

FLY ASH BENEFICATION WITH OZONE: MECHANISM OF ADSORPTION SUPPRESSION

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Introduction

The largest and most lucrative market for coal combustion fly ash is as a pozzolanic additive in concrete where it serves as a partial replacement for cement^{1, 2}. A previous paper documented the beneficial effect of ozone treatment on the air entrainment behavior of concrete made with carbon-containing fly ash³. Ozone is capable of reacting with residual carbon surfaces in ash at or near room temperature to produce surface oxides that reduce the adsorptivity of the ash toward air entraining admixtures (AEAs), the surfactant solutions used in air entrained concrete³. There have been a number of other studies of ozone reaction with various carbon materials, including graphite, carbon fibers, and carbon sorbents. In these studies the applications range from the destruction of ozone waste streams, to the depletion of atmospheric ozone, to surface treatment (of carbon fibers) for improved interfacial bonding in composite materials.

The original paper on fly ash ozonation³ documented the decrease in adsorptivity following ozonation, and presented an argument that the underlying mechanism is change in surface chemistry, since the amount of bulk carbon consumed by oxidation is trivial under the conditions employed. The present paper examines the mechanism of adsorption suppression in more detail, focusing on carbon black as a model substance whose surface oxides can be characterized more readily than those on native residual carbon, which is a minority component in an solid mixture (fly ash) rich in inorganic oxides. The paper also includes data on other, well-characterized surfactants in an attempt to identify the precise mechanism through which ozone treatment suppresses adsorption from aqueous solution.

Experimental

The laboratory upflow fixed bed used for ambient temperature ozonation has been described in detail the previous publication¹. Controlled ozone concentrations from 500 ppm - 2 vol-% were generated in air and passed upward through fixed beds of ash or carbon black (5 - 200 gms), for fixed contact times (1 minute - 20 hrs), while outlet ozone concentration was monitored in real time. The treated carbon surfaces were examined by XPS (Evans East Laboratories), by vapor adsorption techniques, and by wetting experiments (Kruss USA) using standard liquids used to determine surface energies by application of the Owens-Wendt theory⁴. Adsorptivity was determined by titration using methods described previously^{2,3} using Darex II (anionic resin-derived AEA), SDS (a standard anionic surfactant), and Tergitol (a commercial non-ionic surfactant).

Results

The experimental results are presented in Tables 1-3 and Figure 1. The 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

Sample	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

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. The dispersive component of surface energy is observed to increase as well, though only slightly, so the net effect of oxidation is a rather large increase in total surface energy (polar plus dispersive). Figure 1 shows that the effect of ozonation is similar for two model surfactants as for the commercial AEA that has been used in the studies to date³.

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

Sample	surface energy (mJ/m ²)	dispersive component (mJ/m ²)	polar component (mJ/m ²)	surfactant adsorpt. (ml)
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 Owens-Wendt theory⁴ using benzyl alcohol and nitromethane as standard reference liquids.

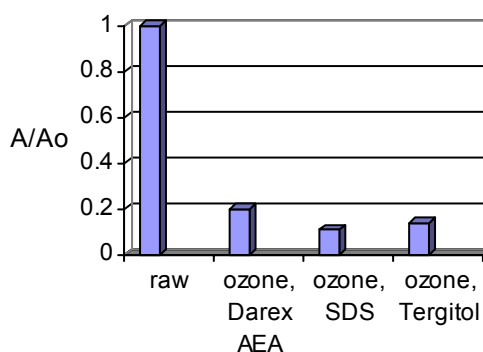


Figure 1. Effect of ozonation on the foam index of carbon black using three different surfactants: Darex II (resin-derived AEA), SDS (commercial anionic), Tergitol (commercial non-ionic). A/Ao is the adsorptivity determined by titration divided by the adsorptivity of the sample prior to ozonation.

Table 3 shows the effect of ozonation on total surface area. For ash #1, total area (by N₂ BET) is not materially affected by ozonation. Ash #2 shows significant area reduction, (similar to that observed by Dietz and Bitner^{5,6} during ozonation of charcoa), but not nearly enough to fully explain the large decreases in surfactant adsorptivity. Both surface area reduction and modification of surface chemistry are thus believed to contribute to the passivation for ash. Ozonation of carbon black produces a slight increase in area, but a similar effect on adsorptivity (see discussion).

