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Measurement of adsorption of air-entraining admixture on fly ash in concrete and cement

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Abstract

A method using UV–Vis spectrophotometry for measuring the adsorption of air-entraining admixture (AEA) on the components of cements was optimized. The method was then used to measure the adsorption of AEA on a series of Class F fly ash samples with carbon concentrations of up to 14.6%. Class F fly ash carbons were found to have a very low capacity for AEA compared to Portland cement. The adsorption capacities of the fly ashes were compared to their carbon concentrations and foam index values. A lack of correlation between adsorption capacity and foam index was primarily due to differences in equilibration times used for the two measurements. Ultimately the Foam Index Test was found to be unsatisfactory for measuring the adsorption of AEA by fly ash carbon. The UV–Vis method is not necessarily a better choice for measuring AEA adsorption by carbon because soluble Ca^{2+} and Mg^{2+} ions from the fly ash were found to interfere with the UV–Vis method due to the formation of precipitates. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Adsorption; Fly ash; Cement; Concrete; Air-entraining admixture

1. Introduction

The amount of air-entraining admixture (AEA) that is added to concrete mixtures is critical to the performance of the final product and an important economic consideration in the production of concrete. That is why there has been considerable study of changes in the amount of AEA required to entrain a given amount of air when coal combustion fly ash is substituted for part of the cement in concrete mixtures [1]. Several studies have ascribed an observed increase in the amount of AEA required in concrete mixtures containing fly ash to various properties of the fly ash, especially its carbon content [1–10]. The degree of AEA adsorption on carbon in fly ash is especially important now that many fly ashes contain increased levels of carbon resulting from the use of low-NO_x burners to control the emission of nitrogen oxides during coal combustion [11].

The test used most often for indirectly measuring the relative adsorption of AEAs by fly ash is the Foam Index Test, or some modification thereof [2]. The Foam Index Test was originally designed to evaluate the influence of cementitious materials on the air-entraining capacity of concrete. The endpoint of the test is difficult to determine, it may be influenced by modifications to the test, and it can be operator dependent. Hence, ASTM Subcommittee CO9.24 on Mineral Admixtures has identified the development of an improved foam index method as a future research need [12]. The Subcommittee also suggested that spectrophotometric method(s) be developed to measure the AEA adsorption rate and capacity of carbon in fly ash, and to correlate the results with foam index and concrete data.

Recently UV–Vis spectrophotometric procedures have been developed to measure the adsorption of AEA by fly ash and carbon [3,10]. While these procedures offer a much more precise measurement of the interaction between the AEA and fly ash components than what is obtained by the Foam Index Test, the research contained in this paper will show that the UV–Vis method can be complicated by a number of factors. Refining the UV–Vis method led to a better understanding of the nature of the interactions between AEA and cement/fly-ash components that influence the Foam Index Test. This information should prove useful in developing improved methods for measuring the most important parameters affecting air entrainment by AEAs.

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2. Experimental

Thirteen samples of Class F fly ash with carbon concentrations ranging from 0.3% to 14.6% were obtained from 13 different units at eight coal-fired power plants. Eight of the fly ashes came from units employing low-NO_x burners. The power plants burned a mixture of eastern bituminous coals, predominantly from the Pittsburgh seam. In another part of the study, two carbon concentrates, CC1 and CC2, from coal combustion fly ash were used. Sample CC1 contained 73% carbon and was obtained by two successive passes of an ash through a triboelectrostatic separation system. Sample CC2 also contained 73% carbon but was obtained by froth flotation separation of a fly ash from a different source. All carbon concentrations were determined by controlled-atmosphere programmed-temperature oxidation.

The AEA was Darex II manufactured by GRACE Construction Products; Darex II is an alkaline solution of fatty acid salts. Unless otherwise noted, fresh dilutions of Darex were used for the experiments. Modified foam index measurements were carried out using a 2-g sample of fly ash. The fly ash sample was mixed with 5 ml of distilled water in a 15 ml i.d. 24 × 45 mm vial, and shaken for 1 min. A 1:40 solution of Darex diluted with distilled water was added to the mixture in 0.05 ml increments using a 2-ml microburet. The vial was shaken for 15 s, placed upright, opened, and the center portion of the foam layer observed using a microscope light source positioned at the side of the vial above the fly ash and below the foam layer. The endpoint was reached when stable foam persisted for 15 s and obscured all but a small fraction of light transmitted at the center of the foam layer.

