

Ozonation for the Chemical Modification of Carbon Surfaces in Fly Ash

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INTRODUCTION

A practical problem with fly ash concrete is the tendency of residual carbon in ash to interfere with the air entrainment process. Porous carbon adsorbs the chemical surfactants (air entraining admixtures, or AEAs) used to generate and stabilize a microvoid system in concrete pastes, as shown by Helmuth (1987), Freeman et al. (1997), and Hill et al. (1997). Without a sufficient network of sub-millimeter air bubbles, concrete fails under internal pressure generated by the freezing and expansion of trapped residual water. About two-thirds of the concrete in North America is air entrained (Dolch, 1995), and this surfactant adsorption phenomenon is the primary driving force for national and regional regulations limiting the carbon content of ash used in concrete. Recent work by Freeman et al. (1997), Gao et al. (1998), and Yu et al. (2000) clearly demonstrate great variability in the extent to which field ash samples adsorb AEAs. This recent work has identified the following four primary factors governing ash adsorptivity:

1. the mass fraction carbon
2. the total surface area of the carbon
3. the accessibility of that surface, as governed by particle size and pore size distribution
4. the carbon surface chemistry.

The inorganic fraction of ash is found to play a minor role in AEA adsorption.

The role of carbon surface chemistry is particularly apparent from the behavior of ash during thermal oxidation in air. Introduction of surface oxides by exposure to air at 350-450 C has been observed by Hachmann et al (1998) to significantly reduce subsequent AEA adsorption without consuming a measurable amount of carbon. In contrast, treatment in inert gas at temperatures sufficient to drive-off many pre-existing surface oxides (900 °C) has been observed to *increase* adsorption. Commercial carbon blacks subjected to surface oxidation processes have also been observed to be less adsorptive than non-treated varieties (Gao et al. 1997). Both of these observations suggests that oxide-free carbon surfaces are the most active for adsorption of surfactants. The important role of non-polar surface is not surprising, as polar functionalities are already abundant in concrete pastes (on inorganic fly ash particles, cement particles, aggregate particles, and in the aqueous solution), whereas the only non-polar components are air bubbles and a portion of the carbon surface. It is likely that the non-polar portions of the carbon surfaces compete directly with the air bubbles for the non-polar portions of the

surfactant molecules. This insight suggests that the deleterious effect of carbon could be suppressed by intentional oxidation of the largely non-polar carbon surfaces.

Possibilities for intentional surface oxidation include dry and wet chemical methods. Many wet oxidation agents have been used to surface treat other carbon materials (Fu et al, 1998, Domingo-Garcia et al, 2000), including HNO_3 , H_2O_2 , CH_3COOH , and $(\text{NH}_3)_2\text{S}_2\text{O}_8$, but for the treatment of ash these wet processes would have practical disadvantages, including high drying costs, and potential problems with self-cementation or loss of pozzolanic activity. Dry oxidation in air requires temperatures above about $300\text{ }^\circ\text{C}$, and is not likely to offer advantages over commercial combustion-based processes, which remove the carbon altogether while operating at only modestly higher temperatures. For these reasons, the authors' efforts have focused on ozone, O_3 , as an oxidant capable of attacking carbon surfaces in ash in the *dry state* and at *ambient temperature*.

There have been a number of studies of ozone reaction with various carbon materials, including graphite (Magne et al, 1988), carbon fibers (Fu et al., 1998, Takeuchi et al., 1993, Rakitskaya et al., 1994), soot and carbon black (Kamm et al., 1999, Mul et al., 1998, Papirer et al. 1967), and carbon sorbents (Dietz et al., 1972, 1973, Stephens et al, 1986). In these studies the applications range from the destruction of ozone waste streams (on fibers or charcoal), to the depletion of atmospheric ozone (on atmospheric soot aerosol), to surface treatment (of carbon fibers) for improved interfacial bonding in composite materials. One goal of the present paper is to demonstrate the effectiveness of ozone for reducing the surfactant adsorptivity of fly ash carbon, and to comment on the potential for a commercial ash treatment process using the same principle.

