CHARACTERIZATION OF CARBON FORMS IN FLY ASH USING CONTROLLED-ATMOSPHERE PROGRAMMED-TEMPERATURE OXIDATION (CAPTO)

Robert B. LaCount, Waynesburg College, and ViRoLac Industries
Douglas G. Kern, ViRoLac Industries
Amanda J. Beisel, Waynesburg College
Keith A. Giles, Waynesburg College
Timothy L. Banfield, Allegheny Power.

SUMMARY

INTRODUCTION

The characterization of carbon forms in fly ash is fundamental to understanding the behavior of air entraining admixtures (AEA's) with unburned carbon in fly ash/cement mixtures. These studies may also lead to prediction of surfactant performance thus minimizing variability in concrete products. Additionally, a correlation between power plant operating conditions or coal blend and one or more unburned carbon forms present in fly ash may exist.

The use of low NOx burners with coal fired boilers, in numerous instances, has resulted in either an increase of unburned carbon in fly ash or more variation in its carbon content. This variation or increased carbon content directly impacts the sale of fly ash used with cement to produce concrete products. Even when fly ash meets loss on ignition (LOI) specifications, variation in the adsorption properties of the carbon forms present may result in variation of the amount of AEA required[1]. Knowledge of the unburned carbon forms present on fly ash may lead to methods for increased utilization of this combustion by-product. Recent studies, using a variety of techniques to characterize fly ash including the unburned carbon content were previously cited[2].

A series of fly ash samples obtained from several different power stations burning pulverized coal were previously characterized, using CAPTO, for forms of carbon present in the unburned carbon on fly ash. Nearly all of the fly ash samples characterized showed carbon oxidation in four different temperature ranges. Several of these temperature ranges are well above those of coals, activated carbon, and other chars and significantly below the oxidation temperature of graphite. The amount of carbon dioxide evolving in each temperature range was evaluated[2].

This CAPTO study centers primarily on thermal (oxidative/non-oxidative) characterization of the carbon forms present in fly ash produced when a Pittsburgh seam coal is burned in a pulverized coal fired utility boiler equipped with Low NO_x Burners. The CAPTO CO_2 evolution profile was used to establish a temperature regime for progressive oxidation and pyrolysis studies of the fly ash. A series of samples of the fly ash were oxidized/pyrolyzed, each to a specific temperature, and the residues recovered and titrated with an AEA using a modified Foam Index Test.

Continuing studies using CAPTO for characterization of coal-fly ash pairs, in conjunction with other characterization studies, may lead to better predictions of the behavior of surfactants with the forms of unburned carbon present in fly ash. Furthermore, these characterizations may suggest routes for minimizing specific forms of unburned carbon in fly ash.

CHARACTERIZATIONS USING CAPTO

The patented controlled-atmosphere programmed-temperature oxidation (CAPTO) method has been used to characterize the carbon, hydrogen, and sulfur forms present in coals, activated carbon, and numerous organic/inorganic mixtures[3,4,5]. The system was originally conceived and effectively used for analysis of treated coals many of which did not respond well to classical coal analysis methods after treatment. Continued research and development resulted in a multiple-sample, one-step method for the direct determination of inorganic and organic carbon, hydrogen, and sulfur forms in coal and other materials.

Typical oxidative and pyrolysis CAPTO profiles of fly ash were produced as previously described[2] and used to establish the temperature intervals (403, 535, 637, and 769ºC) to be used for progressive oxidation/pyrolysis studies. Individual samples of fly ash were treated, using CAPTO, to 403, 535, 637, and 769ºC respectively. Plug flow of both 10% oxygen/90% argon and 100% argon through the samples during thermal treatment ensured uniform reaction throughout the sample plug. The furnace design minimizes temperature variation across the sample zone and a secondary furnace is used to ensure that all gases enter the analysis cells at the same temperature/equilibrium conditions to provide FTIR absorbance/temperature profiles of maximum resolution.

