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AN EXAMINATION OF FLY ASH CARBON AND ITS INTERACTIONS WITH AIR ENTRAINING AGENT

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ABSTRACT

Four fly ash samples, which had previously been found to effect concrete air entrainment in a manner inconsistent with their respective loss on ignition, were investigated using several physico-chemical techniques. This study focused on characterization of the high-carbon fraction of each fly ash, obtained by a triboelectric separation process. While the four samples displayed varying reactivities toward AEA adsorption, the BET specific surface area of all four samples was determined to be essentially the same. Thermal analysis and petrographic examination revealed that the higher demand for air entraining agents exhibited by two of the samples could be directly related to the presence of a higher proportion of optically isotropic, amorphous carbon. Liquid and vapor phase adsorption analysis suggested that the surface chemistry characteristics of the isotropic carbon resulted in a higher adsorption capacity for polar compounds such as air entraining surfactants. © *1997 Elsevier Science Ltd*

Introduction

It is well established that fly ash (FA) improves the properties of concrete both in the fresh and hardened states [1]. That definite benefits accrue from it's usage is evident from it's increasing consumption in the construction industry (from 5.5 Mt/y in 1984 to 9 Mt/y in 1994)[2]. This increasing demand, however, has evolved when the availability of high quality ash is diminishing. The inception of the Clean Air Act Amendments in 1990 has prompted many power generating plants to retrofit their facilities to accommodate low NO_x burners. The resulting changes to the combustion process undoubtedly reduces NO_x emission, but are often accompanied by higher unburned carbon contents.

The carbon content in FA is critical because of it's adverse effect on air entrainment in concrete. It has been proposed that FA carbon, similar to activated carbon, possesses the potential to adsorb surfactants used in air entraining agents (AEA's) [3-5]. This results in a lower percentage of entrained air in concrete. Therefore, high carbon FA, or FA with varying carbon content is avoided when ever air entrainment in concrete is a prerequisite.

While loss on ignition (LOI) continues to be the accepted means for monitoring FA carbon content, and thus it's quality, it's validity as an universal predictive tool remains questionable. For instance both Dodson's foam index test [6] and Meininger's 'easily oxidized carbon' [7] were found to correlate well with mortar air content, but less than satisfactorily with LOI. Spectrophotometric methods to monitor the adsorption of organic constituents and relate it to LOI can also be inconsistent [8,9,10]. More recently, Freeman and others [11] claimed that the foam index correlates better with BET specific surface area than with LOI.

These investigations clearly mark the inadequacy of LOI as a prognostic test. Nevertheless, few published reports address the cause of this phenomenon. A possible reason may be the overall low population of carbonaceous particles (compared to ash particles) in FA which poses instrumental limitations for it's precise analysis. This paper describes an in-depth investigation into the nature of carbonaceous constituents in four FA's that were specifically selected for their tendency to interact with AEA's in a manner inconsistent with the ash's respective LOI values. A new approach to mechanically separate the carbon fraction was adopted.

Experimental

Materials. Initially, a wide range of Class F-FA samples from different sources were evaluated using two different types of AEA's, namely dodecylbenzylsulfonate (DDBS) and vinsol based. The ash performance was found to be significantly different under the same experimental conditions. Based on these results, which will be published separately, four samples were specifically selected for further testing. In order to focus attention on the characteristics of the carbonaceous material in FA, each sample was processed by a triboelectric separation method to produce a high-carbon fraction and a low-carbon fraction. The details of this technique have been reported elsewhere [12]. The differences in LOI resulting from this fractionation method are presented in Table 1. The effectiveness of this method is evident from the low LOI values of the low-carbon fractions. Samples "A" and "B" were from two

TABLE 1

Loss on Ignition of Different Fractions of FA's

Sample	A	B	C_1	C_2
LOI of As-received FA	3.8	4.7	3.0	3.9
LOI of high-carbon fraction	22.0	19.5	19.4	20.5
LOI of low-carbon fraction	0.58	1.7	1.0	0.65

separate sources that were found to perform satisfactorily with respect to air entrainment, whereas "C_1" and "C_2" were from a single source known to produce variable air content when used in concrete. These two were chosen to study the physico-chemical effects as a function of LOI. All of the fly ashes were produced from the combustion of high volatile bituminous coal.

