

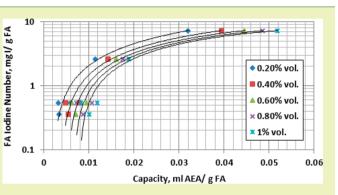
Direct Adsorption Isotherms of AEAs and Fly Ash: α -Olefin Sulfonate and Combination Admixtures

Zeyad T. Ahmed^{*,†,‡} and David W. Hand[†]

[†]Department of Civil & Environmental Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931 United States

[‡]Environmental Protection Department, Saudi Aramco, Dhahran 31311, Kingdom of Saudi Arabia

ABSTRACT: The direct adsorption isotherm test provides a direct measurement of the air entraining admixtures (AEAs) adsorption by fly ash in concrete. This method was developed and tested using a popular Vinsol resin admixture. In this paper, the direct adsorption isotherm test was performed on two other commonly used AEAs of different chemical compositions to verify the applicability of this method to AEAs of other chemical natures. The results showed that, as in the case of the Vinsol resin admixture, the AEAs partitioned between the solid and liquid phase, the partitioning coefficient changed with changing the AEA concentration, and this method was able to quantify the fly ash adsorption capacity



based on the Fruendlich adsorption model. Also, in order to present a practically useful approach for the concrete/fly ash industry, the isotherms results of the three AEAs were correlated to the fly ash iodine number test results. Concrete producers can use these correlations to determine the AEA adsorption capacity, and the AEA dosage adjustment using the fly ash iodine number without the need to perform the direct adsorption isotherm test.

KEYWORDS: Fly ash, adsorption capacity, foam index, direct adsorption isotherms, air entraining admixtures (AEAs), fly ash iodine number

INTRODUCTION

Fly ash is a byproduct generated from coal combustion, mainly in coal fired power plants. As a solid waste, fly ash is usually landfilled and constitutes a burden to the environment, economy, safety, and public health. Stricter regulations of fly ash disposal are often proposed by the U.S. EPA due to the rising concerns about the fly ash landfill safety including the effects of fly ash toxins on groundwater and drinking water sources.¹

On the other hand, the beneficial utilization of fly ash could turn this waste material into a sustainable material for infrastructure. About 45% of the 52 million tons of fly ash produced in the United States (in 2012) was beneficially utilized, mostly by the cement and concrete industry.² Fly ash can be used in the production of cement, and as partial replacement of cement in concrete. The fly ash improves many features in concrete, reduces the amount of cement required by 30-70%, and consequently reduces the carbon footprint and the cost of concrete. Due to its adsorptive properties, fly ash is also used as a low-cost adsorbent for many applications such as the removal of various gaseous pollutants and the removal of organic compounds and metals. Fly ash is also used as a lightweight aggregate, mine backfill, road sub-base, and for zeolite synthesis.³⁻⁵ The beneficial utilization of fly ash also reduces the cost and the environmental impact of landfilling fly ash.

© 2015 American Chemical Society

Highway concrete is a major market for fly ash in the United States. Increased fly ash utilization in concrete is challenged and limited by the tendency of fly ash to adsorb organic admixtures used in concrete. This problem is often reported when high carbon fly ash is used with air entraining admixtures (AEAs).^{6–11} Residual carbon in the fly ash adsorbs some components of the AEAs, reducing their availability to function and entrain the required air void content in the concrete mixture.^{7,8,12–15} Employing low temperature combustion technologies to reduce nitrogen oxides (NO*x*) emissions has increased the unburned carbon content and introduced high adsorption capacity fly ashes.^{16,17}

Air entraining admixtures are used to entrain 4–6% air void content to obtain freeze-thaw resistance. AEAs also improve mixture stability and control concrete density.^{18,19} AEAs interact with cement and fly ash in a complex manner due to the presence of various types of minerals in the concrete mix and also due to the complex composition of AEAs. The adsorption of organic admixtures by fly ash in concrete limits the utilization of fly ash to very low carbon fly ash, which represents a small fraction of the fly ash produced. The lack of fly ash adsorption capacity measurement tools increases the

Received:May 14, 2014Revised:December 27, 2014Published:January 2, 2015

ACS Sustainable Chemistry & Engineering

risks associated with using fly ash in concrete, and therefore, limits the beneficial utilization of fly ash. In practice, the AEA dosage would be adjusted to achieve the target air void content in concrete. This becomes very hard to control if the carbon content or the adsorption capacity of fly ash changes, which could happen frequently. Consequently, it is crucial to have a simple test that can be performed by the concrete producer to determine the adsorption capacity of fly ash and adjust the AEA dosage accordingly.