For the UV–Vis method, approximately 0.05 g of sample was placed in a dry 125-ml filtering flask followed by 25 ml of 0.125% Darex solution and a stirring bar. Initial experiments were carried out in air. Latter experiments were conducted under nitrogen cover. One set of measurements was conducted under carbon dioxide. The procedures were the same in all cases except for the means of introducing the nitrogen and CO_2 covers. For the latter cases, a rubber stopper was placed in the top opening of the flask. A 0.635-cm stainless steel tube was placed through a hole bored in the center of the stopper and connected to the respective gas line with Tygon tubing. Nitrogen or CO_2 gas was allowed to flow into the flask at a rate that just caused the surface of the liquid to move. The gas exited through the arm in the neck of the flask. The solution was stirred under flowing gas with a magnetic stirrer for 10 min. The stopper was then removed and the solution was quickly decanted into a 15-ml glass centrifuge tube. The solution was centrifuged for approximately 1 min at approximately 5500 rpm. The solution was then transferred from the centrifuge tube to a 50-ml glass beaker using a disposable glass Pasteur pipette. The pipette was used in order to remove the liquid that laid between the solid layer at the bottom of the tube and a layer of fine particles that remained suspended at the top of the tube. The beaker was immediately sealed with Parafilm M while blowing nitrogen gas in the top of the beaker in order to remove any air.

The UV–Vis spectra were recorded between 195 and 300 nm. Darex solutions with concentrations of 0.05%, 0.075%, 0.10%, and 0.125% were used for calibration of absorbance versus concentration of Darex. The absorbance was measured at 232.8 nm from a linear background drawn between the minima (approximately 215 and 255 nm, respectively) of the absorption band.

3. Results and discussion

3.1. Optimization of UV–Vis measurements

The initial set of experiments focused on determining the optimal parameters for carrying out UV–Vis measurements. First to be determined was the range of Darex concentrations that produce a linear response of absorbance versus concentration using UV–Vis spectrophotometry. By working in 0.025% concentration increments, it was determined that the maximum concentration of Darex that yielded a linear response of absorbance was 0.125%. A previous study using UV–Vis spectrometry to measure Darex adsorption employed a 0.2% (approximate) Darex solution to treat the samples [10]. That could present a problem unless the concentration of Darex remaining in solution following treatment fell within the linear range of absorbance versus concentration.

Next, the proper amount of sample to be treated was determined. It was generally found that approximately 0.05 g of fly ash was an ideal sample. This was based on an observed change of about 0.2 to 0.3 absorbance units for the solution following treatment. A treatment time of 10 min was selected based on previous results, which showed that adsorption of AEA on fly ash essentially levels off after 10 min of treatment [3]. Because of a discrepancy between that latter work [3] and recently published results [10] showing that adsorption of AEA may still be occurring up to 60 min following treatment, the adsorption equilibrium time was studied in more detail.

The initial experiments were carried out in air with no attempt to blanket the solution with nitrogen during stirring or while it was stored before the UV–Vis measurements. During those experiments, it was noted that the calibration solutions of Darex began to turn cloudy white when stored for more than a few hours. It was also noted that the solutions from the sample treatments turned cloudier the longer the time they were stored under air before the UV–Vis measurements. This may be due to conversion of the fatty-acid salts to their corresponding insoluble free acids by carbonic acid produced from dissolved carbon dioxide. To test this hypothesis, solutions of 0.125% Darex were stirred under air, nitrogen, and CO_2 for 10 min and the absorbances of the resulting solutions were measured and compared to that of the starting solution. The results are reported in Table 1.

