

# Strategies and Technology for Managing High-Carbon Ash

Technical Progress

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## ABSTRACT

The overall objective of the present project is to identify and assess strategies and solutions for the management of industry problems related to carbon in ash. Specific research issues to be addressed include:

- the effect of parent fuel selection on ash properties and adsorptivity, including a first ever examination of the air entrainment behavior of ashes from alternative (non-coal) fuels.
- the effect of various low-NO<sub>x</sub> firing modes on ash properties and adsorptivity
- the kinetics and mechanism of ash ozonation. This data will provide scientific and engineering support of the ongoing process development activities.

During this third project period, an extensive battery of surface analysis tools was used to characterize the surfaces of untreated, air-oxidized, and ozone-treated carbons. Most of the work focused on carbon black chosen as a model carbon material suitable for understanding the fundamental surface mechanisms without interference from inorganic matter. In addition to the XPS work described in previous reports, the overall analytical test battery includes: FTIR spectrometry, thermal desorption in nitrogen and in hydrogen/helium, mixtures, surface acidity, hygroscopic behavior, contact angle measurement with standard liquids to determine surface energy and its polar and dispersive components. Most of this characterization work was completed this quarter, with the remainder planned for next quarter. The present report gives only a brief overview of the new data. By the end of next quarter, a complete picture of the ozone surface mechanism should be at hand and a comprehensive discussion of this phase of the work will be presented in that report - the fourth period covering March 1, 2002 to August 31, 2002.

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## INTRODUCTION

Pulverized coal combustion produces over 75 million tons of fly ash and bottom ash in the U.S. every year. The most widespread and economically attractive option for utilizing fly ash is in concrete manufacture, where the fly ash serves as a partial replacement for Portland cement. In most concrete mixtures, specialty surfactants, or "air entraining admixtures" (AEAs), are added to stabilize sub-millimeter air bubbles, which improve resistance to freeze / thaw cycles (see Fig. 1). The bubbles are believed to provide excess volume to accommodate the expansion of residual water upon freezing in the set concrete. Solid carbon residues, if present in fly ash in high concentration, can adsorb these surfactants and render them unable to fulfill their intended function (see Fig. 2). As a result the stable air volume is too low or the mean bubble separation (spacing factor) is too high to impart the desired freeze/thaw resistance.

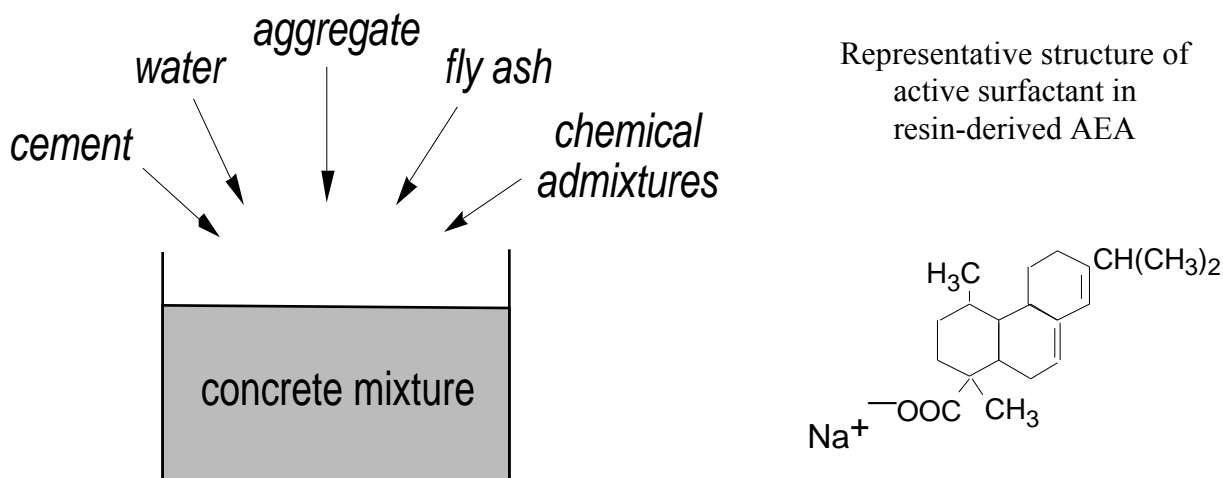


Figure 1. Overview of the composition of fly ash concrete. One class of chemical admixtures are air entraining admixtures (AEA), for which a model structure is shown.

