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INVESTIGATION OF FLY ASH CARBON BY THERMAL ANALYSIS AND OPTICAL MICROSCOPY

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ABSTRACT

A previous study investigated various fly ashes that had comparable loss on ignition values, but significant differences with respect to air entrainment performance. Thermal analysis data suggested that a poorly performing fly ash, with respect to air entrainment, contained a higher proportion of carbon that gasifies (oxidizes) at comparatively low temperatures. A relatively high abundance of isotropic carbon was identified in the poor-performing ash using optical microscopy. The present investigation examined a larger collection of fly ash samples to determine if thermal analysis could be used as a prognostic tool for fly ash performance. An attempt was made to correlate mortar air and foam index values for each sample with differential thermal analysis (DTA) data. Optical microscopy and BET surface area analysis were used as supportive techniques. No clear relationship could be established with the thermal or optical methods, although fly ash performance did correlate well with BET surface area. A low temperature component of the DTA exotherms was considered to be a function of inorganic catalytic species that reside on the carbon surface and lower the ignition temperature. *© 1998 Elsevier Science Ltd*

Introduction

In a previous paper the present authors reported a study of four fly ashes that had been found to affect concrete air entrainment in a manner inconsistent with their respective loss on ignition values (1). Whilst BET analysis revealed that the samples had similar specific surface areas, liquid and vapor phase adsorption tests clearly defined differences in adsorption capacity. The ash that performed the least satisfactorily with regard to air entrainment in mortar exhibited the highest adsorption capacity for a polar dodecylbenzylsulfate-based air-entraining admixture (AEA) in the liquid phase and for polar acetone in the vapor phase. Nonpolar carbon tetrachloride vapor was adsorbed equally by all ashes.

Differential thermal analysis (DTA) conducted in a helium/oxygen atmosphere indicated

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that the poorly-performing ashes produced two distinct exothermic peaks (as a function of temperature), while the better performing ashes produced only one, higher temperature peak. It was suggested that the lower temperature exothermic peak represented a more easily-combusted, structurally disordered, isotropic form of carbon, while the higher temperature peak represented a more ordered, anisotropic form. The worst performing fly ashes were also determined by microscopy to contain a higher proportion of optically isotropic carbon.

Chemical analysis revealed that those ashes exhibiting a higher affinity for AEA had a higher concentration of oxygen in their carbonaceous component. It was proposed that the majority of oxygen resided in the isotropic carbon forms and provided more polar sites for adsorption of polar compounds such as AEAs. It was further hypothesized that the smaller crystallite size and random orientation in the isotropic carbon could provide a more active surface for adsorption. It was concluded that the surface chemistry, as well as surface area, could impart differing adsorption characteristics to fly ash carbon, resulting in variations in behavior between ashes even at comparable LOI values.

Both optical microscopy and thermal analysis appeared to have potential for identifying detrimental forms of carbon in fly ash. Thermal analysis was particularly intriguing because its relative speed and ease of operation would be appropriate for an improved method of fly ash quality control testing. Optical microscopy, with its more time consuming point-count procedure, was deemed more appropriate for research purposes.

Based on the foregoing, an investigation was initiated to conduct thermal analysis on a larger collection of samples, originating from the utility source that produces fly ash containing the highly adsorptive carbon discussed above. The objective was to determine if DTA could be used as a quality control technique providing insight into fly ash carbon activity. If the DTA exothermic peak shapes were in fact a function of carbon forms, it was expected that information on the cause of the air entrainment performance would also be collected.

Experimental Methods

Materials

Fly ash was collected from a single source over a period of several months. The majority of samples were first tested using a foam index (FI) procedure similar to that described by Dodson (2), except that 25% of the cement was replaced with the fly ash sample.

Samples that produced a range of FI values at comparable LOIs were selected for further testing of performance in air-entrained mortar. The admixture used was a commercially available air-entraining admixture, Monex Air 30® after dilution to 1:10.