Many different tests have been utilized to assess the adsorption capacity of fly ash. The loss on ignition (LOI) test and the various forms of the foam index tests are used as surrogate measurements of the fly ash adsorption capacity. However, both tests cannot provide a direct measurement of the adsorption capacity of fly ash. LOI test has been used to measure the carbon content of fly ash, depending on the composition of fly ash, the error between carbon content and LOI can be as low as 1% and can be as high as 75%.^{20,21} Also, the carbon content does not necessarily reflect the adsorption capacity of the carbon. The adsorption capacity of fly ash is governed not only by the amount of carbon content but also by other properties such as the particle size, surface chemistry, pores size distribution, and degree of carbon activation.²²

The many forms and procedures of the foam index test have been used to evaluate the relative performance of fly ash and AEAs in concrete, with various levels of success.^{11,14,17,23–26} Unlike LOI, the foam index test results are affected by the adsorptive properties of the fly ash. Therefore, the foam index results could provide adsorption information not provided by the LOI test. However, the foam index test is not a direct measure of the adsorption capacity because the test is dynamic and the measurement is not done at or near equilibrium.²⁷ In addition, the foam determination in the test is mostly subjective, and although many test procedures exist, there is currently no agreed upon standard procedure.²⁷

The fly ash iodine number test reported by Ahmed^{22,28} provides a direct and accurate measurement of the adsorption capacity of fly ash. This test measures the adsorption capacity of fly ash using iodine adsorption. A similar test, ASTM D4607.94, is widely used by the activated carbon industry for the specification and characterization of carbon.²⁹ The fly ash iodine number test can be used for the specification and characterization of the suitability of the fly ash for use in cement, concrete, and other beneficial uses.²⁸

Iodine is used in adsorption tests because it has very small molecules, which therefore provides a good indication of the microporosity of carbon;^{28,30} it is also easy to measure by simple titration unlike other dyes that require spectroscopy and could pose a health risk.

Because it utilizes iodine rather than AEAs as an adsorbate, the iodine number test does not provide a direct measurement of the AEAs adsorption capacity by fly ash in concrete. However, if it is correlated to the combined adsorption isotherm test results, the fly ash iodine number can be used to predict the AEA dosage adjustment to compensate for the AEA adsorbed by fly ash in concrete.⁵

The combined adsorption isotherm test developed by Ahmed^{22,32} provides a direct method for the measurement of AEAs adsorption by fly ash in concrete. This test measures the difference in AEA concentrations caused by the change of fly ash mass in various isotherm points, and determines the equilibrium relationship between the AEA liquid phase

concentration and the AEA adsorbed phase concentration on the fly ash. This test takes into account the other processes that affect the AEA concentration in the concrete mixture such as AEA precipitation and chemisorption.^{32,33} This test was developed and tested using a popular Vinsol resin admixture.³³ In this study, the test is performed on two other types of AEAs to examine the applicability of this test to AEAs of other chemical natures. In addition, the correlations between the direct adsorption isotherms and the fly ash iodine number test results were developed for these AEAs, these correlations can be used to predict the AEA adsorption capacity based on the iodine number of the fly ash.³¹

The AEAs used in this study are formulated for general use in concrete and were not specifically formulated for the use with fly ash. It is important to emphasize that the compositions of these AEAs are completely different from each other and they are designed to function differently. This study did not assess the performance of any of these AEAs and did not compare any of these AEAs to each other.

The results of this study will assist concrete producers to determine the exact amount of AEA adsorbed by the fly ash in the concrete mix, then estimate the dosage adjustment if any of the studied AEAs was used with fly ash in concrete. Knowing the exact adsorption capacity of AEAs by fly ash eliminates a major variable that hinders the use of fly ash as a sustainable material for infrastructure, facilitate increased use of fly ashes that otherwise considered too risky for use in concrete, reduce the amount of fly ash landfill, and reduce the cost and the carbon footprint of concrete.

MATERIALS AND METHODS

Air Entraining Admixtures. Air entraining admixtures (AEAs) are organic admixtures used to entrain air bubbles in concrete to increase the concrete durability and resistance to freeze—thaw cycles in cold climate. AEAs also increase the workability of concrete in its plastic state. The most common type of AEAs is the Vinsol resin type. α -Olefin sulfonate admixtures are also very common and widely used in the industry. Combination admixtures could a mixture of surfactants, urea, tall oil, and any other AEA categories. Three commonly used AEAs were selected to represent three different chemical compositions of AEAs. These AEAs are preapproved in many states in the U.S. The selected AEAs chemical natures are listed in Table 1.