RESULTS

Using CAPTO, the forms of carbon present in the unburned carbon of fly ash were characterized. Figure 1 compares the CAPTO CO_2 evolution profiles of a Pittsburgh seam coal with the fly ash produced upon combustion of the coal. Fly ash produced low level CO_2 evolution from room temperature up to 403ºC which overlaps with that of the CO_2 evolution derived from oxidation of predominantly non-aromatic organic coal structures. The CO_2 evolution from fly ash observed in the 403-535ºC range overlaps with the CO_2 evolution produced by oxidation of predominantly aromatic organic coal structures. However, the major CO_2 evolutions from fly ash are observed at temperatures well above those encountered during CAPTO characterization of the Pittsburgh seam coal.

Figure 2 shows the fly ash CO_2 evolution profile and the functions that best fit the profile. This figure provides insight for assigning the CAPTO maximum temperature of each partial oxidation experiment. The profiles observed for each partial oxidation are shown in Figure 3 and oxidation up to 769ºC accounts for the 2.93% carbon present in the fly ash sample. The CO_2 evolution profiles observed for the fly ash under non-oxidizing conditions are shown in Figure 4; however, only 0.19% carbon was lost upon pyrolysis to 769ºC.

The fly ash residues from each of the CAPTO oxidation and pyrolysis experiments were recovered and representative samples were used in a Foam Index Test[6]. The AEA titration results from a modified Foam Index Test for the oxidized and pyrolyzed samples are shown in Tables 1 and 2. The ratio of the milliliters of AEA required to produce a stable foam with each sample to the percent carbon remaining in the fly ash sample at each reaction temperature is defined as adsorption "Activity" and shown in Tables 3 and 4. A plot of this "Activity" versus Temperature is shown in Figure 5. A significant decrease in "Activity" was noted between the untreated fly ash samples and the samples treated using oxidizing or non-oxidizing conditions up to 403ºC. The "Activity" of the samples thermally treated above 403ºC using non-oxidizing conditions showed little change throughout the temperature range of the experiments. The "Activity" of the samples thermally treated to 403ºC and 535ºC using oxidative conditions was similar to that of the samples treated using non-oxidizing conditions; however, at 637ºC the "Activity" of the sample showed a significant increase. The carbon forms remaining in the fly ash sample above 637ºC apparently interact with appreciably more AEA than those oxidizing up to 637ºC.

CONCLUSIONS AND CONTINUING WORK

- Evolution of CO_2 at four different temperature ranges is noted for this fly ash sample suggesting that at least four distinct forms of carbon are detectable using controlled oxidation conditions.

- A few percent of fly ash unburned carbon oxidizes in the temperature range normally associated with CAPTO oxidation of non-aromatic and aromatic organic coal structures.

● The major portion of unburned carbon in this fly ash sample oxidizes in CAPTO at temperatures distinct from those of coal, activated carbon, and graphite.

● Changes occurring in the fly ash samples during oxidative or pyrolytic thermal treatment from room temperature to 403ºC where little or no carbon loss is observed result in less AEA required to form a stable foam.

● The carbon forms remaining in the fly ash sample after oxidative treatment up to 637ºC apparently interact with appreciably more AEA than those oxidizing below 637ºC.

● This study is part of a continuing effort to identify new products from fly ash and improve existing fly ash applications. Additional fly ash samples are being examined using the thermal methods described. Initial screening of the fractions is being completed using the Foam Index Test. Differences in morphology of the fractions that show significant changes in adsorption activity are being examined using scanning electron microscopy (SEM) and other techniques with the whole fly ash fractions and carbon concentrates.