Methods

Mortar was made with Ottawa sand and a low-C_3A, low-alkali cement. The majority of testing was performed by maintaining a constant cement content of 375 grams and varying the fly ash content to maintain a constant quantity of 6 grams of carbon (assumed, based on LOI) in the mixture. The total paste volume was maintained constant by varying the sand content to account for changes in fly ash volume. The water content of the mixtures was

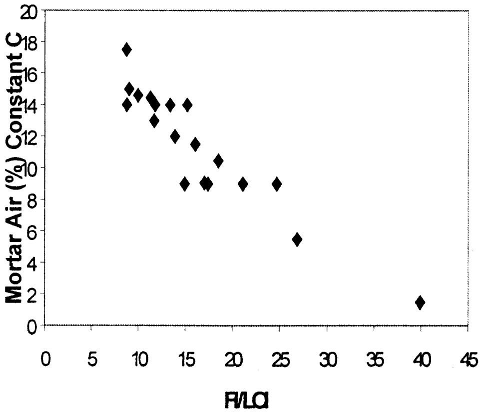

FIG. 1.
Mortar air with a constant carbon mass (6 g) vs. foam index/LOI.

adjusted to maintain a flow of 100 ± 5%. The mixtures were dosed with a constant volume of AEA.

Mixing was accomplished with a Hobart mixer. The volume of mortar air was determined by first calculating the theoretical density of the mixture based on the proportioning of the constituents and their respective specific gravities. The theoretical density was used to calculate the mass of the theoretical air-free mixture that would occupy 400 mL of volume. Next, the mass of the actual test mixture occupying the same volume was experimentally determined by transferring the mixture to a 400 mL brass cup and weighing. The difference in the theoretical and experimental mass was converted to volume as a percentage.

Differential thermal analysis (DTA) and thermogravimetric analyses (TGA) were conducted on a Seiko 320 simultaneous DTA/TGA analyzer. After optimization, the operating parameters were set at a 20°C/min. heating rate with a sweep gas composed of 90% helium and 10% oxygen at a flow of 200 ml/min. Approximately 20–25 mg of each sample was heated to a maximum temperature of 900°C. The thermal analyzer was connected to a quadrapole mass spectrometer for identification of the evolved gasses.

Specific surface area for each fly ash sample was determined from multi-point BET plots of nitrogen adsorption data obtained at 77K using a Quantachrome Automated Gas Adsorption System. The methodology for the microscopical point-count analysis of carbon forms in fly ash was previously described in detail (1). Loss on ignition was determined based on methods described in ASTM C311.

Results and Discussion

Mortar Testing

Comparison of the foam index, normalized to carbon content (FI/LOI), with mortar air (constant carbon) produced with a constant dosage of AEA, provides good correlation (Figure 1). The lack of strong correlation between LOI and mortar air (constant mass)

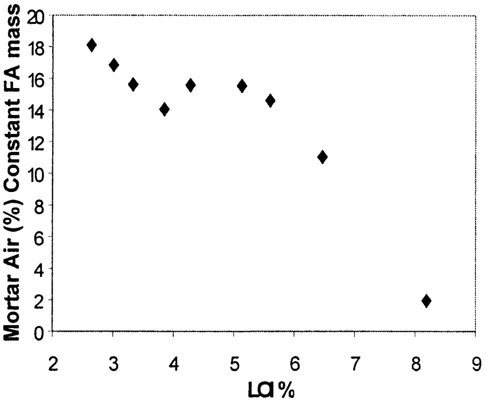

FIG. 2.
Mortar air with a constant fly ash mass vs. LOI.

displayed in Figure 2 underscores the potential inadequacy of LOI as a sensitive indicator of fly ash performance, a conclusion reached by others (3,4). A plot of mortar air containing a constant carbon content (dosed with a constant AEA dosage) vs. LOI should theoretically produce a flat line with a single air content. Figure 3 shows this statement to be true over only a short LOI range (2.6–3.8%). Overall, the ashes with higher LOI values (4–6%) actually had less impact on the initial entrained air content at a fixed carbon concentration than lower LOI fly ashes.

