration/froth flotation. Activation of the carbon concentrate was done to develop further the surface area and porosity of the sample. About 10 g of carbon concentrate was placed in a ceramic boat (1.9 cm x 1.2 cm x 7.5 cm) and centered in a 5 cm ID x 90 cm mullite tube in a Lindberg split-tube furnace. The sample was heated at 20°C/min to 950°C in flowing N₂. The N₂ was replaced by 50% H₂O/50% N₂ for 1 h. The sample was then cooled under N₂ to room temperature.

The SO₂ adsorption capacities of samples were determined by thermogravimetric analysis (Cahn TG-131). In a typical run, a 30-50 mg sample was placed in a platinum pan and heated at 20°C/min in

flowing N_2 to 360°C to remove moisture and impurities. The sample was cooled to 120°C. Once the temperature stabilized, a mixture of gases containing 5% O_2 , 7% H_2O and the balance N_2 was substituted for the N_2 . Once there was no further weight gain due to adsorption of O_2 and H_2O , SO_2 was added in concentrations representative of a flue gas from combustion of high sulfur coal (2500 ppmv SO_2). The weight gain was recorded versus time by a computerized data acquisition system.

Surface areas were determined from the amount of N_2 adsorbed at 77 K using a dynamic sorption method in conjunction with a single point BET adsorption equation. Single point N_2 BET surface areas were determined from N_2 (77 K) adsorption data obtained at a relative pressure (P/P_0) of 0.30 with a Monosorb flow apparatus (Quantachrome Corporation).

RESULTS AND DISCUSSION

The results of analyses of the +90 μm and -90 μm fractions are shown in Table 1. The two major components of the fly ash, silica and alumina, were equally distributed between the two size fractions. Most other elements, except carbon (as evidenced by the LOI), are concentrated in the size fraction with smaller particle diameters. The majority of the carbon in this fly ash had particle diameters larger than 90 μm .

Magnetite

The magnetic concentrate represented about 1% of the feed fly ash. Microscopic evaluation of the concentrate revealed the material was black spherulites (about 90% of the sample) and that no magnetite crystals (octahedrons) were observable, suggesting the particles probably were composed of microcrystalline magnetite. X-ray diffraction spectrometry confirmed that the magnetic concentrate was predominantly magnetite. The spherulites were less magnetic than regular magnetite suggesting they also contained some nonmagnetic material. Semiquantitative analysis of the sample indicated that the concentrate was approximately 90% magnetite and most of the remainder was hematite. The spherulites were somewhat fragile, and could probably be easily ground. This could be a useful property if a simple grinding step could be done to liberate nonmagnetic material and provide a relatively pure microcrystalline magnetite product. Fly ash-derived magnetite has potential for application as a heavy medium in coal cleaning [2, 3]. It has been reported that the most effective magnetite for heavy medium cyclones is magnetite having a mean particle size of 12 μm [4]. A process called the Micromag process was recently patented and specifies that a majority of the magnetite particles be less than 5 μm in size.

Carbon

The unburned carbon in fly ash was concentrated from about 3 wt% to about 70 wt% in this study. Screening at 170 mesh resulted in a 11.6% carbon concentrate (assuming all the LOI is attributed to carbon, Table 1), and flotation increased the carbon content to 70 wt%. Screening has been reported effective for concentrating carbon in fly ash [2] as has air classification [2] and electrostatic separation [5, 6]. Others have used froth flotation to prepare a concentrate of up to 56 wt% carbon [7].

The surface area of the carbon concentrate was about 11 m^2/g . During activation, weight loss was 18%, and surface area of the carbon increased from 11 m^2/g to more than 160 m^2/g . It is known that surface area, corrected for ash content, increases monotonically during activation up to about 80% weight loss [8], suggesting that optimization of separation and activation steps may result in the production of even higher surface area carbons from fly ash.

A low-surface-area carbon has many potential applications. One such application would be in processes for removing air toxics from waste incinerator and utility flue gas [9, 10]. STEAG, a German-based multinational corporation, has licensed technology for carbon-based systems installed on commercial medical, hazardous and municipal waste incinerators in the European Community [9]. The carbon used in the STEAG process, Herdofenkoks, is an activated char produced from lignite, with pore surface area of 300 m^2/g [11]. The SO_2 adsorption capacity of a carbon is reported to be a reliable guide to acceptability in the STEAG process [12]. The kinetics of SO_2 adsorption for a carbon prepared by the ISGS from Illinois coal [13] are compared in Figure 2 with that for Herdofenkoks. The ISGS activated carbon had a N_2 BET surface area of only 110 m^2/g , but had an SO_2 adsorption capacity of 7% by weight after 4 h, almost twice that of the Herdofenkoks. Early pilot scale test results showed that the ISGS activated carbon was effective in the STEAG process. The activated carbon prepared in this study from fly ash adsorbs much more SO_2 than either the ISGS or Herdofenkoks carbons (Figure 2), suggesting that it has potential for application in the STEAG process.

