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TITLE: Kinetics of Fly Ash Beneficiation by Carbon Burnout

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I. ABSTRACT:

OBJECTIVE: To investigate the kinetics of beneficiation of fly ash by carbon burnout

WORK DONE AND CONCLUSIONS: See paper attached.

The three year project that was proposed is a joint venture between Delmarva Power, a power generating company on the eastern shore of Maryland, and the University of Maryland Eastern Shore. The studies have focused on the beneficiation of fly ash by carbon burnout. The increasing use of coal fly ash as pozzolanic material in Portland cement concrete means that there is the highest economic potential in marketability of large volumes of fly ash. For the concrete industry to consider large scale use the fly ash must be of the highest quality. This means that the residual carbon content of the fly ash must have an acceptable loss on ignition (LOI) value, usually between 7-2% residual carbon. The economic gains to be had from low-carbon ash is a fact that is generally accepted by the electricity generating companies. However, since the cost of producing low-carbon in large quantities, based on present technology, far outweighs any financial gains, no electrical power company using coal as its fuel at present

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considers the effort worthwhile. The concrete industry would use fly ash in cement concrete mix if it can be assured of its LOI value. At present no utility company would give such assurance. Hence with several million tons of fly ash produced by a single power plant per year all that can be done is to dump the fly ash in landfills. The kinetics of fly ash beneficiation have been investigated in the zone II kinetic regime, using a Cahn TG 121 microbalance in the temperature 550-750°C. The P_{O_2} and total surface area dependence of the reaction kinetics were determined using a vacuum accessory attached to the microbalance and a surface area analyzer (ASAP 2010), respectively.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Project is related to Advanced Environmental Control Technology for Coal.

PLANS FOR COMING YEAR:

- 1) Continue kinetic measurements
- 2) Investigate reaction rate dependence on different partial pressures of oxygen at $P_{total} = 1$ atm.
- 3) Continue surface area analysis
- 4) Investigate the reaction kinetics using mass spectrometer.

The result from these experiments are being prepared for presentation at the Fourth Annual Historically Black Nd Universities/Private Sector Energy Research and Development Technology Transfer Symposium in April.

A complete technical report will be prepared for submission to a journal and to PETC in the next reporting quarter.

II. HIGHLIGHT OF ACCOMPLISHMENTS:

Successful application of Proportionality Law to kinetic data.

INTRODUCTION

Coal combustion in electric generating power plants results in by-products like bottom ash, broiler slag and fly ash; the latter accounting for over half the total amount of combustion by-products. Fly ash is the material collected in the dust-collection systems that remove particles from the exhaust gases of power plants and consists mostly of small spheres of glass of complex composition involving silica, ferric oxide, and alumina. Each year the electric utility industry generates up to 48 million tons of fly ash, most of which is stored in landfills (1). Storage of fly ash in landfills poses an environmental threat due principally to leaching of heavy metals contained in the fly ash. In addition to the environmental effects, the costs of disposal and the generally finite spaces available for storage of the huge amounts of fly ash produced each year make utilization of fly ash an important consideration for utility companies.

The use of fly ash as a substitute in concrete products seems to be one of the most attractive solutions and is by far the largest market for fly ash today. But the use of fly ash in concrete products is not new. Since the late 1940s, ash from coal plants have been used as an admixture in cement but only small amounts have been allowed as a replacement for some of the cement. Typical specifications state that fly ash may be used to replace up to 15% of the cement (2). There has been a misconception about the value of fly ash that has limited its full exploitation in improving concrete properties. Viewed as a by-product or waste material, the tendency has been to limit the amount of fly ash in a mix instead of optimizing the potential benefits from its use. However, some recent work indicates the possibility of high-volume applications of fly ash (1,3). Cement mixes containing 58% fly ash has resulted in a workable product comparable to conventional concrete in strength and durability. Other uses of fly ash being actively investigated include autoclaved cellular concrete, flowable fill and lightweight aggregate.

