

Characterization of Carbon Concentrates from Coal Combustion Fly Ashes

John P. Baltrus, Arthur W. Wells, Daniel J. Fauth , J. Rodney Diehl and Curt M. White

E-mail: john.baltrus@netl.doe.gov

Telephone: 412-386-4570

Fax: 412-386-4806

U.S. Department of Energy, National Energy Technology Laboratory

P.O. Box 10940

Pittsburgh, PA 15236-0940

A series of nine carbon concentrates having levels of carbon ranging from 24% to 76% and derived from coal combustion ashes plus two high-carbon unprocessed ashes were examined using a variety of physical and spectroscopic characterization methods. The samples originated from a total of seven different coal-fired utilities and six different methods were used to produce the carbon concentrates. All carbon concentrates were derived from class F fly ashes. Three different configurations of triboelectrostatic separators were used to produce the carbon concentrates in addition to two different flotation methods plus a proprietary carbon recovery process.

The properties measured included adsorption activities, density (apparent, bulk, and skeletal), pore volumes (macro, meso, and micro), pore size, surface area, particle size and particle volume/size distributions. The carbon in each sample was further characterized using controlled-atmosphere programmed-temperature oxidation (CAPTO), thermogravimetric analysis (TGA), Raman spectroscopy, X-ray diffraction and optical microscopy.

This study was undertaken to determine the variability, or lack thereof, of some of the most important properties of carbons across a broad spectrum of carbon concentrates from different coal combustion fly ashes and produced by a number of commercial and laboratory separation methods. The results have implications for those who wish to use carbon concentrates from coal combustion fly ashes in secondary markets, especially as sorbents and fillers.

The results of the characterization methods can be summarized as follows:

- The samples did not reveal any activated carbon-like physical or chemical properties. Iodine numbers and carbon tetrachloride activities were extremely low - not existing for all practical purposes.
- The equivalent spherical particle size range for most samples was rather narrow, usually from 0.8 to 5 μm , with a mean particle size of about 2 μm . One sample, a carbon concentrate derived by a proprietary process at Pittsburgh Mineral & Environmental Technology, Inc. (PMET) had a considerably larger particle size (mean diameter of 41 μm).
- Carbon enrichment of a sample usually leads to an increase in the average particle size due to removal of the finer non-carbon ash particles. However the particle size of the product can depend on the

separation method, as observed for a Dale Station ash separated by a triboelectrostatic parallel plate separator where successive passes through that mechanical separation apparatus led to attrition of the carbon particles.

- Although a majority of the carbon concentrate particles were between 0.8 and 5 μm , most of the particle volumes occupied by the samples can be attributed to particles larger than that range.
- Incremental pore volume distributions were remarkably similar for a majority of the samples. Most of the pore volume could be attributed to the carbon portion of the concentrates. The pore volume for each sample was almost evenly distributed between macro pores and micro pores; much less volume could be attributed to meso pores. The macro pore volume was concentrated in pores with diameters between 1 and 11 μm . Again the samples from PMET stood out because they had significantly larger pore volumes per gram of sample both in macro pores and micro pores, as well as having the macro pore volume attributed to pores with diameters in the 20 to 100 μm range.
- All carbon concentrates had relatively low surface areas in the range of 10 to 40 m^2/g . The surface area could be attributed to the carbon portion of the concentrates.
- TGA and CAPTO profiles for the same sample were nearly identical, indicating that the weight loss observed upon heating the samples to 1000°C could be solely attributed to carbon oxidation. This is not surprising for class F fly ashes, which contain little calcium. The CAPTO and TGA profiles for the PMET carbon concentrates were more like those measured for metallurgical cokes.
- Raman spectra of the carbon particles for all samples featured a very broad band at 1360 cm^{-1} and a somewhat less intense and narrower band at 1630 cm^{-1} . Such features are consistent with a highly disordered graphite structure. X-ray diffraction results supported that observation.
- Relative mean-maximum reflectance measurements for the samples ranged from 7.28 to 8.42%. For reference purposes, the carbon forms derived from high volatile coal in metallurgical coke have a relative mean-maximum reflectance of 8.91%.
- Petrographic analysis results showed a significant variation in the size of the carbon cenospheres as well as in the typical cell wall thickness (1 - 100 μm) across the range of samples. The principal char type in most of the samples was anisotropic and consisted of crassisphere and crassinetwork cenospheres, which are characterized by their thick walls and high porosity. However the Kentucky fly ash carbon contained a fair amount of thinner walled tenuisphere cenospheres and was partially isotropic. The cenospheres in several of the samples were broken and the two carbon-enriched PMET samples contained some green (lower temperature) cenospheres; the structure of the particles appeared similar to metallurgical coke in that they were very porous and contained large voids in addition to having the remaining ash embedded within the carbon particles.

- In unprocessed fly ash, optical microscopy also noted the presence of very small carbon particles trapped within larger ash particles in addition to char particles much larger in size than ash particles. As the carbon concentration of the samples increases, a greater fraction of the ash is primarily locked within the carbon particles.

An overall summary of the results can be made by stating that carbon particle size and pore volumes are fairly consistent from sample to sample despite the variety of sources and processing conditions. The particle size can be affected by the processing conditions used to produce the carbon concentrate, with mechanical separation leading to more attrition of particle size than flotation methods. Unprocessed ashes typically contain a mixture of non-carbon and larger char particles. In addition to separate carbon and non-carbon ash particles, part of the carbon is embedded in the non-carbon particles and that carbon is lost upon separation of the ash particles. Ash can also be interlocked within larger carbon particles and will not be liberated unless the carbon particles undergo attrition during separation.

Further studies will be undertaken to further explore the adsorption properties of these ashes, but these initial results indicate that with such low surface areas they are unlikely to be good adsorbents unless activated in some manner.