Methods. The physical performance of these ashes in terms of air entrainment was determined at different AEA dosages; 3-point curves as described by Lane [13] were then constructed. The foam index was tested by slightly modifying Dodson's procedure of using 3 parts cement:1 part FA at w/s = 5 [6].

Chemical analysis was performed in accordance with ASTM C114 (on an ignited basis). Carbon, oxygen, hydrogen and sulfur in the high carbon fractions were analyzed using a LECO analyzer. Differential thermal analysis (DTA) was also carried out on these fractions in a flowing, pure oxygen environment. Selected samples were analyzed by diffuse reflectance FTIR to characterize the carbon bands.

The distribution of carbon forms within the fly ashes, and their separates, was determined using optical microscopy. Samples were prepared by mixing each fly ash with cold-setting epoxy resin and placing this mixture into several cylindrical molds. After hardening, the pellets were extruded from the molds and a surface ground and polished to 0.05µ using silicon carbide abrasive and alumina slurry. The fly ash pellets were examined using a polarizing light microscope in the reflected white light mode at 500x magnification. Quantification of the fly ash components was accomplished using an established point counting technique for the analysis of coal (i.e. ASTM D2799-86) with minor modifications. For this study, at least 1000 counts were completed for each of the raw and high-carbon fly ash samples, whereas only 500 counts were completed on the low-carbon fractions due to the preponderance of one phase (glass).

Liquid adsorption was measured using a UV/Vis spectrophotometer with a photodiode array detector. Fifteen grams of FA mixed with 150 mL of DI H_2O was constantly stirred in a small reaction vessel. This slurry was pumped through a 2 µm prefilter and then through a 10 µL flow cell before returning it to the reaction vessel. A background scan was collected after approximately 3 minutes. After 5 min. an aliquot of the AEA was introduced, which took approximately 30 sec. to reach the flow cell, and 2-5 min. for complete mixing within the cell. The instrument was programmed to record the absorbance over a range of wavelengths corresponding to the maximum absorbance peak for the AEA. Data was collected for 5 sec. (25 scans) at 30 sec. intervals. Background corrections were made simultaneously. This data provided a detailed profile of the concentration of AEA remaining in the solution over time. Absorbance values were converted into concentration by using calibration standards which were designed to match the slurry's chemical matrix.

Surface areas of the high carbon fractions were determined from multi-point BET plots of nitrogen adsorption data, obtained at 77K, using an automated gas adsorption system. Samples were outgassed at 100°C and <10 millitorr for 12 hours prior to analysis. In order to determine the contribution of the carbon to the total surface area, two of the samples were heated in air at 750 C until all of the carbon was removed, and the surface area of the inorganic residue was determined.

Vapor-phase adsorption experiments were conducted on the high-carbon fractions using an apparatus constructed at the University of Kentucky, with carbon tetrachloride and acetone selected as the adsorptives. Approximately 80mg of fly ash was placed in a balance and evacuated to approximately 3×10^{-2} torr, at 100°C, until a constant weight was obtained.

