

Characterization of Differing Forms of Unburned Carbon Present in Fly Ash

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KEYWORDS: unburned carbon types, adsorption properties.

INTRODUCTION

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 agents.^{1,2} In fact, prior petrographic examinations of a number of high-carbon fly ashes have shown that the unburned carbon is not visually uniform.³ 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.^{3,4} The above particle types can be further subdivided according to particle shape, pore volume and wall thickness⁵. Although several studies have been conducted on the characterization of whole fly ash samples,¹⁻² 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.^{6,7} 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 μm), 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.^{6,7}

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) 0.1 - 0.3. The values reported were corrected to a mineral-free basis using the 6 m^2/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.⁸ 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 DGC separation procedure The petrographic data for the Dale and WEPCO parent samples and the carbon-enriched DGC feed samples (Dale-TES and WEPCO-TES) are given in Table 1 on a volume % basis. 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. The amount of glass was reduced from 63 vol% in the Dale parent sample to ~10 vol% following screening and triboelectrostatic (TES) enrichment. A similar reduction was observed from the parent to the enriched WEPCO-TES sample. After DGC separation, enrichments ranged up to 85.5 vol% inertinite in the WEPCO separation, up to 78.5 vol% isotropic coke for the WEPCO separation, and up to 76 vol% anisotropic coke in the Dale and WEPCO carbon-enriched separations. 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.

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 ($1.32\text{-}1.65 \text{ g cm}^{-3}$)	76.5	7.0	1.0	15.5
Fraction #5 ($1.72\text{-}1.75 \text{ g cm}^{-3}$)	13.1	72.1	8.7	6.0
Fraction #12 ($1.92\text{-}1.94 \text{ g cm}^{-3}$)	<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 ($1.50\text{-}1.60 \text{ g cm}^{-3}$)	85.5	8.5	2.5	2.0
Fraction #8 ($1.725\text{-}1.75 \text{ g cm}^{-3}$)	9.5	78.5	11.5	0.5
Fraction #14 ($1.875\text{-}1.90 \text{ g cm}^{-3}$)	2.0	20.0	75.5	2.5

Elemental analyses 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 0.2. The H/C atomic ratios are <0.03 , indicating a high degree of condensation. Any trends that may be present in the hydrogen data 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 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 taken of 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.¹ 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.

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

Fraction #	Average Density (g/mL)	Dominant carbon type (vol%)	%C (daf)	%H (daf)	%N (daf)	%O ^a (daf)
DGC feed		6% in; 24% iso; 61% ani	97.2	0.17	1.77	0.86
#2	1.485	Inertinite (77 v%)	98.4	0.21	1.44	< 0.01
#5	1.738	Isotropic (72 vol%)	95.7	0.22	1.55	2.53
#6	1.763	Isotropic (66 vol%)	96.5	0.13	1.55	1.82
#10	1.895	Anisotropic (71 vol%)	97.8	0.19	1.83	0.18
#11	1.910	Anisotropic (71 vol%)	98.1	0.16	1.77	< 0.01
#12	1.930	Anisotropic (76 vol%)	98.1	0.17	1.73	< 0.01
#13	1.950	Anisotropic (73 vol%)	97.6	0.23	1.86	0.31

^a Determined by difference

Porosity and adsorption properties BET surface area (N₂ at 77K) measurements were carried out on the Dale and WEPCO carbon-enriched separation samples. The surface areas are relatively low (10-60 m²/g). The WEPCO 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 WEPCO fly ash has a surface area of 25 m²/g, compared to only 15 m²/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 1 for selected density fractions from the Dale and WEPCO DGC separations. Inertinites exhibited the lowest surface area (15-25 m²/g), isotropic coke particles presented intermediate surface areas (25-35 m²/g), while anisotropic coke particles exhibited the highest surface areas (35-60 m²/g).