Table 1. Selected AEAs Chemical Natures

no.	chemical nature
1	Vinsol resin admixture
2	α -olefin sulfonate admixture
3	combination admixture

Fly Ash Specimens. Eight coal fly ash specimens with various adsorption capacities were selected for this study; Table 2 illustrates the fly ash specimens' identification numbers, LOIs, fly ash iodine numbers, the silicon, aluminum, ferric, calcium and magnesium oxides, and alkali contents. These are the same coal fly ash materials used in a previous work 32 to develop the combined adsorption isotherm test procedure.

Testing Procedures. LOI tests were performed according to ASTM C311-04.³⁴ The sample was placed in a clean porcelain crucible and dried at 105 °C for 2 h to determine the moisture content, then placed in a muffle furnace for 5 h at 750 °C to determine the LOI. Five hours at 750 °C was found to achieve the constant mass required for all fly ash specimens. Other studies have used 2 h,³⁵ 3 h,³⁶ and several hours²¹ to achieve the constant mass required.

fly ash ID no.	LOI (wt %)	fly ash iodine number (mg/g)	SiO ₂ (wt %)	$Al_2O_3 (wt)$	Fe_2O_3 (wt %)	total SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ (wt %)	CaO (wt %)	MgO (wt %)	alkali (% wt)*
1	0.9	0.0128	60.1	29.9	2.7	92.7	0.9	NA	0.61
7	2.3	0.3541	53.9	27.7	8.29	89.89	1.45	1.15	0.64
8	0.2	0.0040	60.9	25.7	4.66	91.2	3.46	1.12	0.69
10	1.3	0.5450	46	23.6	22.3	91.88	1.28	0.99	0.77
15	1.5	0.5346	58.9	16.2	4.71	79.81	10.3	3.13	0.73
20	0.4	0.0008	44.8	23.1	9.51	77.4	13.6	2.97	0.89
39	10.5	7.2662	39.6	20	12.7	72.3	9.1	2.28	NA
40	3.4	2.6191	53.9	26.3	6.24	86.4	4.0	0.86	NA

Table 2. Fly Ash Specimens' Properties³²

^{*}Alkali is given as Na₂O equivalents; NA = not available.

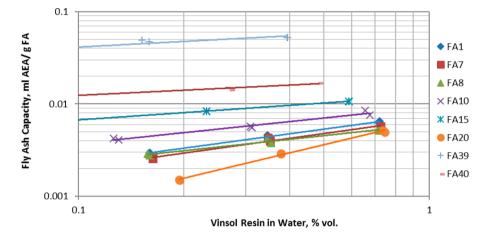


Figure 1. Direct adsorption isotherm results of the Vinsol resin admixture with eight fly ashes³²

The fly ash iodine number and combined adsorption isotherm tests were performed according to Ahmed.^{22,28}

The combined isotherm test is based on equilibrating known masses of a fly ash with various concentrations of an AEA for 60 min to determine the equilibrium correlation between the fly ash adsorption capacity and the liquid phase equilibrium concentration of the AEA. This equilibrium correlation describes the change in the capacity of fly ash in response to the change of the AEA concentration.

Air entraining admixture materials partition between the solid phase (cement and fly ash) and the liquid phase of concrete mixtures. Some of the AEA is chemisorbed by the active minerals surfaces present in the cement and the fly ash, this chemisorption process is driven by chemical bonding (ionic or covalent). Chemisorption is stronger than physical adsorption and is irreversible under normal temperatures. The nonchemisorbed portion of the AEA remains in solution and participates in the air bubbles stabilization during mixing. The chemisorbed part of the AEA on the solid phase stabilizes the air bubbles by attaching them to the solid particles in the system.

The liquid phase AEA concentration is the portion that is susceptible to adsorption by the fly ash carbon.³³ To determine the liquid phase AEA concentration for every initial AEA solution concentration, this test utilizes a blank of AEA solution and 20 g of cement. The 20 g of cement is enough to chemisorb all the chemisorbable portion of the AEA, leaving the liquid phase AEA in solution. The ratio of the equilibrium liquid phase concentration after chemisorption to the initial concentration of the AEA is defined as the AEA partitioning coefficient. The partitioning coefficient is dependent on the type and the concentration of the AEA. The partitioning coefficient for every initial AEA solution is determined by using the following equation:^{22,32}

partioning coefficient =
$$\frac{\text{COD}_{\text{blank}} - \text{COD}_{\text{cement}}}{\text{COD}_{\text{AFA}}}$$

where $\text{COD}_{\text{AEA}} = \text{COD}$ of the AEA solution, mg/L, $\text{COD}_{\text{cement}} = \text{COD}$ of 20 g cement in 200 mL of distilled water, mg/L, and $\text{COD}_{\text{blank}} = \text{COD}$ of the cement blank with the AEA solution, mg/L.