Although increasing surfactant dose may compensate for the adsorption loss, large surfactant doses in practice lead to large and intolerable variations in entrained air when normal variations in ash properties are encountered in the field. Current regulations in the U.S. limit the carbon content in ash streams for concrete applications to 2 to 6 weight-%, depending on region and regulatory body. Carbon content is typically measured by the ASTM Loss-on-Ignition (LOI) test, which reports the extent of weight loss during air oxidation at 700 °C. At high levels, carbon can discolor concrete, or lead to loss of strength, but the first problem encountered as carbon level rises is poor air entrainment behavior and this is the primary driving force for the current regulations. *If the air entrainment problem could be solved in some way, most ashes generated in the U.S. today would be utilized in concrete, even with current carbon levels.*

Almost without exception, combustion research focuses on the *amount* of char consumed and the mass of unburned carbon in ash. Recent studies, however have observed variations in the surfactant adsorptivity of commercial ash samples that cannot be explained by variations in the amount of carbon present, but are related to variations in specific carbon *properties* such as surface

## Surfactant adsorption sites

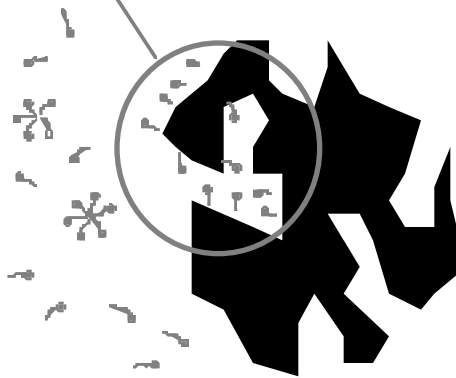


Figure 2. Surfactant adsorption on porous unburned carbon.

area, surface chemistry, and particle size. Very little is known about the effect of combustion conditions, coal type, and post-combustion treatment on carbon adsorptive properties. Several recent studies have measured the relevant adsorptive properties of commercial ash samples, but these samples come from complex and incompletely characterized combustion environments, and, as a result, it has not yet been possible to link surfactant adsorptivity to specific combustion conditions or fuel type.

A number of research and development groups are taking another approach to the carbon problem — they are developing technologies for the physical separation of carbon from the inorganic matter in ash, or for the burnout of carbon in dedicated combustion processes downstream of the boiler. These processes have not been widely adopted in the utility industry, largely due to capital cost and complexity. An alternative to these technologies is the use of ozone as described in the recent Brown University patent (US Patent 6136089). Ozonation at or near room temperature introduces oxygenated surface groups on the unburned carbon surfaces that increase the polarity of the carbon surfaces and reduce the surfactant adsorptivity, without removing significant carbon by full oxidation. In this respect the ozonation process is fundamentally different from all other proposed processes, including those in which carbon is burned out in a separate combustion process downstream of the primary coal-fired boiler. Potential advantages of ozonation include:

- simplicity of concept and operation
- operation under dry conditions, thus preserving the pozzolanic properties of ash.
- operation at ambient temperature, avoiding the need for a heat source.
- low estimated operating costs, consisting primarily of electricity.
- large-scale ozone generation is proven, off-the-shelf technology applied in water treatment, bleaching and disinfecting operations.

