

Strategies and Technology for Managing High-Carbon Ash

Technical Progress

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Principal authors: Robert Hurt, Brown University
Eric Suuberg, Brown University
John Veranth, University of Utah

Ph.D. student Xu Chen, Brown University

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Submitting Organization(s): Brown University (R. Hurt)
Division of Engineering, Box D
Providence, RI 02912

University of Utah
Department of Chemical and Fuels Engineering
Salt Lake City, Utah

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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_x 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 fourth project period we completed the characterization of ozone-treated carbon surfaces and wrote a comprehensive report on the mechanism through which ozone suppresses the adsorption of concrete surfactants.

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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. i). 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. ii). 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.

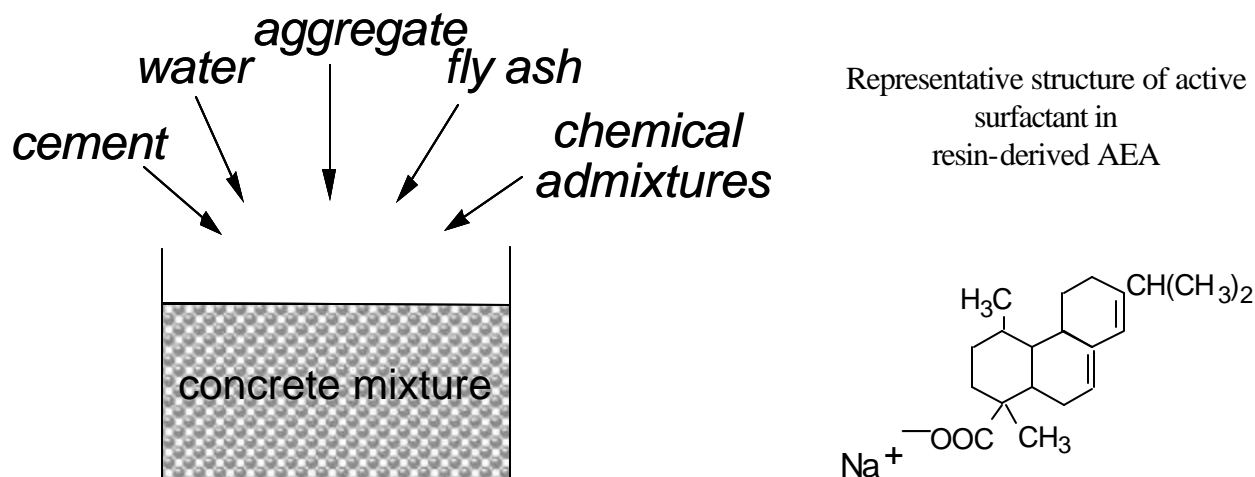


Figure i. Overview of the composition of fly ash concrete. One class of chemical admixtures are air entraining admixtures (AEA), for which a model structure is shown.

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

Surfactant adsorption sites

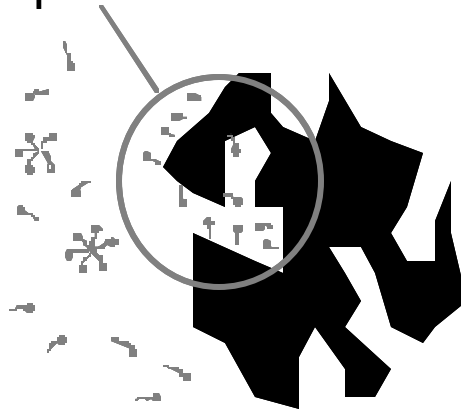


Figure ii. Surfactant adsorption on porous unburned carbon.

surface 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 work 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_x 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

The sections below comprise a comprehensive report on the mechanisms of surfactant adsorption on nonpolar, air-oxidized, and ozone-treated carbon surfaces, with emphasis on the behavior of concrete surfactants that are the origin of the problem with high-carbon fly ash utilization. This material will also form the basis for a journal submission in the near future.

Background

Many soluble organic substances are surface active — i.e. at low bulk concentrations they exert a disproportionate influence on the interfacial and colloidal behavior of solutions. The dual hydrophobic/hydrophilic (amphiphilic) nature of surfactant molecules causes them to accumulate in interfacial regions where both the hydrophobic and hydrophilic segments can participate in favorable intermolecular interactions. Surfactants are widely exploited in industrial processes and in consumer product formulations for emulsion stabilization, foaming, detergent action, wetting enhancement, mineral separations and other purposes. Residual surfactants may interfere with downstream processing and have environmental impacts in wastewater, so there is interest in efficient technologies for their removal. Surfactant adsorption has been the subject of numerous studies [1-4], including several studies in which the sorbent is activated carbon [3,4].

In recent studies, surfactant adsorption on carbon has been identified as a key phenomenon determining the suitability of coal combustion fly ash as a concrete additive [5-9]. Here the carbon is a contaminant and its undesirable adsorption of surfactant from the aqueous concrete paste reduces the surfactant's ability to stabilize sub-millimeter air bubbles that help improve freeze-thaw resistance in set concrete [10]. Previous studies [5,7,11,12] have related the extent of adsorption to four factors: (1) the amount of residual carbon in ash, (2) the total carbon surface area, (3) the accessibility of the surface as governed by pore and particle size distribution, and (4) the state of carbon surface oxidation. Oxidation of carbon surfaces by either air or ozone has been shown to reduce the extent of concrete surfactant adsorption [7].

Intentional surface oxidation by ozone is of potential interest as an ash beneficiation process [7], so there is a motivation for developing a more fundamental understanding of its effects. The literature provides much insight into carbon surface chemistry and its role in adsorption [3,13-16] but this role depends greatly on the adsorbate and very few of these studies have examined surfactants [3,4]. A number of studies have examined carbon surface treatment with ozone [7, 13,17-26], but only our recent work has focused on its effect on surfactant adsorptivity [7]. This previous study did not yield a complete understanding on adsorption mechanism, in large part due to the complexity of the ash/surfactant system. First the abundant inorganic oxides in ash make the characterization of oxides on residual carbon surfaces difficult. Secondly, most commercial concrete surfactants are complex mixtures derived from natural sources, most commonly wood resins, and it is not possible to precisely specify the molecular structure and molecular weight of the active components from these surfactants.

The present work focuses on the mechanisms of surfactant adsorption and especially on the mechanism of its suppression by ozone treatment. This study includes detailed surface characterization of raw and oxidized carbon black samples used as a model adsorbent with low surface polarity and few inorganic impurities. The present work also includes experiments on well-defined, single component surfactants

to complement the previous studies on the multi-component commercial concrete surfactants. The results are used to discuss the driving forces for surfactant adsorption mechanisms, which are relevant both to fly ash concrete and to other situations in which amphiphilic molecules are adsorbed by carbon from the aqueous phase.

Experimental

This study focused on five carbon materials:

1. M120 carbon black (Cabot Corp., Billerica, MA) with BET area 38 m²/gm.
2. M120 oxidized in air at 450 °C for 10 hrs (accompanied by 20% weight loss).
3. M120 oxidized by ozone at ambient room temperature (negligible mass loss).
4. "Ash #1": A commercial carbon-containing fly ash from bituminous coal combustion at the full scale. The fly ash is sample FA21 in the Brown University sample bank with 6.3% loss on ignition (approximately 6.3% elemental carbon), which has been used in previous studies [5,6].
5. "Ash #2": A second commercial fly ash, FA22 in Brown University sample bank, with high residual carbon level (33%).