ACKNOWLEDGMENTS

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Table 1: Foam Index Titration Results for Oxidized Fly Ash

Sample	Temperature (C)	Trial #1 (ml)	Trial #2 (ml)	Avg.	S.D.
1	R.T. (untreated)	1.95	1.89	1.92	0.04
2	403	1.18	1.21	1.20	0.02
3	535	0.96	1.02	0.99	0.04
4	637	0.80	0.83	0.82	0.02
5	769	0.40	0.46	0.43	0.04

Table 2: Foam Index Titration Results for Pyrolyzed Fly Ash

Sample	Temperature (C)	Trial #1 (ml)	Trial #2 (ml)	Avg.	S.D.
1	R.T. (untreated)	1.95	1.89	1.92	0.04
2	403	1.44	1.24	1.34	0.14
3	535	1.18	1.30	1.24	0.08
4	637	1.30	1.43	1.37	0.09
5	769	1.15	1.21	1.18	0.04

Table 3: Percent Carbon and Activity for Oxidized Fly Ash

Sample	Temperature (C)	%C Evolved	%C Remaining	"Activity"
1	R.T. (untreated)	0	2.93	0.65
2	403	0.05	2.88	0.41
3	535	0.60	2.33	0.42
4	637	1.67	1.26	0.65
5	769	2.93	0	-------

Table 4: Percent Carbon and Activity for Pyrolyzed Fly Ash

Sample	Temperature (C)	%C Evolved	%C Remaining	"Activity"
1	R.T. (untreated)	0	2.93	0.65
2	403	0	2.93	0.46
3	535	0.04	2.89	0.42
4	637	0.08	2.85	0.47
5	769	0.19	2.74	0.43