- ozonation does not generate a high-carbon waste stream (as do separation processes), which in most cases must be landfilled

Potential disadvantages of ozonation are:

- ozone is toxic and must be handled in sealed units (note however that ash is already handled in sealed units to prevent dust emissions)
- process leaves carbon in place, thus leaving regulatory hurdles based on LOI in some cases. Even after treatment, if the ash contains carbon above the governing local or federal limit (typically 3 or 4%), additional work is needed to verify its technical suitability for concrete, at least under current regulations.

The second cited disadvantage indicates that the most promising ash streams for initial demonstration are those that meet local LOI specifications, but still behavior poorly in concrete. We have identified a number of such field samples, typically class C ashes, and have focused early work on their treatment. It is anticipated, however, that successful with these low-carbon samples will allow even higher carbon-content ash streams to be considered in the second round of applications.

EPRI is funding the practical development of the ozone technology, but more laboratory work is needed on the kinetics and mechanism to provide the scientific and engineering data for intelligent scale-up and optimization.

### **Project Objective**

The overall objective of the present project is to identify and assess strategies and solutions for the management of industry problems related to carbon in ash. Options for improving or maintaining ash quality include:

- targeted fuel selection (or switching)
- modifications to combustion conditions or ash storage conditions
- post-combustion carbon surface modification by dry ozone

This project brings together a team of researchers from Brown University, the University of Utah, and Southern Company to address the problem of high carbon ash through a combination of bench scale experiments, pilot scale combustion trials with extensive analysis of collected ash samples, and the characterization of field ash samples. Specific scientific issues to be addressed include:

- the effect of parent fuel selection on ash properties and adsorptivity, including a first ever examination of the air entrainment behavior of ashes from alternative (non-coal) fuels.
- the effect of various low-NO<sub>x</sub> firing modes on ash properties and adsorptivity
- the kinetics and mechanism of ash ozonation. This data will provide scientific and engineering support of the ongoing process development activities.

Data from the project will be transferred to industry through close interaction with EPRI and its member companies, the ozonation development team of PCI-Wedeco / Brown and selected ash marketing firms, and Southern Company.

## **PROGRESS THIS PERIOD**

### **Experimental**

Experiments were carried out this quarter to determine the effect of ozonation on the surfactant adsorptivity of carbon black samples. Adsorptivity was measured by the Brown standard titration method used in previous studies and described in Gao et al. [2001]. Ozone treatment was carried out in a laboratory up-flow fixed bed apparatus with continuous monitoring of inlet and outlet concentrations as described in previous semi-annual reports.

Thermal desorption experiments were carried out by heating in inert gas mixtures either in a laboratory tube furnace or a thermal gravimetric analyzer. The TGA experiments were used to provide accurate surface oxide counts and the tube furnace experiments were used to generate large samples for surfactant testing.

Contact angle measurements were made at the external laboratories of Kruss USA using the standard Washburn method. Benzyl alcohol and nitromethane were used as standard probe liquids. The results were used together with the Fowkes theory to determine the surface energies of treated carbon blacks and their and dispersive components.

### **Results and Discussion**

Figure 1 shows the effect of carbon black surface treatment on its adsorption of three commercial surfactants, including a leading air entraining admixture (AEA) used in concrete pastes. Ozone has a similar effect for all three surfactant systems. These results for carbon black are similar to those seen previously for fly ash carbons [Gao et al., 2001], indicating that the phenomenon is quite general on carbon surfaces, and that carbon black will be a suitable model for studying surface chemistry and mechanism.

Figure 2 shows a sample of the thermal desorption results. The ozone effect shown to be reversible upon thermal desorption at 1000 C, but not completely. The lack of reversibility has several possible causes: (1) the presence of refractory oxides that are still present after thermal treatment at 1000 C, (2) the creation of active sites during desorption that subsequently chemisorb oxygen from room air during handling, or (3) changes in the bulk carbon structure. Experiments next quarter using H<sub>2</sub>/He mixtures to 'cap' the active sites should provide useful information to understand this hysteresis phenomenon. The effect of air oxidation can be entirely removed by heat treatment and indeed the surfactant adsorptivity can significantly exceed the value for the untreated surfaces. This result implies either the presence of oxides on the untreated carbon black or the effect of surface area development during air oxidation. More work is needed to understand the complex behavior during thermal desorption.



