UNIVERSITY OF MARYLAND EASTERN SHORE
Department of Natural Sciences

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KINETICS OF FLY ASH BENEFICIATION BY CARBON BURNOUT

FINAL TECHNICAL REPORT

Contract Number:	DE-FG22-94MT94016
Prepared for:	USDOE, Federal Energy Technology Center
FETC Project Officer:	Dr. Phuoc X. Tran
Authors:	Dr. Joseph N.D. Dodoo, Principal Investigator Dr. Joseph M. Okoh, co-Principal Investigator
Private Sector Collaborator:	Delmarva Power

Program Manager: William D. Ferguson
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1. BACKGROUND

This work presented in this report is the result of a collaborative endeavor between Delmarva Power, (now Conectiv), a utility company operating in Virginia, Delaware and Maryland, and the University of Maryland Eastern Shore. The U.S. Department of Energy's fossil energy program for Historically Black Colleges and Universities and Other Minority Institutions, (HBCU/OMI), required collaboration with the private sector. We (the co-Principal investigators), presented our proposal to the management of Delmarva Power at their Wilmington, DE, Headquarters. The company not only agreed to participate in the effort the management also committed to providing summer internship opportunity for a number of students from UMES throughout the duration of the project. We collaborated with the Ash Management Division at Delmarva Power Indian River , DE, Power plant that also supplied the fly ash for the investigations.

2. INTRODUCTION

Coal combustion, the predominant source of energy in the United States and many other countries, results in the production of huge amounts of a waste material known as fly ash. During combustion some minerals present in coal such as clay may be altered thermally, while others, such as silica, remain unaltered. The thermally treated coal impurities, along with small amounts of unburned coal, make up the fly ash. Fly ash is 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. The composition of fly ash varies depending on the parent coal and furnace operating conditions. In general, the major constituents of fly ash are α -quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), hematite (Fe_2O_3), magnetite (Fe_3O_4), lime (CaO), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (1). Fly ash is described as being either Class C, normally produced from lignite or subbituminous coal, or Class F, produced from burning anthracite or bituminous coal, in the American Society for Testing and Materials Standard Specification C618 (2). The basic chemical (1,15, 20,21), requirements set forth for the two classes are listed in Table 1.

Table 1. Chemical Requirements of Fly Ash

Chemical component	Fly Ash Class	
	C	F
$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ -min %	50.0	70.0
SO_3 -max %	5.0	5.0
Moisture content-max%	3.0	3.0
Loss on ignition- max %	6.0	6.0

Source: Reference 2.

The structural configuration of fly ash consists of thin-walled spheres made of silicon dioxide or complex compounds of silicon dioxide, which can be hollow (cenosphere) or filled with smaller solid spheres (plerosphere) as shown in Figure 1.

Figure 1 Typical morphology of a Cenosphere (top) and a plerosphere (bottom) found in fly ash

The majority of fly ash particles collected from an electrostatic precipitator are between 20 and 80 μm in diameter, with specific gravity ranging from 1.59 to 3.10 g/cm^3 (3). The electric utility industry produces nearly 48 million tons of fly ash annually in the United States. Currently 25% of the fly ash produced is utilized while the rest is disposed of in landfills. This practice raises concern as leaching of heavy metals contained in fly ash may contaminate groundwater and water supplies. In addition to this environmental effect, the costs of disposal and the generally finite spaces available for storage of the huge amounts of fly ash produced each year have prompted interest in utilization of fly ash (4-14). Many uses of fly ash have been developed over the years including its use as a pigment in paints and coatings, as filler for plastics and as an agent for removal of contamination from wastewaters (6). 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.

2.1 Use of fly ash in concrete

Typical specifications state that fly ash may be used to replace up to 15% of Portland cement (7-14). Portland cement contains various proportions of four primary compounds: Ca_3SiO_5 , Ca_2SiO_4 , $\text{Ca}_3\text{Al}_2\text{O}_6$, and $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$. Upon setting of concrete, the calcium silicates undergo hydration and hydrolysis to form a gelatinous hydrated silicate on the surface of sand and rock particles, a process known as solidification. A typical reaction is shown below

Over long periods of time, removal of water from the hydrates by dry cement particles lead to hardening of concrete. It is this well-known pozzolanic behavior of fly ash that makes it particularly suitable for the preparation of mortar and concrete. In the presence of moisture, the siliceous and/or siliceous-alumina components in fly ash react with calcium hydroxide, a by-product of the initial reaction between cement and water, at ordinary temperatures to form additional cementitious compounds (7-9). 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 (9).

2.1.2 Permeability reduction

Generally, in concrete, the solubility of calcium hydroxide permits water to leach out from concrete, leaving empty voids and capillaries, which increases its permeability. The pozzolanic reaction prevents this from happening and as a result the concrete is less permeable. The use of fly ash creates a discontinuous pore structure in concrete and clogs pore channels with additional hydration products (10). Consumption of water-soluble calcium hydroxide by the pozzolanic reaction creates additional calcium silicate gel, which is denser than the gel without the pozzolan. The results are dramatically slower transport rates for both water and chlorides through the cementitious paste. Increase in fly ash usage as percentage of total cementitious material enhances the described property (11,12).

2.1.3 Sulfate resistance

Portland cement concrete is attacked by solutions containing sulphate, such as some natural or polluted groundwater, leading to strength loss, expansion, cracking and, ultimately, disintegration. Soluble sulfate ions contained in ground water, sea water or soil diffuse into the concrete and react with calcium hydroxide, produced by the hydrating silicate phases of the cement, resulting in the formation of calcium

sulfate. The newly formed calcium sulfate then reacts with calcium aluminates leading to the formation of CSH_2 (gypsum) and $\text{C}_6\text{AS}_3\text{H}_{32}$ (ettringite), where C, S, A, and H are the abbreviations used in cement chemistry to represent CaO , SO_3 , Al_2O_3 , and H_2O , respectively. These reactions result in expansion because the products have a volume approximately 150 % that of the reactants. The products of these reactions form crystals in the pores and voids in the concrete which ultimately destroy the integrity of the concrete by their expansive force (12). Reduction of the calcium hydroxide content of concrete and decreased permeability as a result of the pozzolanic reaction contributes to the sulfate-resistance of concrete that contains fly ash (13). Through the pozzolanic reaction between fly ash and calcium hydroxide, a refined calcium silicate hydrate binder matrix is formed. As a result, concrete becomes less permeable, and the excess calcium is consumed and rendered unavailable to the expansive formation of ettringite or gypsum compounds. The use of Class F fly ash also reduces the absolute amount of calcium aluminate available to support ettringite formation by reducing the cement content (14,15).