The well-known pozzolanic behavior of fly ash makes it particularly adequate for the preparation of mortar and concrete, and cement production. In the presence of moisture, fly ash reacts with calcium hydroxide, a by-product of the initial reaction between cement and water, at ordinary temperatures to form additional cementitious compounds (2,4). The several types of calcium silicate and calcium aluminate that are formed provide additional bonding and strength. The use of fly ash as a substitute in the preparation of concrete or mortar leads to technical advantages in the final product that are beneficial to the concrete industry. Fly ash having low loss on ignition and high fineness is known to improve the properties of both fresh and hardened concrete. In terms of concrete durability, fly ash interaction reduces permeability, increases sulfate resistance and freezing and thawing resistance among other properties (4).

The mechanism by which the use of fly ash creates a discontinuous pore structure and clogs pore channels with additional hydration products has been described elsewhere (5). The result of these reactions is dramatically slower transport rates for both water and chlorides through the cementitious paste. Consumption of water-soluble calcium hydroxide (produced as a by-product in the hydration of portland cement) by the pozzolanic reaction creates additional calcium silicate gel, which is much denser than the gel without pozzolan. Increases in fly ash usage as a percentage of total cementitious material enhance the described property (6). Reduction of the calcium hydroxide content of the concrete and decreased permeability as a

result of the pozzolanic reaction also contribute to the sulfate resistance of fly ash-containing concrete. Sulfate attack on concrete results in the formation of gypsum compounds and ettringite with subsequent increase in solid volume in the cement matrix, and expansion. The use of Class F fly ash reduces the absolute amount of calcium aluminate available to support ettringite formation by reducing the cement content (7,8). In terms of freezing and thawing resistance, a Bureau of Reclamation study has shown that the use of either Class F and Class C fly ash produces concrete with resistance to freeze-thaw cycles generally superior to portland cement concrete of equivalent strength (9).

In spite of the advantages of the use of fly ash in concrete, currently only 25% of the fly ash generated is subsequently utilized. The key issue for utilization of this material is the availability of high -quality fly ash (2,4). For the concrete market to consider large scale use of fly ash, it must meet certain chemical and physical requirements in relation to chemical constituents, pozzolanic activity, particle size and residual carbon content. While generally fly ash produced from bituminous coal meets the requirements concerning chemical composition and pozzolanic activity, fly ash with the appropriate particle size and residual carbon content is not easily obtained. The amount of carbon or unburned coal constituents in the fly ash is an important parameter as it relates to requirements for proper air entrainment. The carbon present in fly ash adsorbs a portion of the air-entraining agent, which makes it unavailable for creating the needed conditions for stable air bubbles. The amount of adsorption varies with the amount of carbon present and, probably, with the form of such carbon (10). The American Society for Testing and Materials has established a maximum value of 6% residual carbon in fly ash used in concrete, but levels no higher than 3% are generally demanded by the industry when the ash is sold to replace cement in concrete (1,10).

For utility companies production of low-carbon fly ash is an important consideration given the potential economic benefits in terms of cash payments and/or reduced disposal costs. However, as the provisions of the 1990 Clean Air Act Amendments has led to the use of low-NO_x burners, lower, less efficient temperatures are being used in the combustion of coal resulting in increased carbon content of the fly ash (1). Therefore, the need to find an effective method of beneficiation of fly ash in order to render it adequate for large scale commercial application becomes ever more important. Without such large scale use the accumulation of fly ash will overwhelm the landfills and continue to be hazardous to the environment. To this purpose, this project will investigate the kinetics of oxidation of residual carbon present in fly ash as a possible step toward producing low-carbon fly ash from high-carbon, low-quality fly ash.

OBJECTIVE

The main objective of this project was to determine the kinetics of fly ash beneficiation by carbon burnout. The kinetics of the reactions of carbon present in fly ash with air as the reactant gas (oxygen) was investigated at various reaction temperatures and partial pressures of reactant gas and the activation energy of the reaction was determined. By carrying out oxidation experiments on fly ash samples of various sizes, an attempt was made to determine the effect of particle size on reaction kinetics.

