

# OZONATION FOR THE CHEMICAL MODIFICATION OF CARBON SURFACES IN FLY ASH

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## Introduction

Coal combustion fly ash is a useful additive in concrete due to its pozzolanic property — i.e. its ability to react with calcium in concrete mixes to contribute to the formation of the cementitious matrix [1]. Through this mechanism, fly ash serves as a partial replacement for Portland cement, yielding cost savings as well as a variety of concrete property enhancements. A practical problem with this recycling technology is the tendency of residual carbon in ash to interfere with the air entrainment process in concrete. Porous carbon adsorbs the chemical surfactants used in concrete pastes, making them unavailable for the stabilization of a desirable micro-void system. Our earlier work identified non-polar carbon surface as the primary adsorption sites for the surfactant [2]. The present paper describes a new concept for suppressing the surfactant adsorption by the introduction of polar functionalities by reactive treatment at ambient temperature and in the dry state.

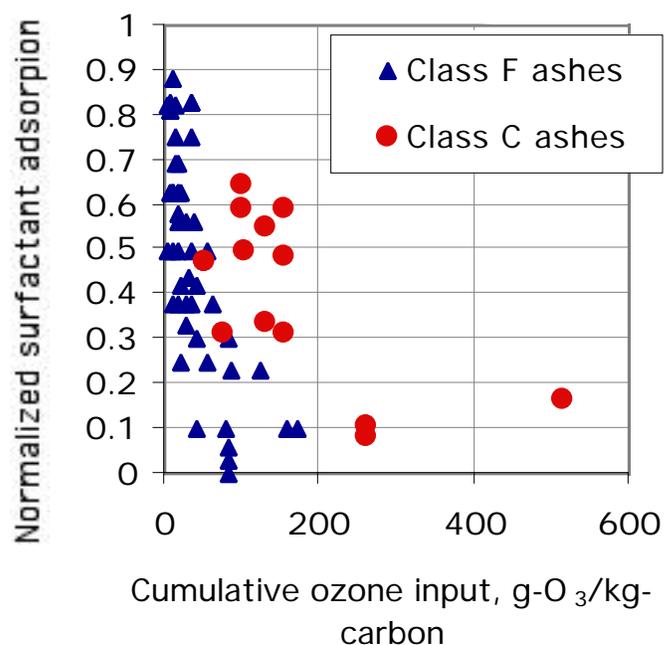
## Experimental

Controlled ozone concentrations from 500 ppm - 2 vol-% were generated in air and passed upward through fixed beds of ash (50 - 200 gms), for fixed contact times (1 minute - 20 hrs), while outlet ozone concentration was monitored in real time. The ozonated ash samples were removed and a standard surfactant adsorptivity determined by a simple titration procedure used previously [3]. Additional experiments were carried out on carbon black under the same ozonation conditions as an inorganic free model carbon for suitable for more detailed surface characterization.

## Results and Discussion

Figure 1 shows surfactant adsorptivity as a function of the total (integrated) amount of ozone charged for a variety of commercial ash samples and ozonation conditions (bed mass, contact time, ozone concentration). Sharp reductions in adsorptivity are observed between 0 and 200 gm-O<sub>3</sub>/kg-carbon. The time-resolved measurements of ozone exit

concentration yield traces which vary with conditions, but typically resemble breakthrough curves in adsorber beds, exhibiting an initial period of near zero



**Figure 1.** The effect of ozone treatment on surfactant adsorptivity of commercial fly ash samples.

concentration followed by a rapid (though not instantaneous) rise. These traces indicate that ozone is consumed during treatment, and the curve shapes suggest relatively rapid kinetics.

There is evidence from several sources that the mechanism of adsorptivity reduction is reactive modification of carbon surfaces. First, the effect is not related to carbon burnout, as carbon consumption is negligible in these experiments up to 20 gm-O<sub>3</sub>/kg-ash (corresponding to about 400 gm-O<sub>3</sub>/kg-carbon). At much higher ozone usages carbon loss does begin to be observed.

Secondly, heating previously-ozonated ash samples to 1000 °C in helium for 10 minutes (a sufficient temperature to drive off most surface oxides) restores

most of the initial adsorptivity. Thirdly, XPS results in Table 1 show greatly enhanced oxygen contents in the near-surface regions of carbon black samples ozonated under the same conditions used for fly ash carbon. High-resolution spectral analysis of the high-binding energy tail of the C1s peak reveals increases in C-O, C=O, and O-C=O functionalities with only subtle differences between thermal (air) oxidation and ozonation.

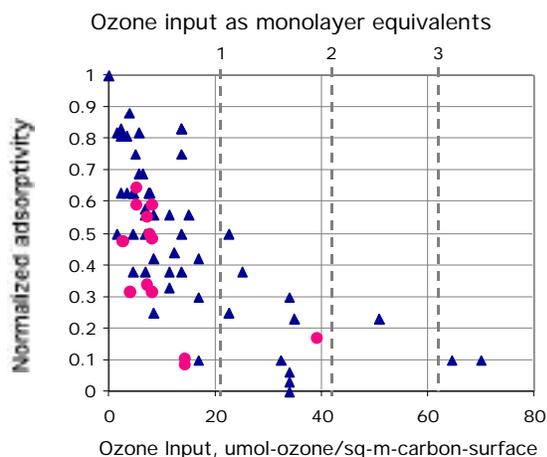
Table 1. XPS results on carbon black

|   | <u>atom-% O<sup>†</sup></u> | <u>atom-% C<sup>†</sup></u> |
|---|-----------------------------|-----------------------------|
| Untreated carbon black                          | 1                           | 98                          |
| air oxidized at 440 C, 8 hrs (20% weight loss)  | 7                           | 92                          |
| 2% ozone, 180 min (600 gm-O <sub>3</sub> /kg-C) | 10                          | 89                          |

<sup>†</sup> near-surface elemental compositions; balance sulfur

Measurements of surface area by vapor adsorption techniques indicate that ozone can decrease total surface for some samples, but the dominant effect is typically due to surface treatment.

Figure 2 provides additional evidence that surface treatment is the underlying mechanism. This plot unifies the data in Fig. 1 by normalizing the ozone requirement by total carbon surface area (by N<sub>2</sub> BET). The ozone required to achieve a given effect is directly proportional to the amount of carbon



**Figure 2.** Effect of ozonation on adsorptivity of carbon-containing ash. Plot shows a unification of the data by normalization by total carbon surface.

surface present. The precise reaction stoichiometry is still under investigation, but from literature data on other carbon materials we estimate one chemisorbed oxygen atom at a Van der Waals diameter of 0.28 nm, per molecule of ozone destroyed [4,5]. On this scale, the major reduction in adsorptivity is seen to occur between zero and one — i.e. during the formation of one oxide layer.

## Conclusions

The combined results indicate the presence of a fast chemisorption that gives rise to the desired surface modification, as well as a slower gasification step that consumes carbon with high ozone usage, as:

- (1)  $C + O_3 \rightarrow \text{surface oxides}$  (fast)
- (2)  $C + O_3 \rightarrow CO/CO_2$  (slow)

These laboratory data suggest the potential for a commercial treatment process. Provided reaction (2) can be minimized, large-scale ozone generation costs are estimated to be much less than the economic benefit of recovering ash sales, composed of the selling price as cement replacement plus avoided costs of landfill disposal.

## References

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