2.1.4 Resistance to freezing and thawing

Concrete may also be damaged by frost, and especially by repeated cycles of freezing and thawing. Damage associated with freezing does not occur unless a sufficient quantity of water is present in pores, and is, therefore, minimal in concrete of low permeability. The reduction in permeability of concrete by fly ash reduces water permeability, which is critical in freeze-thaw damage. A Bureau of Reclamation study

has shown that the use of either Class F or Class C fly ash produces concrete with resistance to freeze-thaw cycles generally superior to Portland cement concrete of equivalent strength (16).

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 (7,9). For the concrete market to consider large-scale use of fly ash, it must meet certain chemical and physical requirements. Key characteristics of particular interest to the concrete market include chemical composition, pozzolanic activity, particle size and residual carbon content (17). The American Society for Testing and Materials has established specifications for use of fly ash as a pozzolan in concrete related to these four characteristics. In terms of chemical composition the sum of silica, alumina and iron oxide must be at least 70 % to ensure that sufficient reactive compounds are present to react with lime. A 3.0% limit is placed on moisture content to minimize caking and packing of the fly ash in shipping and storage (Table 1). The requirement for pozzolanic activity requires that the strength developed by the test mixture in which 35% of the volume of cement is replaced with the same volume of fly ash shall be a minimum of 75% of the strength of the control specimen after storage for 1 day or 7 days. Fineness is one primary characteristic of fly ash that relates to its pozzolanic activity, and the maximum value for fly ash retained when wet sieved on 45 μ m is set at 34 % (17,18).

A product of the combustion of anthracite and bituminous coals, fly ash often contains residual carbon particles. A high carbon content is reported to have a

detrimental influence on certain concrete properties. In addition to their effect on the color of concrete, carbon particles tend to dramatically reduce the efficiency of air-entraining admixtures commonly used to impart desirable properties, including increased durability, to concrete (19). The air-entraining admixtures are organic materials which when added to the gauging water of a concrete mix entrain a controlled quantity of air in uniformly dispersed microscopic bubbles. Air-entraining agents are characteristically long chain molecules with a polar group at one end, and which therefore become concentrated at the air-liquid interface with the polar groups in the liquid and their non-polar parts out of it. This results in the inner surfaces of bubbles being composed of hydrophobic material formed by the non-polar parts of the molecules which act as a barrier to the entry of water during mixing or placing and on any other occasion when the paste is saturated (20). This stable foam of closely spaced, spherical pores has a remarkable effect on the ability of concrete to withstand freeze-thaw cycling. Air entrainment also increases the workability of otherwise similar concrete. The majority of commercial products are based on a relatively small number of raw materials including abietic and pimeric acid salts, fatty acid salts, alkyl-aryl sulphonates, alkyl sulphates and phenol ethoxylates (21). 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 (18). Since a proper air bubble network is not achieved freezing and thawing resistance is decreased in concrete made with high carbon fly ash. Maximum allowable levels of residual

carbon have been set by specifying authorities. These levels are usually designated as Loss on Ignition, which provides a rough estimate of the true value, as the test procedure is designed to oxidize any combustibles by using high temperatures and long residence times. 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 (4-19).

While generally fly ash produced from bituminous coal meets the requirements concerning chemical composition, pozzolanic activity and particle size, fly ash with the appropriate residual carbon content is not easily obtained. 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 (4-18). 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 investigated 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.

3. SCIENTIFIC DISCUSSION

3.1 Kinetics and mechanisms

The reactions of carbon with oxidizing gases are well documented (22-25) and known to be controlled by the following process (26):

- 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.

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 (20-25).

At high reaction temperatures, the rate determining step for the gasification of carbon is the transport of reactant gas molecules to the carbon surface. At lower reaction temperatures, the rate determining step becomes one of chemical control. For a

porous carbon, an intermediate temperature regime occurs at which the reaction may be controlled by chemical processes over the accessible external surface but controlled by diffusion in the less accessible internal surface porosity (25,26). Figure 2 illustrates the three temperature zones for gasification processes with an idealized Arrhenius plot and the corresponding variations in reactant gas concentration through the sample.

Figure 2 (A) Diagram showing the change in rate of the carbon gasification reaction with temperature.

Figure 2 (B) Diagram showing how the concentration of reactant gas in the specimen varies with the rate controlling zone.

Zone I corresponds to low reaction temperatures where rates are low and are chemically controlled over the whole accessible surface, the reactant gas concentration is uniform throughout the bulk of the carbon sample and equals the concentration in the gas phase. The measured activation energy in this zone is the true chemical activation energy of the reaction. Low temperatures and pressures and small particle size are required to obtain a reaction in Zone I. For Zone II reactions, the rate is partially controlled by diffusion in the pores so that the gaseous reactant concentration falls gradually to zero at some point in the pore system. The measured activation energy in this zone, the apparent activation energy, is approximately one half of the true activation energy. At high temperatures, Zone III, the reaction rate is controlled only by diffusion of the gas to the external carbon surface. The activation energy in this zone is lower than that of Zone II. A boundary layer exists within which the gas concentration is depleted from its bulk value (25,26).

While air is the reactant, it is the reaction with oxygen compared to that with carbon dioxide and steam, which predominates. The relative reactivity of these gases and their reaction equations with carbon are presented in Table 2.

Table 2. Relative rates of the gas reaction of carbon at 1073 K and 0.1 atm.

Reaction		Relative Rates at 1073 K and 0.1 atm
C + CO ₂	2CO	1
C + H ₂ O	CO + H ₂	3
C + O ₂	CO ₂	1 x 10 ⁵
C + 2H ₂	CH ₄	3 x 10 ⁻³

Source: Reference 26.

The reaction rate (R) for oxidation of carbon in this project can 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

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

proposed by Hinshelwood (25) for the reaction between a porous solid and gas :

This equation becomes the previous equation if it is assumed that

$$1 \ll k' P_{CO}^n + k'' P_{CO_2}^n$$

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

$$k = A e^{-E_a/RT}$$

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

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

value of the frequency factor will be obtained from the equation:

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 (17,18).

