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Combined Adsorption Isotherms for Measuring the Adsorption Capacity of Fly Ash in Concrete

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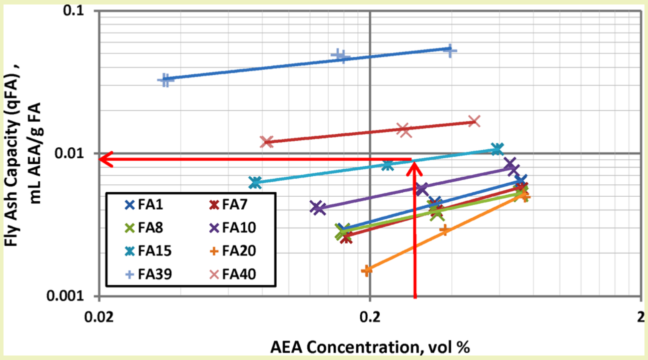
ABSTRACT: Fly ash, a solid waste generated from coal burning, can replace up to 70% of the cement in concrete and reduce environmental impact, cost of construction, and power generation. However, the lack of fly ash adsorption capacity measurement tools limits this type of fly ash beneficial utilization. This article presents the combined adsorption isotherms as a tool for the accurate measurement of the adsorption capacity of fly ash in concrete. The combined adsorption isotherms are simpler yet more accurate than the separate adsorption isotherms for quantifying the adsorption of air entraining admixtures (AEAs) by fly ash in concrete. Instead of performing two separate isotherms, one for cement and another for fly ash, enough mass of cement is added to all fly ash isotherm points to achieve full chemisorption. Blank isotherm points, consisting of the AEA and cement, determine the initial concentrations of AEA available for adsorption. Any AEA concentration reduction caused by the various masses of fly ash in the remainder isotherm points is considered physical adsorption. The difference between the two AEA concentrations is used to determine the adsorption capacity of the fly ash. This approach reduces the fly ash adsorption isotherm test procedure to one isotherm and provides a more simplified form of testing. It also eliminates the need to use judgment in determining the AEA partitioning coefficient from a multipoint cement isotherm. This paper presents the test development and application on Vinsol resin admixture with eight fly ashes. The results obtained from these isotherms were used to make AEA dose adjustment predictions to compensate for the AEA adsorption onto the fly ash for cement mortars and concrete with 25% fly ash replacement. All dose adjustments succeeded in producing the target air void content in cement mortars and concrete mixes.



KEYWORDS: *Fly ash, Concrete, Adsorption capacity, Adsorption isotherms, Air entraining, AEAs, Iodine number, Foam index*

INTRODUCTION

The cement and concrete industries are the main contributors to the beneficial utilization of fly ash.[1] Fly ash, if not beneficially utilized, becomes a costly waste and a burden on the environment and society.[2,3] Fly ash use in concrete is limited by the uncertainty of the fly ash quality, specifically the adsorption capacity of fly ash as its carbon fraction readily adsorbs the concrete organic admixtures such as air entraining admixtures (AESs),[4−9] which consequently alters the final properties of the concrete. The uncertainty of the fly ash quality results from the lack of adequate fly ash adsorption capacity testing tools and methods.[4−9] The development of such testing methods will increase the confidence in the quality of fly ash and facilitate further utilization of ashes otherwise considered risky for use.

Air entraining admixtures are natural or synthetic organic surfactants and common additives to concrete mixtures. These admixtures reduce the surface tension at the air−water interface and "entrain" or capture air from mixing and hydration reactions forming air voids in hardened concrete where migratory water can safely expand during freezing temperatures.[7,10−12] The most common active chemical used in AEAs is Vinsol resin extracted from wood; however, AEAs could instead be made from alpha olefin sulfonate, benzene sulfonate, resin/rosin, and fatty acids or any combination of such chemicals.

Fly ash adsorption capacity indicators such as the loss on ignition test (LOI)[13] and its modifications[14−16] and the various procedures of the foam index test[17−19] provide a relative measure of the adsorption capacity of fly ash. However, these tests do not provide a direct or accurate measurement of the fly ash adsorption capacity. The carbon content of fly ash is often determined by the LOI test according to ASTM C311-11b[13] where 1 g of fly ash is burned in a muffle furnace for 15 min at 750 ± 50 °C. In the LOI test, the decomposition of carbonate ($CaCO_3$) and portlandite $Ca(OH)_2$ and removal of water bound in clay minerals, in addition to combustion of carbon, may contribute to the mass loss observed after burning.