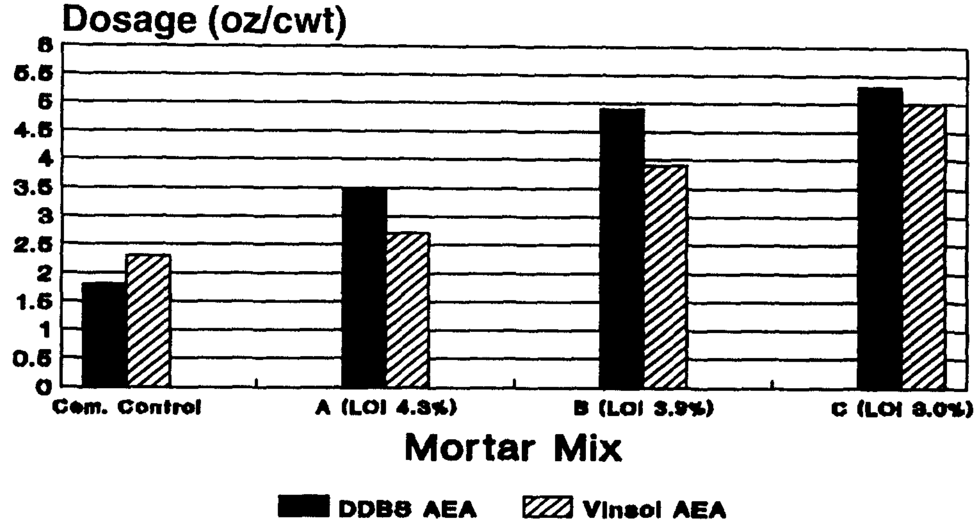

FIG. 1.
AEA dosage required for 16% air entrainment in FA mortars (Samples A, B, C_1).

After the sample had cooled to about 23°C, the adsorptive vapor was introduced at a relative pressure of 0.5, and the weight gain measured at equilibrium. The objective of these experiments was to probe the surface polarity of the fly ash carbons.

Results and Discussion

Air Entrainment Performance. Figure 1 displays the variation in AEA demand required to obtain 16% air entrainment in mortar (an arbitrary value selected by the authors) for the four as-received FA's. Obviously, "A" and "B" mortars produce higher air contents than "C" for both AEA types, although the LOI values of the corresponding FA's are comparable.

Chemical Analysis. The chemical compositions of the as-received FA's were generally similar, except that the "C" samples consisted of marginally lower SiO_2 and SO_3 but distinctly higher Fe_2O_3 contents than A and B. The alkalis were fairly constant (K_2O: 2.1 to 2.5%, Na_2O: 0.3 to 0.5%), whereas CaO ranged from 2.1 to 2.6% except for "C_2" with lower CaO (1.6%). Oxide analysis of the high-carbon fractions indicated changes in constituent concentrations. Closer examination proved these changes to be independent of carbon content; and were in fact artifacts of the separation process; the LOI values of all the four high-carbon fractions were in a narrow band (19.4-22.0% by weight) after the separation (Table 1).

Soluble ions associated with each sample were determined because of the critical impact they could have on air entrainment [14]. The detailed results will be published separately, but of particular relevance to this work are the results from pH analysis of extractions from the enriched carbon samples (Figure 2). Those ashes that required higher AEA dosages, (C_1 and C_2) exhibit lower pH even though their alkali levels are comparable to the other samples. Analysis of the inorganic portions of the "C" samples did not reveal the presence of any obvious pH-lowering compounds such as pyrite. It is postulated that their lower pH is due to

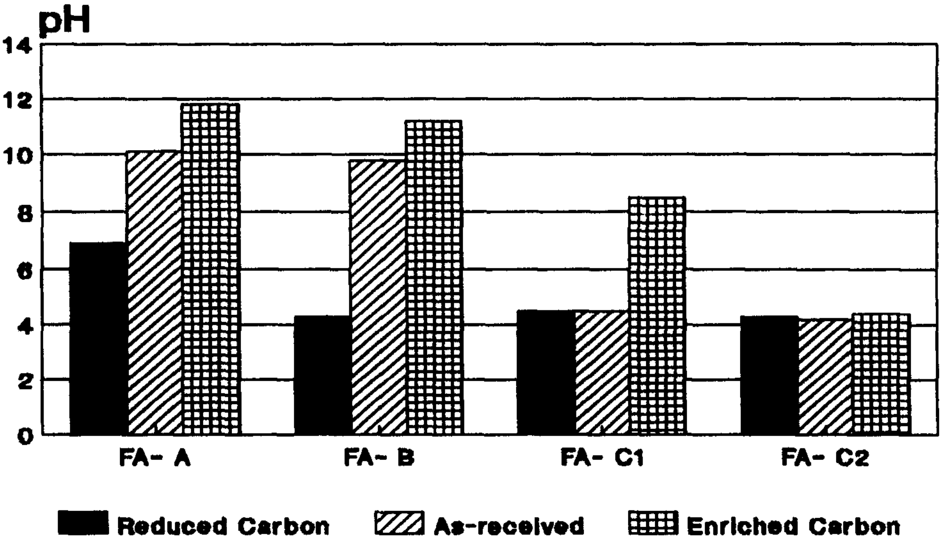

FIG. 2.