The air oxidation was carried out in a horizontal tube furnace in a 1 lit/min flow of compressed air. Ozone treatment consisted of passing 1.5 lit/min of a 2 wt-% O₃ in O₂ mixture in upflow through a small fixed bed of sorbent. The input amount of ozone per weight of carbon black were varied to give different extents of oxidation characterized in terms of ozone dosage, g-ozone-fed/kg-carbon. Three surfactants of varying type were used in this study. Darex II (W.R. Grace, Cambridge, MA) is a commercial surfactant for air entrained concrete applications. It is a complex mixture derived from byproducts of the forest product industry. An example component is the sodium salt of abietic acid, C₁₉H₂₉COOH — a three ring carboxylic acid with short aliphatic side chains found in pine resin. The sodium salt forms a globular organic anion upon dissociation in the basic aqueous medium of concrete pasts. Sodium dodecyl sulfate, [(CH₃(CH₂)₁₁OSO₃⁻][Na⁺], or SDS is a common anionic surfactant with molecular weight 288, whose nonpolar part is an aliphatic chain, in contrast to the globular abietic acid salt. Tergitol (Aldrich Chemical) is a synthetic polyether nonionic surfactant, CH₃(CH₂)₈(C₆H₄)(OCH₂CH₂)₉OH, with molecular weight 616.84.

This study employs both single component surfactants (SDS, Tergitol) and a multi-component natural product that is of special technological interest for concrete (Darex II), the latter product having a complex set of components of varying surfactant activity. For this reason the extent of adsorption is characterized in this work by a titration procedure that measures amount of surfactant required to achieve stable foam in the presence of the sorbent, rather than by assay of the surfactant remaining in solution. The procedure is a modification of the "foam index" titration commonly used in the concrete industry and is described in previous publications [6]. Briefly, the test sorbent is added to 25 ml of distilled water, to which is added 8 gms of cement which provides a standard high-pH aqueous medium, and surfactant solutions are titrated in 0.02 ml per drop until stable foam appears on the surface upon agitation. A blank experiment is conducted without the test sorbent, and the required surfactant amount subtracted. The result is expressed as a "surfactant adsorptivity" in milliliters of standard surfactant solution/gram-sorbent. Alternative approaches using direct surfactant assay by UV adsorption have been attempted [11] but fail to provide an appropriate index of adsorptivity, likely due to differences between the components with strong optical absorbance and those with high surfactant effectiveness

[11]. In the experiments with single component surfactants, results will also be expressed as molar uptakes (mol surfactant / g-carbon) to aid in interpretation.

A variety of tools were used to characterize the carbon surfaces. Total oxide coverage was measured by thermal desorption using a Cahn 2141 TGA with a large sample bed (150 mg) to minimize the effects of sample consumption by trace oxygen as a fraction of total sample mass. XPS was carried out at Evans East Laboratories (East Windsor, NJ) using a Physical Electronics 5700LSci with a 350 Watt monochromatic aluminum source and an exit angle of 65°. To help understand adsorption forces, carbon black surface energies were determined by measurement of contact angles for standard liquids at the analytical laboratories of Kruss USA (Charlotte, NC). It is difficult to obtain fully dense, flat surfaces in carbon black pellets for direct measurement of contact angle, so the standard Washburn technique [27] was used in which liquids are drawn into a porous test solid and the contact angle derived from analysis of the rate of uptake relative to reference liquids that completely wet the substrate (contact angle of zero). Here hexane was used as the reference liquid and the Kruss Processor Tensiometer K12 used to measure the rate of liquid uptake gravimetrically. Water would be a natural choice for a standard liquid since hydrophilicity is of specific interest in this application, but early experiments showed water contact angles greater than 90° on the raw carbon black, and the Washburn technique is restricted to cases where $\theta < 90^\circ$ in which liquid uptake is spontaneous. Therefore benzyl alcohol and nitromethane were chosen as standard reference liquids, as they each wet the carbon black samples ($\theta < 90^\circ$) and have significantly different polarities (see Table 1). Knowing the surface tensions of the two standard liquids and their polar and dispersive components, the measured contact angles can be used to derive total surface energy and its polar and dispersive components by application of the Fowkes/Owens-Wendt theories as described later.

Table 1.
Properties of standard wetting liquids and their contact angles on untreated and oxidized carbon blacks

<i>Properties of Standard Liquids</i>	Benzyl alcohol	Nitromethane
Surface tension, mJ/m ²	39	36.5
Dispersive component, mJ/m ²	30.3	22.0
Polar component, mJ/m ²	8.7	14.5
Polar fraction	22%	40%
<i>Contact Angles on Carbon Blacks</i>		
Untreated carbon black	64.4 °	68.3 °
Air oxidized at 450 °C, 10 hrs	48.8 °	48.9 °
Treated in 2 wt-% O ₃ (600 g- O ₃ /kg-C)	34.6 °	30.5 °

Differential scanning calorimetry was performed using a DuPont DSC 2910. 13-15mg of sample was loaded onto a non-hermetic aluminum pan after equilibration at 25 °C. The temperature was ramped at 5-25 °C/min to a final temperature of 600 °C. Prior to each set of runs, the calorimeter was calibrated with 10 mg of indium and 15 mg of zinc. FT-IR spectra of the carbon surfaces were obtained using a

Nicolet Magna-IR 560 Spectrometer in transmission mode. KBr was mixed with 0.1 wt-% of the carbon test sample and milled, after which pellets were made in a laboratory press at 10 tons for 10 minutes. The pellet was dried at 90 °C for 8 hours. A set of 10 spectra was obtained for each sample. The hygroscopic nature of the carbon surfaces was examined by placing freshly prepared or freshly dried surfaces in a closed chamber with an open dish of water and the moisture uptake measured gravimetrically by drying at 110 °C for 2 hours. Surface acidity was measured using the sonic slurry method in ASTM1512-95, the standard pH test for carbon black samples. Carbon black (1.5g) was placed into a beaker with 20 ml distilled water. Several drops of acetone were added to help dispersion. After 3 minutes of agitation in an ultrasonic bath, the pH of the slurry was measured by using Corning 455 pH meter, which was calibrated by using buffers at pH of 4.0 and 10.0.

Results and discussion

Adsorption behavior

Figs 1-4 show the effects of surface oxidation on surfactant adsorptivity. Carbon black and fly ash carbon behave in similar fashion (compare Figs. 1 and 2), so the choice of carbon black as a model for fundamental surface studies is appropriate. The suppression is largely reversible upon thermal desorption of the oxides in N₂, but a significant hysteresis is also seen; the adsorptivity after 1000 °C thermal desorption ranges from 60% - 130% of the initial (pre-oxidation) value. Thermal desorption of the oxides in 1%v/v H₂/He atmosphere increased the surfactant adsorptivity relative to desorption in N₂ (Fig. 2). Air and ozone are both effective oxidants for adsorption suppression, and the somewhat greater effect seen for ozone in Fig. 2 correlates with the near-surface concentration of oxygen atoms by XPS (Fig. 3). Fig. 4 shows that the extent of suppression by ozone is similar for the three surfactant types. Overall, surfactant adsorption is strongly suppressed by surface oxidation for each of the surfactant/carbon/oxidant systems studied here.