SCIENTIFIC DISCUSSION

Reactions of carbon with the normal constituents of air have been studied in detail 1 (11-14). The rates of these reaction may be diffusion controlled or reaction controlled or both. In this project, the chosen reactions conditions are such that the rate is partially controlled by pore diffusion. This means that the gaseous reactant concentration fall gradually to zero to some point in the pore system of the fly ash, putting the reaction into the Zone II kinetic regime, where the rate determining step becomes one of chemical control (15).

Although air is mentioned as the reactant, it is the reaction with oxygen compared to that with carbon and steam, which predominates. The relative reactivities of these gases and their reaction equations with carbon are presented in Table 1 (15).

Reaction	Relative Rates at 1073 K and 0.1 atm.	ΔH (kJ mol ⁻¹)
$C + CO_2 \rightarrow 2CO$	1	170.7
$C + H_2O \rightarrow CO + H_2$	3	130.3
$C + O_2 \rightarrow CO_2$	1×10^5	-393.4
$C + 2H_2 \rightarrow CH_4$	3×10^{-3}	-74.8

KINETICS AND MECHANISM

The reactions of carbon with oxidizing gases are well documented and known to be controlled by the following processes (15):

- Mass transfer of gaseous reactants from the bulk gas phase to the carbon surface.
- Adsorption of reactants on the surface
- Occurrence of chemical rearrangements (reactions) on the surface mobility and formation of adsorbed products
- Desorption of products
- Mass transport (by diffusion) of the gaseous products away from the carbon surface.

By controlling process parameters such as temperature, the diffusion of reactant gas from and away from the carbon surface can be ignored. At low temperatures then the reaction is chemically controlled and the true activation energy of the reaction can be determined. The adsorption process may be considered as molecular involving an atom or a molecule from the gas phase and an active carbon atom on the carbon surface. The energy of activation required

may be used to form an activated complex between the oxygen molecule or atom and the active carbon atom. Desorption from an immobile layer involves an activated state in which a molecule attached to an adsorbing center acquires the proper configuration and activation energy to permit it to escape from that surface.

The reaction rate (R) will be evaluated in terms of the rate of mass loss:

$$R = -\frac{dm}{dt} = k_{air} \Sigma(O) P^n$$

where k_{air} is the reaction rate coefficient, P is the pressure of the reacting gas, n is the reaction order and $\Sigma(O)$ the surface area. This equation is based on the rate law proposed by Hinshelwood (14):

$$R = -\frac{dm}{dt} = \frac{k_{air} \Sigma(O) P^n}{[1 + k' P^n_{CO} + k'' P^n_{CO_2}]}$$

for the reaction between a porous solid and gas. This equation becomes the previous equation if it is assumed that

$$1 \gg k' P^n_{CO} + k'' P^n_{CO_2}$$

The temperature dependence of carbon gasification will be evaluated from the Arrhenius equation:

$$k = A e^{-(Ea/RT)}$$

where k is the rate constant, R is the universal gas constant and T is the absolute reaction temperature. This equation will enable us to calculate the respective values of the energy of activation and the frequency factor A . By using the absolute rate theory, a value of the frequency factor will be obtained from the equation:

$$AN_o = \frac{k_B T}{h} \frac{f^*}{f}$$

Where N_o is Avogadro's number, k_B is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, and f^* and f_a are the partition functions of the transition state complex and the absorbed species, respectively (16).

EXPERIMENTAL PROCEDURE

FLY ASH SAMPLES

The fly ash samples for this study were obtained from the Delmarva Power Indian River plant. Samples were collected from the landfill and fractioned according to particle size. The sieve sizes that were used have openings of 5, 10, 45, 75 and 125 μm . The fly ash samples were dried at 200 °C under nitrogen for 3 hours using a Lindberg furnace. The samples were kept in airtight containers until the experiments.

The fly ash produced in this plant is classified as Type F fly ash. Elementary analysis was carried out on the fly ash before and after reaction.

CARBON OXIDATION REACTIONS

Rate data were collected by following the weight loss of fly ash samples under the experimental conditions with a thermogravimetric analyzer Cahn TG-121. This instrument has a readability of 0.1 μg and can attain temperatures up to 1100 °C with a readability of ± 3 °C. Data analysis was carried out with a PC interfaced to the TG. Ultra-pure Carrier Grade Air was used as the reactant gas in all runs, while the balance chamber of the TG was flushed with He during the course of each run. Table 2 shows the analysis of the reactant gas used for the carbon oxidation.