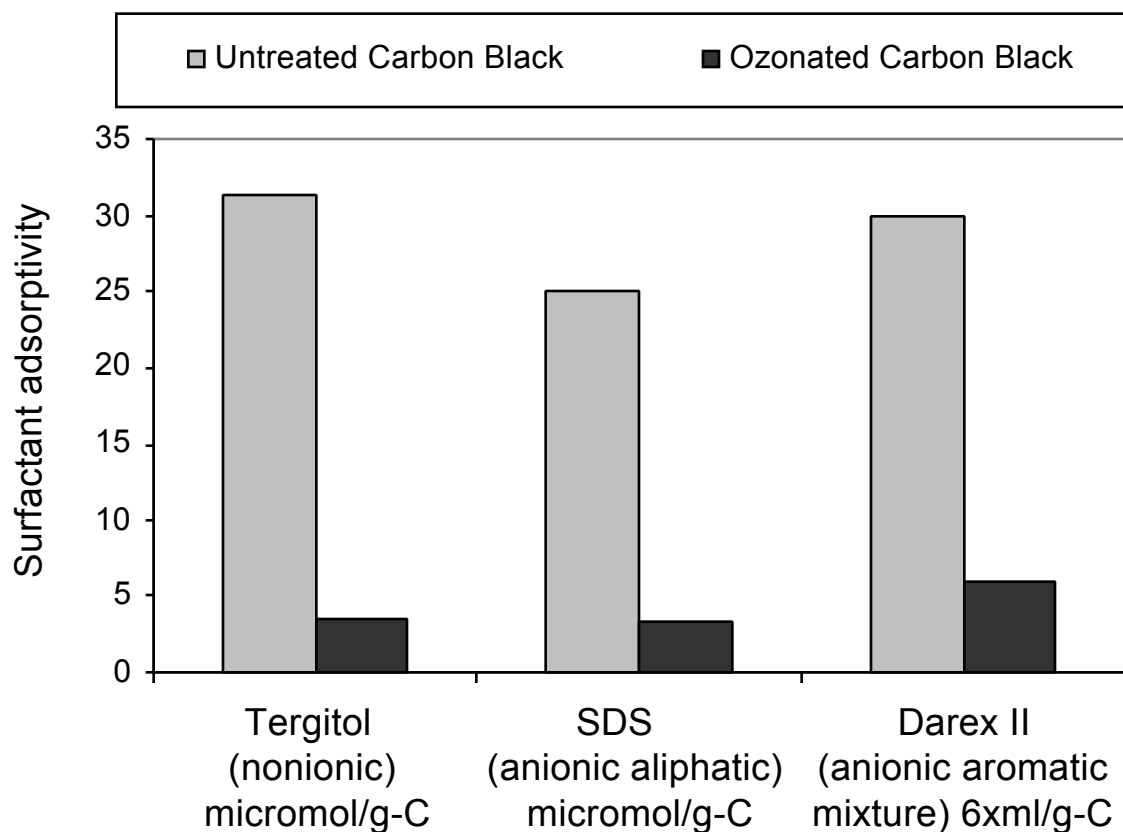


Figure 1. Effect of ozonation on the standard adsorptivity toward three surfactants of differing type.

Table 1 shows contact angles measurements and surface energy analysis based on Fowkes theory for three carbon black samples: untreated, thermally oxidized in air, and ozonated under typical conditions used in this study. Both forms of oxidation increase the total surface energy, primarily by increasing the polar component. Although high surface energy is often associated with high adsorptivity, here the opposite effect is observed. We believe this is related to the competitive nature of adsorption from solution, where it is the relative affinity for water and surfactant that governs adsorption, not the total binding energy. As such there is a good inverse correlation between the fractional polarity and the surfactant adsorptivity (Table 1).