Surface area and porosity

A possible physical mechanism of absorption suppression is the blockage of fine porosity by surface oxides [28,29]. Table 2 shows that ozonation does decrease the total carbon surface area for ash #1, but not by a large enough factor to explain the loss in adsorptivity. Neither ash #2 nor the carbon black decreases in surface area upon ozonation. In this respect carbon black is a useful model substance for isolating the effects of surface chemistry, because its surface area is located primarily on the external surfaces of the primary particles (75 nm in diameter) and is thus primary meso- and macro-porosity which is not easily blocked by sub-nanometer scale surface oxides. It is notable in Table 2 that air oxidation greatly increases carbon black surface area, presumably due to the creation of micro-porosity, but that the surfactant adsorptivity is decreased nevertheless. It is clear that the primary mechanism through which surface oxidation suppresses surfactant adsorption must be related to surface chemistry rather than pore blockage.

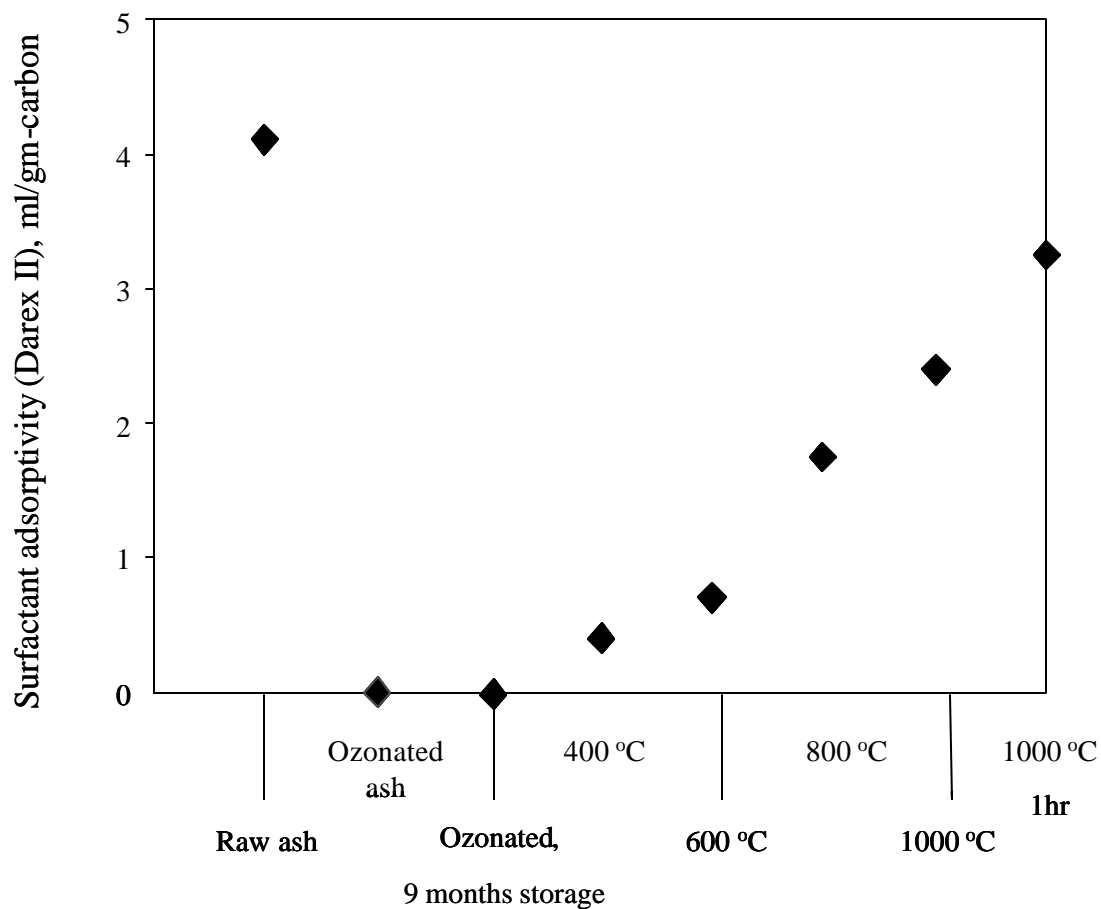


Figure 1. Effect of O_3 treatment on the adsorptivity of carbon-containing fly ash (Ash #1) toward the commercial anionic concrete surfactant, Darex II. The fly ash sample contains 6.3% carbon and derives from full-scale combustion of a bituminous coal. O_3 treatment at 20 °C: 20 gm-ozone/kg-ash. The figure shows the stability of the complexes at room temperature — 9 months of laboratory storage produced no measurable recovery of the adsorptivity. Data labeled 400-1000 °C represent ozonated samples subsequently treated in a preheated tube furnace in N_2 at the given peak temperature for 30 min except where marked.

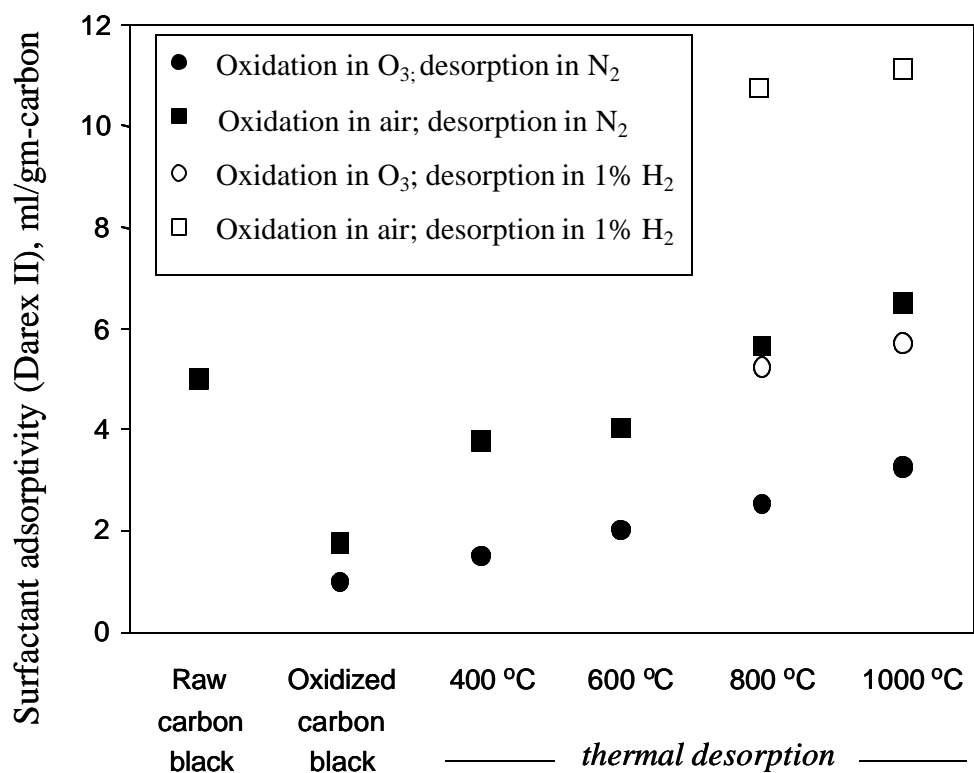


Figure 2. Effect of oxidation and subsequent thermal desorption on the surfactant adsorptivity of M120 carbon black. Air oxidation at 450 °C for 10 hrs (20% weight loss). O₃ treatment at 20 °C; 600 gm-O₃/kg-carbon. Data labeled 400-1000 °C represent ozonated samples subsequently treated for 30 min in a preheated furnace in N₂ or 1%v/v H₂/He at the given peak temperature.