The LOI measurement of the carbon content can have a percent error ranging from 1% to 75%.[16] This is largely

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Table 1. Fly Ash Properties

fly ash	SiO_2 (wt %)	Al_2O_3 (wt %)	Fe_2O_3(wt %)	Total %: SiO_2, Al_2O_3, Fe_2O_3	CaO(wt %)	SO_3(wt %)	MgO(wt %)	LOI(wt %)
1	60.1	29.9	2.7	92.7	0.9	NA	NA	0.87
7	53.94	27.66	8.29	89.89	1.45	0.08	1.15	2.25
8	60.85	25.7	4.66	91.2	3.46	0.29	1.12	0.17
10	45.95	23.61	22.31	91.88	1.28	0.77	0.99	1.26
15	58.92	16.17	4.71	79.81	10.24	0.86	3.13	1.5
20	44.81	23.08	9.51	77.4	13.58	0.96	2.97	0.39
39	39.6	20	12.7	72.3	9.1	1.1	2.28	10.49
40	53.9	26.3	6.24	86.4	4	0.2	0.86	3.35

dependent on the composition of fly ash, and even without analytical error, the correlation between LOI and adsorption is not assured. The adsorption capacity of fly ash is governed not only by the amount of carbon present but also by other properties such as the carbon particle size and porosity, surface chemistry, and degree of liberation for each carbon particle. The use of carbon content as estimated by LOI is not an accurate measurement of either the carbon content or the adsorption capacity of fly ash for various organic compounds such as AEAs.

The fly ash adsorption capacity measurement for the purpose of characterization and specification can be accurately determined using the fly ash iodine number test.[20,21] However, this test utilizes iodine for measurement and therefore is unable to directly quantify the adsorption of AEAs by fly ash. A direct measurement of the fly ash adsorption capacity of AEAs was reported by Ahmed[20] and Ahmed et al.[22] using direct adsorption isotherms. These isotherms provide a direct measurement of the fly ash adsorption capacity of AEAs and enable users to determine the exact volume of AEAs adsorbed by the fly ash in a fly ash-containing concrete mix. Consequently, a dose adjustment can be made to compensate for the adsorbed volume of the AEA, which ultimately solves the fly ash−AEA adsorption problem in concrete.

The direct adsorption isotherms procedure requires performing two sets of isotherms. The first set is performed using AEA and cement to determine the AEA partitioning coefficient and the initial aqueous-phase concentration of the AEA that is available for physical adsorption by the fly ash. The second set of isotherms, which exhibits higher levels of adsorption than the first set, is performed using the AEA and fly ash to determine the adsorption capacity of the fly ash. The initial AEA aqueous concentration used was determined from the first set.[20,22]

In this paper, a simplified, yet more accurate, fly ash adsorption isotherm procedure is presented. The simplification is due to the use of only one set of combined cement−fly ash isotherms instead of two. The improved accuracy resulted from the elimination of the chemisorption process completion uncertainty.

■ MATERIALS AND METHODS

Fly ash samples and AEA type were chosen by preliminary testing and survey results. Measurement of AEA concentration and basic isotherm test setup are also discussed. Most importantly, methodology for discerning between chemisorption of AEA solution by cement, COD of solid materials, and fly ash adsorption of AEA is discussed here. These are necessary parameters included in the mass balance of the isotherm.

Fly ash and AEA. Forty fly ash samples were obtained from coal-fired power plants across the United States and characterized by LOI because it was the most closely related existing test that could provide an initial measurement and some initial indication of carbon content. Eight fly ash samples, with LOIs ranging from 0.17% to 10.49%, were selected from these 40 to develop these isotherms. These eight samples represented the range of LOI presented among the 40 fly ash samples. Table 1 shows some of the properties of the fly ash samples used in this study.[21,23] Common AEAs were chosen from specifications provided from a nationwide survey. MB VR, a Vinsol resin AEA manufactured by BASF, was the most commonly identified AEA and was utilized to develop the combined isotherm experimental procedure.

Measurement of AEA Concentration. The chemical oxygen demand (COD) test was used to measure the concentration of the AEA. A HACH COD kit (TNT821 and TNT 822) along with a HACH spectrophotometer DR5000 were utilized for this purpose. More details regarding the utilization of COD for the measurement of AEA concentrations are reported by Ahmed.[20]

Isotherm Points Setup. All isotherm tests were performed in 250 mL Erlenmeyer flasks. For each isotherm point, a volume of 200 mL of the solution (water or AEA solution), measured using a volumetric flask, was equilibrated with the adsorbent (cement and/or fly ash) for 1 h at 20 °C. The contents of the flask were kept mixed using a magnetic stirrer. After equilibration, the mixture was filtered using grade 1, 11 μm, 90 mm diameter, cellulose, Whatman qualitative filter paper in a vacuum apparatus. The volume of filtrate was measured using a graduated cylinder, and the COD measurements of the filtrate were taken. The same procedure was followed for the cement blanks with the three AEA concentrations and for the COD of solid materials (fly ash or cement) with distilled water.

