

CHARACTERIZATION OF FLY ASH CARBONS DERIVED DUE TO THE IMPLEMENTATION OF NO_x CLEAN AIR ACT AMENDMENTS

M. Mercedes Maroto-Valer¹, Darrell N. Taulbee² and James C. Hower²

¹The Energy Institute, The Pennsylvania State University,
405 Academic Activities Building, University Park, PA-16802

²University of Kentucky - Center for Applied Energy Research, 2540 Research Park Drive,
Lexington, KY-40511

Keywords: NO_x Clean Air Act Amendments, fly ash carbons, properties.

One of the more extensively used approaches for meeting the Title IV of the 1990 Clean Air Act Phase-I has been the installation of low-NO_x burners. Although these technologies have been proven effective in reducing NO_x emissions, they have also resulted in an increase in the concentration of unburned carbon in the fly ash. This has restricted the principal use of ash in the cement industry, since the unburned carbon tends to adsorb the air-entrainment admixtures (AEAs), that are added to the cement to prevent crack formation and propagation. However, very little is known about the properties of fly ash carbons and any information regarding their properties is watched closely by the utility industry. Accordingly, the work reported here represents the first characterization of the bulk properties of unburned carbon concentrates that have been isolated to purities up to 86% by using density gradient centrifugation. The density of like carbon forms isolated from two fly ashes appears to be quite similar, regardless of the source of the fly ash. The H/C atomic ratios are ~ 0.028-0.016, indicating a high degree of condensation. The BET surface areas are relatively low, ranging from 10 to 60 m²/g, and most of the pores are in the mesopore range (2-50 nm in width). For both series of fly ash samples, the surface area was found to increase linearly with increasing particle density.

INTRODUCTION

The Environmental Protection Agency (EPA) issued, under Title IV of the 1990 Clean Air Act Amendment, a two-phase strategy to reduce NO_x emissions from coal-fired utility boilers. Phase I took effect on January 1996 and promulgated that emissions levels from Group-1 boilers should be reduced by over 400,000 tons/year between 1996-1999 [1]. Group-1 is formed by dry-bottom wall-fired boilers and tangentially fired boilers and their emissions levels were reduced to 0.50 and 0.45 lb NO_x / MM Btu, respectively. Phase II, that began last January, will achieve an additional reduction of ~ 900,000 tons of NO_x annually. Phase II has lowered the emission levels for Group-1 boilers to 0.46 - 0.40 lb NO_x / MM Btu, and established limits for Group-2 boilers, that include cell, cyclones, wet bottoms and vertically fired boilers to levels down to 0.68, 0.86, 0.84, and 0.80 lb NO_x / MM Btu, respectively [2]. Nevertheless, Phase II regulation has been dormant during a litigation process that was originated by eight upwind states and a number of utilities, that sued EPA's authority to issue the rule [3]. However, a federal appeals court has recently upheld EPA's rule and the administration has requested to reactivate the rule. It is expected that facilities in 19 states could be affected by the implementation of this regulation.

One of the more extensively used approaches for meeting the Title IV of the 1990 Clean Air Act Phase-I has been the retrofitting of several hundred existing boilers with low-NO_x burners. Furthermore, EPA has projected that around 85-90% of the boilers in both Group-1 and 2 could meet the required NO_x reduction levels by installing low-NO_x burners [2], leaving other technologies, such as Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR) suitable complementary approaches to meet the required NO_x reduction levels. The installation of low-NO_x burners changes the flame-temperature profile as well as the flame chemistry since, in essence, a hot oxygen-rich flame is replaced by a cooler and longer, fuel-rich flame. While these modifications have proven effective in reducing NO_x emissions, they have also resulted in a lower combustion efficiency, leading to an increase in the concentration of unburned carbon in the fly ash [4]. Although the unburned carbon is known to preclude the use of fly ash in the cement industry, very little is known about the properties of this material and any information regarding its properties is watched closely by the utility industry.

