Engineering controls on fly ash chemistry: Examples from Kentucky power plants

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The chemistry of fly ash is controlled by a number of factors: 1/ chemistry of the feed coal (and added fuels, such as petroleum coke, tires, biomass, etc.), 2/ size consist of the fuel feed (controlled by pulverized fuel vs. cyclone combustion, maintenance of pulverizers, etc.), 3/ design of the boiler and pollution control system, and 4/ temperature of the flue gas at the collection point. In general, for any electrostatic precipitator (ESP) or baghouse system, the concentrations of volatile trace elements in fly ash will increase with a drop in the flue gas temperature and a decrease in the particle size. Mercury is an exception, requiring carbon to be present in the fly ash for any appreciable amount of Hg to be captured.

Changes in the design of two Kentucky power plants, both originally using central Appalachian coal sources, and the consequent impact on the fly ash chemistry were examined through sampling for a number of studies from 2000 to 2012. One plant, typically burning medium-S eastern Kentucky coals, bypassed two rows of mechanical (cyclone) collectors, consequently sending coarser fly ash to the ESPs. Among the consequences of the design change are a $1^{\rm st}$ -row ESP C, As, and Hg content than in the ESP fly ash without the coarse ash. The utility is currently installing dry scrubbing to control SO_2 emissions, allowing them to broaden their fuel supply to include high-S coals.

A second plant was burning low-S coal, but installed fluegas desulfurization (FGD) in anticipation of more stringent regulation of emissions. As with the first plant, this change allows them to pursue a wider range of coals than the central West Virginia sources previously utilized; over 2.5% total S vs. 0.8% prior to the FGD installation. The post-FGD-installation fly ash contains much higher Fe $_2$ S and CaO and lower Al $_2$ O $_3$ and SiO $_2$ than the pre-FGD fly ash. The Hg content, while never as high as at some power plants, is below the detection limit in the post-FGD fly ash.

The Coupling of Voltammetric Microelectrodes with Optical Microscopy: A Novel Combination as Applied to the Study of Neutrophilic Iron Oxidizers

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Voltammetric solid-state Au/Hg microelectrodes measure multiple analytes, including dissolved oxygen, sulfide, thiosulfate, polysulfides, iodide, Fe²⁺, Mn²⁺, and FeS simultaneously at the (sub)millimeter scale. These electrodes are ideal for the *in situ* quantification of the chemical gradients within redox transition zones, ubiquitous in the natural environment or created in the laboratory, and have been used to examine Fe(II) oxidation by neutrophilic iron oxidizers. Use of Au/Hg microelectrodes alone in redox transition zones have inherent limitations as the exact location of the electrode tip where analytes are detected cannot be pinpointed.

To advance chemical and microbial studies we have coupled voltammetric solid-state Au/Hg microelectrodes with optical microscopy using an optical resolution of $0.55~\mu m$ in specially designed microslide growth chambers. Higher optical resolutions can be used on the microslides alone. The resulting microslide profiles yield quantifiable chemical gradients including O2 and Fe(II) associated with both isolated species in artifical media and with samples of naturally occuring flocculent material in freshwater believed to contain iron oxidizers. These profiles are consistent with other profiles obtained from sediments and microbial mats. This novel combination allows for high resolution images to be simutaneously aquired with the electrochemical measurements and the exact location of the electrode tip is known. The coupling of voltammetric microelectrodes with high resolution microscopy is applicable to the study of the chemistry of the microenvironments of other types of microbes as well as microbial biofilms.