Cement Blanks. At least two blanks with 20 g of cement and no fly ash were performed for each initial AEA concentration. The goal of these blanks was to quantify the chemisorption demand of the cement and to determine the partitioning coefficient at that AEA concentration. The chemisorption was determined by measuring the AEA aqueous-phase concentration left in solution after equilibrating the AEA solution with cement. This AEA aqueous-phase concentration was considered to be the initial AEA concentration available for adsorption. For the i^{th} AEA concentration, $COD_{Blank,i}$ was determined by performing an isotherm point using 20 g of cement with 200 mL of the i^{th} AEA concentration. The measured COD of the filtrate was simply $COD_{Blank,i}$.

COD of Solid Materials (CODs). When in solution, both cement and fly ash contain some level of soluble oxidizable materials that contribute to the COD values of the isotherm points, and because COD is used to represent the concentration of the AEA, the COD contribution of the solid materials (fly ash and cement) must be subtracted from the total COD measurement. To determine the COD contribution caused by the presence of cement, 20 g of cement was equilibrated with 200 mL of distilled water for 1 h. The measured filtrate COD, called COD_{cement} (mg/L), was multiplied by the volume of water used (0.2 L) and divided by the mass of cement used (20 g) to determine $COD_{s,cement}$ (mg COD/g). The same procedure was repeated with the fly ash instead of cement, and COD_{FA} and $COD_{s,FA}$ was determined.

$COD_{s,cement}$ and $COD_{s,FA}$ represented the background COD released by these solid materials. This background COD was subtracted from the COD value of any AEA solution wherever fly ash and/or cement were present to obtain the net AEA concentration.

Fly Ash Isotherm Points. In the finalized test procedure, three different AEA concentrations were used to generate a three-point isotherm that measures the change in AEA concentration due to the adsorption by fly ash. For the first isotherm point and the first AEA concentration, 20 g of cement and an amount of fly ash between 10 and 40 g of fly ash were used. If the resulting AEA concentration of the fly ash isotherm point dropped to near the lower detection limit of the HACH COD test measurement system, the isotherm point was repeated using less fly ash. If the resulting fly ash isotherm point AEA concentration was more than 80% of the AEA concentration of the cement−-AEA blank filtrate, the isotherm point was repeated using more mass of fly ash, up to a maximum of 100 g. The same procedure was repeated with the other two AEA concentrations to obtain a three-point isotherm for three different AEA concentrations.

RESULTS AND DISCUSSIONS

This method is based on providing enough mass of cement to chemisorb all the chemisorbable portion of the AEA solution in every isotherm point in all AEA concentrations. A cement−AEA blank of every AEA solution concentration utilized is required to determine the AEA aqueous-phase concentration after chemisorption at that AEA solution concentration. Any reduction of the AEA aqueous-phase concentration in any fly ash−cement isotherm point below the cement−AEA blank concentration is then considered loss due to adsorption by that mass of fly ash.

Test Development and Optimization. Chemisorption fulfillment was important so as not to interfere with fly ash physical adsorption. Chemisorption tests were performed to obtain the correct amount of AEA susceptible to physical adsorption. Next, tests with different amounts of fly ash were performed with different AEA concentrations to quantify the physical adsorption. Combinations were limited to the measurable range within the HACH COD kit and HACH spectrophotometer DR5000 system.

This section describes the development of the test, determination of the appropriate mass of cement to achieve full AEA chemisorption, and selection of the masses of fly ash and AEA concentrations.

Mass of Cement in the Isotherm Points. Previous research showed that for several commercially available AEAs less than 10 g of cement in all isotherm points was enough to achieve full chemisorption and to bring the AEA aqueous-phase concentration to a constant level.[20,22] Fly ash adsorption isotherms with 10, 20, and 30 g of cement combined with various masses of fly ash were performed to determine the appropriate mass of cement to fulfill the chemisorption requirements of cement−fly ash isotherm points.

The results of these combined isotherms are illustrated in Figure 1. MB VR at a concentration of 0.8 vol %, which is a relatively high concentration, was utilized in this set of isotherms to ensure that the mass of cement utilized could achieve full chemisorption at high AEA concentrations. The three masses of cement exhibited the same behavior and produced identical results within the experimental error of the COD test at this AEA concentration, which confirms the findings of Ahmed et al.[22] However, as a conservative measure, 20 g of cement was chosen to be the standard amount of cement added to each isotherm point to ensure the availability of at least twice the amount of cement needed to achieve full chemisorption. Twenty grams of cement was used with all remainder isotherms in this study.

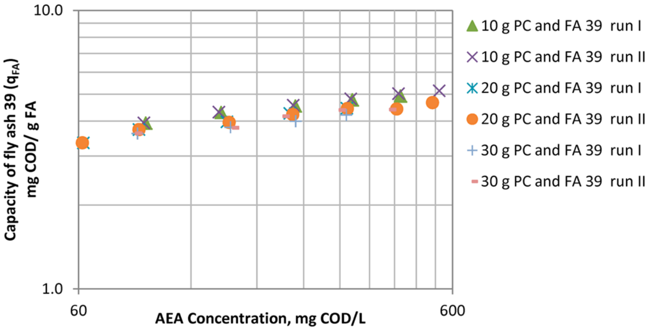

Figure 1. Combined adsorption isotherm results of 0.8% MB VR, fly ash 39, and various masses of Portland cement.