It is generally known that the ASTM LOI specification is not sufficient to identify the suitability of a fly ash for the cement industry, since this criterion only gives a rough approximation to the carbon content of a sample and does not directly correlate with the capacity to adsorb air entrainment admixtures (AEAs), that are added to the cement to prevent crack formation and propagation [5,6]. In fact, prior petrographic examinations of a number of high-carbon fly ashes have shown that the unburned carbon is not visually uniform [7]. Three microscopically distinct carbon types have been identified: (i) inertinite particles, which appear to have been entrained from the combustor prior to melting or combustion; (ii) isotropic coke; and (iii) anisotropic coke, the latter two being extensively reacted particles, which appear to have passed through a molten stage [7,8]. The above particle types can be further subdivided according to particle shape, pore volume and wall thickness [9]. Although several studies have been conducted on the characterization of

whole fly ash samples [5,6], very little is known about the relative properties of the three carbon types, as their isolation is not a trivial task. For example, it is not known whether a fly ash that contains mainly inertinite has the same capacity to absorb air entrainment agents as an otherwise equivalent fly ash containing predominantly isotropic carbon. If in fact the capacity to absorb air entrainment agents varies substantially for the differing forms of unburned carbon, it may be possible to establish a criterion based on the relative properties of the differing carbon types to identify suitable fly ashes for the cement industry, regardless of their LOI value. Accordingly, this work presents the first characterization of these differing forms of unburned carbon, that have been previously separated by Density Gradient Centrifugation (DGC). The authors have successfully developed a method to isolate the three differing forms of unburned carbon [10,11]. The methodology used includes a preliminary triboelectrostatic enrichment or acid digestion, followed by DGC with a high-density lithium polytungstate media (2.85 g cm^{-3} max). Two fly ashes, identified as Dale and WEPCO, obtained from different power plants, were separated by the above procedure. In this work, the highest purity fractions from these separations were extensively analyzed by several analytical techniques, including elemental and surface area analyses.

EXPERIMENTAL

Two fly ashes, identified as Dale and WEPCO, were examined in this study. For the Dale sample, approximately 12 kg of fly ash were collected from the mechanical precipitators of a 70 MW boiler (Dale unit #3) operated by Eastern Kentucky Power. The WEPCO (Wisconsin Electric Power Co.) sample was collected from the electrostatic precipitators of a 136 MW unit at Valley Power Station. A series of preliminary enrichments were conducted to increase the amount of carbon in the ash and thereby, minimize the number of DGC runs. These steps included an initial screening of the sample with a 140 mesh sieve ($106 \mu\text{m}$), with the 140+ fraction being triboelectrostatically separated to obtain a sample (Dale-TES) with an inorganic matter content below 10%. This carbon-enriched fraction was then used as the feed for subsequent DGC separations. The WEPCO (Wisconsin Electric Power Co.) sample was processed directly through the triboelectrostatic separator without the initial screening step. Again, the carbon-enriched fraction (WEPCO-TES) was used as the feed material in a subsequent DGC separation, using a lithium heteropolytungstate high-density media. Details of the DGC separation procedure can be found elsewhere [10, 11].

Petrographic analyses of the fly ash parent samples and DGC fractions were performed on epoxy-bound polished pellets using oil-immersion objectives at a final magnification of 500-625x. The elemental analyses were carried out on a Leco CHN-600 analyzer. The porosity of the samples was determined via N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASiT. The BET surface areas were calculated using the adsorption points at the relative pressures (P/P_0) 0.05 - 0.25. The values reported were corrected to a mineral-free basis using the $6 \text{ m}^2/\text{g}$ surface area measured for the 2.5 g cm^{-3} density fraction of the fly ash and the TGA-derived inorganic contents for the respective density fractions [11]. The total pore volume, V_{TOT} , was calculated from the amount of vapor adsorbed at the relative pressure of 0.95. The mesopore (pores 2-50 nm in width) volume was calculated using the BJH equation.