Analysis of slurry pH for reduced carbon and carbon rich fractions and as-received FA samples A, B, C, and C_2..

the presence of a different carbon species. For instance, both basic and acidic activated carbons are known to exist [15], depending on the processing conditions.

Analysis of the organic portion of the high-carbon fractions are provided in Table 2. The higher oxygen content of samples "C_1" and "C_2" suggests that the carbonaceous constituent in these ashes has been substituted with oxygen, possibly as weakly-bound functional groups, or incorporated as heterocycles [16]. The presence of heteroatoms, such as oxygen, in the unburned carbon fraction of these two samples could explain their relatively low pH. Examination of the high-carbon fractions by diffuse reflectance FTIR, however, did not detect the presence of bands characteristic of carbonyl functional groups, thus implying that the oxygen is most likely bound as heterocyclic compounds. The slightly elevated total carbon level in sample "A" is attributed to experimental error. The variation in sulfur content is marginal, whereas hydrogen in all the samples is less than 0.5%.

Table 2
Analysis of organic constituents in high-carbon fractions of FA's

Sample/LOI	**Total** C(%)	**H** (%)	**S** (%)	**O_2** (%)
A (22.0)	24.6	<0.5	0.4	1.4
B (19.5)	18.3	<0.5	0.4	1.7
C_1 (19.4)	19.7	<0.5	0.3	3.6
C_2 (20.5)	19.7	<0.5	0.3	4.1

TABLE 3

BET Specific Surface Areas of FA's

Sample Identification	Total Surface Area (m^2/g)	Residual Ash Surface Area (m^2/g)	Carbon Surface Area (m^2/g)
A	7 ± 1	0	7 ± 1
B	5 ± 1	na	na
C_1	9 ± 1	3 ± 2	6 ± 2
C_2	8 ± 1	na	na

Surface Area. Differences in air entrainment performance have often been attributed to differences in the specific surface area of the carbon fraction of fly ash. Nonetheless, nitrogen adsorption data (Table 3) indicate that these samples are similar to the extent that gross variations in AEA as observed in Figure 1 are not predicted based on surface area values.

Thermal Analysis. Thermal analysis was used to further characterize the carbon in these FA's. The exotherms in Figure 3 depict an intrinsic difference in samples "A" and "B" as compared to the "C" series of ashes. Although the exothermic peak at ≈590C is present in all four samples, the distinct, additional low temperature exotherm (540C) unique to samples C_1 and C_2 suggests a relatively larger concentration of a more easily-oxidized form of carbon; sample "B" had a detectable but minor shoulder at 540C. This relationship was confirmed from quality control testing performed at the source of the sample "C" FA's. Foam index testing of daily samples over approximately a two month period are presented in Figure 5.

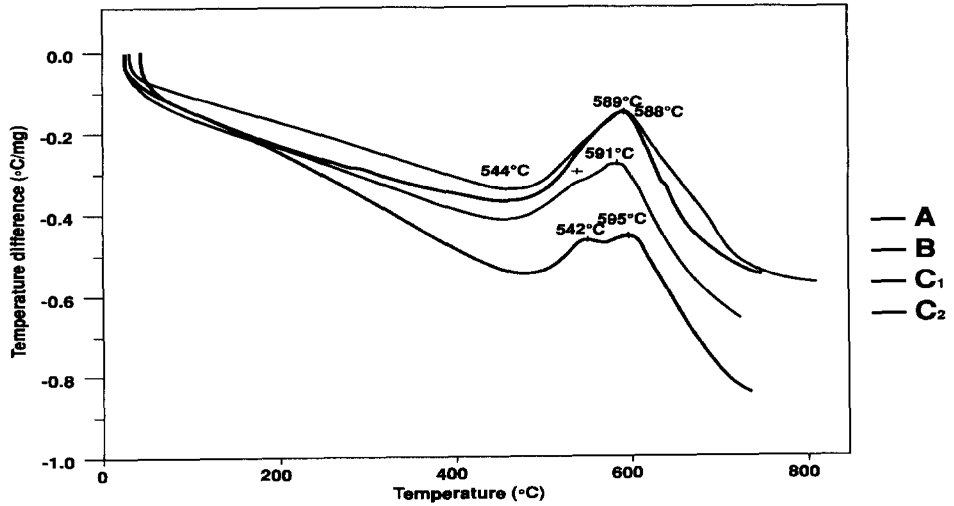

FIG. 3.