EXPERIMENTAL PROCEDURES AND RESULTS

Figure 1 shows the laboratory equipment for ash ozonation. 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. In these thick bed experiments, the ozone usage is typically limited by the rate of supply, and therefore the cited contact times do not reflect the true reaction kinetics, which are believed to be fast. The ozonated ash samples were removed and a standard surfactant adsorptivity determined by the foam index test, a simple titration procedure used previously to quantify ash adsorptivity (Freeman et al., 1997, Gao et al., 1997). 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 by XPS and surface energy analysis by contact angle with standard reference liquids.

Figure 2 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 3 gm- O_3 / kg-ash. 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 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. Based on these continuous measurement of outlet ozone concentration, a very high fraction of the charged ozone reacts within the bed for the subset of data in Fig. 2 lying below 3 gm- O_3 /kg-ash on the abscissa. Thus the initial

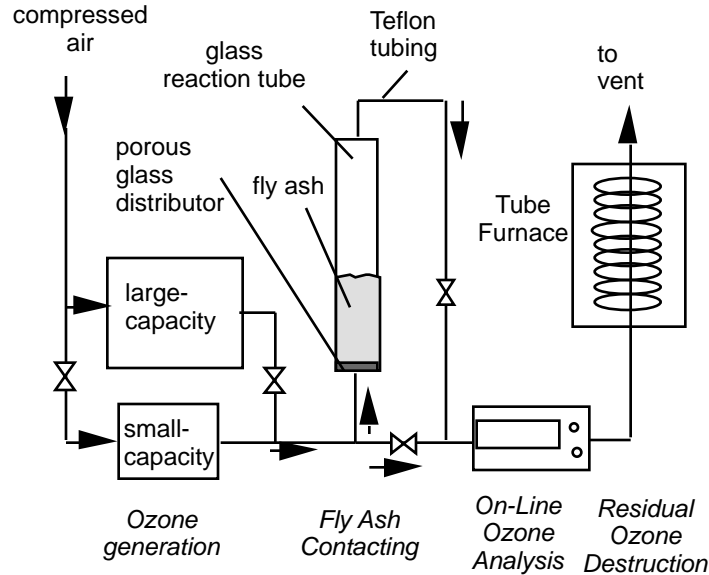


Figure 1. Sketch of the laboratory apparatus for ash ozonation.

portion of Fig. 2 (0 - 3 gm-O₃/kg-ash) can be reasonably regarded as an intrinsic relation between adsorptivity and amount of ozone reacted for these ashes, while the data beyond 3 gm-O₃/kg-ash overstate the actual ozone requirement due to unreacted reagent loss. Figure 3 plots the same data per unit mass of *carbon*, rather than unit mass of *ash*, and shows that carbons in class C ashes (all of which in this study derive from subbituminous coals) are seen to require more O₃ to achieve the same effect observed with class F ashes (all of which in this study derive from bituminous coals). This trend is consistent with the higher specific surface adsorptivity of carbons in most class C ashes (Kulaots et al., 2000). The similar behavior of class F

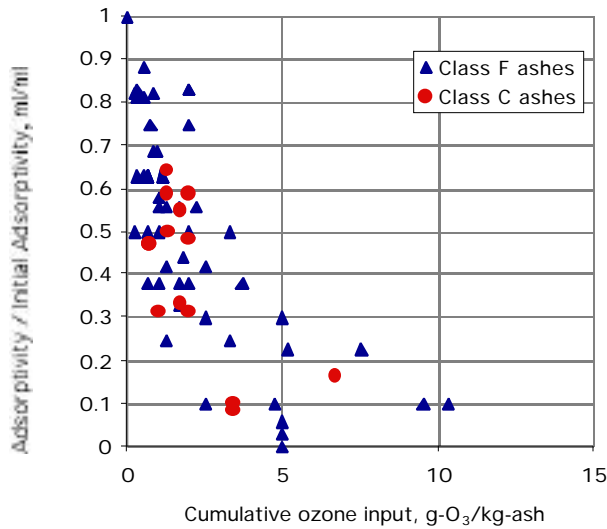


Figure 2. The effect of ozone treatment on surfactant adsorptivity of commercial fly ash samples. Data points represent a range of ash types, bed masses (50 - 400 gm), ozone concentrations (500 ppm - 2 vol-%), and contact times (10 - 800 min). All data are for fixed bed treatment (see Fig. 1) at ambient temperature and pressure. Class F ashes are low calcium ashes derived from bituminous (or occasionally anthracitic) coals, while class C ashes are high calcium ashes derived from subbituminous or lignitic coals.