Mass of Fly Ash. The mass of fly ash in any isotherm point has to be large enough to adsorb some of the AEA and produce a measurable reduction in the AEA aqueous-phase concentration. Also, fly ash absorbs water, and even though this absorbed water was considered in the calculations, it was important to minimize the water volume change to minimize the consequent impact on the AEA concentration. Fly ash mass of 10−40 g was found to be sufficient to produce measurable change in the aqueous AEA concentrations. The sufficient mass of fly ash was dependent on two factors: the carbon content of the fly ash and the concentration of the AEA solution. For example, 40 g of fly ash 20 (0.39% LOI) was enough to produce change in MB VR solution concentrations of 0.2, 0.4, and 0.8 vol % without driving the MB VR concentration to near the COD test lower detection limits. This is because fly ash 20 has little carbon content; therefore, relatively large quantities are needed to adsorb the AEA significantly. On the other hand, 40 g of fly ash 40 (3.35 wt % LOI) drove the 0.2 vol % MB VR concentration to near the COD test lower detection limits because that mass of fly ash 40 has enough carbon content to adsorb almost all the AEA available in the 200 mL of the 0.2% AEA concentration. On the basis of that, 20 g should be used with the 0.2 vol % AEA concentration and 40 g can be used with 0.4 and 0.8 vol % AEA concentrations. For high carbon fly ash such as fly ash 39 (10.49 wt % LOI), 5 g should be used with the 0.2 vol %, 10 g with the 0.4 vol %, and 20 g with the 0.8 vol % MB VR concentration because fly ash 39 has a very high carbon content. A relatively small mass of it can adsorb large quantities of the AEA. Results are illustrated in Table 2.

In general, if the equilibrated concentration of the AEA drops to near the lower detection limits of the COD test, the isotherm point should be repeated using less mass of fly ash. Also, if the drop in AEA concentration was less than 20%, the isotherm point should be repeated using more mass of fly ash, up to a maximum of 100 g.

AEA Solution Concentrations. Due to the relatively low adsorption capacity of some fly ashes, it is sometimes impossible to obtain a good representative isotherm by using only one initial AEA concentration. Therefore, this combined isotherm procedure required the utilization of three different AEA concentrations in order to obtain an isotherm that represents a wide range of practical AEA concentrations. It is recommended to use the average practical AEA concentration used by the concrete industry for the first set of isotherms, and then use 50% of that for the second set and 200% for the third set of isotherms. This produced a three-point isotherm that covered all the possible practical concentrations.

Combination Isotherm Calculations. Mass balances of isotherms were used to calculate all parameters using eqs 1−6.[20,23] The amount of AEA available for adsorption, for each

Table 2. Fly Ash Properties

fly ash	LOI (wt %)	FA (g)	0.2 vol % MB VR	0.4 vol % MB VR	0.8 vol % MB VR
20	0.39	20	x	x	x
		40	measurable/detectable change	measurable/detectable change	measurable/detectable change
40	3.35	20	measurable/detectable change	x	x
		40	x	measurable/detectable change	measurable/detectable change
39	10.49	5	measurable/detectable change	measurable/detectable change	
		20	x	x	measurable/detectable change

initial AEA concentration, was determined from the cement−AEA blanks using eq 1.

$$\mathrm{COD}_{\mathrm{available},i} = \mathrm{COD}_{\mathrm{blank},i} \times V_{\mathrm{f\,blank},i} - \mathrm{COD}_{\mathrm{s,cement}} \times M_{\mathrm{cement}} \tag{1}$$

where, COD $_{\mathrm{available},i}$ = available mass of AEA for adsorption for the i^{th} initial concentration, mg COD. COD $_{\mathrm{blank},i}$ = COD of the cement−AEA blank (isotherm performed in AEA solution) with the i^{th} initial AEA concentration, mg/L. $V_{\mathrm{f\ blank},i}$ = volume of the filtrate of the cement blank for the i^{th} initial concentration, L. COD $_{\mathrm{s,cement}}$ = COD released by cement in water, mg (COD)/g cement. M $_{\mathrm{cement}}$ = mass of the cement used in the blank, g.