RESULTS AND DISCUSSION

Purities and densities of the fraction separated by DGC The petrographic data for the Dale and WEPCO parent samples and the carbon-enriched DGC feed samples (Dale-TES and WEPCO-TES) are presented in Table 1 on a volume % basis. The parent Dale fly ash contained approximately 64% glass, while its -140 fraction had ~91% glass. The glass content was reduced to ~59% in the +140 mesh fraction and to less than 10% following the triboelectrostatic separation. The predominant carbon type is anisotropic coke. The relative proportions of the three carbon types in the parent and the beneficiated Dale samples are very similar, with the exception of a slight reduction in inertinites in the +140 fraction and resultant subsamples. However, even these minor changes were not statistically significant as they stay within the experimental error of the petrographic measurements ($\pm 5\%$). The WEPCO sample was selected for this study for two reasons. First, to determine if like carbon forms exhibited the same densities regardless of the source of the fly ash. Second, the WEPCO sample contained a higher proportion of isotropic relative to anisotropic coke, which, assuming like carbon forms do in fact have the same density, should be reflected by the weight recovery curve. For the WEPCO sample, a similar reduction in the glass content was observed after the triboelectrostatic separation, going from ~60% to ~10% (Table 1). The predominant carbon form in the WEPCO sample is isotropic coke. However, there seems to be somewhat higher beneficiation of the anisotropic carbon, compared to the other carbon types, during the triboelectrostatic separation. Nevertheless, this difference stays within the experimental error. Whether triboelectrostatic separations truly discriminate certain carbon types has not been fully investigated.

Figure 1 shows the petrographic composition for all the density fractions recovered for the WEPCO-TES fractions. The highest enrichment is for inertinites (densities $< 1.60 \text{ g cm}^{-3}$ with purity of ~85%) and is similar to that found for Dale-TES. Isotropic coke particles partitioned predominantly at densities $\sim 1.725\text{-}1.750 \text{ g cm}^{-3}$, similar to the Dale-TES sample, but presented higher purities (79% cf. 72%), due in part to the higher proportion of isotropic carbon present in the parent sample, as well as the smaller particle size and lower frequency of mixed particles. Anisotropic coke particles maximized at similar densities and purities to those observed for the Dale separations. The higher density fractions are dominated by inorganic particles, with spinel being the most dense mineral. This is consistent with the values reported for spinel and glass minerals, where the former has a specific gravity of 3.55 g cm^{-3} , while the latter is $\sim 2.50 \text{ g cm}^{-3}$. Previous centrifugal separations have also reported a higher partition of non-glassy particles, consisting primarily of iron oxides, at densities $> 2.40 \text{ g cm}^{-3}$ [12, 13].

The petrographic analysis of the three highest purity carbon-type fractions from each separation along with the density range over which these highest purity fractions were recovered are also shown in Table 1. After DGC separation, enrichments ranged up to 85.5 vol% inertinite in the WEPSCO separation, up to 78.5 vol% isotropic coke for the WEPSCO separation, and up to 76 vol% anisotropic coke in the Dale and WEPSCO carbon-enriched separations (Table 1). Note that the differences in the fraction number in which the highest purities were obtained for the three separations is due to changes made in the cut-point densities for the three separations and not necessarily to differences in particle density. Maximum purities were obtained at similar densities for both samples. That is, inertinite purity maximizes in the lowest density fractions ($<1.65 \text{ g cm}^{-3}$), isotropic-coke purity maximizes between 1.72 and 1.78 g cm^{-3} , and anisotropic-coke purity maximizes between 1.88 and 1.94 g cm^{-3} . Thus, these data indicate that the density of the three unburned carbon types to be similar in these two fly ash samples despite the differences in the starting coal or the utility combustor from which they were derived.

Elemental analyses and atomic ratios CHN analyses were carried out only on the Dale carbon-enriched separation samples. The results of these analyses conducted on the DGC feed and selected higher-purity carbon-type fractions are shown in Table 2. The elemental analyses show that the three types of unburned carbon consist primarily of C, while the H content is below 0.23. The H/C atomic ratios range between 0.028 to 0.016, indicating a high degree of condensation. Any trends that may be present in the hydrogen data and atomic H/C ratios are masked by the error of the analysis stemming from the very low hydrogen concentrations coupled with potential interferences from adsorbed moisture. However, there does appear to be a correlation between nitrogen concentration and carbon type (or fraction density), where higher nitrogen concentrations and N/C atomic ratios are associated with increasing density. In addition, there also appears to be a higher level of oxygen in the isotropic coke particles (fraction nos. 5 and 6). FT-IR spectra were conducted on selected density fractions in an effort to determine if the isotropic-rich fractions were measurably greater in carbonyl (C=O) functional groups, the only oxygen functionality to which infra-red analysis would be sufficiently sensitive to detect, but these analysis were inconclusive. Nevertheless, similar trend has been found previously by other authors, where fly ashes with predominant isotropic coke presented higher oxygen levels than ashes with predominantly anisotropic coke [5]. In this previous study, diffuse reflectance FT-IR was also used, but again this technique did not detect carbonyl functional groups, implying that the oxygen was most likely bound as heterocyclic compounds. The reason for these trends in the nitrogen and oxygen levels is unclear, but these distinctive concentrations as a function of unburned carbon type may be reflected in differences in adsorption properties.