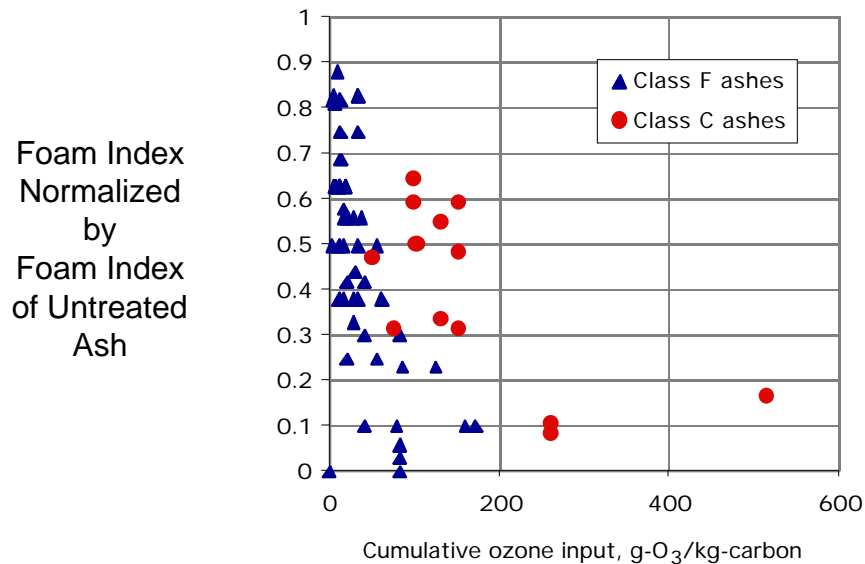


Figure 3. The effect of ozone treatment on surfactant adsorptivity of commercial fly ash samples. Data from Fig. 2 plotted per kg of *carbon*, rather than *ash*.

and C ashes in Fig. 2 is believed to be the fortuitous result of two offsetting effects — the class C ashes have lower carbon contents but higher specific carbon adsorptivities. Additional experiments indicate that the reduction in adsorptivity persists during ash storage in bottles under ambient conditions for up to nine months (the longest time examined).

There is evidence from several sources that the mechanism of adsorptivity reduction is reactive modification of carbon surfaces leading to loss of accessible area and changes in surface chemistry. First, the effect is not related to carbon burnout, as carbon consumption to be negligible in these experiments up to at least 20 gm-O₃/kg-ash (corresponding to about 400 gm-O₃/kg-carbon). At much higher ozone usages carbon loss does begin to be observed.

Secondly, 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.

Thirdly, surface energy analysis in Table 2 show greatly enhanced polar contributions in carbon black samples ozonated under the same conditions used for fly ash carbon. Air oxidation at 440 C is also seen to increase surface polarity and to decrease adsorptivity, but to a lesser extent than ozonation. Finally, 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

Table 1. XPS results on carbon black

<i>Sample</i>	Atom-% O*	Atom-% C*
Untreated carbon black	1	98
air oxidized at 440 C, 8 hrs (20% weight loss)	7	92
2% ozone, 180 min (600 gm-O ₃ /kg-C)	10	89

* near-surface elemental compositions; balance sulfur

Table 2 Surface energies* of carbon black samples oxidized under similar conditions to the fly ash carbon.

<i>Sample</i>	<i>surface energy (mJ/m²)</i>	<i>dispersive component (mJ/m²)</i>	<i>polar component (mJ/m²)</i>	<i>surfactant adsorpt. (ml)</i>
Untreated carbon black	21.8	20.9	0.9	10
air oxidized at 440 C, 8 hrs	27.0	22.7	4.3	3.5
2% ozone, 90 min (430 gm-O ₃ /kg-C)	32.4	24.4	8.1	2

* determined by Fowkes theory using benzyl alcohol and nitromethane as standard reference liquids.