For each fly ash isotherm point, the remaining mass of AEA in solution after equilibration with cement and fly ash can be determined from eq 2.

$$\mathrm{COD}_{\mathrm{final},i} = \mathrm{COD}_{\mathrm{eq},i} \times V_{\mathrm{f},i} - \mathrm{COD}_{\mathrm{s,FA}} \times M_{\mathrm{FA}} - \mathrm{COD}_{\mathrm{s,cement}} \times M_{\mathrm{cement}} \tag{2}$$

where $\mathrm{COD}_{\mathrm{final},i}$ = mass of AEA COD remaining in solution after equilibration with cement and fly ash, mg. $\mathrm{COD}_{\mathrm{eq},i}$ = COD of the equilibrated isotherm point, mg/L. $V_{\mathrm{f},i}$ = volume of equilibrated isotherm point filtrate, L. COD $_{\mathrm{s,FA}}$ = COD released into solution by the fly ash, mg/g. M_{FA} = mass of fly ash used in the isotherm point, g.

The capacity at each fly ash isotherm point is the AEA mass COD adsorbed divided by the mass of fly ash used in the isotherm point. The capacity (adsorption capacity) can be determined from eq 3.

$$q_{\mathrm{FA},i} = (\mathrm{COD}_{\mathrm{available},i} - \mathrm{COD}_{\mathrm{final},i})/M_{\mathrm{FA}} \tag{3}$$

where q $_{\mathrm{FA},i}$ = fly ash capacity for the isotherm point, mg (COD)/g (FA).

At this point, the capacity at the i^{th} AEA concentration is determined, and repeating the procedure using two more AEA concentrations will be enough to produce the required three-point isotherm. However, the capacity has units of mg (COD)/g (FA), and the AEA concentration is in mg/L COD, which are not typical units used in the concrete industry. The next steps can be performed to convert the capacity and concentration units to typical units used in the industry, and for this purpose, the AEA partitioning coefficient (PC_i) has to be used.

The AEA partitioning coefficient (PC_i) is the concentration of AEA remaining after full chemisorption is achieved by cement divided by the initial concentration of the AEA before chemisorption.[20,22] It can also be defined as the portion of the AEA available for adsorption. The AEA partitioning coefficient is concentration dependent and must be determined for each initial AEA concentration used. The AEA partitioning coefficient can be determined from the COD of the cement−AEA blank and the COD of the AEA solution using eq 4.

$$\text{Partioning Coefficient}_i\ (\mathrm{PC}_i) = \frac{\mathrm{COD}_{\mathrm{blank},i} - \mathrm{COD}_{\mathrm{cement}}}{\mathrm{COD}_{\mathrm{AEA},i}} \tag{4}$$

where COD $_{\mathrm{AEA},i}$ = COD of the AEA solution for the i^{th} initial concentration, mg/L. COD $_{\mathrm{cement}}$ = COD of 20 g cement in 200 mL distilled water.

Equation 5 can be used to convert the capacity form mg COD/g FA to mL AEA/g FA. The conversion factor can be obtained from the COD measurement of the AEA solution.

$$q_{\mathrm{FA},i}\left(\frac{\mathrm{mL}_{\mathrm{AEA}}}{\mathrm{g}_{\mathrm{FA}}}\right) = q_{\mathrm{FA},i}\left(\frac{\mathrm{mg}_{\mathrm{COD}}}{\mathrm{g}_{\mathrm{FA}}}\right) \div \left[\mathrm{PC}_i \times \frac{\mathrm{COD}_{\mathrm{AEA},i}}{\mathrm{AEA}\ i^{\mathrm{th}}\mathrm{conc.}}\right] \tag{5}$$

where AEA i^{th} conc. = i^{th} initial concentration of the AEA, mL/L.

The AEA aqueous-phase concentration, represented as vol % in water, can be obtained from eq 6 in which the i^{th} initial concentration of the AEA is represented as vol %.

$$\text{AEA conc., vol \%} = (\mathrm{COD}_{\mathrm{eq},i} - \mathrm{COD}_{\mathrm{cement}} - \mathrm{COD}_{\mathrm{FA}}) \div \left[\mathrm{PC}_i \times \frac{\mathrm{COD}_{\mathrm{AEA},i}}{\mathrm{AEA}\ i^{\mathrm{th}}\mathrm{conc.}}\right] \tag{6}$$

where AEA i^{th} conc. = i^{th} initial concentration of the AEA, vol %. $\mathrm{COD}_{\mathrm{FA}}$ = COD of the fly ash used in the isotherm point in 200 mL distilled water, mg/L.

Performing the previous procedure on three AEA concentrations produces three fly ash capacities for three AEA concentrations. A flowchart for the combined direct adsorption isotherm testing procedure is presented in Figure 2.

Combined Cement and Fly Ash Isotherm Results Analysis. The adsorption isotherm was obtained by plotting the fly ash capacity of all isotherm points versus their corresponding final equilibrated aqueous-phase AEA concentration on a log−log scale, as shown in Figure 3. A power line data fit produced a Freundlich equation (eq 7) that describes the equilibrium partitioning between the AEA solid-phase concentration (capacity of fly ash) and the AEA aqueous-phase concentration.[24]

$$q = K \times C^{1/n} \tag{7}$$

where K = Freundlich capacity parameter, mL/g × (1/vol %)$^{1/n}$. $1/n$ = Freundlich intensity parameter, unitless.