DTA plots of high-carbon fractions, where the lower temperature exotherm at 540C represents amorphous carbon, and the higher temperature exotherm (590C) is due to the crystalline variety.

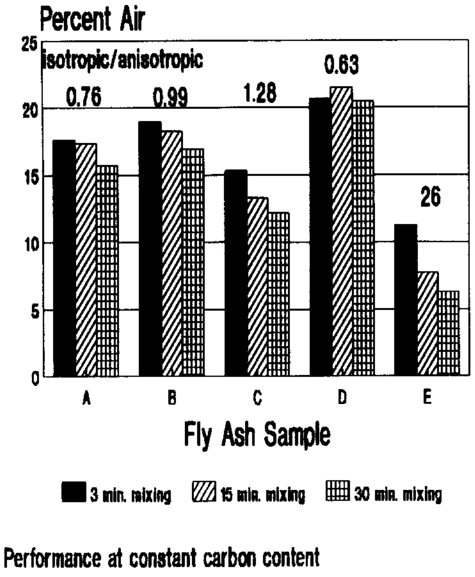

FIG. 4.
Mortar air entrainment performance at constant dosage (5.5 oz/cwt) of DDBS AEA.

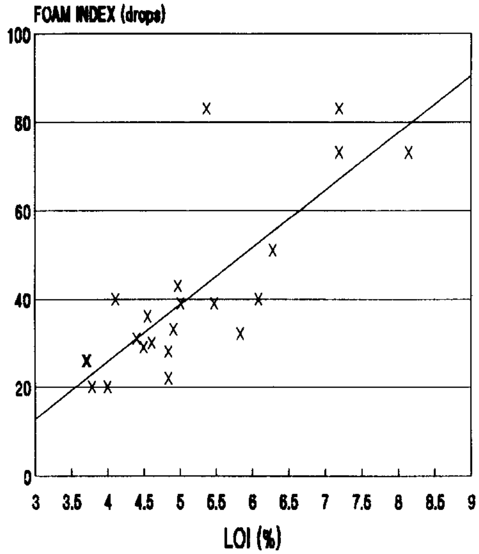

FIG. 5.
Foam index vs LOI quality control program at the source of FA sample “C”.

Of interest is the outlying data point (FA sample $\approx$5.3% LOI) which represented a particularly poor air entrained mortar sample. It’s DTA curve is compared with another with slightly lower LOI (5.0%) but with a "normal" foam index of 40, in Figure 6. The anomalous sample (high foam index of over 80) had a distinctly larger low temperature exotherm at 540C.

The exotherms at 540 and 590C corresponded to the production of CO_2, CO and H_2O, as determined by a mass spectrometer interfaced with the DTA. However, under a pure He atmosphere none of the samples expelled CO_2 upon heating to 900C. This eliminated the possibility that the lower temperature exotherm was due to decarbonation, and corroborated FTIR results.

Optical Microscopy. Carbons in fly ash are actually composed of several microscopically distinguishable forms. One type is called inertinite, and comprises particles that are more-or-less unaltered in appearance from the feed coal. The other types are particles that have melted, devolatilized and swelled to varying degrees, and re-solidified; these are figuratively referred to as "coke". They are subdivided based on degree of structural order: isotropic coke is disordered on the microscopic scale, as is inertinite, whereas anisotropic coke has more developed alignment of the molecules. Commercial adsorbent carbons are inherently isotropic, whereas carbons with negligible adsorptive capacity, such as petroleum coke, are generally highly anisotropic. It was hypothesized that fly ash containing a large proportion of isotropic coke and inertinite has a greater adsorptive capacity for air entraining reagent than fly ash with a greater proportion of anisotropic coke.