3.2 Application of proportionality law of processes

Since the time dependent traces (weight loss versus time) of kinetic data in thermogravimetry are sigmoid, it is customary of investigators to calculate reaction rate

(dm/dt) from the linear portion of such curves. Thus the rates that are calculated are not really representative of the physical events that are reflected in the sigmoid curve. The proportionality law of processes (27-29),, that circumvents this problem was used in the analysis of kinetic data from this study. The proportionality law of processes states that for certain natural phenomena, the change of variable Y with respect to change of variable X (i.e., dY/dX) is proportional to Y_t (i.e., the value of Y remaining to be processed at a given X , or the difference between the reference value of Y_i and of Y at given X) and inversely proportional to X .

Figure 3. Direct Plot of Y vs X

In the above graph dY/dX is the slope of the points on an asymptotic curve, which represents a typical kinetic change. The slope at point P1 is larger than the slope at P2 and so is the distance from the asymptote Y_i , where $(Y_i - Y_t)$ is larger at point P1 than at point P2; however the large slope at point P1 corresponds to a small X and a smaller slope at point P2 corresponds to a larger X. That is

$$dY/dX \propto (Y_i - Y)$$

$$dY/dX \propto 1/X$$

A true proportionality exists when dY/dX is proportional to the product of the two terms above, that is:

$$dY/dX \propto (Y_i - Y)/X$$

or, when a proportionality constant K is introduced, one obtains:

$$dY/dX = K(Y_i - Y)/X$$

In the above equation the term $(Y_i - Y)$ can be called a driving force and the term X can be called a dragging force. Usually, in a general asymptotic process with continuity, as X approaches infinity, Y will approach Y_i . On the other hand, Y never reaches or crosses over asymptote Y_i because this would be a violation of the principle of continuity. Integration of the preceding equation yields:

$$\log [1/(Y_i - Y)] = K \log X + \log C$$

where C is a constant equal to $1/(Y_i - Y)$, since at $X=1$, $\log 1=0$. When a true proportionality constant exists, the plot of $1/(Y_i - Y)$ versus X on a log-log graph will be linear. The value of Y_i which enables a linear plot is the true value of the asymptote. The values of K and Y_i can be obtained either graphically by integration or by regression.

Applying the foregoing principles, the rate of oxidation of carbon present in fly ash can be determined by measuring the weight loss W of fly ash exposed to oxygen. At the beginning of the oxidation reaction, the rate of weight loss is expected to be fast. As the oxidation of carbon progresses, the number of reactive sites diminishes, leading to a decrease in the rate of weight loss. The weight loss continues, however, until all the carbon is oxidized. The final weight reached is the asymptotic value W_i .

4 INSTRUMENTATION

4.1 Accelerated Surface Area and Porosimetry system

The surface area and porosity of fly ash samples were determined by means of a Surface Area and Porosimetry system ASAP 2000 from Micromeritics. Nitrogen at its boiling point of 77 K was used as the adsorptive; other operating conditions are listed in Appendix A. This instrument employs an automated volumetric technique for determining surface areas. The basis of surface area determinations is the physical adsorption of gases to solids. Before adsorption of nitrogen is measured, physically adsorbed gases are removed from the surface of samples by outgassing; heating under vacuum. To start measurements of adsorption, the outgassing heater is replaced by a liquid thermostat. When a steady-state condition has been achieved, nitrogen gas is admitted to the sample tube and the quantity calculated from pressure, volume and temperature measurements using the equation of state for the gas. When the gas is admitted to the sample holder the pressure falls due to expansion and adsorption by the sample. The decrease due to expansion can be calculated from a prior dead volume calibration of the sample holder. When equilibrium is re-established, the amount of unadsorbed gas remaining can be calculated and hence the amount of gas adsorbed can be deduced. The molar amount adsorbed, n , and the equilibrium pressure, p , are the first data pair from an adsorption isotherm. The process is then repeated to provide further data pairs until the required pressure range has been covered. A desorption isotherm is obtained by reversing this procedure and progressively reducing the adsorbate gas pressure by removing gas using the vacuum pumps (30, 31). Surface

areas are, then, calculated from adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) equation (32) presented in Appendix A.

4.2 Thermogravimetric Analyzer

Rate data were collected by following the weight loss of fly ash samples under the experimental conditions with a thermogravimetric analyzer Cahn TG-121. A diagram of this instrument is included in Appendix B. This instrument has a readability of 0.1 g and can attain temperatures up to 1100 °C with a readability of ± 3 °C (See Appendix B). Ultra-pure Carrier Grade Air was used as the reactant gas in all runs, while the balance chamber of the TG was flushed with Helium during the course of each run. Table 3 shows the analysis of the reactant gas used for the carbon oxidation.

Table 3. Typical analysis of the reactant gas (air) used for carbon oxidation experiments

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

Source: Reference 31.

5 EXPERIMENTS

5.1 Fly ash samples

The fly ash samples used in this study were obtained from the Delmarva Power Indian River plant. Samples were collected from the landfill, oven-dried at 100 °C to remove moisture and fractioned according to particle size. The sieve sizes used had openings of 44, 74, 149 and 250 μm (U.S. mesh sieve sizes #325, #200, #100 and #60, respectively). The fraction of fly ash particles greater than 250 μm was discarded.

The three size-fractionated fly ash samples obtained were then heated at 200 °C under nitrogen for 3 hours using a Lindberg furnace to drive off water absorbed in interstitial spaces of the bulk sample or water physically adsorbed on the surface of individual particles. Three hours were considered ample time for complete removal of moisture since a 50 mg-sample of fly ash heated at 200 °C under nitrogen in a thermogravimetric analyzer lost all adsorbed water, indicated by no weight loss, after approximately one hour.

For convenience and easy handling of data, the three size-fractionated fly ash samples were labeled as follows: fly ash particles with diameters between 149 μm and 249 μm were labeled s#100; fly ash particles with diameters between 74 μm and 148 μm, #200; fly ash particles with diameters between 44 μm and 73 μm, s#325. The samples were kept in airtight containers until ready for use.

