THE UNDESIRABLE ADSORPTION OF CONCRETE SURFACTANTS ON POROUS CARBON IN COAL COMBUSTION FLY ASH

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Introduction

The most important commercial outlet for coal ash is in the concrete industry as a partial replacement for Portland cement. In many concrete mixtures careful control of air entrainment is required, but the presence of solid carbon disrupts the air entrainment process by adsorbing "air entraining admixtures" (AEAs), the specialty surfactants used in concrete applications. Commercial AEAs are typically complex mixtures of soluble (typically anionic) organic surfactants derived from natural sources (e.g. neutralized wood resins) or, increasingly, synthetic materials.

The interaction of unburned carbon in fly ash with AEAs represents a unique case, in which the adsorptive properties of carbon are detrimental to an industrial process. This paper presents experimental results on the dynamics of this adsorption process, on the dependence on carbon form and type, and on possible techniques for mitigating the effects of this undesired adsorption.

Experimental Procedures

The foam index test was used to measure the adsorptivity carbon-containing fly ash samples and a variety of model carbon materials toward a commercial air entraining admixtures. The test is a laboratory titration procedure, in which air entraining admixture is added dropwise to a premixed aqueous suspension of cement and fly ash until stable bubbles appear on the suspension surface following agitation. The milliliters of AEA required is reported as the foam index, a measure of the activity of the given fly ash or model compound.

Results

It is observed that the foam index is a strong function of the amount of carbon present in the fly ash sample. It is correspondingly very low for samples in which the carbon has been removed by air oxidation at 700 ^{o}C. At a given weight-% carbon, the foam index is also seen to vary significantly as function of the origin and properties of the carbon solid present. There is signficant variation in activity amoung fly ash samples from the field that cannot be explained by the amounts of carbon present. In some samples, elevated levels of activity appear to be related to the presence of other products of incomplete combustion (e.g. soot, tar). In most samples, the variability is believed to be caused by variable properties (surface chemistry, pore structure) in the char derived carbon, which is the bulk of unburned carbon in the vast majority of cases. Much but not all of the sample-to-sample variability can be eliminated by surface area normalization, as seen in Figure 1.

In Figure 1, the fly ash carbons and untreated carbon black samples lie on a common curve of foam index vs. nitrogen BET surface area. An exception to this relationship (not shown) are commercial activated carbons, which have a high weight-normalized activity, but an exceptionally low area-normalized activity. This trend suggests that the entire microporous surface area in the

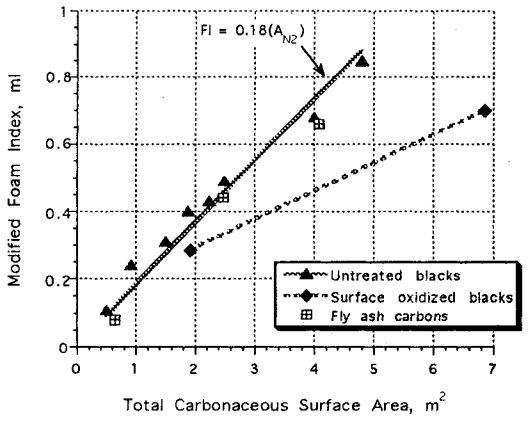

Figure 1. Summary of foam index measurements on various fly ash carbons and carbon black samples of varying primary particle size.

commercial products in not active —consistent with the size of the organic surfactant molecules of interest.

A second exception to the curve in Figure 1 are the surface-treated carbon blacks, with lower activities. These materials have undergone a post-combustion oxidative treatment to aid in wettability and dispersion in aqeuous media. The accompanying reduction in activity suggests that nonpolar surface is primarily responsible for the AEA adsorption.

This observed effect of surface chemisty opens post-combustion oxidation as an interesting possiblity for minimizing AEA adsorption and the negative effects of carbon in concrete. Figure 2 shown the effect of air oxidation (one hour at increasing temperatures from 200 to 600 °C) on the foam index of a carbon-containing ash sample. Oxidation above 500 °C removes carbon and decreases the foam index as expected. Below 500 °C, however,there is a temperature range in which foam index is signficantly decreased before the onset of gasification. The presentation in Figure 2 (foam index vs. conversion) shows clearly the initial decrease in foam index prior to weight loss — an effect attributed to increasing hydrophobicity of the carbon surfaces.

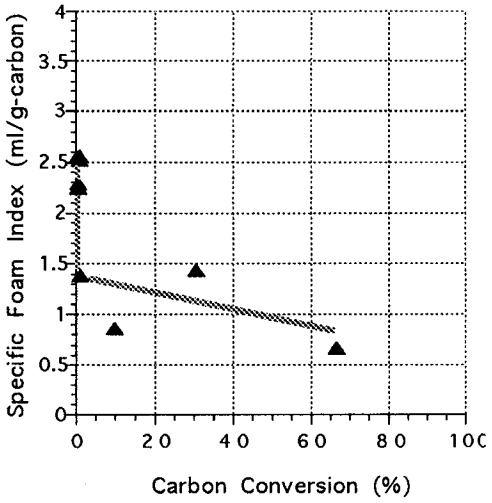

Figure 2. Effect of thermal oxidation on the mass-specific foam index of fly ash carbon. Samples are heat treated in air for one hour at a series of increasing temperatures from 200 to 600 °C.

Figure 3 illustrates another concept for suppressing the sorptive activity of carbon — the use of sacrificial adsorbates. Certain additives have been found that reduce the foam index without exhibiting surfactant action of their own. It is believed that these substances adsorb on carbon surfaces, blocking sites for the subsequent adsorption of AEAs. In addition to the reduction in absolute amount of AEA, is a reduction in sensitivity of AEA requirement to changes in fly ash properties, an important practical consideration.

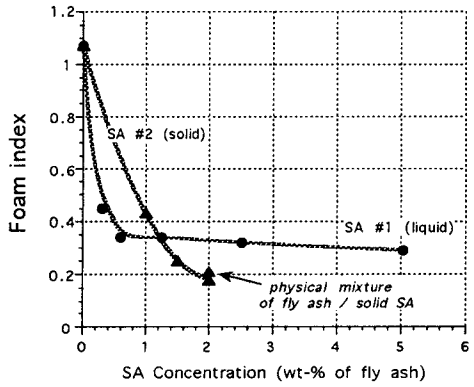

Figure 3. Effect of sacrificial adsorbate dosage and type on concrete surfactant adsorptivity of fly ash.

Summary

The widespread problems experienced with the use of high carbon-content fly ash in concrete are largely due to a liquid phase adsorption process, in which specialty surfactants added for air entrainment are adsorbed by the porous carbonaceous particulate that are residues from incomplete combustion. The adsorption process is still poorly understood, but appears to require carbonaceous, hydrophobic, surface area. The range of carbon pore sizes that participate in the adsorption process is still unknown, but has been shown to exclude the ultra-micropores. Exciting opportunties exist for suppressing this detrimental adsorption by oxidative surface treatment or by the addition of certain competetive, "sacrificial" adsorbates.