Several other isotherm points are made by adding various masses of fly ash to 20 g of cement and three different AEA concentrations. The fly ash capacity determined from these isotherms are represented using Fruendlich isotherm equation.^{37,38} After developing Fruendlich isotherm model form the isotherm data points, the liquid phase AEA concentration is used for the determination of the fly ash adsorption capacity at that specific AEA equilibrium concentration.

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

where q = fly ash adsorption capacity, mL AEA/g fly ash, C = AEA concentration, vol %, K = Freundlich adsorption capacity parameter, $(mL/g)(1/vol \ \%)^{1/n}$, and 1/n = Freundlich adsorption intensity parameter, unitless.

The combined adsorption isotherm test utilizes the chemical oxygen demand (COD) test for the measurement of AEAs concentration. The COD measurements were made using the HACH COD kit (TNT821 and TNT822) and HACH DR 5000 UV–vis spectrophotometer. COD measurements were taken at least twice for every sample; a third measurement was taken if the difference between the first two readings exceeded 1%.

A matrix of 8 fly ash materials and 3 AEAs was tested in this study, two direct adsorption isotherm tests were performed for each fly ash-AEA combination, and therefore, 48 direct adsorption isotherm tests results are presented in this study. Each isotherm presented was generated using 6-8 isotherm data points; typically, three points isotherms are considered representative by standard isotherm tests such as the iodine number test (ASTM D4607-94).²⁹

RESULTS AND DISCUSSIONS

AEAs vary in terms of their partitioning between the solid phase (cement and fly ash) and the liquid phase in the concrete

Table 3. Freundlich	Isotherm Model	Parameters for	the Three	AEAs and	the Eight Fly	v Ashes
---------------------	----------------	----------------	-----------	----------	---------------	---------

	Vinsol resin			lpha-olefin sulfonate			combination AEA		
fly ash no.	K	1/n	R^2	K	1/n	R^2	K	1/n	R^2
1	0.0076	0.52	1	0.0083	0.59	0.89	0.006	0.74	0.99
7	0.0069	0.53	0.99	0.0101	0.68	0.95	0.0053	0.73	0.98
8	0.0060	0.41	0.98	0.0083	0.78	0.92	0.0041	0.64	0.86
10	0.0093	0.40	0.97	0.0091	0.71	0.93	0.0039	0.44	0.94
15	0.0123	0.26	1	0.0118	0.44	0.95	0.0052	0.34	0.98
20	0.0068	0.91	1	0.0061	0.99	0.96	0.0029	0.79	0.94
39	0.0658	0.20	0.95	0.0519	0.30	0.95	0.0217	0.32	0.93
40	0.0190	0.18	0.97	0.0188	0.31	0.96	0.0086	0.32	0.98

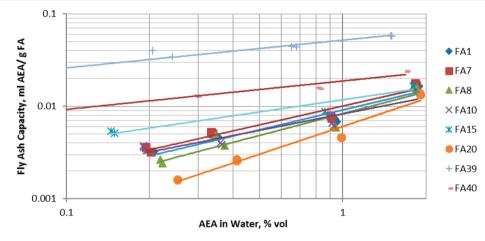


Figure 2. Direct adsorption isotherm results of the α -olefin sulfonate admixture with eight fly ashes.

mixture, some AEAs are designed to maintain high liquid phase AEA concentration, while others maintain a lower liquid phase concentrations and rely heavily on the AEA portion chemisorbed by the solid phase. The AEA partitioning coefficient is dependent on the type and the concentration of the AEA.³⁴ This fact was verified in this research and a unique partitioning coefficient was obtained for each of the three concentrations of the AEAs utilized in this study.