5.2 Surface Area Measurements

Before measurement, approximately 0.2 grams of each fly ash sample were degassed at 150 °C for twenty-four hours. The sample tube was then transferred to the analysis port for surface area and porosity determinations (See Appendix A for analysis conditions). The ASAP instruments calculate volume as a function of a change in pressure. From this volume the information necessary to determine the surface area characteristics of a sample is generated. The following reports were obtained from the N₂ adsorption-desorption isotherms of fly ash samples:

BET Surface Area report: listing the relative pressures, volumes adsorbed and BET transformations at the points selected for use in surface area data reduction. From these points a plot is generated which defines the BET characteristics (Appendix A).

Micropore Area and Micropore Volume (t-plot) report: listing the statistical thickness calculated at each relative pressure selected for micropore data reduction. A plot of the volume adsorbed at the pressure of interest provides micropore volume, area, and external surface (30, 34).

BJH Pore Volume and Area Distribution report: based on the method developed by Barrett, Johner, and Halenda to determine the mesopore volume/area distribution which accounts for both the change in adsorbate layer thickness and the liquid condensed in pore cores (36).

5.3 Carbon oxidation reactions

Reaction rates for the oxidation of carbon present in the fly ash samples were determined in the temperature range of 550-750 °C for the three fly ash samples. At each selected temperature the reaction rate was determined at three different partial pressures of the reacting gas (0.213 atm, 0.168 atm, and 0.126 atm).

Tarring was carried out with and without gas flow. The gas flow was set at 60 standard cubic centimeters. For each run, approximately 50 mg fly ash samples were placed in the quartz cup within the TG chamber. Previous analysis had indicated 50 mg to be an adequate sample size given that the average carbon content of the fly ash was about 9% (See Table 4). The amount of carbon in the fly ash was confirmed by analysis

with a Scanning Electron Microscope with an Energy Dispersive X-ray Analyzer (See Appendix C for determination of carbon content in fly ash using electron microscopy analysis). The sample was held in a nitrogen gas flow for 5-10 minutes to allow its weight to stabilize. The chamber was then heated at a rate of $25^{\circ}\text{C min}^{-1}$ until the desired temperature was reached. At this point, the gas flow was manually switched from nitrogen to air. The sample was held at this final condition until there was no weight loss, from 1-4 hours. The presence of a nitrogen atmosphere during the temperature ramp in the TGA prevented oxidation of carbonaceous materials until the sample reached the selected temperature, when air is admitted to the chamber.

Table 4. Chemical composition of Delmarva Power fly ash

Variable analyzed	Percentage of total weight
Silica (SiO_2)	40.34
Aluminum (Al_2O_3)	27.59
Iron (Fe_2O_3)	9.75
Calcium (CaO)	2.49
Magnesium (MgO)	0.42
Sodium (Na_2O)	0.62
Potassium (K_2O)	2.36
Titanium (TiO_2)	2.60
Sulfur (SO_3)	0.40
Loss on Ignition	8.93
Loss on Drying	27.99
PH	8.0

Source: Reference 37.

Figure 4 shows an example of the temperature versus time profile and parameters used in a typical TG run at 750 °C. 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 with a PC interfaced to the TG. The TG files were exported to MicroSoft Excel for analysis.

Segment	Initial Temp °C	Rate °C/min	Final Temp °C	Time (m)	Nitrogen
1	25	0.0	0	20	On
2	25	25	750	29	On
3	750	0.0	750	10	On
4	750	0.0	750	240	Off
Segment	Air	Samp. Int (s)	Data Ave	Furn Cool	Cooling Fan
1	Off	10	On	Off	On
2	Off	10	On	Off	On
3	Off	10	On	Off	On
4	On	10	On	Off	On

Figure 4 Temperature vs time profile and parameters used in the TGA tests

6. RESULTS AND DISCUSSION

6.1 Surface Area Measurements

Surface area and porosity results for fly ash samples are listed in Tables 5-7. For the fly ash samples studied, surface area increases as particle size increases. At high size ranges, irregular porous fly ash particles of carbonaceous origin are expected to be predominant contributing to the high surface area found for large particles (38). The higher surface areas for fly ash s#100 can be then attributed to the presence of highly porous carbonaceous particles. Figure 5 shows a plot of surface area vs. carbon content and particle size and illustrates this dependence of surface area on carbon content.

The adsorption-desorption isotherms of fly ash samples s#100, s#200 and s#325 are shown in Figures 6, 7 and 8, respectively. All three isotherms show closed-loop hysteresis in the range $P/P_o = 0.40-1.00$. Hysteresis occurs because the mechanism of adsorption in pores is different from that for desorption and may be understood as a capillary condensation phenomenon in which the capillary empties during desorption at a lower P/P_o than that at which it fills during adsorption (30). Therefore, the hysteresis loops observed on the isotherms point out to the presence of porosity in the fly ash samples analyzed.

Experimental isotherms can be analyzed by the t-plot method devised by deBoer and co-workers (39), in which the volume of adsorbed gas is plotted vs. film thickness, calculated from the Harkins and Jura equation (34), for a reference solid. The slope of the line yields the effective surface area. Deviation from this line is indicative of porosity: points above the line indicate additional volume held by capillary

condensation and points below the line indicate blockage of pore throats, occluding the interior surface area. The t curves of the three fly ash samples used in this study, plotted in Figure 9 A-C, show deviations from linearity which suggest that the fly ash samples are porous. Figures 10, 11, and 12 show pore size distribution curves obtained for fly ash samples s#100, s#200 and s#325, respectively. BJH adsorption pore size distribution reports indicated that no pores were open at both ends. Average pore diameters were similar for the three fly ash samples: Average pore diameters obtained from adsorption data were approximately 115 Å.