Carbon monoxide	2 ppm
Carbon dioxide	400 ppm
Nitrogen oxides	not detected
Sulfur dioxide	not detected
Water vapor	0.05
Total hydrocarbons	2.5 ppm
Oxygen	21 %
Odor	not detected
Oil	not detected

Reaction rates for the oxidation of carbon present in the fly ash samples were determined in the temperature range of 550-750 °C for various particle sizes. At each selected temperature the reaction rate was determined at four different partial pressures of the reacting gas (atmospheric, 0.8, 0.6 and 0.4 atm). Mass transport effects were investigated by analyzing samples of different weights.

Tarring was carried out with and without gas flow. The gas flow was set at 60 sccm. For each run, approximately 50 mg fly ash samples were placed in the quartz cup within the TGA chamber. The sample was held in a nitrogen gas flow for a few minutes to allow its weight to stabilize. The chamber was then heated at a rate of 20-25 C min⁻¹ until the desired temperature was reached. At this point, the gas flow was manually switched from nitrogen to air. The sample

was held at the selected temperature for 1-4 hours. For runs at different partial pressures of oxygen, vacuum was applied to the chamber during the isotherm period of the run. Data was collected for each run as a continuous record of the sample mass, temperature and time.

SURFACE AREA MEASUREMENTS

The surface area of fly ash samples will be determined from their N₂ adsorption isotherms by means of a Surface Area and Porosimetry system (ASAP 2000 by Micromeritics).

ENERGY DISPERSIVE X-RAY ANALYSIS

An energy dispersive X-ray analyzer attached to the SEM was used to obtain spectra corresponding to the elements in the sample. Comparison of the spectra from different particles would give semiquantitative information as to the relative concentration of elements in each by comparing relative intensities of the X-ray lines. A map of the distribution of a particular element throughout the sample was obtained by collecting only the X-rays that originate from the element of interest. Elemental X-ray maps was also produced to provide information of the spatial distribution of the element of interest to the rest of the sample.

Data

Table 3 shows a summary of data for area, pore volume and pore size collected for the fly ash. Figure 1 shows variation of Adsorbed-Desorbed volume cm³/g at STP versus relative pressure. Fig. 2 and 3 are the desorption pore area and desorption cumulative Pore area respectively. The adsorption pore area and cumulative adsorption pore area are shown in figs 4 and 5 respectively. The desorption pore volume and cumulative desorption pore volume are shown in figs 6 and 7 respectively.

Sample Id: fly ash #200
 Operator Id: A. Diaz
 Submitter Id: UMES
 File Name: C:\ASAP2010\DATA\000-036.SMP

Started: 05/24/96 14:53:30 Analysis Adsorptive: N2
 Completed: 05/24/96 16:45:57 Analysis Bath: 77.35 K
 Report Time: 05/28/96 10:44:24 Thermal Correction: No
 Sample Weight: 0.2362 g Smoothed Pressures: No
 Warm Freespace: 17.1845 cm³ Cold Freespace: 54.9296 cm³
 Equil. Interval: 5 secs Low Pressure Dose: None

Summary Report

Area

Single Point Surface Area at P/Po 0.20000000 :	3.8379	m ² /g
BET Surface Area:	3.9922	m ² /g
Langmuir Surface Area:	5.5979	m ² /g
BJH Adsorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 A Diameter:	2.2145	m ² /g
BJH Desorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 A Diameter:	3.1105	m ² /g

Volume

Single Point Total Pore Volume of pores less than 783.5396 A Diameter at P/Po 0.97465899:	0.004470	cm ³ /g
BJH Adsorption Cumulative Pore Volume of pores between 17.000000 and 3000.000000 A Diameter:	0.006431	cm ³ /g
BJH Desorption Cumulative Pore Volume of pores between 17.000000 and 3000.000000 A Diameter:	0.006934	cm ³ /g