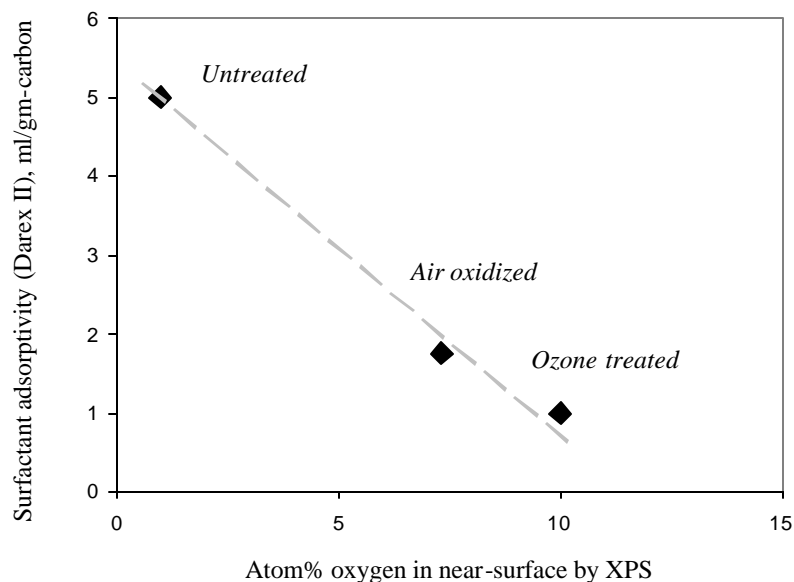


Figure 3. Near-surface atomic oxygen concentration by XPS and its inverse correlation with surfactant adsorptivity for M120 carbon blacks.

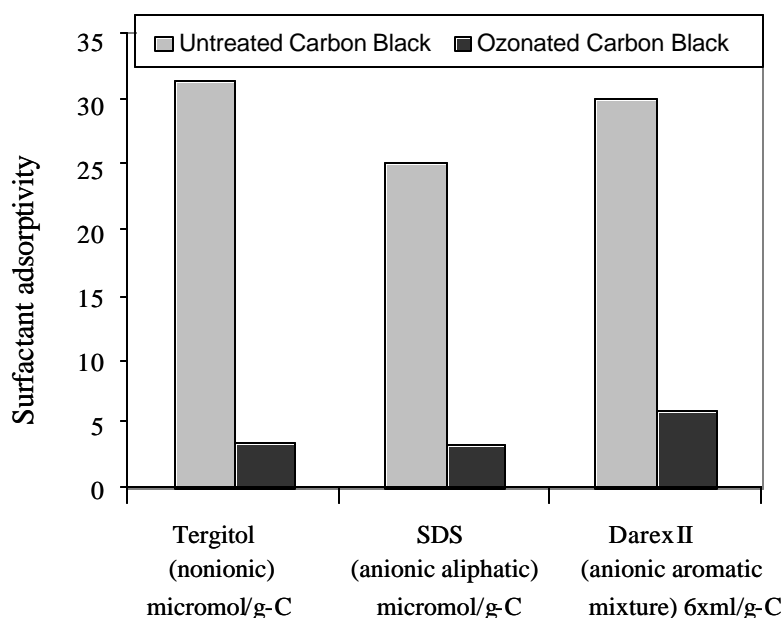


Figure 4. Effect of ozonation on the standard adsorptivity toward three surfactants of differing type. For the natural surfactant mixture, Darex II, the adsorbed amounts are presented as titrated solution volumes (6x ml surfactant solution/gm-carbon). Because of the need for different units, the absolute values in this figure are not meaningful, but rather the relative effect of ozonation for the three surfactants.

Table 2.
Effect of ozonation on total carbon surface areas

<i>Sample</i>	<i>Surfactant Adsorptivity (ml / gm-carbon)</i>	<i>Carbon Surface Area (N₂ BET) (m² / gm-carbon)</i>
Ash #1 (FA21) from bitum. coal, 6.1% LOI	3.9	51.3
Ash #1 ozonated (2g O ₃ /kg ash)	0.8	38.1
Ash #1 heavily ozonated (20g O ₃ /kg ash)	0.0	26.3
Ash #2 (FA22) from bitum. coal, 33% LOI	2.8	50.4
Ash #2 ozonated (8g O ₃ /kg ash)	1.0	53.4

M120 Carbon black:		
Untreated	5	38.5
Air oxidized	1.75	234
Ozonated	1	36.7

Thermal desorption

Fig. 2 shows a rapid rise in adsorptivity with increasing thermal desorption temperature in the range of 600-1000 °C, consistent with previously observed peaks in TPD curves in that temperature range [21], which mark a region of significant surface oxide decomposition. Thermal desorption at 1000 °C in N₂ atmosphere reverses most of the effects of oxidation, but a modest hysteresis in surfactant adsorptivity was still observed. Using 1% H₂ atmosphere for thermal desorption makes the process fully reversible, suggesting that the hysteresis was due to the creation of new active sites during oxide decomposition which became chemisorptive sites for oxygen in room air during cooling or sample handling. H₂ treatment at high temperature is known to remove oxides, gasify the most reactive surface carbon atoms and to minimize O₂ re-adsorption at room temperature [30].

For air oxidized samples, thermal desorption at 1000 °C in N₂ raises the surfactant adsorptivity to values 30% above the pre-oxidation level, an effect which is likely related to the very significant surface area development accompanying air oxidation under our conditions. Finally, after treatment with 1% H₂ at 1000 °C, the surfactant adsorptivity of air oxidized carbon black is 225% of its initial value, which is not surprising, considering the effects of both the oxygen-free surface and the enhanced total surface area developed during air oxidation.

The large-sample thermal desorption experiment provides a useful count of the surface oxides (Fig. 5). Following either light ozonation (50 g-ozone/kg-carbon) or heavy ozonation (200 g-ozone/kg-carbon) the oxide count is 0.45-0.84 millimole oxide/g-carbon, which is comparable to the theoretical surface site density of 0.63 millimole/g estimated from the total surface area. It is noteworthy that ozone can quantitatively cover most of carbon black surfaces with oxides while there is insignificant carbon consumption by gasification. This behavior is in contrast to oxygen chemisorption, which typically covers only a fraction of the total surface when the chemisorption is carried out below gasification temperatures [31]. The quantitative surface coverage suggests that ozone can attack or reside not only on edges and defect sites but also on graphene basal sites. Such non-selective chemisorption has previously been observed for atomic oxygen [32]. Previous studies with ozone, however, have shown much smaller fractional surface coverage on graphite [21], a difference that may reflect the very different degrees of structural perfection in graphite and carbon black.