Table 5. Results of surface area analysis of fly ash particles s#100

Area	
BET Surface Area	5.5348 m ² /g
BJH Adsorption Cumulative Surface Area of Pores ¹	2.6233 m ² /g
BJH Desorption Cumulative Surface Area of Pores ¹	3.0693 m ² /g
Volume	
BJH Adsorption Cumulative Pore Volume ¹	0.007592 cm ³ /g
BJH Desorption Cumulative Pore Volume ¹	0.007853 cm ³ /g
Pore Size	
Average Pore Diameter (4V/A by BET)	44.6874 Å
BJH Adsorption Average Pore Diameter (4V/A)	115.7567 Å
BJH Desorption Average Pore Diameter (4V/A)	102.3468 Å

¹ Pores between 17 and 3000 Å Diameter

Table 6. Results of surface area analysis of fly ash particles s#200

Area	
BET Surface Area	3.9922 m ² /g
BJH Adsorption Cumulative Surface Area of Pores ¹	2.2145 m ² /g
BJH Desorption Cumulative Surface Area of Pores ¹	3.1105 m ² /g
Volume	
BJH Adsorption Cumulative Pore Volume ¹	0.006431 cm ³ /g
BJH Desorption Cumulative Pore Volume ¹	0.006934 cm ³ /g
Pore Size	
Average Pore Diameter (4V/A by BET)	44.7863 Å
BJH Adsorption Average Pore Diameter (4V/A)	116.1695 Å
BJH Desorption Average Pore Diameter (4V/A)	89.1701 Å

¹ Pores between 17 and 3000 Å Diameter

Table 7. Results of surface area analysis of fly ash particles s#325

Area	
BET Surface Area	3.0028 m ² /g
BJH Adsorption Cumulative Surface Area of Pores ¹	1.8355 m ² /g
BJH Desorption Cumulative Surface Area of Pores ¹	2.2171 m ² /g
Volume	
BJH Adsorption Cumulative Pore Volume ¹	0.005284 cm ³ /g
BJH Desorption Cumulative Pore Volume ¹	0.005536 cm ³ /g
Pore Size	
Average Pore Diameter (4V/A by BET)	49.8128 Å
BJH Adsorption Average Pore Diameter (4V/A)	115.1592 Å
BJH Desorption Average Pore Diameter (4V/A)	99.8740 Å

¹ Pores between 17.000 and 3000.000 Å Diameter

Figure 5. Plot of surface area vs. particle size (diamonds) and surface area vs. carbon content (squares). Actual values for particle size are ten-times values shown in graph.

Figure 6. Adsorption-desorption isotherm of fly ash sample s#100. Crosses are the adsorption leg; circles are the desorption leg.

Figure 7. Adsorption-desorption isotherm of fly ash sample s#200. Crosses are the adsorption leg; circles are the desorption leg.

Figure 8. Adsorption-desorption isotherm of fly ash sample s#325. Crosses are the adsorption leg; circles are the desorption leg.

Figure 9. T-plots for fly ash samples s#100 (A), s#200 (B) and s#325 (C).

Figure 10. Barret-Johner-Halenda (BJH) pore size distribution curve of fly ash sample s#100.

Figure 11. Barret-Johner-Halenda (BJH) pore size distribution curve of fly ash sample s#200.

Figure 12. Barret-Johner-Halenda (BJH) pore size distribution curve of fly ash sample s#325..

6.2 Carbon oxidation reactions

Oxidation reactions were carried out on three different size-fractioned fly ash samples at temperatures of 550°C, 650 °C and 750 °C. At each given temperature, runs were performed at reactant gas pressures of 0.213 atm, 0.168 atm and 0.126 atm. For each of the three size-fractioned fly ash samples nine oxidation reactions were

performed for a total of twenty seven runs. Figures 13-15 show typical weight vs. time traces for oxidation of fly ash s#100, s#200 and s#325 at a reaction temperature of 750 °C. These figures depict the weight changes in fly ash after oxygen was introduced in the heating chamber of the TG. Before that, the weight remained stable in the presence of nitrogen.

Reaction rates were determined for each oxidation reaction using the initial rate law and the proportionality law. For the initial rate law method, the slope of the linear portion of the sigmoid curve of wt vs. time was used to calculate reaction rates. For example, the linear portion of the weight vs. time curve for the oxidation of fly ash s#200 used to calculate the reaction rate is shown in Figure 16. For the proportionality law method, the sigmoid curve of weight vs. time was converted to a straight line by plotting $\ln t$ vs. $\ln (\ln W - \ln W_i)$, or qt vs. $q(qW - qW_i)$, where W is the weight at any given time and W_i is the asymptote. The slope of the line obtained, which comprised the whole reaction event, was used to calculate reaction rates. Figure 17 shows the qt vs. $q(qW - qW_i)$ plot for the oxidation of fly ash s#200 (Figure 16). In each case, the rate of weight loss was normalized to initial weight and the surface area of the specific size-fractioned fly ash for the purpose of allowing meaningful comparisons among the reaction rates under varied conditions.

Figure 13. Weight vs. time plot for oxidation of fly ash s#100 at a reaction temperature of 750 °C and reactant gas pressure of 0.213 atm. Total run time = 40.1 min.

Figure 14. Weight vs. time plot for oxidation of fly ash s#200 at a reaction temperature of 750 °C and reactant gas pressure of 0.213 atm. Total run time = 89.2 min.

Figure 15. Weight vs. time plot for oxidation of fly ash s#325 at a reaction temperature of 750 °C and reactant gas pressure of 0.213 atm. Total run time = 67.5 min.

Figure 16. Weight vs. time plot for oxidation of fly ash s#200 at a reaction temperature of 750 °C and reactant gas pressure of 0.213 atm. The slope of the linear portion of the sigmoid curve was used to calculate the reaction rate according to the initial rate law.

Figure 17. Application of the proportionality law of processes to the oxidation of fly ash s#200. The sigmoid curve of weight vs. time was converted to a straight line by plotting qt vs. $q(qW - qW_i)$, that is, the natural logarithm of t vs. the natural logarithm of the difference of $\ln$ weight and $\ln W_i$ (asymptote). The slope of this line, which comprised the whole reaction event, was then used to calculate the reaction rate.

6.3 Rate dependence on temperature

Reaction rates obtained from the initial rate method and proportionality law method at the temperatures and pressures of oxygen used in this study are presented in tables 8, 9, and 10 for fly ash samples s#100 , s#200 and s#325, respectively.

Table 8. Rate dependence on temperature at three different partial pressures of reactant gas (oxygen) for fly ash particles s#100.