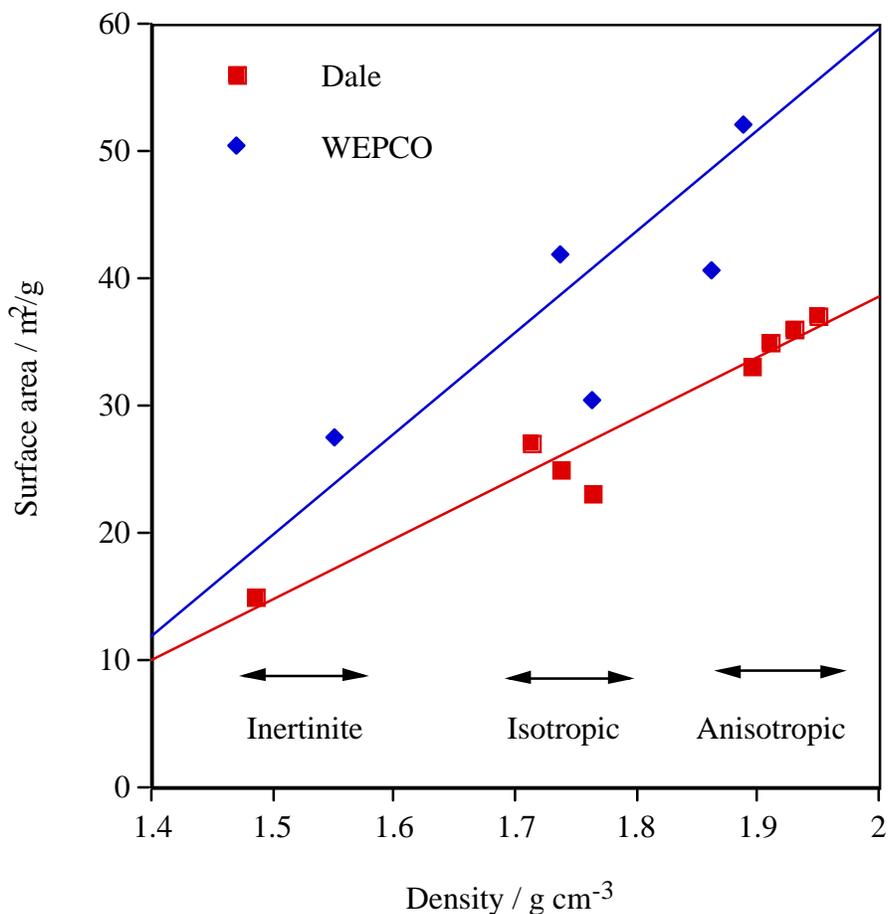


Figure 1 Relationship between surface area and density for selected density fractions from the Dale and WEPCO DGC separations.

The N₂ 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. 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 2 for selected density fractions from the Dale separation. Figure 2 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 WEPCO DGC fractions.

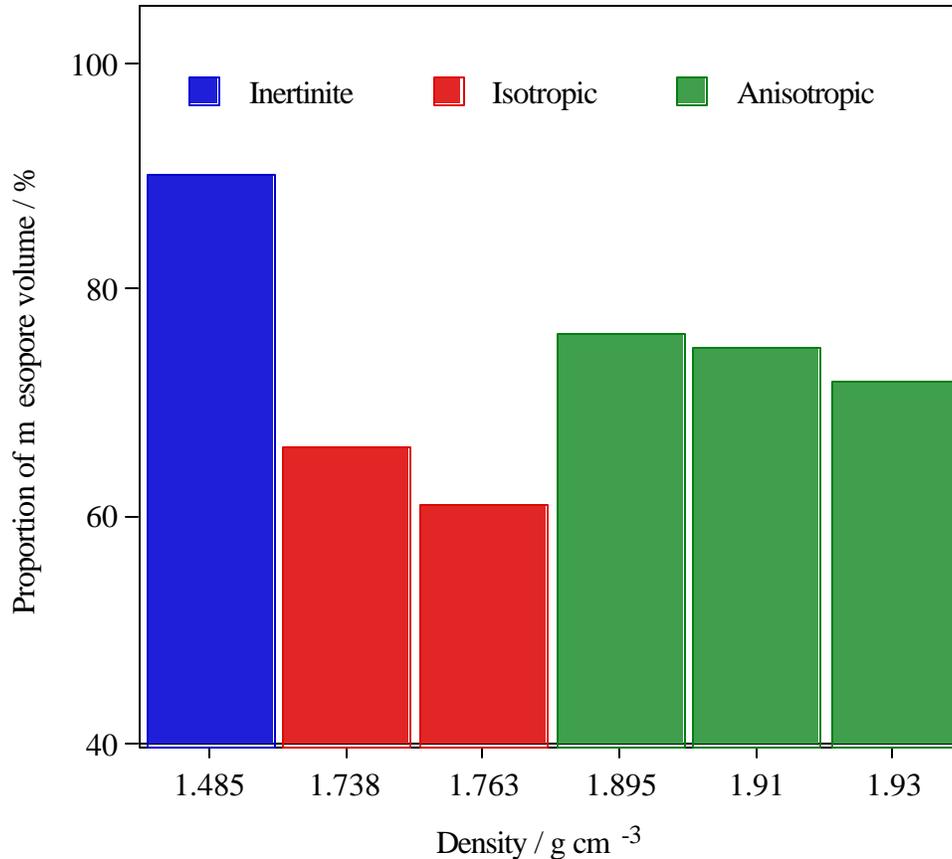


Figure 2 Proportion of mesopore (2-50 nm) volume for selected density fractions from the Dale DGC separation.

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 ~ 0.03-0.02, 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 absorption 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, 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. Ongoing work is focused on the development of routes for the generation of premium carbon products, like activated carbons and carbon artifacts, from the unburned carbon present in fly ash. Work conducted in these novel areas is also presented in these Proceedings.^{9, 10}

ACKNOWLEDGEMENTS

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

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