XPS analysis

Near-surface oxygen concentrations by XPS are much less than 100%, varying from 1% for the untreated carbon black to a maximum of 10% for the ozonated carbon black. The apparent discrepancy between XPS and thermal desorption reflects the sampling depth (electron escape depth) of the XPS technique which is about 8 nm under these experimental conditions and thus captures as many as 8 nm / 0.34 nm (single carbon atom layer thickness) ~ 23 subsurface carbon layers in addition to the oxygen-rich surface.

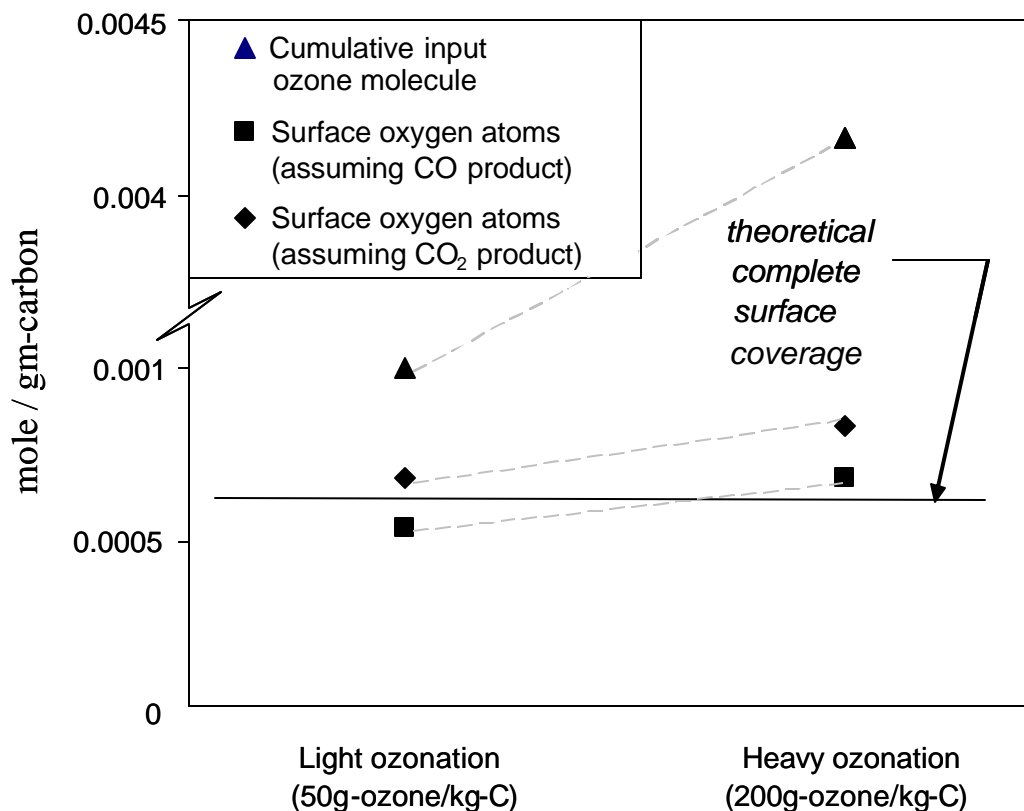


Figure 5. Oxide counts by thermal desorption. Weight loss determined by heating 150 mg sample in ultra high purity N_2 at 50 °C /min to 850 °C with a hold time of 30 min. Weight losses are 0.34% (untreated carbon black), 1.50% (light ozonation) and 1.85% (heavy ozonation). Plotted are the moles of surface oxygen atoms calculated from the above weight loss values assuming either CO or CO₂ product as bracketing cases. The total site number is estimated from N_2 BET area (38 m²/g) assuming 10 Å² per surface oxygen atom [41]. Ozone quantitatively covers the total surface with oxides. Also plotted for comparison are the total moles of O₃ introduced in the feed gas giving a measure of O₃ conversion efficiency to oxides.

The high-resolution C1s peak at around 285 eV shown in Fig. 6 exhibits a long tail on the high energy side similar to that reported by Wu et al [3]. Spectral analysis suggests a variety of band modes on the oxidized surfaces including C-O, C=O, and O-C=O. A clear feature in the C1s tail is the rise of a peak at around 289 eV during oxidation (by either air or ozone), a peak normally associated with O-C=O (carboxyl, anhydride or lactone). The lack of other distinct features makes the full quantitative spectral analysis uncertain, but it does suggest a higher concentration of C-O containing groups (e.g. phenol) in the air oxidized sample and a higher concentration of O-C=O groups in the ozone sample. Additional information is provided by the high resolution O1s peak, whose spectral analysis is shown in table 3. The fraction of O-C is slightly higher for both the air oxidized and ozone treated samples than O=C.