Pressure of reactant gas (atm)	Temperature (°C)	R(initial rate law) (mg/g.m ² sec)	R(Proportionality law) (mg/g.m ² sec)
0.213	550	0.0188	2.267
	650	0.0736	12.165
	750	0.1520	28.630
0.168	550	0.0302	3.182
	650	0.1036	19.787
	750	0.1830	121.462
0.126	550	0.0345	3.533
	650	0.1710	23.9084
	750	0.2320	123.012

Table 9. Rate dependence on temperature at three different partial pressures of reactant gas (oxygen) for fly ash particles s#200.

Pressure of reactant gas (atm)	Temperature (°C)	R(initial rate law) (mg/g.m ² sec)	R(Proportionality law) (mg/g.m ² sec)
0.213	550	0.0069	7.306
	650	0.0219	165.032
	750	0.1586	618.738
0.168	550	0.0100	3.953
	650	0.0213	59.323
	750	0.1629	320.759
0.126	550	0.0147	37.093
	650	0.1100	19.099
	750	0.1724	143.103

Table 10. Rate dependence on temperature at different partial pressures of reactant gas (oxygen) for fly ash particles s#325.

Pressure of reactant gas (atm)	Temperature (°C)	R(initial rate law) (mg/g.m ² sec)	R(Proportionality law) (mg/g.m ² sec)
0.213	550	0.0035	12.098
	650	0.0290	72.420
	750	0.1462	584.638
0.168	550	0.0265	7.757
	650	0.1296	79.421
	750	0.2252	504.078
0.126	550	0.0675	60.793
	650	0.2110	343.650
	750	0.2455	828.588

A trend of increasing rates with increasing temperatures under same pressure of reactant gas was observed for the three fly ash samples used in this study. In each case, the reaction rates obtained with the proportionality law were consistently higher than the initial rates calculated from the linear portion of the curve throughout the temperature range analyzed. This is an expected result given that the proportionality

law method comprises the whole reaction event and not only the initial weight loss as does the initial rate method. The dependence of reaction rate on reaction temperature was evaluated with the Arrhenius equation. For each of the three fly ash samples, the activation energy at various pressures of reactant gas was evaluated from Arrhenius plots. Activation energies for the size-fractionated fly ash samples used in this study ranged from 43 kJ/mol to 131 kJ/mol. Tables 11, 12 and 13 list the values of Arrhenius parameters obtained at various pressures of reactant gas for fly ash samples s#100, s#200, and s#325, respectively. Other studies have found activation energies for coal fly ash to be about 59 kJ/mol for the temperature range 275 °C-350 °C. In the same study higher activation energies were found for MSW fly ash (104 kJ/mol-142 kJ/mole) (40). Activation energies were found to be inversely proportional to pressure for the three fly ash samples. Indeed, these values decrease with decreasing pressures indicating some effect of mass transport on activation energy. For porous materials, the concentration of reactant gas decreases to almost zero inside the pores at low partial pressures of reactant gas limiting the reaction and lessening the effect of increasing temperatures on reaction rate. In our samples, pores ranged from 44 Å to 116 Å in diameter. BHJ adsorption/desorption pore distribution reports revealed that no pores were open at both ends, only one end of the pores was open to the external surface. This implies that the oxygen concentration decreases inside the pores at low oxygen pressures thus confirming that carbon burnoff occurred in the zone II kinetic regime.

Table 11. Arrhenius parameters for oxidation reaction of fly ash particles s#100 at various partial pressures of reactant gas.

Po ₂ (atm)	Initial rate data		Proportionality data	
	Ea (kJ/mol)	A	Ea (kJ/mol)	A
0.213	73.85	13.55	135.06	22.12
0.168	68.28	7.61	146.43	23.45
0.126	63.81	4.21	92.37	17.69

Table 12. Arrhenius parameters for oxidation reaction of fly ash particles s#200 at various partial pressures of reactant gas.

Po ₂ (atm)	Initial rate data		Proportionality data	
	Ea (kJ/mol)	A	Ea (kJ/mol)	A
0.213	108.40	10.69	157.43	25.18
0.168	95.78	9.16	154.91	24.09
0.126	88.07	8.84	**	

**no regression

Table 13. Arrhenius parameters for oxidation reaction of fly ash particles s#325 at various partial pressures of reactant gas.

Po ₂ (atm)	Initial rate data		Proportionality data	
	Ea (kJ/mol)	A	Ea (kJ/mol)	A
0.213	131.44	13.55	135.06	22.12
0.168	76.12	7.61	146.43	23.45
0.126	43.92	4.21	92.37	17.69

No consistent trend was observed for the change in activation energy with particle size so that it is not possible to determine how the rate effects of temperature varied with particle size. At a reactant gas pressure of 0.213 atm, the value of the energy of activation decrease with increasing particle size, but this does not apply to reactant gas pressures of 0.168 atm and 0.126 atm. These inconsistencies in activation energies demand a close look at the rate data obtained for the oxidation of carbon in fly ash. Throughout this study, it has been assumed that the weight loss of fly ash is due exclusively to the oxidation of carbon present in fly ash. Calculations of weight loss for fly ash sample s#100 at 550 °C, 650 °C and 750 °C resulted in values of 9.5 mg, 11.4 mg, and 12.2 mg, respectively. The greater values of weight loss at high temperatures (650 °C and 750 °C) suggest that weight loss in fly ash at these temperatures is not caused only by carbon oxidation. In a study of the accuracy of the loss-on-ignition test,

Brown and Dykstra (41) performed thermogravimetric analysis on fly ash samples produced by four distinctive kinds of coal boilers. Samples were heated under nitrogen to a temperature of 725 °C. For all the fly ash samples analyzed, large weight losses were observed between 600-710 °C originating from the calcination of limestone or dolomite in the fly ash. All of the samples showed weight losses from processes other than just water desorption and carbon oxidation. In fact, portlandite $[\text{Ca}(\text{OH})_2]$, occurring at 400 °C, and carbonate calcination were the largest contributors to weight loss. Limestone, which is mostly calcite (CaCO_3) or dolomite $[\text{CaMg}(\text{CO}_3)_2]$ is usually added as fine particulate material to fluidized bed combustors. It's generally calcinated at the high temperatures of the boilers to lime, CaO, but fine particulate matter can be entrained in the gas flow through the boilers and , therefore, lime and limestone can appear in fly ash. Lime is extremely hygroscopic and will readily form portlandite $[\text{Ca}(\text{OH})_2]$ in the presence of water. High levels of naturally occurring carbonates in coal can also contribute to the presence of limestone and dolomite in fly ash. From the ongoing discussion, it becomes obvious that at temperatures above 600 °C weight losses from these minerals will yield overestimates of unburned carbon content in fly ash. Therefore, it is reasonable to suspect that carbonate calcination may have contributed to weight losses during reactions carried out at 650 °C and 750 °C, and consequently, confounded the calculations of reaction rates for oxidation of carbon in fly ash. Given that the calculated reaction rates correspond to total weight loss and not only to carbon oxidation, it is not possible to evaluate the rate dependence on temperature based on the data collected.