Vinsol Resin Admixture. Vinsol resin admixtures are a dark reddish-brown in color, natural thermoplastic resins extracted from pinewood. A large fraction of the Vinsol resin composition is of phenolic nature, such as phlobaphenes, carboxylated phlobaphenes, and substituted stilbenes; also, there is a considerable rosin fraction such as rosin acides, oxidized and polymerized rosin acids with a smaller fraction of terpenoids such as wax, dimethoxystilbene, and polymerized terpenes.³⁹

Two separate sets of combined adsorption isotherms were performed with the Vinsol resin solution with initial concentrations of 0.2, 0.4, and 0.8 vol %. The blank cement— AEA isotherm points produced partitioning coefficients of 0.375, 0.348, and 0.3, respectively, for the three concentrations. Each milliliter of this AEA contains 270 mg of COD; therefore, the COD of the 0.2, 0.4, and 0.8 vol % AEA solutions were 540, 1080, and 2160 mg/L, respectively.

The remaining liquid phase AEA concentration is the initial AEA concentration available for adsorption, and the combined adsorption isotherm equations³³ were used to determine the capacity of the other isotherm points with fly ash. Figure 1 illustrates the combined adsorption isotherm results for the Vinsol resin with the eight fly ash specimens.

The isotherms, represented as Fruendlich isotherm equation, of the eight fly ashes exhibited very good correlations, with R^2 value of 0.95 for FA39, 0.97 for FA 40 and FA10, 0.98 for FA8, and 0.99 and over for the rest. Five isotherm points of FA 20 and six isotherm points for the rest were utilized to construct these isotherms. The Freundlich isotherm model parameters for the Vinsol resin admixture with the eight specimens of fly ash in addition to the R^2 values for each model are presented in Table 3.

α-Olefin Sulfonate Admixture. α-Olefin sulfonate admixtures are ionic surfactants that have a hydrophilic group or groups and a hydrophobic hydrocarbon group.⁴⁰ These admixtures are highly soluble in water and their hydrophilic groups dissociate into cations and anions in water. One popular example is sodium α-olefin sulfonate, which has the composition $C_nH_{2n-1}SO_3Na$ (n = 14-16).⁴¹

Four different initial concentrations of the α -olefin sulfonate admixture were utilized to develop the isotherm, 0.25, 0.4, 1, and 2 vol %. The resulted partitioning coefficients for these initial AEA concentrations equilibrated with 20 g of Portland cement are 0.147, 0.132, 0.105, and 0.102, respectively. Each milliliter of this AEA contains 300 mg of COD; therefore, the COD of the 0.25, 0.4, 1, and 2 vol % AEA solutions are 750, 1200, 3000, and 6000 mg/L.

As the low partitioning coefficients indicate, this AEA is designed to retain a low AEA liquid phase concentration. This implies that this type of AEA is more reliant on the AEA chemisorbed to the minerals active sites (on the cement and fly ash) to entrain air bubbles, and stabilize the air bubbles by electrochemically attaching them to the solid mineral materials. The results of the adsorption isotherm performed using these

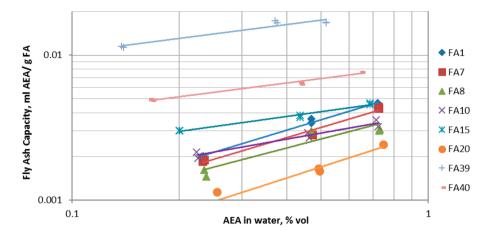


Figure 3. Direct adsorption isotherms results of the combination admixture with eight fly ashes.

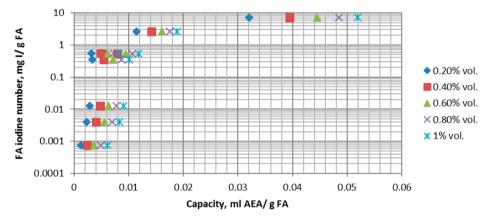


Figure 4. α -Olefin sulfonate admixtures adsorption capacity vs fly ash iodine number.

four AEA concentrations and the eight specimens of fly ash are presented in Figure 2.

The isotherms of the eight fly ash materials exhibited good correlations, with R^2 value of 0.89 for FA7, and 0.92–0.96 for the rest. The number of isotherm points used to develop these isotherms is eight for all fly ash specimens except for FA20, in which six points were utilized. The Freundlich isotherm model parameters for the α -olefin sulfonate admixtures with the eight specimens of fly ash in addition to the R^2 values for each model are presented in Table 3.

Combination Admixture. The combination admixture selected for this study is an aqueous solution of neutralized resin/rosin, amine, and fatty acids salts. The composition of this AEA includes dipropylene glycol, resin and rosin acids, maleated, potassium salt, rosin polymer with formaldehyde, tall oil, triethanolamine, and less than 1% of diethanolamine and sodium hydroxide.⁴²

Three different initial concentrations were utilized to develop the isotherm correlations, 0.25, 0.5, and 0.75 vol %. The corresponding partitioning coefficients for these initial concentrations are 0.395, 0.362, and 0.342, respectively. One mL of the raw AEA solution contains 476 mg of COD, therefore the COD of the 0.25, 0.5, and 0.75% volume AEA solution are 1190, 2380, and 3570 mg/L.

