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_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.

This first project period, experiments were carried out to better understand the fundamental nature of the ozonation effect on ash. Carbon surfaces were characterized by surfactant adsorption, and by X-ray Photoelectron Spectroscopy before and after oxidation, both by air at 440 C and by ozone at room temperature. The results strongly suggest that the beneficial effect of ozonation is in large part due to chemical modification of the carbon surfaces.

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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_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 thorough 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

During this first project period, e-mail communications were carried out among the PIs to coordinate early activities and sample exchanges. Technical work in the first period focused on understanding the fundamental origin of the ozonation effect — the relative contribution of surface area changes, surface polarity changes, or other factors. Carbon black samples were used as a model system for detailed surface characterization, after it was demonstrated in our laboratory that carbon black shows the same essential adsorptiivty behavior and response to ozone as does the native unburned carbon in ash.

X-ray photoelectron spectroscopy (XPS) was used to obtain information on the number of surface oxides and their mode of bonding before and after ozonation. Wetting studies were carried out to determine surface energies and their polar and dispersive components before and after ozonation. The sections below combine these new results with earlier results on fly ash ozonation to produce a dataset that begins to reveal the fundamental surface mechanism. Additional surface characterization by temperature programmed desorption and FTIR is planned for upcoming periods. During the second period we also plan to initiate work on the analysis of pilot-scale ashes and to begin the laboratory study of ash behavior from selected coals and alternative (non-coal) fuels.

Experimental

Ash ozonation experiments were carried out in the apparatus shown in Fig. 1. 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.

The carbon black sample was Cabot M120 with 75 nm primary particle size. Ozonated samples were prepared at Brown using the apparatus in Fig. 1 under the following conditions: 2 wt-% ozone in air, 180 min contact time, 20 gm carbon black, and 1.5 lit/min flow rate. These conditions correspond to 600 gm-ozone per kg carbon. An additional sample was air oxidized at 440 C for 8 hrs, leading to 20% weight loss. Both air oxidation and ozonation reduced the surfactant adsorptivity, as shown in Table 1.

Surfactant titration

The degree of interaction between an AEA and a specific fly ash or carbon solid sample can be estimated using the foam index test [3], a simple laboratory titration procedure. This procedure was used in this study to investigate the interactions between a commercial AEA (Darex II, trademark of W.R. Grace & Co., Cambridge, MA) and a variety of model carbonaceous materials and carbon-containing fly ash samples. The original foam index test⁹ was modified to accommodate smaller amounts of fly ash; the procedure is as follows: 2 grams of fly ash are place in a 70 ml cylindrical

Figure 1. Laboratory apparatus for ash ozonation

weighing bottle with I.D. 40 mm x 80 mm (Fisher Scientific) along with 25 ml of distilled water. The sample is ultrasonically dispersed for 5 minutes, after which 8 grams of Portland cement is added. The weighing bottle is then capped and thoroughly shaken for one minute to completely wet the cement and fly ash. A 10 vol-% aqueous solution of Darex II is then added one drop at a time from a 2 ml microburet. After each addition the bottle is capped and shaken vigorously for 15 seconds after which the lid is removed and the liquid surface observed. Prior to the endpoint of the test, the foam on the liquid surface is extremely unstable, the bubbles bursting within a few seconds. The endpoint is realized when a constant foam is maintained on the surface for at least 45 seconds. The volume of diluted Darex II required to produce this stable foam is referred to as the foam index of the fly ash / cement mixture. The entire procedure is repeated using 8 grams of cement and no fly ash yielding a foam index value for the cement alone (typically very low). Subtraction of the two values yields an effective foam index for the fly ash which serves as a measure of the degree to which any given ash adsorbs AEAs. The same procedure was used in the tests involving carbon blacks, in which no ash was used, and the carbon black type and sample weight were varied as test parameters.

XPS

Surface chemistry of raw, thermally oxidized, and ozonated carbon black samples were investigated by X-ray photoelectron spectroscopy (XPS). XPS was performed by Evans East Laboratories in East Windsor, N.J., using a Physical electronics 5700LSci with monochromatic aluminum as the X-ray source. Low resolution scans were acquired to determine the elements present, followed by high resolution scans to determine binding energies and concentrations from the C1s and O1s peaks.

Results and Discussion

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 200 gm-O₃/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 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-O₃/kg-ash (corresponding to about 400 gm-O₃/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. 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 chemical surface modification.

Figure 2. The effect of ozone treatment on surfactant adsorptivity of commercial fly ash samples.

Table 1. XPS Results on Carbon Black

	<u>atom-% O[†]</u>	<u>atom-% C[†]</u>	<u>Surfactant Adsorptiv. (ml/gm-carb)</u>
Untreated carbon black	1	98	10
air oxidized at 440 C, 8 hrs (20% weight loss)	7	92	3.5
2% ozone, 180 min (600 gm-O ₃ /kg-C)	10	89	2

[†] these are near-surface elemental compositions — the approximate escape depth of carbon electrons was 8 nm. The balance is sulfur.

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 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 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.

Figure 3 shows the effect of heavy ozone exposure on the carbon content of ash. At high ozone / carbon ratios ozone consumes the carbon, converting it to gaseous CO and CO₂ (gasification). This carbon consumption may be expected to further improve ash behavior somewhat, but consumes an excessive amount of ozone and is prohibitively expensive.

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

Figure 3. Gasification (consumption) of fly ash carbon under heavy ozonation conditions. Reaction in 2 mole-% ozone in air; 1.5 liter/min; ash bed: 50 gm. At 1.5 hr the cumulative ozone fed is 115 gm/kg ash; after 23 hr it is

Conclusions

The new surface characterization data combined with the earlier results indicates that the probably mechanism in chemical surface modification, but that this effect may be enhanced in some cases by reduction in total surface area due to oxide obstruction. The results further suggest the presence of 2 reaction steps: 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:

Step 2 removes bulk carbon, which eventually will help reduce adsorptivity, but the step is stoichiometric in ozone and would be prohibitively expensive if it were the dominant route. 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. Pilot scale studies of large scale contacting schemes are underway. The pilot studies are being supported by further laboratory investigation focused on the mechanism of adsorption suppression and the kinetics of surface oxidation.

References

1. Helmuth, R. Fly Ash in Cement and Concrete, The Portland Cement Association, Skokie, Illinois, 1987.
2. Hachman, L., Burnett, A., Gao, Y., Hurt, R., Suuberg, E. Surfactant adsorptivity of carbon solids from pulverized coal combustion under controlled conditions", Proceedings of the Combustion Institute, Vol 27 2965-2971, The Combustion Institute, Pittsburgh, 1998.
3. Gao, Y.; Shim, H.; Hurt, R.H.; Suuberg, E.M.; Yang, N.Y.C. Effects of Carbon on Air-Entrainment in Fly Ash Concrete: The Role of Soot and Carbon Black," Energy and Fuels, 1997;11: 457-462.
4. Kamm S., Möhler, O., Naumann, K.H., Saathoff, H., Schurath, U., Atmospheric Environment 1999; 33:4651-4661.
5. Stephens, S., Rossi, M.J., Golden, D.M. International Journal of Chemical Kinetics, 1986; 18:1133-1149.