The results of microscopical analysis of the carbon enriched fractions and as-received FA’s are shown in Table 4. Samples "C_1" and "C_2" generally comprised a larger proportion of isotropic coke and a correspondingly smaller amount of the anisotropic species. They also contained a slightly larger amount of inertinite compared to sample A or B. This was par-

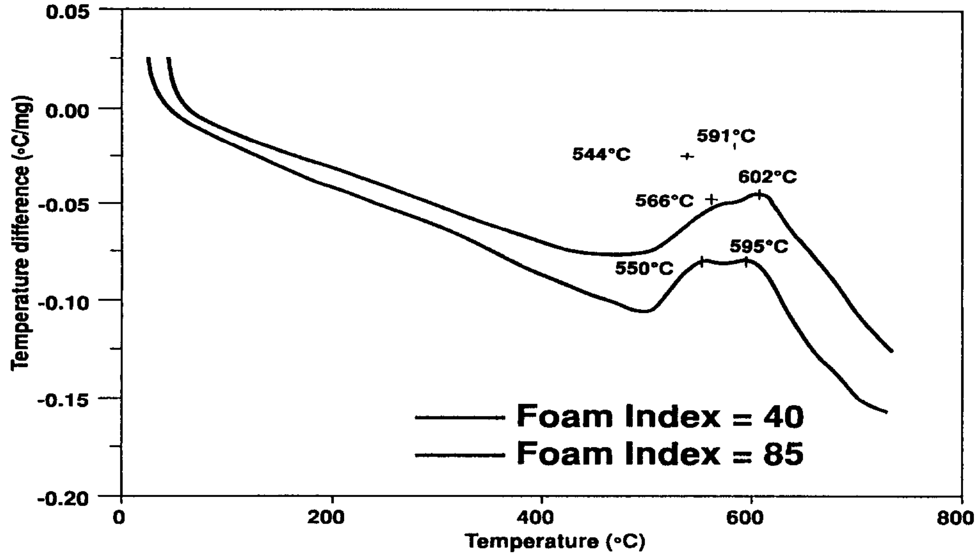

FIG. 6.

DTA plots of anomalous FA (LOI = 5.0%) and another with higher LOI but normal foam index of 40. Note the difference in the carbon exotherms.

ticularly evident in the high-carbon fractions where the high carbon content led to statistically more reliable determinations. The samples' isotropic/anisotropic coke ratio illustrated a trend consistent with their demand for AEA's as follows:

$$C_1>C_2>B>A$$

In order to further investigate the relationship between isotropic/anisotropic carbon ratio of FA and air entrainment properties, two additional FA samples were selected. These samples referred to as "D" and "E" had previously been classified as having distinctly different isotropic/anisotropic coke ratios, 26 for E versus 0.6 for D. The mortar air entrainment results, along with their respective isotropic/anisotropic coke ratios, presented in Figure 4 again illustrate that the sample with the highest isotropic carbon content has the greatest impact on air entrainment. Longer mixing times appears to increase the demand still further when the isotropic/anisotropic coke ratio is high.

Liquid Phase Adsorption. Liquid phase adsorption of a commercial AEA (DDBS based) monitored over a period of time (Figure 7) clearly demonstrates ash "A" and "C" as having markedly different adsorption capacities for the same AEA. Sample "A" produced a profile (within the limits of this semiquantitative method) which quickly reached it's initial dosage concentration and then gradually depleted over approximately one hour. At the lower dosage, the slope of the concentration curve was slightly reduced at early ages (prior to the maximum), which can be related to competition between "adsorption" and the "mixing and transport process" occurring within the test cell. In contrast, the adsorption capacity of

TABLE 4

Point Count Results for Carbon in Different Fractions of FA Samples

Sample (LOI %)	**Isotropic Coke (Vol. %)**	**Anisotropic Coke (Vol. %)**	**Inertinite (Vol. %)**	**Isotropic/ Anisotropic (Vol. %)**
A (3.8)	1.8 ± 0.6	2.6 ± 0.2	0.3 ± 0.1	0.69
A (22.0)	14.5 ± 1.4	19.2 ± 0.6	2.9 ± 0.8	0.76
B (4.7)	1.9 ± 0.9	2.5 ± 0.3	0.7 ± 0.1	0.76
B (19.5)	14.2 ± 2.0	14.3 ± 2.8	3.2 ± 0.6	0.94
C_1 (3.0)	1.6 ± 0.4	1.9 ± 0.7	0.6 ± 0.2	0.84
C_1 (19.4)	19.9 ± 3.9	15.5 ± 5.7	4.4 ± 0.5	1.28
C_2 (3.9)	1.9 ± 0.7	2.3 ± 0.8	0.7 ± 0.1	0.83
C_2 (20.5)	15.1 ± 2.3	12.2 ± 2.4	4.5 ± 0.1	1.24