This AEA, similarly to the Vinsol resin AEA, retained about one-third of its composition in liquid phase. The results of the direct adsorption isotherms of the combination admixture with the eight fly ash specimens are illustrated in Figure 3. The isotherms of the eight fly ashes exhibited good correlations, with R^2 value of 0.86 for FA8, and 0.93–0.99 for the rest. The number of isotherm points used to develop these isotherms is six for all fly ash specimens except for FA20, for which five points were utilized. The Freundlich isotherm model parameters for the combination admixture with the eight specimens of fly ash in addition to the R^2 values for each model are presented in Table 3.

It is clear that all isotherms in Figures 1-3 exhibited very good fit to the power regression correlation that represents the Fruendlich isotherm equation. This indicates that the direct adsorption isotherm procedure can be used to quantify the AEA adsorption by fly ash for these different types of AEAs.

The results of the direct adsorption isotherm tests performed on several AEAs were utilized by another team of researchers to make AEA dosage adjustments for cement mortars and concrete mixes, with various specimens of fly ash. The research team concluded unless factors other than adsorption dominate "The results of the mortar and concrete experiments indicate the test could be used to predict AEA adsorption and provide an estimate for the associated adjustment in AEA dosage".⁴³ The details of the mortar and concrete tests and results are available in NCHRP 18-13 project final report.⁴³

Correlation to Fly Ash lodine Number. The Fruendlich isotherm model was utilized to determine the AEA adsorption capacities of the three AEAs at equilibrium concentrations of 0.2, 0.4, 0.6, 0.8, and 1 vol %. with each of the eight fly ash specimens. The resulted capacities were plotted against the fly

ACS Sustainable Chemistry & Engineering

ash iodine number for each fly ash specimen as presented for the α -olefin sulfonate admixtures in Figure 4.

The results presented in Figure 4 shows that even for an extremely small fly ash iodine number, there is a corresponding small AEA adsorption capacity. However, the adsorption of that small fraction of the AEA may not be perceptible in the concrete mixture for two reasons; the first is that the change in the AEA concentration is small, and the second is that the concrete air void content is not very sensitive to such small changes in the AEA concentration. Ahmed et al.⁴ suggested that "a fly ash with a fly ash iodine number less than 0.1 mg/g can be considered a good fly ash with low adsorption capacity" as this correspond to LOI less than 2%, and therefore adsorption of AEAs by such low capacity is not likely to cause adsorption problems.

Accordingly, correlations for each AEA with respect to iodine number can be constructed and used to determine the AEA adsorption capacity of fly ash materials as shown in Figures 5-7.

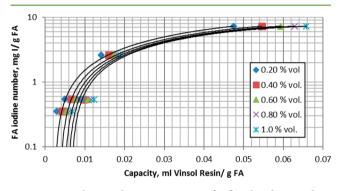


Figure 5. Vinsol resin adsorption capacities for fly ash iodine numbers higher than 0.1 mg/g.

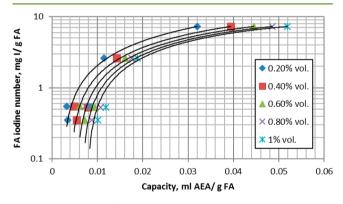


Figure 6. α -Olefin sulfonate admixture adsorption capacities for fly ash iodine numbers higher than 0.1 mg/g.

Figures 5–7 demonstrate a simple methodology to predict the AEA adsorption capacity from the fly ash iodine number of any fly ash. Unlike the fly ash iodine number, the direct adsorption isotherm test is a relatively complicated procedure. Predicting the adsorption of AEAs by fly ash without the need to perform a direct adsorption isotherm would be a more practical method to use.

To use these graphs, the fly ash iodine number test has to be performed on the fly ash of interest, then the fly ash iodine number can be used, along with the appropriate graph to determine the AEA adsorption capacity of that fly ash at that AEA concentration.

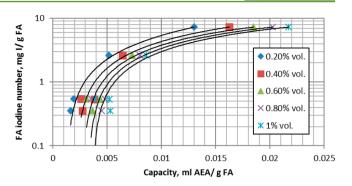


Figure 7. Combination admixture adsorption capacities for fly ash iodine numbers higher than 0.1 mg/g.