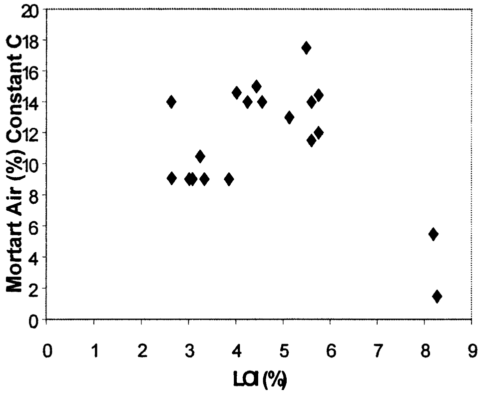

FIG. 3.
Mortar air with a constant carbon mass (6 g) vs. LOI.

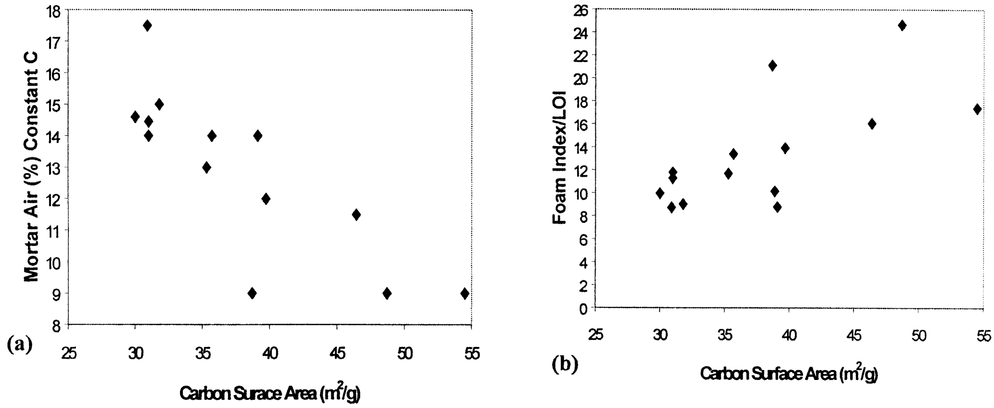

FIG. 4.
Mortar air constant carbon mass (6 g) vs. *a*) carbon surface area or *b*) foam index/LOI.

BET Analysis

The adsorption isotherms indicated that the samples were non-porous or macro-porous in nature. Comparisons of calculated carbon surface area (based on LOI) with mortar air (at constant carbon content), and FI/LOI as shown in Figures 4a and b mark clear trends. Figure 4b also identifies several fly ashes that have similar surface areas ($\sim$40 m^2/g), but have significantly different adsorption capacities (FI/LOI = 8 to 22).

The correlations in Figures 4a and b could possibly be improved by directly determining carbon content rather than using LOI as an indicator. However, it should be noted that the potential effects of carbon chemistry on AEA adsorption capacity cannot be elucidated using an inert gas such as N_2.

Thermal Analysis

The TGA weight loss was found to be about 0.5% (absolute) less than the corresponding LOI value. TGA weight loss plotted against DTA exotherm response produced a linear relationship with a y-intercept of essentially zero. These data, coupled with the fact that the exothermic reaction was associated primarily with CO_2 evolution, confirmed that the exotherm was produced from the oxidation, or gasification, of fly ash carbon. The DTA instrument was unable to precisely detect the exothermic reaction in fly ash samples with an LOI value of less than 0.5%.