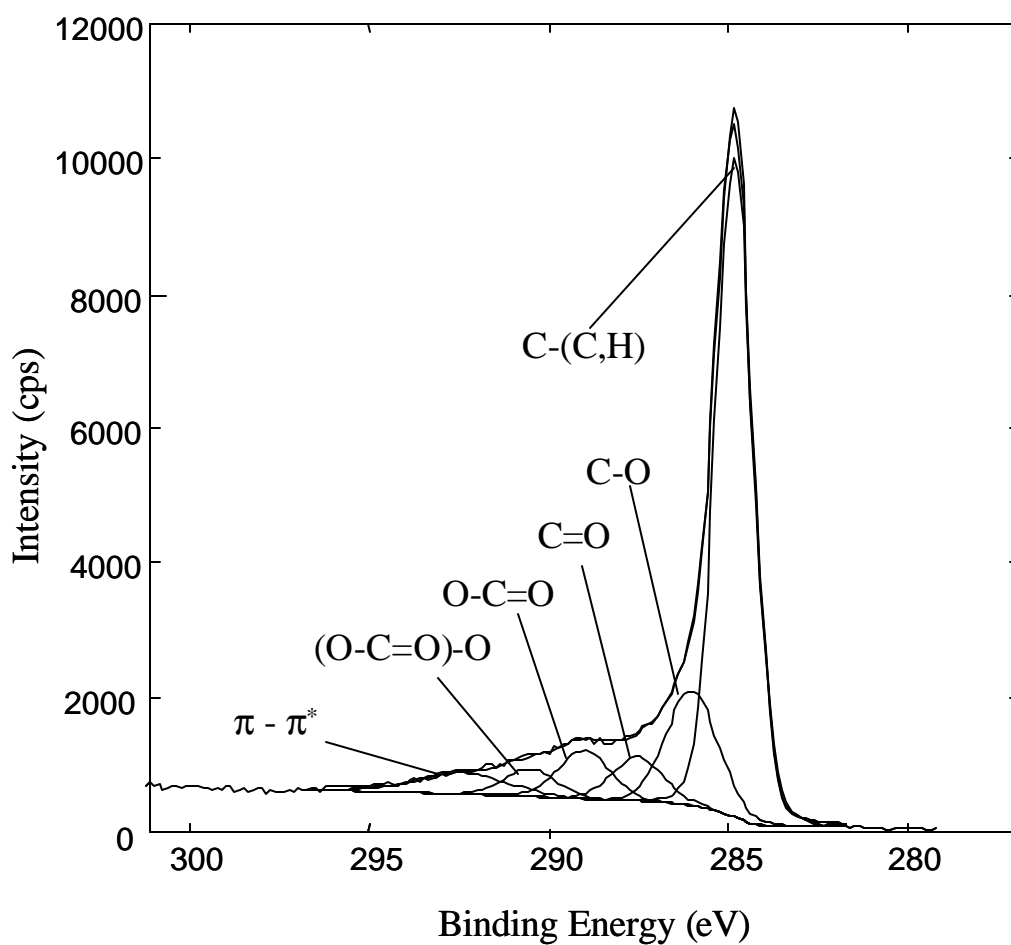


Figure 6. High resolution C1s XPS spectra of O₃ treated carbon black

Table 3.
Area of O1s peak and near surface oxygen concentration of carbon blacks

Carbon black	Normalized area of the O1s peaks (%)			Oxygen (atom%)
	O-C	O=C	Others ¹	
Untreated	66	28	6	1
Air oxidized	50	38	13	7.3
O ₃ treated	50	40	10	10

¹ Chemisorbed O₂/H₂O

Table 4 shows selected results of FT-IR characterization. A gross classification would associate the bands from 1600-1800 cm^{-1} primarily with carboxyl/carbonyl structures (C=O), and those from 1100-1400 cm^{-1} with phenolic or etheric structures (C-O) [33-35]. This is in agreement with the features seen in the XPS O1s peak and with some earlier studies of ozone treatment on carbon fibers [17]. Within the bands are specific peaks whose spectral locations vary between the air oxidized and ozonated carbon black samples. Table 4 gives possible assignments.

Table 4.
Possible FT-IR peak assignments [30-32]

Wave number, cm^{-1}	Possible Peak Assignments
<i>Air oxidized sample</i>	
2340	CO ₂ Contamination
1745	carboxylic acid – carbonyl stretch (C=O)
1600	carboxylate (COO-) –COO- stretch OR aromatic ring vibrations
1260	phenol –C-O stretch and O-H bend
<i>O₃ treated sample</i>	
2340	CO ₂ Contamination
1890	lactone or anhydride or phenyl
1725	carboxylic acid C=O stretch
1690	aryl ketone C=O stretch
1640	aromatic ketone
1405	phenol COH bend or carboxylic acid

Previously published FT-IR spectra of oxidized carbons surfaces share many of the peaks identified in Table 4 [36, 37-41]. A notable difference is a peak around 1220 cm^{-1} in the ozonation studies of Smith [37,39], Sutherland [41] and Mawhinney [42] but absent here. Also, the peak around 1890 cm^{-1} that was observed here was not detected in previous studies. Previous authors assigned the peak around 1220 cm^{-1} to ester, lactone, aromatic ketone, or cyclic anhydride – consequences of a C-O stretch and an O-H bend. The differences between the spectra observed here and previous spectra may relate to reaction conditions (temperature, time) or to water/humid air exposure during handling. The peak around 1890 cm^{-1} was assigned to lactone or anhydride, suggesting these groups may be more prevalent during ozone treatment than during air oxidation. Indeed ozone can break unsaturated C=C bonds to yield unstable ozonides as intermediates, which may rearrange to produce anhydrides or lactones [40,42,43]. The presence of the 1260 cm^{-1} in the air oxidized but not the ozone treated sample suggests formation of more phenolic groups.

Although the oxygen bonding modes have been characterized by XPS and FT-IR, it should be mentioned that there is no evidence shows that the bonding mode is a deciding variable in the suppression of surfactant adsorption. Although ozone is somewhat more effective than oxygen under

the conditions used, the degree of adsorption suppression correlates adequately with the different *amounts* of surface oxides, as also seen by Wu et al. [3] for the anionic surfactant dodecanoic acid on carbon.

Hygroscopic and acidic properties

DSC traces were obtained for untreated and oxidized carbon black samples. No large heat effects are seen relative to untreated carbon black except for the temperature at 100-180 °C, which is just visible for the ozonated sample and quite pronounced for the air oxidized sample. Repeated experiments on a single air oxidized sample show this peak only on the first scan, so it represents an irreversible process. The temperature range suggests water desorption, so a special test was devised to characterize the hygroscopic nature of the oxidized samples.

Fig. 7 shows that both methods of oxidation make the carbon black samples quite hygroscopic. The large difference between 12 hour and 7 day exposure in almost saturated humidity for ozone treated sample may reflect a slow hydration of anhydride sites. Heating at 1000 °C removes the hygroscopic behavior for the ozonated sample as expected, but surprisingly the air-oxidized sample retains much of its hygroscopic behavior after thermal desorption. The surface areas of the air oxidized samples are 234-246 m²/g — a factor of about 7 times higher than the ozonated samples (34-40 m²/gm) and it is likely that the high water uptake in the air oxidized/thermally desorbed sample is due to adsorption and capillary condensation in fine porosity developed during air oxidation. Integration of the DSC difference curve of air oxidized sample gives an amount of heat that is somewhat greater than but of the same order of magnitude as the vaporization of bulk water at about 20% of the sample mass. Overall, thermal desorption of adsorbed/condensed water in fine porosity is thus the most likely explanation for the main origin of the irreversible endotherm at 130 °C seen in the DSC of air oxidized samples and, to a much less extent, for the ozonated samples. The absence of other peaks indicates that no significant endothermic/exothermic rearrangement or desorption occurs. This result suggests that any removal of unstable ozonides or peroxides must have occurred during reaction or sample handling (prior to DSC) and that much of the oxide desorption does not occur under 600 °C, the maximum DSC temperature.