Surface area, pore volume and adsorption properties The N_2 adsorption isotherms of all the samples investigated were Type II according to the BDDT classification and they are typical for nonporous or macroporous adsorbents, on which unrestricted monolayer-multilayer adsorption can occur. BET surface area (N_2 at 77K) measurements were carried out on the Dale and WEPSCO carbon-enriched separation samples. The surface areas are relatively low, ranging from 10 to 60 m^2/g . The WEPSCO parent fly ash and subsequent subsamples present slightly higher surface areas than those observed for their counterparts of the Dale separations. For example, the inertinite fraction derived from WEPSCO fly ash has a surface area of 25 m^2/g , compared to only 15 m^2/g for the inertinite fraction derived from Dale fly ash. For both series of fly ash samples, the surface area was found to increase linearly as a function of particle density, as illustrated in Figure 2 for selected density fractions from the Dale and WEPSCO DGC separations. Inertinites exhibited the lowest surface area (15-25 m^2/g), isotropic coke particles presented intermediate surface areas (25-35 m^2/g), while anisotropic coke particles exhibited the highest surface areas (35-60 m^2/g). The fly ashes investigated here are class F and were derived from high volatile bituminous coals. Studies on class C fly ashes, that are generally derived from subbituminous coals, have shown much higher surface areas (200-400 m^2/g) [14], indicating that the properties of fly ashes are not only dependent of petrographic composition, but also on the rank of the coal they are derived from. In a previous study, we showed that anisotropic coke, with the greatest BET surface area, appears to adsorb the greatest amount of Hg from the flue gas stream, while inertinite, derived from the coal with little alteration in the combustion process, is the least adsorptive carbon form. Although the relationship between sample density and BET surface area is essentially linear, for Hg adsorption while generally increasing with the density and surface area, does deviate from a simple, linear relationship [15].

Pore size distribution studies were also conducted on the above samples and the proportion of mesopore (pores 2-50 nm in width) volume over total volume is presented in Figure 3 for selected density fractions from the Dale separation. Figure 3 shows that for the three carbon types, the pore volume is mainly due to mesopores, with the mesopore volume accounting for over 60% of the total pore volume. This indicates that the extensive and rapid devolatilization that coal undergoes in the combustor, seems to promote the generation of meso- and macropores. There does appear to be a correlation between mesopore volume and carbon type, with inertinites exhibiting the highest proportion of mesopores (~90%), while isotropic coke particles present the lowest fraction of mesopore volume (~60%) and anisotropic coke presenting intermediate values (70-80%). A similar trend has been found for the WEPSCO DGC fractions.

CONCLUSIONS

Concentrates of three microscopically identifiable forms of unburned carbon (inertinite, isotropic coke, and anisotropic coke) have been generated from two high-carbon-content fly ash samples using the technique of density gradient centrifugation (DGC). The density of like carbon forms isolated from the two fly ashes appears to be quite similar, regardless of the source of the fly ash. The H/C atomic ratios are ~ 0.028-0.016, indicating a high degree of condensation. The surface