It can be seen that stirring the Darex solutions in air and pure CO_2 led to a significant decrease in absorbance as opposed to stirring under nitrogen. A visual comparison of the stirred solutions showed the ones stirred in air and CO_2 to be cloudy while the solution stirred in nitrogen remained clear. In order to quantify the degree of cloudiness, the background absorbance of each solution was recorded at 300 nm, where there is no absorption by Darex, and also reported in Table 1. There was a significant increase in background of the solution stirred under air, and even more so under CO_2, while only a minimal increase occurred for the solution stirred under nitrogen. Conversion of the AEA to its acid form is limited by the amount of carbon dioxide that dissolves in the solution. It appears to be proportionally insignificant for standing solutions containing concentrations of Darex greater than about 5%.

As a final confirmation that 10 min is sufficient for equilibration of Darex adsorption, a fly ash was treated for 10 and 20 min under air or nitrogen. The results, also reported in Table 1, show that when the experiment is carried out in air, additional loss of Darex from solution is observed between 10 and 20 min. However, when the treatment is done under nitrogen, no further adsorption is observed after 10 min of equilibration in the Darex solution.

The above results contradict those of other researchers [10] who concluded, based on a continued decrease in Darex concentration measured by UV–Vis for treatment times of 60 min, that solutions containing Darex and fly ash or activated carbon are slow to reach equilibrium. More likely the additional decrease beyond 10 min of treatment results from conversion of the surfactant to its insoluble acid form due to dissolution of carbon dioxide from the air. Our results are in agreement with those of another study [3] which showed that AEA adsorption levels off within 10 min of treatment. The AEA in that study was not affected by exposure to air because the treatment and UV–Vis measurement was done in a closed system.

The initial experiments carried out in air focused upon using UV–Vis to measure the relative adsorption of Darex on 13 different fly ashes with carbon concentrations ranging from 0.3% to 14.6%. Before those treatments were conducted, the precision of the treatment method incorporating UV–Vis measurement of Darex in solution was determined. Ten separate treatments were done using the same fly ash sample. The average adsorption of Darex by the fly ash was 0.186 ± 0.009 ml/g fly ash (RSD = 4.8%). The same fly ash was also used in a similar measure of precision of the Foam Index Test. The results of 10 separate measurements of foam index, which yielded an average value of 2.78 ± 0.20 ml (RSD = 7.2%), indicated somewhat better relative precision for the UV–Vis method.

Table 1
Effects of atmosphere and treatment time on Darex solutions

	Absorbance			Absorbance (300 nm)		
Treatment/stirring time (min)	Air	N_2	CO_2	Air	N_2	CO_2
Solution only						
0	0.517	0.532	0.520	0.200	0.130	0.121
10	0.426	0.546	0.415	0.340	0.158	0.444
Fly ash L						
0–blank	0.517	0.558				
10	0.226	0.279				
20	0.185	0.284				

3.2. Comparison of foam index and adsorption measurements

The results of the measurements of Darex adsorption and foam index for the various fly ashes are reported in Table 2. For most of the fly ashes the adsorption values are very similar, ranging from 0.198 to 0.225 ml per gram of fly ash. Only four samples fall outside that range. There is no correlation between the amount of Darex adsorption and the carbon concentrations of the fly ashes or between the amount of Darex adsorption and foam index. Others have attempted to establish a correlation between foam index or specific foam index (ml AEA/gram carbon) and loss-on-ignition, carbon surface area, and particle size with varying degrees of success [3–6]. However, almost no correlation between the parameters measured in the present study was found. This led to further experiments to determine the reasons for the difficulty in correlating carbon concentration with Foam Index and Darex adsorption measurements.

3.2.1. Equilibration time effects

The factor that readily became apparent as an important difference between the foam index and UV–Vis adsorption measurements was the time allowed for equilibration of adsorption of the AEA solution. The foam index value of 5.27 ml, the highest value in Table 2, measured for fly ash M corresponds to only 0.066 ml of Darex per gram of fly ash when the foam index value is converted using the dilution and treatment information in the Experimental section. This value is less than half the Darex adsorption measured by the UV–Vis method for the same sample. Because the other foam index values are lower, and the corresponding adsorption values measured by UV–Vis are higher than that measured for fly ash M, the differences in Darex adsorption as measured by foam index versus UV–Vis are even greater for the other fly ash samples. The correspondingly lower adsorption capacities measured by the Foam Index Test are probably due to an insufficient equilibration time being allotted for adsorption of the AEA. The Foam Index Test allots only 15 s for equilibration of the last addition of AEA compared to the UV–Vis method, which allots 10 min for equilibration of all the AEA in solution.