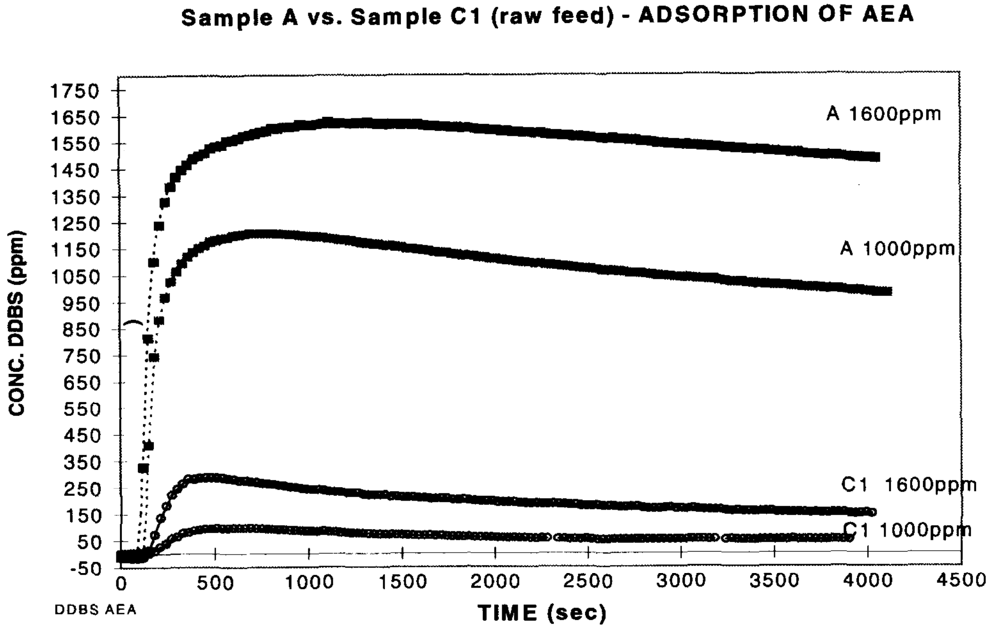

FIG. 7.

Liquid adsorption plots of as-received FA samples A and C_1 as a function of time at two AEA (DDBS) dosages. The AEA was DDBS.

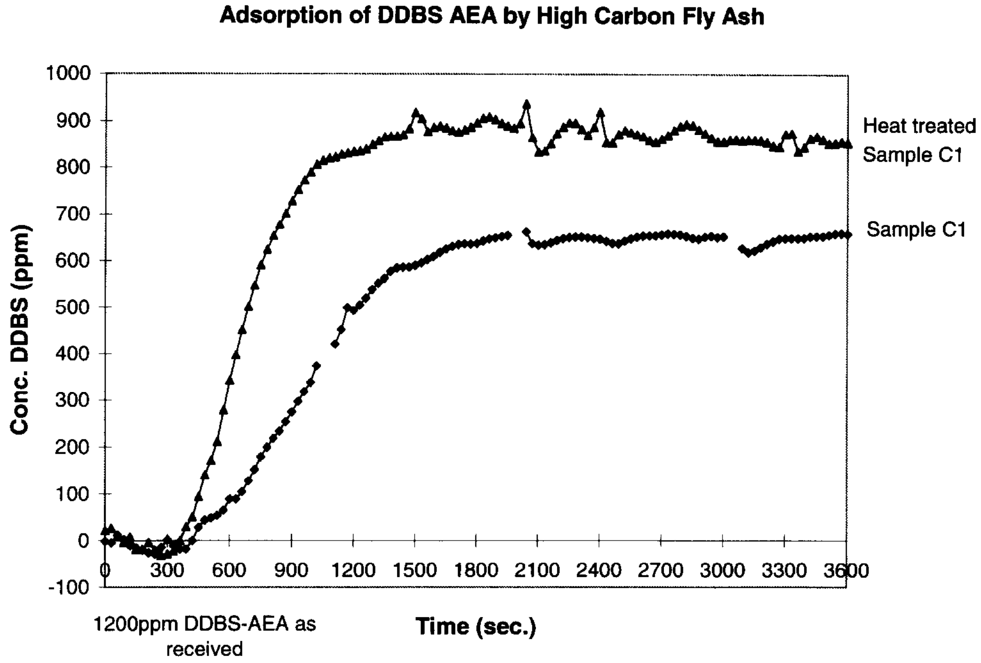

FIG. 8.