Inspection of a typical DTA curve (Fig. 5a) reveals that the overall exothermic response of carbon gasification comprised three separate regions that were resolved as three individual, overlapping peaks by using a curve-fitting program. Each of the three determined peaks was integrated to obtain its proportion of the total exotherm. The data were then plotted against FI/LOI and mortar air content (at constant carbon) to ascertain if the exotherm peak distributions could predict fly ash performance. A plot of the lowest temperature peak area, normalized to 100%, vs. mortar performance is shown in Figure 6. It is evident from the

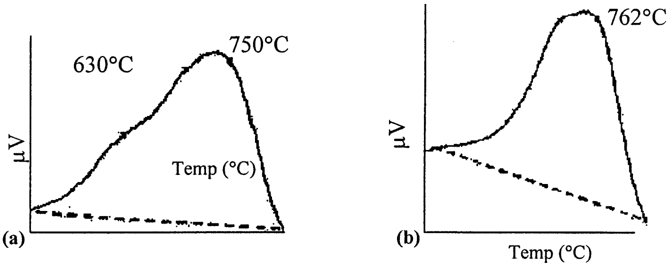

FIG. 5.
Differential thermal analysis exothermic peak profile of *a*) fly ash carbon or *b*) fly ash carbon after HCl wash.

graph that no correlation between these variables exists, and that the distribution of the resolved exothermic peaks bears little relation to the fly ash's performance.

Based on these results, it was concluded that DTA is not useful for predicting air entrainment performance of fly ash in concrete. Furthermore, it is apparent that the lower temperature DTA exothermic peak is not produced by the oxidation of a relatively adsorptive or "active" form of carbon. According to the literature, carbon gasification rates are primarily influenced by several factors: 1) concentration of active sites, 2) crystallinity and structure, 3) inorganic impurities, e.g., catalyst, and 4) diffusion of reactive gasses to active sites (5).

The working hypothesis, on which this study was established, assumed that the difference in the DTA exotherms were mainly a function of factors 1 and 2. Diffusion of reactive gasses was thought to be constant because particle size distribution, which had previously been found to be reasonably consistent among the samples tested, was expected to lead to

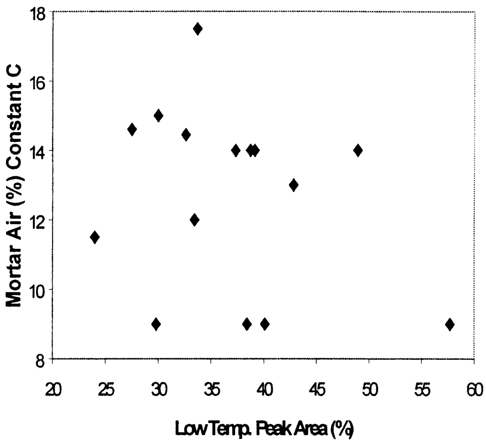

FIG. 6.
Mortar air at constant carbon mass (6 g) vs. low temperature DTA exothermic peak area (% of total peak).

relatively uniform packing. However, the possible influence of inorganic "impurities" warranted further study.

It is well established that iron oxides, and certain alkali- and alkaline earth metal salts can catalyze the oxidation of carbon (6–8). The influence of a catalyst on the DTA peaks produced in this study was investigated by acid washing (HCl 10% v/v) eleven of the previously characterized samples. Thermal analysis was conducted on the acid-washed samples for comparative purposes.

Significant concentrations of cations were extracted from each ash. Moreover, acid washing consistently reduced the low temperature exothermic peak, in most cases almost completely eliminating it (Figs. 5a and b).

Statistical analysis of the thermal data on the eleven samples found the following trends to be significant for the samples after acid washing: 1) TGA weight loss was increased and 2) low temperature peak area decreased.

Comparison of the off-gas composition, as determined by mass spectrometry, to the weight loss curves indicated that the majority of the weight loss after 500° was due to carbon oxidation. The general increase in TGA weight loss, and the DTA exotherm intensity, after HCl washing implies that the treatment removed mainly inorganic material and that the reduction in the low temperature peak area is not due to carbon loss.

Based on the above, it is proposed that the HCl washing altered the carbon surface, probably removing catalytic species such as calcium, magnesium and iron. The removal of the majority of the catalysts significantly raises the ignition temperature of a portion of the fly ash carbon, and thus reduces the proportion of the lower temperature exotherm region. The higher temperature "peaks" represent carbon not in contact with catalytic species and so are essentially unaffected by acid washing.