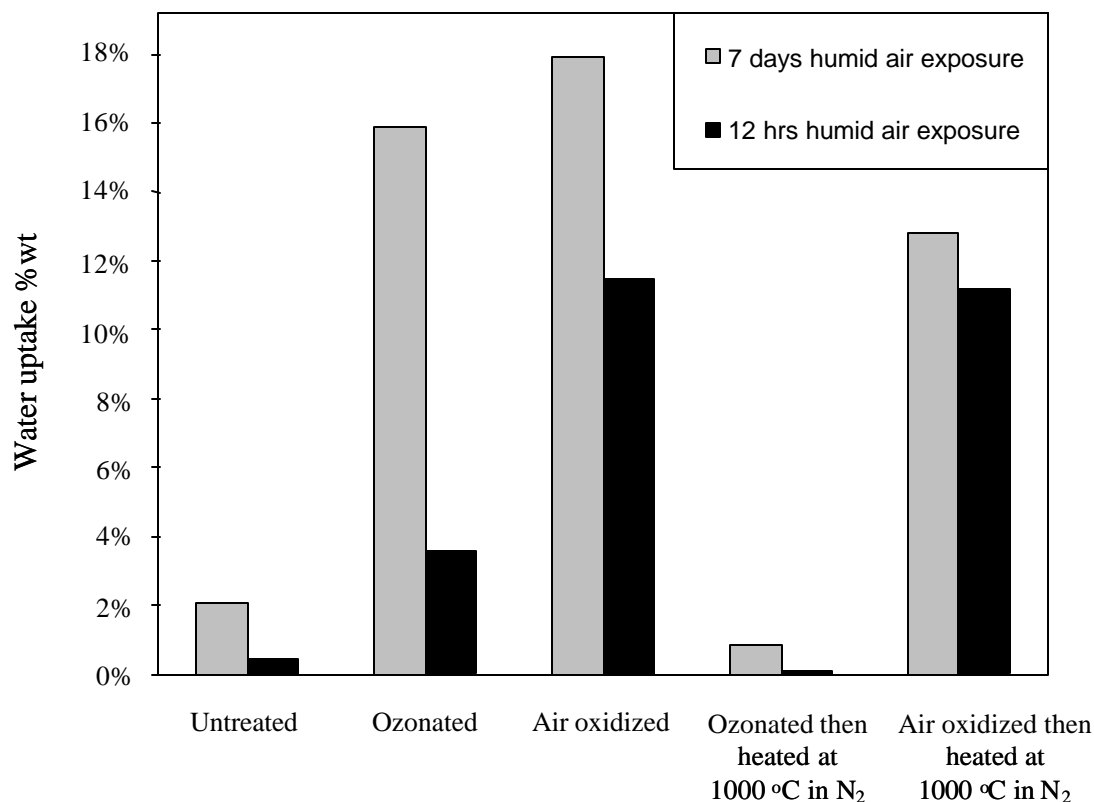


Figure 7. Effect of surface oxidation and subsequent thermal desorption on hygroscopic behavior of carbon black samples.

Fig. 8 shows the pH of raw and treated carbon black slurries. Both oxidation methods introduce primarily acidic oxygen complexes, which is consistent with the carboxylic functionalities seen by FT-IR. It is notable that the ozonated sample after thermal desorption not only loses its acidity but exhibits a pH of 9.2. This significant basicity is due either to residual refractory basic oxides, or more likely to the higher concentration of oxygen-free Lewis base sites associated with π cloud systems [15, 44].

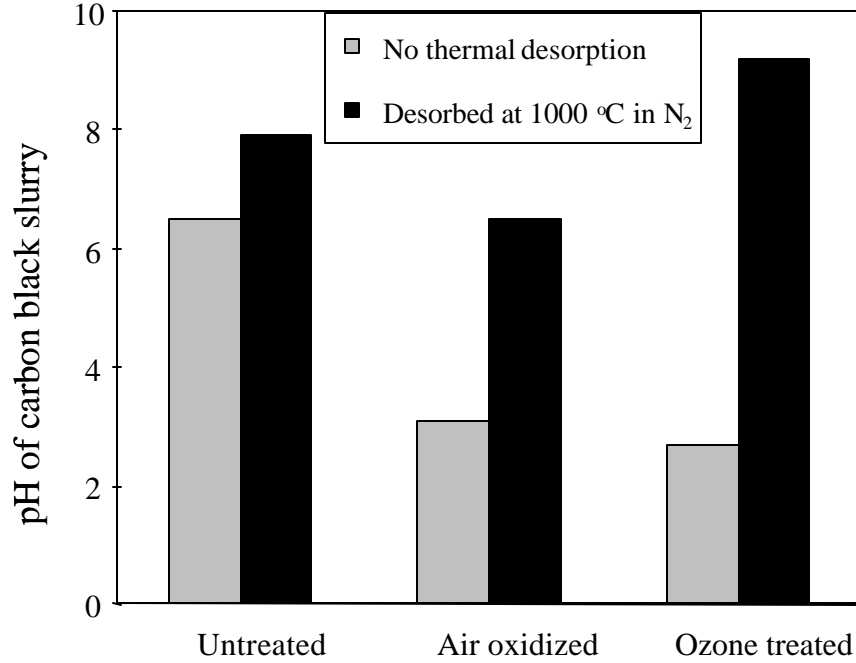


Fig. 8. The pH of raw, oxidized, and thermally desorbed carbon blacks by ASTM 1512-95.

Carbon surface energy analysis

Table 1 shows that both modes of surface oxidation improve the wetting (reduce the contact angle) of the two standard liquids: benzyl alcohol and nitromethane. Because benzyl alcohol and nitromethane have different fractional polarities (22% vs. 40%), they can be used to derive the polar and dispersive components on solid surface tension.

The determination of carbon surface energies by the Fowkes / Owens-Wendt theory [45] will prove useful for elucidating the mechanism of oxidative adsorption suppression. This theory of interfacial interaction divides the total solid surface energy into polar and dispersive components:

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (1)$$

The liquid surface tension is likewise divided into polar and dispersive components:

$$\gamma_l = \gamma_l^p + \gamma_l^d \quad (2)$$

The liquid/solid interfacial energy is expressed as:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} - 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (3)$$

Combining these relations with the Young equation:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta \quad (4)$$

yields:

$$(\cos\theta + 1) \gamma_l = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (5)$$

If contact angle, θ , is measured for a test liquid of known γ_l^d and γ_l^p , only two unknowns remain in Eq. 5: γ_s^d and γ_s^p . Measuring θ for a second test liquid provides the second equation needed to calculate γ_s^d and γ_s^p and their sum, the total solid surface energy, γ_s .

The result of this calculation for our carbon surface is shown in Table 5. Both air and ozone oxidation greatly enhances the polar contribution to carbon black surface energy, with ozone treatment showing the larger effect. The dispersive component of surface energy is observed to increase as well, though only modestly, so the net effect of oxidation is a rather large increase in total surface energy (polar plus dispersive). An increase surface energy normally brings about an increase in the strength of interfacial forces, which thus promotes wetting (as observed) and promotes adsorption from the vapor phase. The opposite behavior in solution (adsorption suppression) has been attributed to the fact that adsorption from solution is governed not only by surface/adsorbate forces, but also by surface/solvent interactions and solvent/adsorbate interactions. This idea is discussed in detail below.