Figure 4 unifies the data in Fig. 3 by normalizing the ozone requirement by total carbon surface area (by N₂ BET). The ozone required to achieve a given effect is directly proportional to the amount of carbon surface present. The precise reaction stoichiometry is still under investigation, but it is nevertheless useful to assume a likely stoichiometry from literature data (on other carbon materials) and to convert the abscissa in Fig. 4 from mol-O₃-charged/m²-carbon-surface to an equivalent number of oxide layers on the carbon surface. The alternate abscissa at the top of Fig. 4 was calculated assuming one chemisorbed oxygen atom at a Van der Waals diameter of 0.28 nm, per molecule of ozone destroyed (Kamm et al., 1999, Mul et al., 1998). On this scale, the major reduction in adsorptivity is seen to occur between zero and one — i.e. during the formation of an oxide monolayer, providing a check on the

reasonableness of our proposed mechanism. (Note that the data in Fig. 4 extend to superficial surface coverage values much greater than one. This is certainly due in part to the loss of unreacted ozone from our fixed bed reactor at long times, but may also be due to secondary chemical pathways for ozone destruction — a possibility that requires further investigation.)

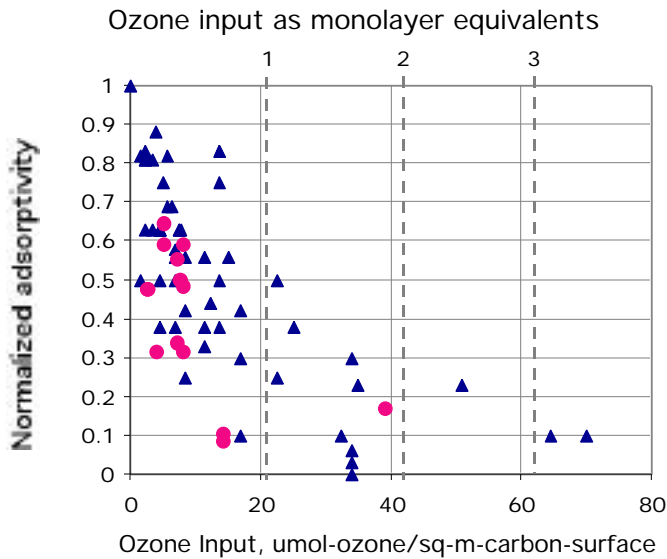


Figure 4. Effect of ozonation on adsorptivity of carbon-containing ash. Data from Fig. 3 with ozone feed expressed per unit carbon surface area (by N₂ BET). Also shown is the ozone feed expressed as number of monolayer equivalents (top axis) calculated assuming one chemisorbed oxygen atom (0.28 nm Van der Waals diameter) per molecule of O₃ reacted.

The laboratory data suggest the potential for a commercial treatment process, as illustrated by the following calculation. A factor of two reduction in adsorptivity would make many currently marginal ash streams saleable for concrete application, and this level of treatment would require an ozone usage of 1 - 2 gm-O₃/kg-ash by the data in Fig. 2A. The primary cost of ozone generation is for electricity, estimated from equipment vendor data at about 7 kW-hr / lb ozone. For electricity costs of 1 - 2 cents/kW-hr (utility service cost on-site from Lesky, 1999) these assumptions lead to an estimate of 0.3 - 1.2 \$/ton ash for electrical power required for ozone generation. This cost is much less than the potential economic benefit of recovering ash salability, which is related to sales revenues, and avoided disposal costs. These are highly region and site-specific, but can be estimated at 20 \$/ton for sales in the concrete market and 30 \$ / ton for disposal (1992 national average from Fitzgerald et al., 1995).

Based on these results, fly ash ozonation warrants further investigation as a commercial alternative to physical carbon separation or carbon burnout processes. Work is underway on the detailed kinetics and mechanism and on the evaluation of contacting methods for large scale application through pilot scale trials at PCI-Wedeco of West Caldwell, N.J..

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