Petrographic Characterization of Carbon in Fly Ash

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In a general sense fly ash is the small particles entrained in the gases generated in the combustion of coal. Fly ash is viewed differently by workers with different backgrounds and approaches. Some see fly ash as a waste material that must be disposed of at a cost. Others see fly ash as mixtures of inorganic ash and organic unburned coal. The latter believe that the marketability of fly ash can be increased by benefeciation to recover the unburned coal that may have a variety of uses including recovered heat units. Once the carbon is reduced, the inorganic ash has more uses and may be used as a pozzolon extender for cement. Emission control on NOx resulted in lowered combustion temperatures which tends to increase carbon in fly ash. Since tens of millions of tons of fly ash are produced each year in the U.S.A., there is considerable effort being expended to turn fly ash into marketable products.

Fly ash is mostly inorganic ash materials obtained from the mineral matter in coal. The minerals in coal are mostly aluminosilicates or clays, silica or quartz, carbonates such as calcite and sulfates and sulfides. In addition, there is a variety of minor minerals in coal. Ashes are commonly analysed for the oxides. Acid or refractory ashes which have high softening temperatures are high in Al₂O₃ and SiO₂ while basic or lignite type ashes have low ash softening temperatures and are rich in alkali elements and iron. The analytical procedures for the characterization of the inorganics in fly ash are widely used and fairly well standardized. In contrast the procedures for the characterization of organic carbon in fly ash are not as well developed. The loss on ignition or LOI of fly ashes are attributed to unburned coal/coke carbons.

ICCP and ISO are working on developing microscopic procedures to characterize the morphology of unburnt coal in fly ash.

When coals are heated they produce combustable gases which burn until the coked carbon residue surface ignites. It is more difficult to combust an some of the coke ends up in fly ash.

In general, bituminous coals are partially coked during combustion. The heated coal particles form a thermobitumen which plastizes part of the coal and entrapped gases in the softened coal expand to produce relatively symmetrical, porous or foamed coke particles which are called cenospheres, as suggested by Sinnatt in 1928. The name comes from cenosphaera which is a single celled organism that has a shell with a lattice pattern. Coked cenospheres from coal have been recognized in coal dust explosions, in blast furnaces with coal injection, in thermally dried coal and in the tars from coal carbonization as well as in fly ash.

Coals consist of macerals which are considered to be the organic equivalents of minerals in rocks. The macerals are broadly classified as reactive and inerts. In coke making the reactives form the coke binder phase and the inerts act as filler. The reactive macerals are vitrinite from woody material and liptinite from reproductive organs and leaf and stem coatings. The inerts are called inertinite. The vitrinite forms the binder in cenospheres. The high hydrogen liptinite forms the most gas and tar when heated and leaves a small coke residue. The low hydrogen and carbon rich inerts are the most difficult to burn and retain the same form in coke as they displayed in the coal.

The morphology of cenospheres is determined by the amounts of reactives and inerts in the precursor coal particles. In general, the wall thickness decreases and the porosity and symmetry of the cenospheres increase as the vitrinite increases. Wall thickness and porosity as well as the wall shapes and distributions are used to classify cenosphere microstructures. In addition, the wall carbons contain microtextures that range from optically isotropic to increasing anisotropism as the coal rank increases.

The morphology or microstructure and microtexture of cenospheres in an unburned fly ash carbon are due to the rank (maturity) and type (maceral content) of coal being burned and on process variables. The thinner walled and porous, isotropic carbon cenospheres have the highest reactivity to CO2 while the high inert, thick walled, dense, anisotropic forms have the lowest reactivity.

The current work describes a simple and useful classification of carbon in fly ash. The system can be expanded to include ash forming minerals. Petrographic characterization of the fly ash should aid in selecting coals and in adjusting combustion conditions to minimize carbon or BTU losses to fly ash. Similar data should be useful in beneficiation of fly ash to recover carbon and render the carbon-free fly ash more marketable and desirable for use.