

The Role of Unburned Carbon in AEA Adsorption as Measured by Foam Index and UV-Vis Methods

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Fly ashes with elevated levels of carbon are unsuitable for concrete mixtures. One of the reasons given is that concrete mixtures containing such ashes require increased amounts of costly air-entraining agents (AEA) to achieve a given level of air entrainment.¹ It has been suggested that the reason for an increase in the AEA requirement is due to AEA adsorption by the unburned carbon.^{2,3} That is somewhat surprising given that fly ashes in general, and especially carbon from class F fly ashes have low surface areas and poor adsorption capacities.⁴ The Foam Index Test has been used to determine the amount of AEA to add to concrete mixtures.⁵ Because of the presumed influence of unburned carbon on AEA adsorption, the Foam Index Test has also been used as a measure of the degree of interaction between an AEA and fly ash or carbon.^{2,3} Recently UV-Vis spectrophotometry has been used as an alternative method for measuring the adsorption of AEA from solution by fly ash.^{6,7}

A linear relationship between AEA concentration and absorbance at 232.8 nm was found for solutions of Darex II up to 0.125% using UV-Vis spectrophotometry. Optimization of the UV-Vis method for determining AEA adsorption capacities of fly ash showed that an equilibration time of 10 min. was sufficient. Finally, dissolved CO₂ from the air can interfere with the UV-Vis determined adsorption capacity because of reaction of carbonic acid in solution with the AEA fatty acid salt to convert it to its insoluble free-acid form.

UV-Vis determined adsorption capacities and foam index values of 13 class F fly ash samples with carbon concentrations ranging from 0.3% to 14.6% were measured using Darex II. It was immediately obvious that there was no correlation between the carbon concentrations of the samples and their foam index values. This is important because of the past use of foam index values as a measure of interaction between AEA's and fly ash. There was also no correlation between the carbon concentrations and adsorption capacities as measured by UV-Vis spectrophotometry. Finally, no correlation was observed between foam index values and adsorption capacities.

Conversion of the foam index values to adsorption capacities yielded values that were significantly lower than those measured by UV-Vis spectrophotometry for all ashes, probably because of the difference in equilibration times used for adsorption of the AEA by the two methods. The Foam Index Test allots only 15 seconds for equilibration of the last addition of AEA compared to the UV-Vis method, which allots 10 minutes for equilibration of all the AEA in solution. The effect of the differences in equilibration times was measured by using the foam index test variables to carry out an UV-Vis measurement of Darex adsorption. The results showed that an amount of Darex II, 12% in excess of that required to reach the Foam Index Test endpoint, was adsorbed entirely by the fly ash. The results imply that had the Darex been allowed to equilibrate for a longer time in the Foam Index Test, the endpoint would have produced a higher foam index value.

The presence of soluble Ca²⁺ and Mg²⁺ ions in solution may also pose a problem when using either UV-Vis or foam index to measure Darex adsorption, and especially when trying to correlate adsorption values to carbon content of the fly ashes. This is because the ions form insoluble complexes with the fatty acids in the AEA.⁸ The

degree of interference by soluble alkaline-earth ions was first measured by adding soluble Ca^{2+} to a standard Darex solution. The absorbance of Darex decreased and formation of a cloudy-white precipitate was observed. Next, soluble Ca^{2+} and Mg^{2+} ions were washed from a fly ash sample. Its Darex adsorption capacity, as measured by UV-Vis spectrophotometry, decreased by 90%. These results indicate that precipitates can have a significant effect on the measured adsorption values of AEA's.

The Darex adsorption capacities of two carbon concentrates (73% C), as measured by the UV-Vis method, were only at most 40% greater than the highest value reported for the 13 fly ash samples even though the carbon concentrates contained at least five times as much carbon. The adsorption capacity measured by the UV-Vis method for a commercial Portland cement was more than twice that measured for any of the 13 fly ash samples. The results indicate that on a weight replacement basis, the adsorption capacity of cement for Darex would be lowered by the substitution of the fly ashes used in this study for some of the cement.

The results of this study clearly show that the Foam Index Test does not measure a material's adsorption capacity for AEA. Because of the short amount of time allowed for equilibration with AEA, the Foam Index Test primarily measures those reactions that result in removal of AEA from solution and which occur in a very short time frame. For the samples used in this study, the "instantaneous" reaction of air-entraining agent with soluble Ca^{2+} and Mg^{2+} ions probably influences the foam index values the most.

Controlled-atmosphere programmed-temperature oxidation (CAPTO) of fly ash in conjunction with measurement of foam index as a function of temperature showed that the greatest decrease in foam index occurs prior to significant loss of carbon. In order to determine the effects of thermal treatments in general on the foam index of fly ash, the series of 13 fly ash samples was oxidized or pyrolyzed to 500°C and 800°C followed by measurement of the foam index on the residue. There were significant changes in foam index values upon heat treatment of samples with very little carbon and upon pyrolysis, under which conditions the carbon content of the sample remains constant. The thermal treatments may have affected the foam index by altering the solubility of alkaline-earth ions (e.g. by locking them into the fly ash matrix). The effect of carbon on foam index was minor as determined by comparison of foam index values following oxidation at 800°C with those following pyrolysis at 800°C for the same fly ash.

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