Pore Size

Average Pore Diameter (4V/A by BET):	44.7863	A
BJH Adsorption Average Pore Diameter (4V/A):	116.1695	A
BJH Desorption Average Pore Diameter (4V/A):	89.1701	A

Table 3 Sumary of surface area and pore volume data

Started: 05/24/96 14:53:30
Completed: 05/24/96 16:45:57
Report Time: 05/28/96 10:44:24
Sample Weight: 0.2362 g
Warm Freespace: 17.1845 cm³
Equil. Interval: 5 secs

Analysis Adsorptive: N2
Analysis Bath: 77.35 K
Thermal Correction: No
Smoothed Pressures: No
Cold Freespace: 54.9296 cm³
Low Pressure Dose: None

10

Fig 1 Adsorption and desorption volume at various relative pressures

Sample Id: fly ash #125

Operator Id: A. Diaz

Submitter Id: UMES

File Name: C:\ASAP2010\DATA\000-040.SMP

Started: 06/01/96 09:12:11

Analysis Adsorptive: N2

Completed: 06/01/96 11:03:42

Analysis Bath: 77.35 K

Report Time: 06/03/96 09:52:33

Thermal Correction: No

Sample Weight: 0.2100 g

Smoothed Pressures: No

Warm Freespace: 17.0693 cm³Cold Freespace: 52.7881 cm³

Equil. Interval: 5 secs

Low Pressure Dose: None

Fig. 2 Variation of pore area with pore diameter (Adsorption)

Sample Id: fly ash #125

Operator Id: A. Diaz

Submitter Id: UMES

File Name: C:\ASAP2010\DATA\000-040.SMP

Started: 06/01/96 09:12:11

Analysis Adsorptive: N2

Completed: 06/01/96 11:03:42

Analysis Bath: 77.35 K

Report Time: 06/03/96 09:52:33

Thermal Correction: No

Sample Weight: 0.2100 g

Smoothed Pressures: No

Warm Freespace: 17.0693 cm³Cold Freespace: 52.7881 cm³

Equil. Interval: 5 secs

Low Pressure Dose: None

Fig. 3

Variation of cumulative pore area with pore diameter (Adsorption)

Sample Id: fly ash #125

Operator Id: A. Diaz

Submitter Id: UMES

File Name: C:\ASAP2010\DATA\000-040.SMP

Started: 06/01/96 09:12:11

Analysis Adsorptive: N2

Completed: 06/01/96 11:03:42

Analysis Bath: 77.35 K

Report Time: 06/03/96 09:52:33

Thermal Correction: No

Sample Weight: 0.2100 g

Smoothed Pressures: No

Warm Freespace: 17.0693 cm³Cold Freespace: 52.7881 cm³

Equil. Interval: 5 secs

Low Pressure Dose: None

Fig. 4 Variation of pore area with pore diameter (Desorption)

Sample Id: fly ash #125
Operator Id: A. Diaz
Submitter Id: UMES
File Name: C:\ASAP2010\DATA\000-040.SMP

Started: 06/01/96 09:12:11 Analysis Adsorptive: N2
Completed: 06/01/96 11:03:42 Analysis Bath: 77.35 K
Report Time: 06/03/96 09:52:33 Thermal Correction: No
Sample Weight: 0.2100 g Smoothed Pressures: No
Warm Freespace: 17.0693 cm³ Cold Freespace: 52.7881 cm³
Equil. Interval: 5 secs Low Pressure Dose: None

Fig. 6

Variation of pore volume with pore diameter (Desorption)

Sample Id: fly ash #125

Operator Id: A. Diaz

Submitter Id: UMES

File Name: C:\ASAP2010\DATA\000-040.SMP

Started: 06/01/96 09:12:11

Analysis Adsorptive: N2

Completed: 06/01/96 11:03:42

Analysis Bath: 77.35 K

Report Time: 06/03/96 09:52:33

Thermal Correction: No

Sample Weight: 0.2100 g

Smoothed Pressures: No

Warm Freespace: 17.0693 cm³Cold Freespace: 52.7881 cm³

Equil. Interval: 5 secs

Low Pressure Dose: None

Fig. 7 Variation of cumulative pore volume with pore diameter (Desorption)

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