areas are relatively low (10-60 m²/g), and most of the pores are in the mesopore range (2-50 nm in width). For both series of fly ash samples, the surface area was found to increase linearly as a function of particle density. This work has shown that the three carbon types are not only visually different, but also present distinctive physical and chemical properties (density, nitrogen and oxygen concentrations, as well as surface area and mesopore volume). Furthermore, these distinctive properties may be reflected in differences in adsorption properties, and therefore, the ASTM LOI specification, that is only based on the total carbon content, is not sufficient to identify the suitability of a fly ash for the cement industry. Our immediate goal is to measure the relative capacity of the different carbon types to adsorb air-entrainment reagents. For this purpose, we are developing a micro-technique to measure in-situ the adsorption of such agents directly. Finally, this characterization work has indicated that the unburned carbon can also be considered as a valuable precursor for the production of premium carbon products, since it consists basically of carbon and it has gone through a devolatilization process while in the combustor. Accordingly, we have investigated two potential routes for the generation of premium carbon products from the unburned carbon present in fly ash [16]. The first route focuses on the use of fly ash carbons as precursors for activated carbons by steam activation at 850°C, while the second route concentrates on the utilization of fly ash carbons as a replacement for calcined petroleum coke in the production of carbon artifacts.

ACKNOWLEDGEMENTS

The authors wish to thank Drs. H. Ban and J. M. Stencil (CAER-University of Kentucky) for conducting the triboelectrostatic separation and to the Research Council of the Basque Government for financial support.

LITERATURE CITED

1. The U.S. Department of Energy, 1996, Clean Coal Technology, Reducing emissions of nitrogen oxides via low-NO_x burner technologies, Topic report no. 5.
2. U.S. Environmental Protection Agency, 2000, <http://www.epa.gov/ardpublic>.
3. Hogue, C., 2000, Chemical and Engineering News, **78**, 10.
4. Hower, J.C., Rathbone, R.F., Robl, T.L., Thomas, G.A., Haeblerlin, B.O., and Trimble, A.S., 1997, Waste Management, **17**, 219.
5. Hill, R.L., Sarkar, S.L., Rathbone, R.F. and Hower, J.C., 1997, Cement and Concrete Research, **27**, 193.
6. Freeman, E., Gao, Y-M, Hurt, R.H. and Suuberg, E.M., 1997, Fuel, **8**, 761.
7. Hower, J.C., Rathbone, R.F., Graham, U.M., Groppo, J.G., Brooks, S.M., Robl, T.L. and Medina, S.S., 1995, Proceedings International Coal Testing Conference, 49.
8. Maroto-Valer, M.M., Taulbee, D.N. and Hower, J.C., 1998, Proceedings Conference on Unburned Carbon on Utility Fly Ash, 49.
9. Bailey, J.G., Tate, A., Diessel, C.F.K. and Wall, T.F., 1990, Fuel, **69**, 225.
10. Maroto-Valer, M.M., Taulbee, D.N. and Hower, J.C., 1999, Energy & Fuels, **13**, 947.
11. Taulbee, D.N., Maroto-Valer, M.M. and Hower, J.C., 1999, Proceedings 13th International Symposium on Use and Management of Coal Combustion By-Products, **1**, 24/1-15.
12. Ghosal, S., and Self, S.A., 1995, Fuel, **74**, 522.
13. Palmer, S.R., Sivanandan, S., and Huggett, W., 1997, Proceedings 1997 International Conference on Coal Science, **2**, 1999.
14. Kulatos, I., Gao, Y-M, Hurt, R.H. and Suuberg, E.M., 1998, Prepr. Am. Chem. Soc. Fuel Division, **43**, 980.
15. Hower, J.C., Maroto-Valer, M.M., Taulbee, D.N. and Sakulpitakphon, T., 2000, Energy & Fuels, **14**, 224.
16. Maroto-Valer, M.M., Andrésen, J.M., Andrésen, C.A., Morrison, J.L., and Schobert, H.H., 2000, Prepr. Am. Chem. Soc. Fuel Division, **45**, In Press.

Table 1: Petrographic analysis for the parent samples, carbon-enriched feeds and the highest purity carbon-type density fractions from each separation.