Table 5.
Carbon black surface energies
and their dispersive and polar components¹

	γ_s^d (mJ/m ²)	γ_s^p (mJ/m ²)	γ_s (mJ/m ²)
Untreated	20.9	0.9	21.8
Air oxidized at 450 °C, 10 hrs	22.7	4.3	27.0
Treated in 2 wt-% O ₃ (600 g- O ₃ /kg-C)	24.4	8.1	32.5

¹Determined by Owens-Wendt theory using benzyl alcohol and nitromethane as standard reference liquids

Mechanisms of Adsorption Suppression

Carbon surface oxidation can either promote or inhibit adsorption of organics from aqueous solution depending on the nature of oxide, adsorbate, and the solution chemistry. Adsorption can be influenced by surface charge, van der waals forces, hydrogen bonding, π - π bonding (for aromatic surfactants on carbon), hydrophobic interactions, chemisorption and electron transfer complexes[14]. In principle the same factors are relevant for surfactant adsorption, along with additional factors such as adsorption of hemi-micelles and dual site adsorption involving adjacent polar and nonpolar surface functionalities. However, in the search for mechanism, the experimental result shows that oxidation suppresses

adsorption with almost equal effectiveness for a variety of carbon types, oxidants, and surfactant types. It suggests a simple mechanism common to all surfactant/carbon systems studied here. Based on other aqueous phase adsorption systems, several possible mechanisms have been considered about the surfactant adsorption suppression by surface oxidation:

1. Micropore blockage. Surface oxide formation decreases total area by blocking fine pores or pore mouths.
2. Electron withdrawal. The addition of electronegative oxygen atoms to graphene layer edges withdraws electron density from the π clouds and reduces dispersion forces that bind the adsorbate to graphene basal surface [14].
3. Electrostatic repulsion. 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 anionic (negatively charged) surfactant molecules [14].
4. Reduction of hydrophobic interactions. Introduction of oxides destroys nonpolar surface area that is responsible for adsorption, leaving hydrophilic surface sites that participate in strong hydrogen bonding with water and are effectively unavailable for surfactant adsorption.
5. Steric hindrance. Introducing surface functionality disrupts the close geometric accommodation between the adsorbate and the surface thus reducing the overall strength of attractive forces. This effect would be most important for large adsorbates and those capable of π - π bonding which relies on the atomic flatness of graphene basal plane segments.

The present data allows a critical evaluation of these completing explanations for our system as follows. Mechanism 1 (pore blockage) is a contributor for at least some fly ash carbons, but is not believed to be the primary mechanism, since carbon black and some other fly ash carbons exhibit the same beneficial effect of ozonation, but do not show any decrease in area.

Mechanism 2 (electron withdrawal) can be ruled out by the surface energy results derived from wetting studies (Table 5). 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 ozonation is expected to slightly *enhance* the dispersive attractive forces for adsorption, not *suppress* them.

Mechanism 3 (electrostatic repulsion) likely plays a role for resin-derived concrete surfactants, since they are anionic and would be repelled by the negative surface charges expected on the oxidized carbon surfaces at the high pH of concrete paste. This mechanism is not believed as the primary effect, since surface oxidation by ozone is also effective at suppressing the adsorption of Tergitol, a nonionic surfactant.

Mechanism 4 (reduction of hydrophobic interactions) is believed to be the primary mechanism sufficiently to explain the main effects observed in this study. It can be arrived by basic consideration of the nature of surfactants. Any solution adsorption process can be broken down into three conceptual steps: 1.

desolvation of solute, 2. desolvation of surface, and 3. solute/surface interaction. The total driving force for adsorption is the sum of the driving forces (chemical potential differences) of the three steps. Unlike other solutes, surfactants have a highly insoluble nonpolar part, for which step 1 (desolvation) is highly favorable, and thus the driving force for step 1 can be sufficient to drive adsorption. This fact is evident from the propensity that surfactant molecules collect at the gas interface, chiefly in bubble cavities, which offer no attractive interfacial forces (no driving force component for step 3). Nonpolar solid surfaces behave in similar fashion. Step 1 and 2 are the “hydrophobic forces” that drive surfactants to nonpolar surfaces, and when these "forces" are strong the adsorption is not dependent on the driving force for step 3 or on the detailed nature of the surface, as long as it is nonpolar. It is believed that the surfactant adsorptivity of carbon is most directly related to the fraction of its surface that is hydrophobic (nonpolar) with other characteristics of the surface being of secondary importance, as also cited by Wu[3]. Ozonation destroys this nonpolar surface and replaces it with oxidic surface that is hydrophilic and capable of strong hydrogen bonding with the solvent water. Since adsorption in aqueous solution is intrinsically a competitive process in which the surfactant and water molecules compete for adsorption 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.

Mechanism 5 (steric hindrance), or geometric mismatch between sorbent/surface, is not believed to be the primary mechanism here. Oxidation most certainly changes the atomic topology of the carbon surface, but the wetting studies show enhanced dispersion interactions with both benzyl alcohol and nitromethane. The surfactant molecules being larger are more prone to steric effects, but the two chain surfactants should have flexibility to adapt to irregular surfaces. This mechanism is expected to be most important for aromatic or polyaromatic solutes that adsorb on carbon through π - π bonding, which is not the case for the surfactants investigated here. Although steric effects are not the primary mechanism, it is believed that they play a role in determining the amount of surface oxides needed for the hydrophobic mechanism (mechanism 4) to engage. As oxide coverage increases, it becomes increasingly difficult for the large nonpolar segments of the surfactant to find a nonpolar surface patch lying between oxide sites. Further, oxides serve as nucleation sites for hydrogen-bonded clusters of water molecules, thus enlarging their effective size for the disruption of the continuous nonpolar surface. Through this mechanism significant adsorption suppression is expected at coverage much less than 100%, as observed in our previous study [7].

The results in this report help explain the origin of apparently contradictory reports of the effects of surface oxidation in the literature on fly ash carbon [8,9,12]. It is believed that the enhanced uptake of polar compounds from the vapor phase (acetone) [9] is driven by the increased surface energy and polarity of oxidized carbon surfaces, while the decreased uptake of surfactant from solution is related not to the magnitudes of the energies but to the increased polar/dispersive ratio. Vapor phase adsorption is driven only by step 3 — surface/vapor attractive forces, which are increased by oxidation and adsorption (like wetting) is enhanced. In solution the overall surface energy is less important than the polar/dispersive ratio since adsorption is competitive and the polar/dispersive ratio governs the relative affinity for water and surfactant molecules. More detailed surface characterization would yield further insight into the nature of the specific oxygen functionalities, but may not contribute significantly to the understanding of surfactant adsorption.

Because the proposed mechanism is based on hydrophobic interactions, which are the essence of surfactant action, it offers a convenient explanation for the general nature of the phenomenon observed

— the fact that surface oxidation is effective over a range of carbon/surfactant/oxidant types. Surface oxygen complexes may still interact with the polar or ionic groups in surfactants [3, 46], but the dominance of hydrophobic interactions makes these specific interactions of secondary importance in the present system, and indeed their effects are difficult to discern in the data.

Conclusions

A battery of carbon surface analyses has been used to study the underlying mechanisms behind the previously reported ozone treatment effect on surfactant adsorption [7]. Ozone increases surface energy but suppresses adsorption in each carbon/surfactant system studied. Air oxidation produces a similar effect although it produces somewhat different surface species, notable more phenol and less lactone/anhydride. The overall extent of adsorption suppression correlates with surface oxygen concentration by XPS and is largely, though incompletely, reversible upon thermal desorption in N₂. The effects of surface oxidation are quite similar for three surfactant types: a nonionic, an aliphatic chain anionic, and a globular anionic mixture derived from natural sources. The combined data indicate that the primary mechanism of adsorption suppression is the destruction of nonpolar carbon surface area with possible contributions from blockage and increased negative surface charge for some systems. While the polar/ionic portion of surfactants can undergo specific interactions with surface oxygen complexes, here these effects are secondary compared to the amount of nonpolar surface on which surfactant adsorption is strongly favored by hydrophobic interactions.

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