CONCLUSIONS

A quality adsorbent carbon and a quality magnetite concentrate were recovered from an Illinois utility fly ash. There remains significant room for improvement in the quantity and quality of both these products recovered from fly ash. The quantity of recoverable cenospheres has not yet been evaluated. Co-recovery of cenospheres, currently a commercial product, could make the economics of processing fly ash even more attractive. Adsorbent carbons sell for up to \$2,500 per ton, magnetite for approximately \$60-\$70 per ton and cenospheres for as much as several hundred dollars per ton. Removing these valuable products from fly ash may improve the characteristics of the remaining ash for application in cement and concrete products. Future efforts will focus on recovery of products from fly ashes with a wide range of characteristics.

ACKNOWLEDGMENTS

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Table 1. Composition of +90- μm and -90- μm fly ash (wt%).

Oxide	+90 μm	-90 μm
SiO ₂	45.91	44.86
Al ₂ O ₃	25.15	26.91
Fe ₂ O ₃	4.38	7.10
CaO	6.31	9.46
MgO	1.61	2.26
K ₂ O	0.67	0.76
Na ₂ O	0.91	1.37
TiO ₂	1.07	1.53
P ₂ O ₅	1.12	2.12
MnO	0.01	0.01
SO ₃	0.43	0.71
SrO	0.17	0.32
BaO	0.24	0.47
Loss on Ignition (carbon)	11.62	1.75

FLY ASH: AN INDUSTRIAL CHEMICAL RESOURCE

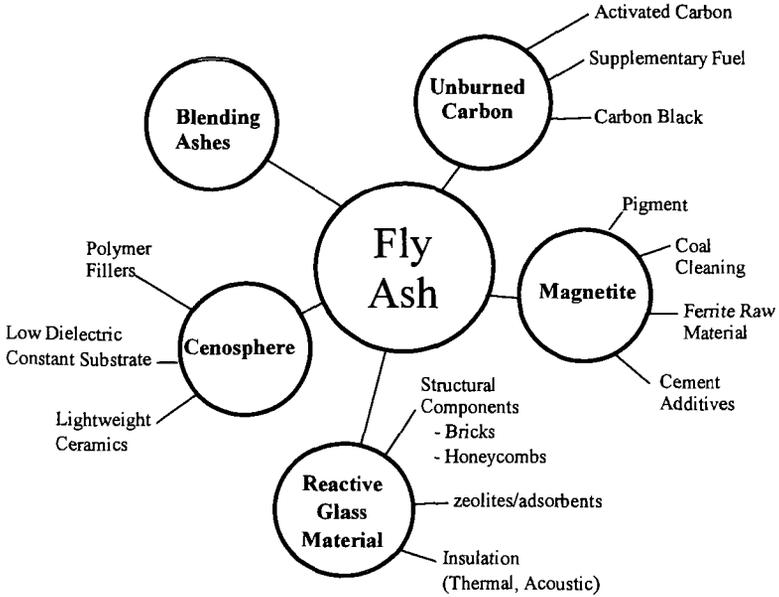


Figure 1. Components of fly ash.

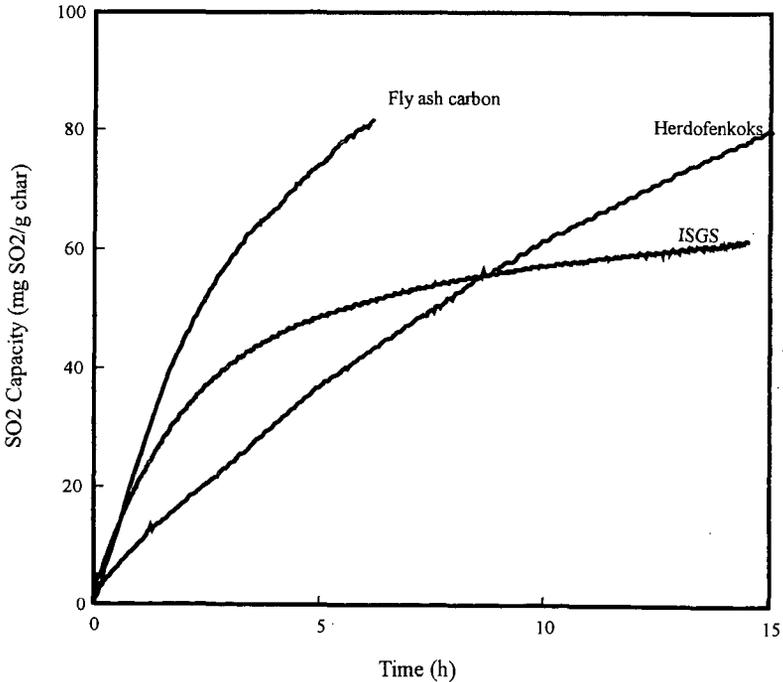


Figure 2. SO₂ adsorption for activated carbons.