Table 2
Darex adsorption and Foam Index Test results for fly ash samples

Fly ash	Percentage carbon	Darex adsorption (ml/g)[a]	Foam index (ml)
A	0.3	0.217	3.98
B	1.0	0.217	4.71
C	2.6	0.205	3.77
D	3.8	0.206	1.37
E	4.0	0.225	1.95
F	4.5	0.205	2.85
G	5.4	0.198	2.53
H	7.0	0.216	2.34
I	7.7	0.250	2.43
J	8.1	0.214	3.24
K	9.0	0.179	4.29
L	12.2	0.254	2.67
M	14.6	0.143	5.27

[a] Experiments were done in air; adsorption values were corrected by using a blank.

The effect of the difference in equilibration times between the two methods was measured by using the Foam Index Test variables to carry out an UV–Vis measurement of AEA adsorption. Two grams of fly ash L were placed in a test tube along with 3 ml (0.23 ml more than the foam index measured for this fly ash) of the 1:40 diluted Darex solution and 22 ml of deionized water. The solution was stirred for 10 min and then centrifuged. It is important to note that the solution turned cloudy white initially, but after 10 min of stirring it was clear. The resulting liquid was analyzed by UV–Vis spectrophotometry. The spectrum showed no absorption peak in the region used to measure Darex. The liquid was also shaken and bubbles could not be produced. Both observations indicate that all of the Darex was adsorbed by the fly ash. The results imply that had the Darex in the Foam Index Test been allowed to equilibrate with the fly ash for a longer time, the endpoint of the test would have produced a higher foam index. The results of the comparison are also consistent with an observation in another study that "quick addition of a large amount of AEA would lead to an apparent endpoint at a lower foam index value than when the drops were added slowly" [7].

3.3. *Comparison of carbon content, foam index, and adsorption*

3.3.1. *The effects of soluble Ca^{2+} and Mg^{2+} ions*

Next, the apparent lack of correlation between the carbon content of the samples and their corresponding UV–Vis adsorption or foam index values was examined. Darex II is an alkaline solution of fatty acid salts, more commonly categorized as a "soap." It has long been known that alkaline earth ions such as Ca^{2+} and Mg^{2+} form insoluble complexes with soap. Therefore, they present problems to detergent manufacturers. The potential problems that could arise from precipitation of AEAs by calcium ions in cements were recognized some time ago [2,13].

To test the effect of Ca^{2+} and Mg^{2+} on Darex solutions, a few milligrams of nitrate salts of each ion were added separately to a 0.125% Darex solution. When either salt was added, the solution immediately turned cloudy. If sufficient salt were added, the solution did not foam upon shaking. As a comparison, Na^{+} and K^{+} nitrate salts were similarly tested. Neither salt turned the solution cloudy and shaking the solution after significant amounts of either salt were added could still produce foam. Finally, because the nitrate ion causes a spectral interference in the region used to measure Darex adsorption, 0.0035g of $Ca(OH)_2$ was added to 25 ml of a 0.125% Darex solution and the resulting solution was measured for the presence of Darex using UV–Vis spectrophotometry. The absorbance of Darex in solution decreased from 0.559 to 0.297 as a result of the Ca^{2+} addition. The decrease in absorbance by Darex was accompanied by an increase in the background absorbance at 300 nm from 0.100 for the 0.125% Darex solution to 0.450 upon addition of Ca^{2+}. Therefore, changes in background absorbance at 300 nm could be used as a relative measurement of the degree of formation of alkaline earth Darex salts. Based on the results of these experiments, it is clear that soluble Ca^{2+} and Mg^{2+} ions in fly ash will result in precipitation of Darex from solution.