Figure 1

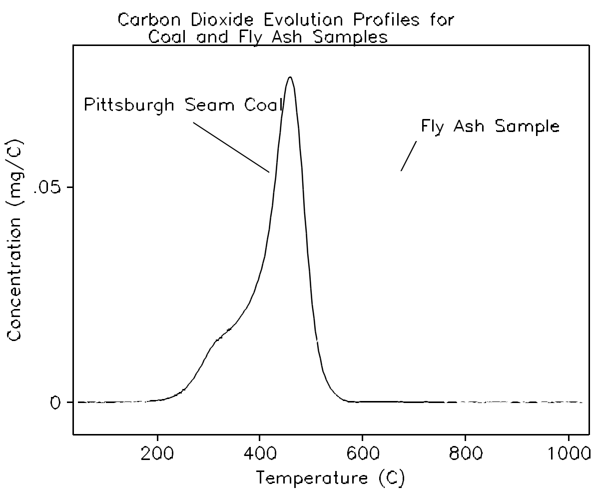


Figure 2

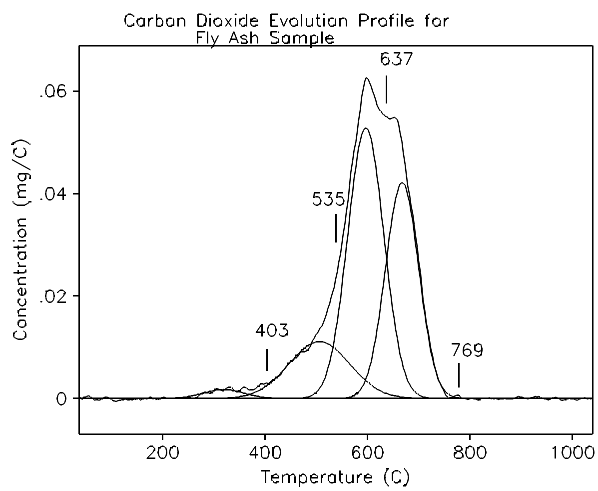


Figure 3

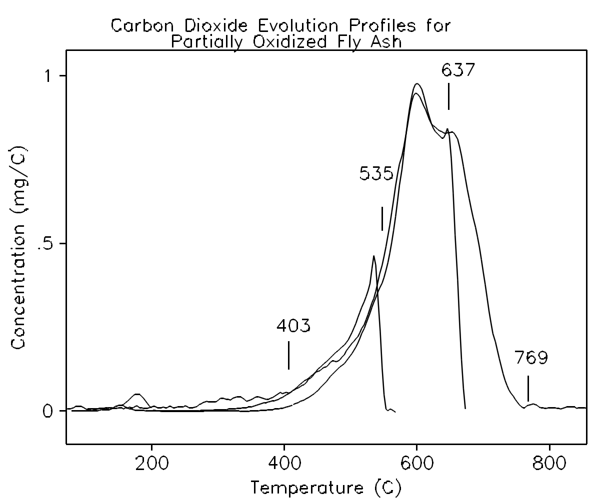
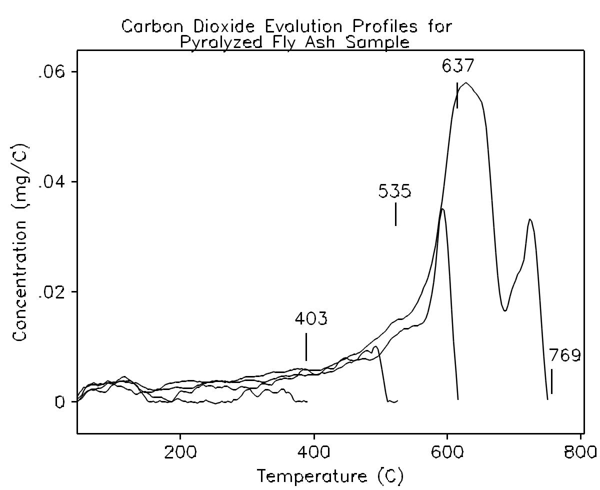


Figure 4



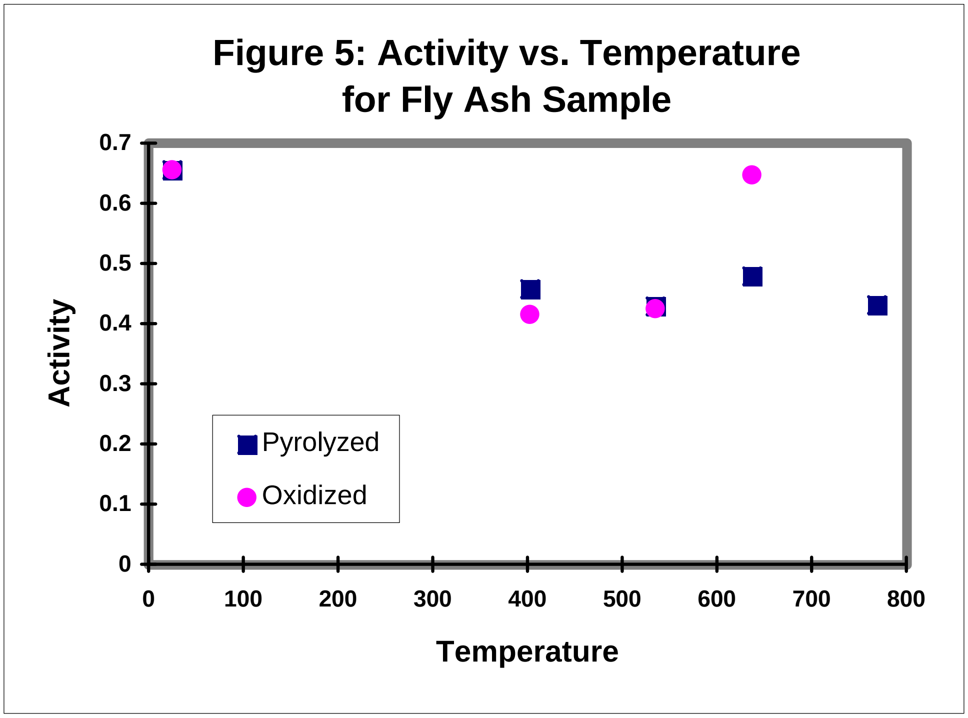


Figure 5: Activity vs. Temperature
for Fly Ash Sample
Activity
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
100
200
300
400
500
600
700
800
Temperature
Pyrolyzed
Oxidized