The Freundlich equation as well as the graph by itself was used to determine the capacity at any AEA concentration. This isotherm procedure was adopted as the final procedure and was used for the rest of this research. This procedure was conducted on MB VR with eight different fly ashes. The results are illustrated in Figure 3.

Adsorption Isotherms Utilization. The isotherm results presented in Figure 3 provided a precise quantification of the

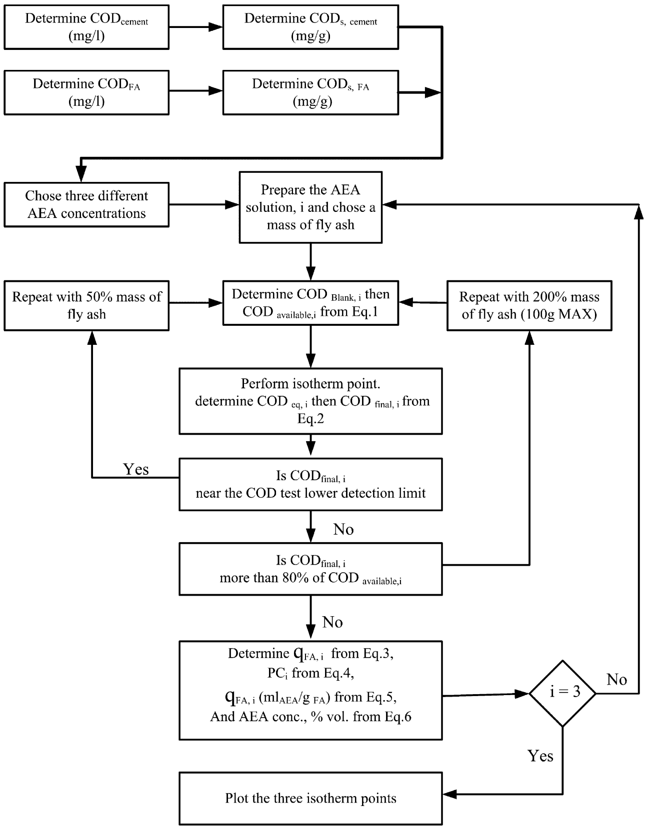

Figure 2. Flowchart representation of the combined direct adsorption isotherm procedure.

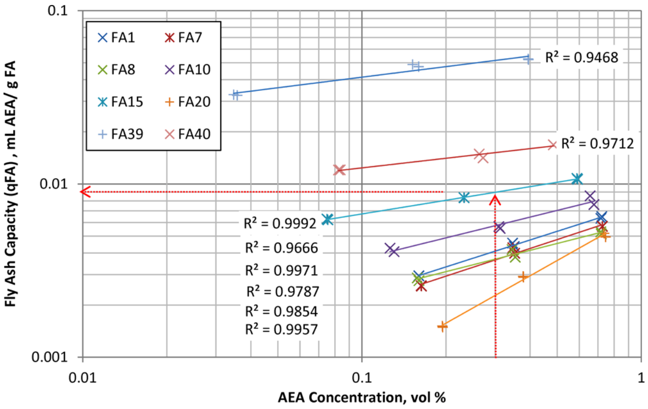

Figure 3. Combined adsorption isotherms for MB VR with eight fly ashes.

amount of AEA adsorbed by the fly ash as a function of the AEA concentration. To determine the fly ash adsorption capacity specific to the mix condition, an isotherm must be developed for the specific fly ash and the specific AEA used in the concrete mix. AEA dosages are often specified in terms of volume AEA/100 kg of cement used in the mix. To determine the AEA solution concentration, the volume of AEA used must be divided by the volume of water used in the concrete mix. The fly ash capacity at this concentration can be determined from the isotherm graph. For example, the adsorption capacity of FA40 for MB VR at a concentration of 0.5 vol %. AEA/water is 0.017 mL AEA/g FA. This capacity multiplied by the total mass of fly ash used in the mix results in the volume of MB VR adsorbed by FA40 at this concentration.

Effect of Temperature on Fly Ash Adsorption Capacity. Adsorption isotherm tests were conducted at various temperatures to assess the effect of temperature on the adsorption capacity of fly ash. MB VR was tested with fly ash 39 in solution temperatures of 5, 20, 30, and 40 °C, and the results of these isotherms are illustrated in Figure 4. Results showed that the adsorption capacity of fly ash at 5 and 40 °C were almost identical, and there was no significant effect of temperature on the adsorption capacity of AEA on fly ash.