Optical Microscopy

Microscopy was utilized to classify the fly ash carbon population as comprising anisotropic coke, isotropic coke and inertinite. Inertinite represents material from the coal maceral inertinite that is more or less unaltered in appearance from feed coal. Coke has undergone, to various degrees, partial volatilization and swelling. Anisotropic coke is structurally ordered on the microscopic scale, while isotropic coke is disordered. Inertinite is also an isotropic form of carbon. Commercial adsorbents are inherently isotropic (9), whereas carbons with negligible adsorbent activity, such as petroleum coke, are generally highly anisotropic.

The results of the microscopic analysis are presented in Table 1. Glass is the predominant phase in all the samples with lesser amounts of quartz, mullite, spinel (also includes hematite), and carbon. To determine if the carbon form distribution relates to air entrainment performance, the isotropic carbon content (inertinite and isotropic coke) was divided by the total carbon content, and these values were compared with mortar air data obtained at a constant carbon content. The results, as depicted in Figure 7, show considerable scatter with only weak evidence of a relationship between isotropic carbon abundance and mortar air.

If a relationship exists between carbon structure and air entrainment performance, optical microscopy is unable to resolve it. One reason for this lies in the low carbon content in the fly ashes. Previous testing was performed on ashes in which the carbon had been concentrated by triboelectric means to approximately 20% (mass basis). Samples in this study generally had LOI values less than 6%, which makes it difficult to obtain statistically

TABLE 1
Results from microscopical point count analysis of fly ash.

Smp. I.D.	Glass vol. %	Mullite vol. %	Spinel vol. %	Quartz vol. %	Iso. coke vol. %	Aniso coke vol. %	Inertinite vol. %	Tot. C vol. %
K355	90.2	0.2	2.4	0.2	3.5	3.0	0.6	7.0
K356	90.6	0.2	1.6	0.0	4.0	2.8	0.8	7.6
K357	86.6	0.6	2.8	0.2	4.8	4.0	1.1	9.8
K358	92.6	0.2	2.2	0.0	1.5	2.6	0.9	5.0
K359	93.4	0.4	1.6	0.0	2.5	2.0	0.2	4.6
K360	89.6	0.4	2.4	1.0	2.8	3.6	0.3	6.6
K361	95.0	0.2	2.1	0.0	1.2	1.3	0.2	2.6
K362	95.4	0.0	1.8	0.0	1.5	1.1	0.2	2.8
K363	92.8	0.2	0.4	0.2	3.2	2.9	0.4	6.4
K364	90.4	0.2	1.8	0.6	3.5	3.2	0.3	7.0
K365	91.6	0.2	1.0	0.2	3.5	2.8	0.8	7.0
K366	96.0	0.0	0.8	0.2	1.7	1.1	0.3	3.0
K367	91.6	0.4	1.2	1.0	2.7	2.7	0.4	5.8
K368	96.6	0.0	1.4	0.0	1.0	0.8	0.3	2.0
K369	92.8	0.6	2.0	0.2	1.9	2.5	0.1	4.4
K370	93.6	0.2	1.0	1.0	1.9	2.0	0.4	4.2

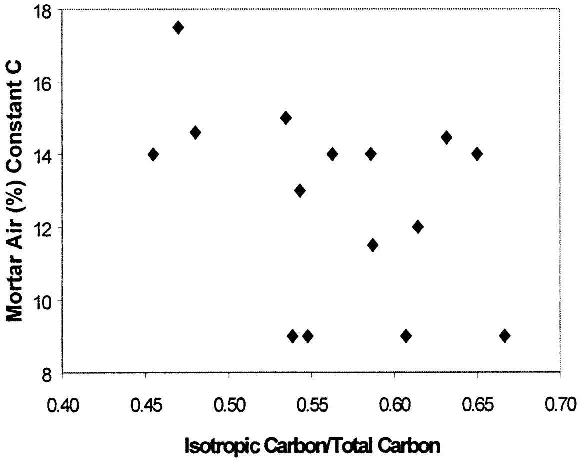

FIG. 7.
Mortar air constant carbon mass (6 g) vs. percent isotropic carbon.