6.4 Rate dependence on pressure

The information presented in the tables 8, 9, and 10 also provide information on the dependence of the reaction rate on oxygen pressure. The rate dependence of oxidation of fly ash s#100 on partial pressure of oxygen revealed a trend of increasing rate with decreasing concentration of reactant for both rate estimates. The higher rates at lower partial pressures of oxygen may be accounted for by the presence of volatiles in the fly ash. At low concentrations of oxygen (high vacuum), volatile compounds such as adsorbed organic species entrained in the porous system of the fly ash evolved rapidly, contributing to weight loss in fly ash. The increasing rate with decreasing pressure may also be due to the ease of transport of products away from reaction sites within pores with lowering pressure. This trend of increasing rate with decreasing concentration of reactant is also observed in fly ash s#200 and fly ash s#325 for the initial rate estimates only.

The effect of reactant gas concentration on reaction rates of fly ash was evaluated using the equation

$$R = k[O_2]^a$$

where $[O_2]$ is the concentration of oxygen. The slope of the plot of the $\ln R$ vs. $\ln O_2$ represents the dependence on oxygen concentration, a . Figures 18, 19, and 20 show the results for fly ash s#100, s#200, and s#325 at 550 °C, respectively.

Table 14. Results from regression analysis of $\ln R$ vs. $\ln O_2$ for oxidation of fly ash s#100, s#200, and s#325 at 550 °C. The slope, a , represents the oxygen concentration dependence.

Fly ash sample	A	R^2
s#100	-1.132	0.87
s#200	-1.437	0.99
s#325	-5.553	0.93

Regression analysis of $\ln R$ vs. $\ln O_2$ for oxidation of fly ash reveal an inverse relationship, where the oxygen concentration dependence has a negative value ranging from -1.132 to -5.57.

Figure 18. Effect of oxygen concentration on reaction rate for fly ash s#100. Data are plotted as $\ln R$ vs. $\ln O_2$; the slope represents the oxygen concentration dependence (slope = -1.132).

Figure 19. Effect of oxygen concentration on reaction rate for fly ash s#200. Data are plotted as $\ln R$ vs. $\ln O_2$; the slope represents the oxygen concentration dependence (slope = -1.437).

Figure 20. Effect of oxygen concentration on reaction rate for fly ash s#325. Data are plotted as $\ln R$ vs. $\ln O_2$; the slope represents the oxygen concentration dependence (slope = -1.132).

7 CONCLUSIONS

7.1 Surface Area Analysis

Surface area analyses performed on fly ash samples reveal that the surface area is controlled by carbon content. The higher surface areas found in large particles are

due to the presence of highly porous carbonaceous particles. Adsorption-desorption isotherms and t-plots of fly ash samples indicate that fly ash is porous. BJH Adsorption/Desorption pore size analysis reveal that pore diameters are independent of sieve size. They appear to be dependent only on the nature of the material which confers porosity.

7.2 Carbon oxidation reactions

Based on the results of Brown and Dykstra (41) it is reasonable to assume that calculations of reaction rates at temperatures above 550 °C were confounded by weight losses from processes other than carbon oxidation and, therefore, are not useful in determination of the temperature dependence of carbon oxidation in fly ash. The results of the present study indicate that temperatures below 550°C should be used for future studies in order to satisfactorily assess the temperature dependence of carbon oxidation in fly ash. Furthermore, it is also advisable that percent carbon determinations be performed on fly ash samples after the oxidation reactions to determine whether all carbon present in fly ash is oxidized. This will ensure that reaction rates are representative of the complete oxidation of carbon.

An inverse relationship was determined between reaction rates and oxygen concentration for this study. As discussed, this may be due to volatilization of volatiles from fly ash and ease of transport of products away from the reaction sites by the action of the vacuum applied to the samples. A more accurate determination of oxygen dependence of carbon oxidation can be accomplished by the use of specialty gases

containing different concentrations of oxygen which could eliminate the need to apply vacuum to the samples.

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APPENDIX A

POROSIMETER ANALYSIS CONDITIONS

Analysis Adsorptive	Nitrogen
Dose from Psat tube	No
Maximum manifold pressure	925.00 mmHg
Non-ideality factor	0.000066
Density conversion factor	0.0015468
Ther. tran. hard-sphere diameter	3.860 Å
Molecular cross-sectional area	0.162 nm ²
Fast evacuation	Yes
Crossover pressure	5.0 mmHg
Leak test	No
Leak test duration	120 sec
Evacuation time	0.1 hours
Backfill Gas	Analysis
Equilibration interval	5 sec
Maximum volume increment	No
Target tolerance	5.0% or 5.0 mmHg
Min. equil. delay at P/Po >= 0.995	600 sec
Free space group	Measured
Warm free space	16.0000 cm ³
Cold free space	45.0000 cm ³
Post-free space	No
Evacuation time	0.1 hours
Leak test	No
Leak test duration	180 sec
Low pressure dosing	No
Dose amount	0.00 cm ³ /g STP
Minimum equilibrium delay	0.00 hours
Maximum equilibrium delay	999.00 hours
Po type	Measured
Po	740.000 mmHg
Measurement interval	120 minutes
Temperature type	Entered
Temperature	77.35 K
Measurement gas	Nitrogen

APPENDIX B

TGA OPERATING PARAMETERS

BALANCE

Capacity	1.5 grams
Low Weighing Range	0-150 mg
Readability	0.1 μ g
High Weighing Range	
Temperature Drift	1 μ g/ $^{\circ}$ C
Full Range Zeroing	Yes

FURNACE

Maximum Temperature	1100 $^{\circ}$ C
Maximum Heating Rate	100 $^{\circ}$ C/min
Maximum Cooling Rate	50 $^{\circ}$ C/min
Temperature Repeatability	$\pm$ 3 $^{\circ}$ C