The capacity obtained from Figures 5-7 represents the amount of AEA required to fulfill the adsorption capacity of the fly ash in the concrete mixture, and adding this specific amount of AEA will bring the AEA concentration to the same level of the fly ash free concrete base mixture, eliminating the effect of the adsorption of AEAs by the fly ash. These graphs represent the relative adsorbability of various concentrations of the AEA to iodine.

Although the data presented exhibited good correlations, more work is needed to populate such graphs by using more specimens of fly ash to increase the confidence in the correlation and to examine the data in a more comprehensive statistical approach.

Assuming relatively consistent production and little variation in AEAs compositions, the direct adsorption isotherm test can be performed on the AEA with a suit of fly ashes that covers a wide range of adsorption capacities, as done in this study, and the results can be used to predict the AEA adsorption by similar ashes, based on the fly ash iodine number. This ideally should be done and supplied by the AEA manufacturers in order to promote the use of their products and to make it easier for concrete producers to use their admixtures with fly ash in concrete.

CONCLUSIONS AND RECOMMENDATIONS

The direct adsorption isotherm test was successful in quantifying the adsorption capacity of the α -olefin sulfonate and the combination air entraining admixtures used in this study, very good fits to the Freundlich adsorption isotherm model were obtained.

The α -olefin sulfonate admixture exhibited low partition coefficients (0.102–0.147) compared to Vinsol resin (0.3–0.375) and the combination admixture (0.342–0.395). However, this does not necessarily mean that the latter two are better to use with fly ash, because the activity of the AEA left in solution also vary among the AEAs.

The graphical representation of the AEA adsorption capacity versus the fly ash iodine number represents the fly ash adsorbability of various concentrations of the AEA relative to iodine. This correlation can be developed for any AEA and used to estimate the fly ash adsorption capacity of the AEA using the iodine number of the fly ash of interest. However, an exact measurement can only be done through performing the direct adsorption isotherm test on the specific AEA and fly ash.

This study quantifies the adsorption of AEA, or some portion of the AEA, by fly ash in concrete. It does not study the performance of these AEAs in fly ash containing concrete because the performance in concrete is dependent on whether the adsorbed part of the AEA is active or not, which is not the focus of this study. This study present a method of determining the AEA dosage adjustment needed to compensate for the adsorbed part of the AEA, which eliminates the effect of AEA adsorption by fly ash in concrete.

There is a great deal of effort given to examining the various properties of fly ash and AEAs in order to understand the effect of various materials properties on adsorption of AEAs by fly ash. The methods used in this study provide a direct tool for adsorption measurement, this will assist concrete materials researcher to understand the impact of material properties on adsorption, and ultimately air entrainment in fly ash containing concrete.

AUTHOR INFORMATION

Corresponding Author

*Z. T. Ahmed. E-mail: ztmahmou@mtu.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Part of this work was done through a research project 18-13 funded by the National Cooperative Highway Research Program (NCHRP), the Transportation Research Board of The National Academies. The authors thank NCHRP for their cooperation and support. The researchers also express their thanks to the department of civil and environmental engineering at Michigan Technological University for hosting the research, Dr. Melanie Kueber Watkins and Mrs. Angela Keranen for their help and continuous support, and for BASF's Construction Chemicals and Grace Concrete Products for their support and providing the AEAs used in this study.

REFERENCES

(1) Hopey, Don. Proposal would restrict disposal of coal fly ash. *Post-Gazette Journal*. [Online]; PG Publishing Co., Inc.: Pittsburgh, PA. http://www.post-gazette.com/stories/local/state/proposal-would-restrict-disposal-of-coal-fly-ash-264890/ (accessed March 3, 2014).

(2) American Coal Ash Association. 2012 Coal combustion product production & use survey report. http://www.acaa-usa.org/Portals/9/ Files/PDFs/revisedFINAL2012CCPSurveyReport.pdf (accessed March 3, 2014).

(3) Ahmaruzzaman, M.; Gupta, V. K. Application of coal fly ash in air quality management. *Ind. Eng. Chem. Res.* **2012**, *51*, 15299–15314.

(4) Ahmaruzzaman, M. A review on the utilization of fly ash. *Prog. Energy Combust. Sci.* **2010**, *36*, 327–363.

(5) Ahmaruzzaman, M. Role of fly ash in the removal of organic pollutants from wastewater. *Energy Fuels* **2009**, *23*, 1494–1511.

(6) 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, 135–154.