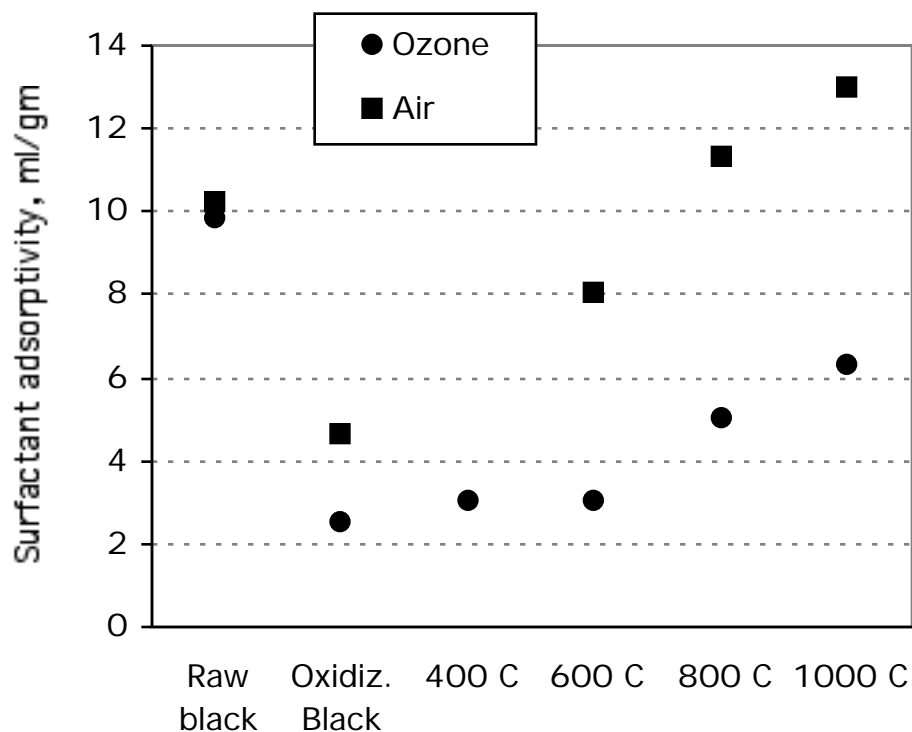


Figure 2. Effect of oxidation and subsequent thermal desorption on the standard adsorptivity of carbon black samples.

Table 1. Surface Energy Analysis\* of Untreated and Oxidized Carbon Black

Sample	relative surfactant adsorptiv.	total surface energy (mJ/m <sup>2</sup> )	polar component (mJ/m <sup>2</sup> )	dispersive component (mJ/m <sup>2</sup> )	% polarity
Untreated carbon black	10	21.8	0.86	20.9	3.9
air oxidized at 440 C, 8 hrs (20% weight loss)	3.5	27.0	4.3	22.7	16.0
2% ozone, 90 min (430 gm-O <sub>3</sub> /kg-C)	2	32.4	8.1	24.4	24.9

\* Determined by the Washburn method using benzyl alcohol and nitromethane as standard wetting liquids.

## Conclusions

Carbon black has been shown to be a suitable model for understanding the fundamental surface processes during ozonation of fly ash carbon without interference from inorganic matter. It shows a similar adsorption behavior with respect to concrete surfactants and an analogous sharp decrease in that adsorption during ozone treatment. The tests carried out so far (FTIR, contact angle measurement, thermal desorption) show significant surface modification during ozonation and air oxidation. The entire battery of surface analytical tests will be complete next quarter, and the resulting data set should allow a sound interpretation of the ozone effect. A comprehensive report on this phase of the project will be written at that time.

## References

Gao, Y., Külaots, I., Chen, X., Aggarwal, R., Mehta, A., Suuberg, E.M., Hurt, R.H., "Ozonation for the Chemical Modification of Carbon Surfaces in Fly Ash," *Fuel* 80 765-768 (2001).