REACTION CHAMBER

Sample Volume	11 cc
Reactor Tube Volume	125 cc
Automatic Gas Switching	4 gases
Oxygen Free Environment	Yes
Pressure	5 psi
Vacuum	5 x 10 ⁻⁶
Reducing Gases	Yes
Oxidizing Gases	Yes
Corrosive Gases	Yes with precautions

DATA ACQUISITION

Temperature Program Segments	60
Type of Segments	Isotherms, Ramps
Method Storage	Unlimited
Data Point Storage	Over 2 Million
Data Display	VGA Monitor
Run Time	48 hours
Data Analysis Commands	21

BRUNAUER-EMMETT-TELLER (BET) THEORY

The BET theory describes multilayer adsorption of gases on a wide range of porous and non-porous solids. The BET equation expressed in the linear form is:

$$\frac{1}{V[(P_o/P)-1]} = \frac{1}{(V_m c^1)} + \frac{(c^1-1)P}{V_m c^1 P_o}$$

where V is the volume adsorbed, V_m is the monolayer capacity, P is the pressure of the adsorbate, P_o is the normal vapor pressure of the gas, and c^1 is a constant.

Figure B1 BET Surface Area plot

APPENDIX C

DETERMINATION OF CARBON CONTENT BY ELECTRON MICROSCOPY

The following analyses were carried out at the US Bureau of Mines, Pittsburgh Research Center, using the scanning electron microscope/energy dispersive X-ray unit at the Fires and Explosions Division.

The carbon content of fly ash was determined by electron microscopy with energy dispersive X-ray analysis using dolomite [$\text{CaMg}(\text{CO}_3)_2$] as the standard compound as follows:

Table 15 Relative number of atoms contained in dolomite and percent carbon in Fly Ash

Element	Ca	Mg	C	O
Mass	40	24	12	16
Relative amount	1	1	2	6
Weight	40	24	24	96
Material	Formula Weight	C count rate m^{-1}	% Carbon	
$\text{CaMg}(\text{CO}_3)_2$	184 g/mol	7.8×10^3	13.043	
Fly Ash		4.9×10^3	8.19	

Percent carbon by mass in dolomite

$$24/184 \times 100 = 13.043\%$$

Count rate of carbon dolomite $7.8 \times 10^3 \text{ C/m}$

Count rate of carbon in fly ash $4.9 \times 10^3 \text{ C/m}$

The count rate for the 13% carbon in Dolomite was $7.8 \times 10^3 \text{ m}^{-1}$. The percent of carbon in the fly ash was determined from the ratio,

$$\frac{4.9 \times 10^3}{7.8 \times 10^3} \times 13.043 = 8.19\%$$

Figure 1C shows electron micrographs for dolomite and fly ash, respectively. The X-ray spectra are shown in figures 2C through 6C.

Figure C1 Scanning electron micrograph of Delmarva Power Indian River Power plant fly ash

$\text{CaMg}(\text{CO}_3)_2$ [1:1:2:6]

MEM1: Dolomite 1/12/96
 Livetime = 150 s

WINDOW LABEL	START keV	END keV	WIDTH CHANS	GROSS INTEGRAL	NET INTEGRAL	EFF. FACTOR	%AGE TOTAL
C	.191	.352	17	10040	3631	.94	19.93
O	.432	.592	17	14041	3586	2.85	59.79
Mg	1.172	1.332	17	16138	4196	.40	9.79
Ca	3.592	3.78	20	22083	6653	.27	10.50

Figure C2 Characteristic x-ray spectrum for Dolomite

MEM1: Delmarva Power Fly Ash (1/17/96)

Livetime = 150 s

WINDOW LABEL	START keV	END keV	WIDTH CHANS	GROSS INTEGRAL	NET INTEGRAL	EFF. FACTOR	%AGE TOTAL
C	.19	.35	17	985	237	.94	13.32
O	.43	.59	17	1390	489	2.85	83.45
Mg	1.17	1.33	17	1017	74	.40	1.76
Ca	3.59	3.77	19	1108	92	.27	1.48

Figure C3 Characteristic x-ray spectrum for Delmarva Power Indian River Fly Ash

MEM1: Delmarva Power Fly Ash (1/17/96)

Livetime = 150 s

WINDOW LABEL	START keV	END keV	WIDTH CHANS	GROSS INTEGRAL	NET INTEGRAL	EFF. FACTOR	%AGE TOTAL
C	.19	.35	17	985	237	.94	13.32
O	.43	.59	17	1390	489	2.85	83.45
Mg	1.17	1.33	17	1017	74	.40	1.76
Ca	3.59	3.77	19	1108	92	.27	1.48

Figure C4 Characteristic x-ray spectrum for Delmarva Power Indian River Fly Ash

APPENDIX D

PLOTS FOR OXIDATION OF FLY ASH AT 550 °C AND THREE DIFFERENT PARTIAL PRESSURES

WEIGHT VS. TIME CURVE FOR OXIDATION OF FLY ASH S#100 AT 550°C AND 0.213 ATM

Figure D1

Figure D2

Figure D3

PROPORTIONALITY PLOT FOR OXIDATION OF FLY ASH S#100 AT 550°C AND 0.168 ATM

Figure D4

WEIGHT VS. TIME CURVE FOR OXIDATION OF FLY ASH S#100 AT 550°C AND 0.126 ATM

Figure D5

PROPORTIONALITY PLOT FOR OXIDATION OF FLY ASH S#100 AT 550°C AND 0.126 ATM

Figure D6

Figure D7

Figure D8

Figure D9

PROPORTIONALITY PLOT FOR OXIDATION OF FLY ASH S#200 AT 550°C AND 0.168 ATM

Figure D10

WEIGHT VS. TIME CURVE FOR OXIDATION OF FLY ASH S#200 AT 550°C AND 0.126 ATM

Figure D11

PROPORTIONALITY PLOT FOR OXIDATION OF FLY ASH S#200 AT 550°C AND 0.126 ATM

Figure D12

Figure D13

Figure D14

Figure D15

PROPORTIONALITY PLOT FOR OXIDATION OF FLY ASH S#325 AT 550°C AND 0.168 ATM

Figure D16

Figure D17

Figure D18