

Characterization of the carbon types present in fly ash separated by density gradient centrifugation

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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 uniform³. 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 stage³. The above particle types can be further subdivided according to particle shape, pore volume and wall thickness⁴. Although several studies have been conducted on the characterization of whole fly ash samples¹⁻², 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. 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). A preliminary account of this separation method was presented in the 1998 Conference on Unburned Carbon on Utility Fly Ash⁵ and a more detailed description can be found elsewhere⁶. 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 thermogravimetric, elemental and surface area analysis, and the results are presented in this summary.

Characterization studies

1. Purities and densities of the separation procedure For the DGC separations, the maximum purities ranged from 77-85 vol% for inertinite, 63-79 vol% for isotropic coke, and 69-76 vol% for anisotropic coke. Maximum purities were obtained at $\sim 1.50\text{-}1.65 \text{ g cm}^{-3}$ for inertinite, at $1.72\text{-}1.78 \text{ g cm}^{-3}$ for isotropic coke, and at $\sim 1.88\text{-}1.95 \text{ g cm}^{-3}$ for anisotropic coke. 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.

2. Thermogravimetric and CHN analysis These analyses were conducted only on the Dale carbon-enriched separation samples. The elemental analyses show that the three types of unburned carbon consist primarily of C (>98%), while the H content is below 0.02. The H/C atomic ratios are <0.04, indicating a high degree of condensation. Analogous elemental analyses measurements for the density fractions from the WEPCO sample are currently being conducted.

3. Surface area measurements BET surface area ($\text{N}_2\text{-}77\text{K}$) were carried out on the Dale and WEPCO carbon-enriched separation samples. The surface areas are relatively low ($10\text{-}60 \text{ m}^2/\text{g}$), and most of the porous are in the mesopore range ($20\text{-}500 \text{ \AA}$ in width). 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 $25 \text{ m}^2/\text{g}$, compared to only $15 \text{ m}^2/\text{g}$ for the inertinite fraction derived from Dale fly ash. However, for both series of fly ash samples, the surface area was found to increase linearly as a function of particle density, that is, inertinites exhibited the lowest surface area ($15\text{-}25 \text{ m}^2/\text{g}$) with anisotropic coke exhibiting the highest ($35\text{-}60 \text{ m}^2/\text{g}$), while isotropic coke presented intermediate surface areas ($25\text{-}35 \text{ m}^2/\text{g}$).

Future directions

A more detailed description of the porosity, including pore size distribution analysis, of the differing carbon types will be presented. Our immediate goal is to measure the relative capacity of the different carbon types to adsorb air-entrainment reagents. Ultimately, we hope to adapt or develop a micro-technique to measure the adsorption of such agents directly. Furthermore, these carbon materials could also be valuable precursors for

the production of activated carbons, since they have already undergone devolatilization, and only require further activation. A preliminary assessment of the potential use of unburned carbon as precursor for high value premium carbon products will also be presented.

Literature cited

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