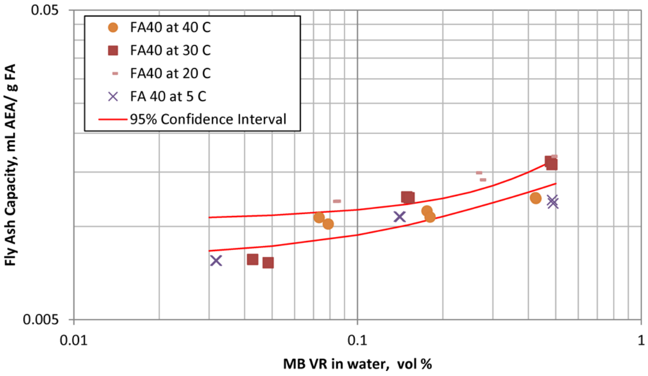

Figure 4. Effect of temperature on the adsorption capacity of fly ash.

In conventional activated carbon applications, the majority of the surface area available for physical adsorption is within the adsorbent particles. Within an activated carbon particle both multilayer adsorption and adsorbate condensation take place at the adsorbent surface and inside the adsorbent pores where the adsorption potential is extremely high. In this case, the limiting factor for adsorption becomes the solubility limit of the solute because the solute is present in its pure form at the high adsorption potential sites. The solubility limit is very sensitive to temperature; therefore, temperature affects the capacity of activated carbon significantly. Fly ash carbon has very little pore space, and it possesses very low adsorption capacity because it is not activated. In addition, AEA molecules are very large, and the adsorption is most likely characterized by monolayer coverage. Therefore, solubility limit is not an issue for fly ash, and fly ash capacity is not sensitive to temperature.

Although the AEA adsorption is not sensitive to the temperature change, this test must be performed in a constant temperature because the test utilizes volumetric measurements that could be affected by high temperature variation.

AEA Dosage Adjustment. Because the fly ash will adsorb a certain amount of AEA in the concrete mix, this same amount of AEA must be added to the mix to compensate for this AEA loss and bring the AEA concentration to the required mix design concentration. The amount of the AEA adsorbed can be determined from the capacity of the fly ash at the target AEA concentration. This fly ash capacity multiplied by the mass of fly ash used in the concrete mix produces the amount of AEA adsorbed by the fly ash, which is the same as the required dosage adjustment.

For example, and as is pointed in Figure 3, if FA15 is to be used with MB VR concentration of 0.3%, the isotherm graph can be used to determine the capacity of FA15, which is 0.009 mL MB VR/g FA15. This capacity multiplied by the mass of fly ash per unit volume of concrete produces the volume of MB VR, per unit volume of concrete, needed as a dosage adjustment.

RESULTS VERIFICATION

The combined direct fly ash and cement adsorption isotherm results presented in Figure 3 were utilized to determine the dosage adjustments for cement mortars and concrete with 25% fly ash replacement. A 25% replacement level was utilized because it is the maximum acceptable fly ash−cement replacement level according to the Federal Highway Administration.[25] All adjusted dosages succeeded to achieve the target air content, and in most cases, these adjusted dosages were lower than the adjusted dosages determined using the conventional trial mix approach. A detailed results verification study is presented in NCHRP 18-13 project final report.[23]

CONCLUSIONS AND RECOMMENDATIONS

The newly developed combined adsorption isotherm test provides an accurate and direct measurement of the adsorption capacity of AEAs onto fly ash. This simple test can be performed in a laboratory that has the capability of measuring COD. The results obtained from this test provide the capacity of fly ash to adsorb AEAs, and the capacity can be used along with the mass of fly ash utilized to determine the amount of AEA needed to compensate for the adsorbed portion of the AEA. This amount is the dosage adjustment that needs to be added to the base AEA dose to achieve the required air content. This adjustment can be made for any fly ash−cement replacement ratio because it is only dependent on the capacity of the fly ash and the mass of fly ash utilized. It is recommended that concrete mixers perform this test on the specific fly ash and the specific AEA utilized in their mixes. This procedure gives a product-specific dosage that is direct and accurate without the need to use any approximation of adsorption capacity or inaccurate indicators.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) 2011 Coal Combustion Product (CCP) Production and Use Survey Report. American Coal Ash Association. http://www.acaa-usa.org/Portals/9/Files/PDFs/Final2011CCPSurvey.pdf (accessed April 18, 2013).

(2) Nisbet, M. A.; Marceau, M. L.; VanGeem, M. G. Environmental Life Cycle Inventory of Portland Cement Concrete. http://www.nrmca.org/taskforce/Item_2_TalkingPoints/Sustainability/Sustainability/SN2137a.pdf (accessed January 7, 2013).

(3) Climate Change 2013: The Physical Science Basis. Intergovernmental Panel on Climate Change. http://www.ipcc.ch/report/ar5/wg1/#.Uk4aSRa_PG4 (accessed February 20, 2014).

(4) Perdersen, K. H.; Jensen, A. D.; Skjøth-Rasmussen, M. S.; Dam-Johansen, K. A. Review of the interference of carbon containing fly ash with air entrainment in concrete. *Prog. Energy Combust. Sci.* **2008**, *34* (2), 135−154.