The degree of interference by soluble Ca^{2+} and Mg^{2+} ions in a fly ash sample was then measured using UV–Vis spectrophotometry and a 0.125% Darex solution. Fly ash "L" was chosen because it exhibited the highest background absorbance at 300 nm of all the fly ashes tested earlier. In order to determine the effect of the soluble ions, the fly ash was stirred in 100 ml of deionized water, filtered, and then washed repeatedly with deionized water while it was on a suction filtration device in order to wash away the soluble ions. The washed fly ash was then dried. Both the washed and unwashed samples of fly ash L were then treated with the Darex solution. The Darex adsorption values measured for the two fly ash samples are reported in Table 3 along with the corresponding values of the background absorbance at 300 nm. The adsorption of Darex decreases to one-tenth the original value after the sample is washed. A corresponding drop in the background absorbance, which is attributed to the interference by Ca^{2+} and Mg^{2+} precipitates, accompanies the decrease in adsorption of Darex. In fact, the background absorbance measured for the washed fly ash is nearly identical to what was measured for the 0.125% Darex solution, indicating the complete removal of all of the soluble interfering ions from the fly ash. The Darex solution was also added to some of the filtrate. The filtrate turned from clear to cloudy white immediately upon addition of Darex.

Table 3
Adsorption of Darex on fly ash L

	Darex adsorption (ml/g)	Absorbance (300 nm)
Unwashed	0.254	0.285
Washed	0.030	0.102

The results of the washing experiment have important implications regarding the adsorption capacity of carbon in fly ash for air-entraining agents. Fly ash L had the second highest carbon concentration of all the fly ashes tested, yet when the interfering ions were washed away the resulting adsorption capacity for Darex was extremely low. In a separate leaching experiment followed by ion chromatographic analysis, fly ash A was found to solubilize the equivalent of 0.0035g of $Ca(OH)_2$ into 25 ml of deionized water, the same amount used earlier to demonstrate a sizeable interference by Ca^{2+} ions on Darex adsorption. The interference probably accounts for most of the measured adsorption by fly ash A reported in Table 2. Therefore, it can be suggested that the apparent lack of correlation between Darex adsorption values and carbon concentration in Table 2 is due to the overall poor adsorption capacities of unburned carbon for Darex. It is further suggested that most of the variation in measured adsorption values reported in Table 2 is most likely due to variation in the amounts of interfering soluble ions.

The results above should be examined with respect to the results of an earlier study on the effects of precipitated calcium surfactants on air entrainment in portland cement pastes and what is known about surfactant–particle interactions [13,14]. The mechanism by which AEA entrains air is through its adsorption onto the cement particles with its polar groups oriented towards the particles [14]. The surfactant remaining in solution forms bubbles on agitation with the surfactant molecules stabilizing the air–liquid interface with their hydrophobic tails oriented towards the center of the bubble. The bubbles then adhere to the hydrophobic surface created on the cement particles. In the study on the affects of precipitated calcium surfactants, it was shown that AEA–calcium salts with very low solubility form when AEA is added to cement mixtures [13]. The study concluded that some of the AEA are precipitated by calcium ions in solution, some are adsorbed onto the cement particles and the rest remain in solution to aid in the formation of air bubbles. As AEA is adsorbed onto the cement particles some of it is replaced in solution through dissolution of the AEA–calcium salts even though their solubility is very low. That is why air entrainment has been reported in concrete even at the low levels of AEA present when there is an excess of calcium ions and an AEA–calcium precipitate has formed [13]. This behavior was also observed in the present experiments. When a calcium-containing fly ash was added to an AEA solution in excess of the amount needed to absorb all of the AEA, a precipitate was immediately formed. The precipitate slowly dissolved until eventually all of the AEA was adsorbed by the fly ash. The formation of a precipitate is very quick compared to the rate of adsorption of AEA from solution. Depending on the AEA, the precipitate can be nearly insoluble and excessive amounts of AEA must be added to a cement mixture to make up for both AEA adsorption and precipitate formation.