Table 3: Properties of Raw and Ozonated Ashes

Ash sample	Specific Surfactant Adsorptivity (ml / gm-carbon)	Carbon Surface Area (N ₂ BET) (m ² / gm-carbon)
Ash #1, class F, from bituminous coal, 33% LOI	2.8	50.4
Ash #1 ozonated	1.0	53.4
Ash #2, class F, from bituminous coal, 6.1% LOI	3.9	51.3
Ash #2 ozonated	0.8	38.1
Ash #2 heavily ozonated	0.0	26.3
Ash #2 heavily ozonated then heated at 1000 °C in He	3.0	not measured
Carbon black, raw	10	38
Carbon black, ozonated (600 g-ozone/kg-C)	2.5	40

Discussion

At the outset of this study, there were four candidate mechanisms to explain the observed suppression of adsorptivity by ozone:

1. "pore blockage" – surface oxide formation decreases total area by physically blocking pores or pore mouths.
2. "electron withdrawal" – the addition of electronegative oxygen atoms to graphene layers withdraws electron density from the aromatic systems and reduces dispersion forces that bind the surfactant to the surface.
3. "electrostatics" – the acidic nature of most carbon surface oxides leads to a negatively charged surface in the high-pH concrete solution. The net negative surface charge repels the AEA molecules which are anionic (negatively charged) surfactants.
4. "reduction of hydrophobic forces" – introduction of oxides destroys non-polar surface area that is responsible for adsorption, leaving only polar surfaces that are hydrophilic and solvated (hydrogen bonded to water) and thus effectively unavailable for surfactant adsorption.

One or more of the latter three mechanisms are often cited to explain the observed effects of surface oxidation on activated carbon adsorption from solution⁷. The present work allows us to evaluate these competing explanations. Mechanism 1 (pore blockage) is a likely contributor for at least some fly ash samples, since Table 3 shows a case in which ozone treatment markedly reduces total area. It is not believed to be the primary mechanism, however, since carbon black exhibits the same beneficial effect of ozonation, but does not show decreases in area (see Table 3). The different area behavior of

carbon black and fly ash carbon is not surprising, since most area in carbon black is mesoporous, lying on the external surfaces of the nanoscale primary spheres, thus giving little opportunity for micropore blockage by surface oxides.

Mechanism 2 (electron withdrawal) can be ruled out by the surface energy results derived from wetting studies (Table 2). Ozonation is seen to add a polar component to the surface energy without decreasing the dispersive component. Indeed the dispersive component increases slightly and the overall effect is a large increase in total surface energy. Thus we expect ozonation to slightly *enhance* the dispersive attractive forces for adsorption, not suppress them.

Mechanism 3 (electrostatics) can be ruled out as the primary driver since the same effect of ozone is also observed when using the non-ionic surfactant Tergitol (Fig. 1). This uncharged molecule should not be greatly affected by changes in net surface charge.

Mechanism 4 (reduction of hydrophobic forces) is believed to be the primary mechanism, in part by process of elimination and in part from basic considerations about the nature of surfactants. Unlike other soluble organics, surfactants have a highly insoluble nonpolar part ("tail"), which is strongly driven by hydrophobic forces to leave the aqueous phase. It thus collects at the air interface, chiefly in bubble cavities, and on any other available non-polar surface. Because of its very low solubility (high hydrophobic forces) we believe the surfactant is not particularly selective about the nature of the non-polar surface and does not require strong adsorption interactions. Indeed in the case of the air interface the surfactant molecules collect by hydrophobic forces alone, with no attractive forces present between the surfactant and the interface whatsoever. We therefore believe that the adsorptivity of carbon is directly related to the fraction of its surface that is non-polar regardless of its other characteristics. Ozonation destroys this non-polar surface and replaces it with oxidic surface that is hydrophilic and capable of strong hydrogen bonding with the solvent. Since adsorption from solution is intrinsically a competitive process in which the surfactant and solvent (water) compete for sites, the water molecules have a strong advantage over the surfactant molecules on oxide-covered surfaces and the overall effect is suppression of the surfactant adsorptivity.

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