	Inertinite	Isotropic	Anisotropic	Glass
Dale Parent	3.8	13.4	19.2	63.6
-140 mesh Dale	1.2	2.6	5.2	91.0
+140 mesh Dale	2.0	13.0	25.5	59.5
Dale TES (DGC feed)	5.5	24.0	61.0	9.5
Fraction #2 (1.32-1.65 g cm ⁻³)	76.5	7.0	1.0	15.5
Fraction #5 (1.72-1.75 g cm ⁻³)	13.1	72.1	8.7	6.0
Fraction #12 (1.92-1.94 g cm ⁻³)	<0.5	19.5	76.0	4.5
WEPCO parent	4.0	27.3	7.3	61.5
WEPCO TES (DGC feed)	8.5	51.5	27.5	12.5
Fraction #4 (1.50-1.60 g cm ⁻³)	85.5	8.5	2.5	2.0
Fraction #8 (1.725-1.75 g cm ⁻³)	9.5	78.5	11.5	0.5
Fraction #14 (1.875-1.90 g cm ⁻³)	2.0	20.0	75.5	2.5

Table 2: Elemental analyses of selected density fractions from the Dale carbon-enriched separation.

Fraction #	Dominant carbon type (vol%)	%C (daf)	%H (daf)	%N (daf)	%O* (daf)	H/C	N/C
DGC feed	6%in; 24% iso; 61% ani	97.2	0.17	1.77	0.86	0.021	0.016
#2	Inertinite (77 v%)	98.4	0.21	1.44	< 0.01	0.025	0.013
#5	Isotropic (72 vol%)	95.7	0.22	1.55	2.53	0.027	0.014
#6	Isotropic (66 vol%)	96.5	0.13	1.55	1.82	0.016	0.014
#10	Anisotropic (71 vol%)	97.8	0.19	1.83	0.18	0.024	0.016
#11	Anisotropic (71 vol%)	98.1	0.16	1.77	< 0.01	0.019	0.015
#12	Anisotropic (76 vol%)	98.1	0.17	1.73	< 0.01	0.021	0.015
#13	Anisotropic (73 vol%)	97.6	0.23	1.86	0.31	0.028	0.016

* Determined by difference

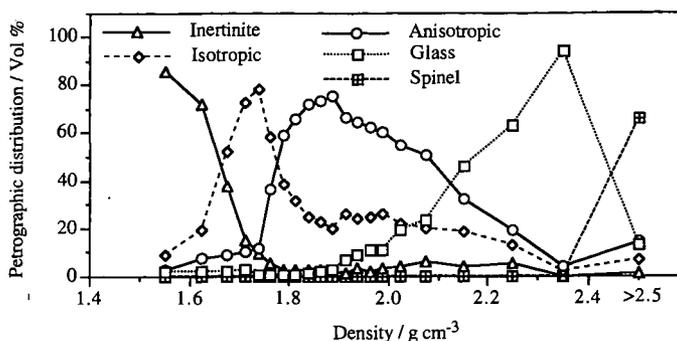


Figure 1: Petrographic distribution of the recovered density fractions for the separation of the WEPCO-TES sample.

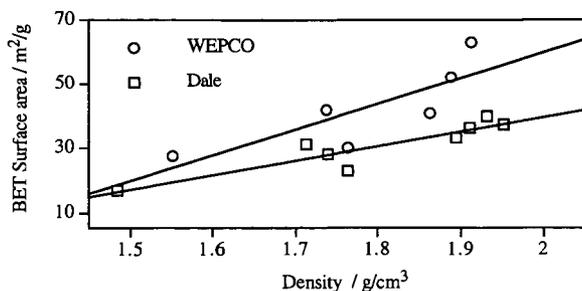


Figure 2: Relationship between surface area and density for selected density fractions from the Dale and WEPCO DGC separations.

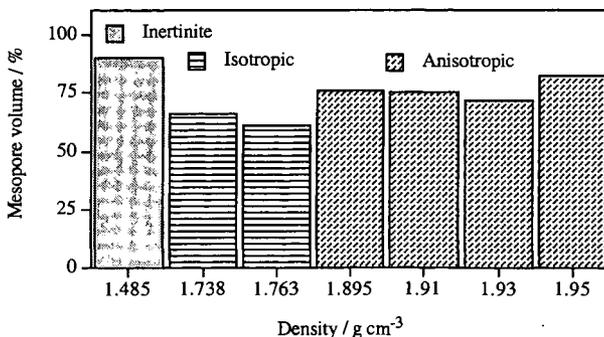


Figure 3: Proportion of mesopore (2-50 nm) volume for selected density fractions from the Dale DGC separation.