3.3.2. *The effects of unburned carbon*

It has been shown that unburned carbon in Class F fly ashes has poor adsorption properties and that it must be activated to create significant adsorption capacity [15–18]. The experiments above suggest similar behavior. To further support this observation, Darex adsorption experiments were conducted with carbon concentrates from two different fly ashes. Their measured Darex adsorption capacities and corresponding carbon concentrations are reported in Table 4. The adsorption values in Table 4 are only at most 40% greater than the highest value reported in Table 2 even though the carbon concentrates contain at least five times as much carbon as the fly ashes in Table 2.

In order to determine the relative importance of adsorption of air entrainment agent by unburned carbon compared to portland cement, the latter's adsorption capacity was measured using UV–Vis spectrophotometry and a 0.125% Darex solution. The adsorption value measured for the portland cement was 0.583 ml Darex per gram of cement. The background absorbance at 300 nm was 0.287, indicating some interference from soluble Ca^{2+} and Mg^{2+} ions. The overall results indicate that on a weight replacement basis, the adsorption capacity of the cement for Darex would be lowered by substitution of the fly ashes in Table 2 for some of the cement. The amount of Darex that would required to achieve a given level of air entrainment would be less if some of the soluble Ca^{2+} and Mg^{2+} ions were removed from the fly ashes prior to their addition to cement. It is interesting to note that some previous studies have indicated that good air entrainment was achieved using high-calcium, Class C fly ashes [1]. That may be possible if the calcium in those fly ashes is not in a soluble form, such as amorphous glass-like structures or present as oxides and hydroxides, which are relatively insoluble.

It should be noted that the foam index of the portland cement was determined to be 0.37 ml. There is a greater disparity between foam index and the measured Darex adsorption value for the cement than seen in any of the results in Table 2. Clearly, all of the results in this study show that foam index does not measure a material's total adsorption capacity for air entrainment agent. Based on the short time frame allowed for equilibration with the AEA, the Foam Index Test primarily measures fast reactions that result in the removal of AEA from solution. For the samples used in this study, the "instantaneous" reaction of AEA with soluble Ca^{2+} and Mg^{2+} ions probably influence the foam index values the most.

Table 4
Adsorption of Darex on carbon concentrates from fly ash

Carbon Concentrate	Percentage carbon	Darex adsorption (ml/g)
CC1	73.0	0.354
CC2	73.3	0.293

4. Summary

This study provides important information on how a common AEA used in concrete is affected if the concrete contains fly ash having significant levels of unburned carbon. The Foam Index Test, which has traditionally been used to determine the influence of materials on the air-entraining capacity of concrete, appears to be a poor choice for measuring the interaction between AEA and unburned carbon. Some previous studies have shown that there is a good correlation between foam index and air entrainment in concrete mixtures, implying based on the present results that the most important reactions leading to air entrainment occur in a short time frame. The present study shows that adsorption of AEA by unburned carbon requires an equilibration time longer than that used for the Foam Index Test. A slow adsorption of AEA by unburned carbon may explain the decrease in entrained air that is observed over time for some concrete mixtures made using fly ash with higher levels of unburned carbon [1]. Poor adsorption of AEA on unburned carbon can lead to less air entrainment if adsorption of AEA on cement particles is critical to stabilization of entrained air [14]. Also, poor results may be obtained if the AEA attaches to the carbon surface through its hydrophobic end [5], opposite the orientation of its attachment to cement particles.

This study does not provide enough evidence to suggest that the Foam Index Test should not be used to predict air entrainment. In fact, the Foam Index Test appears to accurately measure the effects of precipitation of AEA from solution by soluble Ca^{2+} and Mg^{2+} ions. Although a UV–Vis method has been suggested as an alternative to measure AEA adsorption, the present study has identified possible complications to developing such a method. Further development of the UV–Vis method must address potential problems caused by the formation of AEA precipitates with soluble Ca^{2+} and Mg^{2+} ions, as well as precipitation of AEA from solutions exposed to air. It will also be important to determine the relationship between AEA adsorption, as measured by UV–Vis spectrophotometry, and actual air entrainment in the concrete product.

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