(5) Clendenning, T. G.; Durie, T. G.; Hower, J. Properties and Use of Fly Ash from a Steam Plant Operating Under Variable Load. *Proc., Am. Soc. Test. Mater.* **1963**, *62*, 1019−1040.

(6) Maroto-Valer, M.; Taulbee, D.; Hower, J. Characterization of differing forms of unburned carbon present in fly ash separated by density gradient centrifugation. *Fuel* **2001**, *80* (6), 795−800.

(7) Bouzoubaa, N.; Zhang, M. H.; Malhotra, V. M. Laboratory produced high volume fly ash blended cement: Compressive strength and resistance to the chloride ion penetration of concrete. *Cem. Concr. Res.* **2000**, *30* (7), 1037−1046.

(8) Zhang, D. S. Air entrainment in fresh concrete with PFA. *Cem. Concr. Compos.* **1996**, *18* (6), 409−416.

(9) Gebler S.; Klieger, P. *Effects of Fly Ash on the Air-Void Stability of Concrete*. In Proceedings of the International Conference on the Use of Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete, Montebello, Quebec, Canada, July−Aug, **1983**, Volume *1*, pp 103−142.

(10) Du, J.; Folliard, K. J. Mechanisms of air entrainment in concrete. *Cem. Concr. Res.* **2005**, *35* (8), 1463−1471.

(11) Hewlett, P. C. *Lea's Chemistry of Cement and Concrete*; Buuerworth-Heinemann/Elsevier: Oxford, 2004; p 32.

(12) Külaots, I.; Hsu, A.; Hurt, R. H.; Suuberg, E. M. Adsorption of surfactants on unburned carbon in fly ash and development of a standardized foam index test. *Cem. Concr. Res.* **2003**, *33* (12), 2091−2099.

(13) Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete; ASTM C311-04; ASTM International: West Conshohocken, PA, 2004.

(14) Fan, M.; Brown, R. C. Comparison of the loss-on-ignition and thermogravimetric analysis techniques in measuring unburned carbon in coal fly ash. *Energy Fuels* **2001**, *15* (6), 1414−1417.

(15) Zhang, Y.; Lu, Z.; Maroto-Valer, M. M.; Andrésen, J. M.; Schobert, H. H. Comparison of high-unburned-carbon fly ashes from different combustor types and their steam activated products. *Energy Fuels* **2003**, *17* (2), 369−377.

(16) Brown, R. C.; Dykstra, J. Systematic errors in the use of loss-on-ignition to measure unburned carbon in fly ash. *Fuel* **1995**, *74* (4), 570−574.

(17) Baltrus, J. P.; LaCount, R. B. Measurement of adsorption of air entraining admixture on fly ash in concrete and cement. *Cem. Concr. Res.* **2001**, *31* (5), 819−824.

(18) Harris, N. J.; Hover, K. C.; Folliard, K. J.; Ley, M. T. The use of the foam index test to predict AEA dosage in concrete containing fly ash: Part I—Evaluation of the state of practice. *J. ASTM Int.* **2008**, *5* (7), DOI: 10.1520/JAI101601.

(19) Watkins, M. K. *Characterization of a Coal Fly Ash-Cement Slurry by the Absolute Foam Index*. Ph.D. Dissertation, Michigan Technological University, Houghton, MI, 2013.

(20) Ahmed, Z. T. *The Quantification of the Fly Ash Adsorption Capacity for the Purpose of Characterization and Use in Concrete*. Ph.D. Dissertation, Michigan Technological University, Houghton, MI, 2012.

(21) Ahmed, Z. T.; Hand, D. W.; Sutter, L. L.; Watkins, M. K. Fly ash iodine number for measuring adsorption capacity of coal fly ash. *ACI Mater. J.* **2014**. URI: http://www.concrete.org/Publications/ACIMaterialsJournal/ACIJournalSearch.aspx?m=details&ID=51686582.

(22) Ahmed, Z. T.; Hand, D. W.; Watkins, M. K.; Sutter, L. L. Air entraining admixtures partitioning and adsorption by fly ash in concrete. *Ind. Eng. Chem. Res.* **2014**.

(23) Sutter, L. L.; Hooton, R. D.; Schlorholtz, S. *Methods for Evaluating Fly Ash for Use in Highway Concrete*; NCHRP Report 749; Transportation Research Board of the National Academies: Washington, DC, 2013.

(24) Crittenden, J. C.; Trussell, R. R.; Hand, D. W.; Howe, K. J.; Tchobanoglous, G. *MWH's Water Treatment Principles and Design*; John Wiley & Sons, Inc.: Hoboken, NJ, 2012.

(25) Fly Ash. Federal Highway Administration (FHWA), U.S. Department of Transportation. http://www.fhwa.dot.gov/infrastructure/materialsgrp/flyash.htm (accessed February 2, 2014.

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