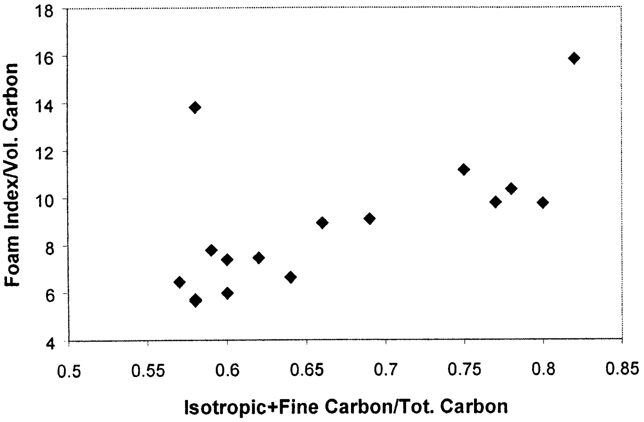

FIG. 8.
Foam index/carbon volume vs. fine carbon and isotropic carbon.

significant values. Another problem is one of scale. The optical microscope has a nominal resolution of about 0.3 μm, which dictates that anisotropic domains must be at least this size in order to be resolved. An optically isotropic carbon at this scale may in fact have a high degree of structural order on a smaller, macromolecular scale.

Resolution also became important with respect to detecting carbon in the fly ash. A plot of carbon volume, determined optically, vs. carbon mass (based on LOI) did not correlate as well as anticipated. The discrepancy was attributed to the existence of fine carbon ($<$1 μm), which is not easily detected microscopically. Gao et al. previously reported the detection of fine carbon and soot in fly ash and related it to high surface area and foam index values (10).

By assuming a reasonable "microscopical" density of 1.6 g/cm^3 for carbon and utilizing known densities for the other fly ash phases, the LOI yields were converted mathematically to a "true" volume-based carbon content. The optically determined carbon content was then subtracted from the calculated value to get an estimate of the volume fraction of fine carbon that was "overlooked" microscopically. When this inferred fine carbon plus isotropic carbon content is plotted vs. foam index normalized to calculated carbon volume (Figure 8), an improved correlation is obtained.

Conclusions

The primary conclusions from this work are:

1. The majority of BET nitrogen surface area resides in fly ash carbon particles. Fly ashes with comparable LOIs can have significantly different surface areas. Calculated carbon surface area correlates well with both mortar air and foam index results yielding an inverse and positive relationship, respectively. It should be noted that nitrogen adsorption is relatively insensitive to differences in carbon chemistry, which can also influence the adsorption of air entraining admixtures.
2. Differential thermal analysis was not found to be a useful prognostic tool for the

performance of fly ash in air entrained mortar. The hypothesis that the lower temperature region of the multi-peaked exotherm, produced during fly ash oxidation, represents highly adsorptive, isotropic carbon, was not substantiated in this study. No correlation between exothermic peak areas and performance was found.

3. Further study of the low temperature shoulder of the exotherm found that acid washing significantly reduced its area. Preliminary data suggests that this phenomenon is primarily related to the removal of catalytic species from the carbon surface which can lower the ignition temperature of the carbon.
4 Microscopical characterization of the forms of carbon in fly ash did not provide data that could be related to fly ash performance with respect to air entrainment. It is possible that a relation does exist but that there were not enough carbon particles per sample to produce statistically significant data. Optical microscopy did provide evidence that a significant portion of carbon in fly ash is sub-micron in size. Mortar air entrainment appeared to be reduced in proportion to the concentration of combined fine carbon and isotropic carbon.

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