Liquid adsorption curves of high-carbon fractions of unheated C_1 and heat-treated C_1 to remove the amorphous carbon phase.

sample "C_1" was significantly stronger as evidenced by the lower maximum solution concentration achieved (by a factor of 10^3), and the greater effect on the initial slope. Furthermore, this strong rate of adsorption continued over an extended time period.

Figure 8 shows the liquid adsorption profiles of two high-carbon fractions of the same sample "C_1". One of these fractions was carefully ignited to 545°C to remove the amorphous carbon phase yet retain the crystalline carbon; this was subsequently confirmed by thermal analysis. The adsorption test was performed at constant carbon contents. The increase in AEA concentration in solution for the ignited sample represents a lower adsorption capacity of this carbon species, thus confirming the results of the previous experiment. Comparison of Figures 7 and 8 also suggests that it is mostly the carbonaceous constituent in FA which is responsible for adsorbing the AEA.

Vapor Phase Adsorption. Table 5 clearly illustrates that although all four high-carbon fractions had the same affinity for non-polar carbon tetrachloride, samples "C_1", and "C_2" had a definite higher adsorption capacity for polar acetone. Since surfactants in AEA are also polar compounds, it can be surmised that this carbon species behaves similarly when it comes in contact with AEA.

Conclusions

This study has demonstrated the inadequacy of LOI as an indicator of FA's air entraining performance. The air entraining properties of the fly ashes studied here varied significantly

TABLE 5

Vapor Phase Adsorption of High-Carbon Fractions of FA's

Sample ID	**LOI (%)**	**CCl_4 (cc/g) Total**	**CCl_4 (cc/g) (LOI Basis)**	**C_3H_6O (cc/g) (Total)**	**C_3H_6O (cc/g) (LOI Basis)**
A	20.3	0.003	0.015	0.003	0.015
B	19.5	0.003	0.015	0.003	0.015
C_1	19.4	0.004	0.021	0.011	0.054
C_2	20.5	0.004	0.020	0.010	0.049

in spite of their similar LOI values, and can be related to the adsorption properties of the carbon species present. Whereas BET analysis revealed that the samples had similar specific surface areas, liquid and vapor phase adsorption tests clearly defined differences in adsorption capacity. These differences correspond to differences in carbon forms distribution; an inverse relationship was observed between air entraining performance and the isotropic (amorphous)/anisotropic (crystalline) carbon ratio. The existence of several types of fly ash carbon was also suggested by thermal analysis, based on gasification reactivity. A lower temperature exothermic peak is more prominent in fly ashes exhibiting poorer air entrainment performance, and is possibly produced from isotropic, disordered carbon that is more reactive to oxygen than anisotropic coke. Chemical analysis established that the carbonaceous material in those fly ashes exhibiting a higher demand for AEA also has a relatively high oxygen content. It is proposed that the majority of this oxygen is in the isotropic coke, and possibly inertinite, and provides more polar sites on these carbons compared to the anisotropic coke. Furthermore, an overall smaller crystallite size and random orientation of the optically isotropic carbon may result in the exposure more aromatic edge sites with valence electrons available for bonding. Therefore, the surface chemistry and structure of this disordered carbon imparts a greater "active surface area" for polar compounds such as AEA's, and is responsible for it's' enhanced reactivity toward these reagents. This phenomenon directly contributes to the higher adsorption capacity of some carbon in fly ash for AEA's even at comparable LOI's.

Research is in progress to further evaluate the influence of carbon specific surface area and chemistry for a wide variety of FA's. Studies along these lines are crucial to properly define FA's potential to interact with different types and dosages of AEA.

Acknowledgments

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