(7) 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.

(8) 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*, 795–800.

(9) 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*, 1037–1046.

(10) Zhang, D. S. Air Entrainment in Fresh Concrete with PFA. Cem. Concr. Compos. **1996**, 18, 409–416.

(11) 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 31–Aug 5, 1983; Vol. 1, pp 103–142.

(12) Gao, Y. M.; Shim, H. S.; Hurt, R. H.; Suuberg, E. M. Effect of carbon on air entrainment in fly ash concrete: The role of soot and carbon black. *Energy Fuels* **1997**, *11*, 457–462.

(13) Hill, R. L.; Sarkar, S. L.; Rathbone, R. F.; Hower, J. C. An examination of fly ash carbon and its interactions with air entraining agent. *Cem. Concr. Res.* **1997**, *27*, 193–204.

(14) Freeman, E.; Gao, Y. M.; Hurt, R. H.; Suuberg, E. M. Interactions of carbon containing fly ash with commercial airentraining admixtures for concrete. *Fuel* **1997**, *76*, 761–765.

(15) Yu, J.; Kűlaots, I.; Sabanegh, N.; Gao, Y.; Hurt, R.; Suuberg, E. Adsorptive and optical properties of fly ash from coal and petroleum coke co-firing. *Energy Fuels* **2000**, *14*, 591–596.

(16) Veranth, J. M.; Pershing, D. W.; Sarofim, A. F.; Shield, J. E. Sources of unburned carbon in the fly ash produced from low-NOx pulverized coal combustion. *Proc. Combust. Inst.* **1998**, *27*, 1737–1744.

(17) Kűloats, I.; Hurt, R. H.; Suuberg, E. M. Size distribution of unburned carbon in coal fly ash and its implicatoins. *Fuel* **2004**, *83* (2), 223–230.

(18) Rixom, R.; Mailvaganam, N. Chemical Admixtures for Concrete; E. & F. N. Spon: London, 1999.

(19) Nasvik, J.; Pistilli, M. Are we placing too much air in our concrete? *Concr. Constr. World Concr.* 2004, 49, 51–55.

(20) Dobson, V. H. *Concrete Admixtures*; Van Nostrand Reinhold: New York, 1990.

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

(22) Ahmed, Z. T. Quantification of the fly ash adsorption capacity for the purpose of characterization and use in concrete. Ph.D. Thesis, Michigan Technological University, Houghton, MI, 2012.

(23) 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*, 819–824.

(24) Dobson, D. H.; LaCount, R. B.; Kern, D. G. *Economical Treatment of High Carbon Fly Ash to Produce a Low Foam Index Product with Carbon Content Retained*; DOE Technical Report; Waynesburg College: Waynesburg, PA, 1999.

(25) 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.

(26) Stencel, J. M.; Song, H.; Cangialosi, F. Automated foam index test: Quantifying air entraining agent addition and interactions with fly ash-cement admixtures. *Cem. Concr. Res.* **2009**, *39*, 362–370.

(27) Watkins, M. K. Characterization of a coal fly ash-cement slurry by the absolute foam index. Ph.D. Thesis, Michigan Technological University, Houghton, MI, 2013.

(28) 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**, *11*, 383–390.

(29) Standard Test Method for Determination of Iodine Number of Activated Carbon; ASTM D4607.94; ASTM International: West Conshohocken, PA, 1994.

(30) Sontheimer, H.; Crittenden, J. C.; Summers, R. S. Activated Carbon for Water Treatment; DVGW-Forschungsstelle and AWWA: Karlsruhe, Germany, 1988.

(31) Ahmed, Z. T.; Hand, D. W. The quantification of the adsorption capacity of fly ash. *Ind. Eng. Chem. Res.* **2014**, *53*, 6985–6989.

(32) Ahmed, Z. T.; Hand, D. W.; Watkins, M. K.; Sutter, L. L. The combined adsorption isotherms for measuring adsorption capacity of fly ash in concrete. *ACS Sustainable Chem Eng.* **2014**, *2*, 614–620.

(33) Ahmed, Z. T.; Hand, D. W.; Watkins, M. K.; Sutter, L. L. Air entraining admixtures partitioning and adsorption by fly ash inconcrete. *Ind. Eng. Chem. Res.* **2014**, *53*, 4239–4246.

ACS Sustainable Chemistry & Engineering

(34) 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.

(35) 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*, 1414–1417.

(36) 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*, 369–377.

(37) Freundlich, H. Über die adsorption in lösungen. J. Phys. Chem. A 1906, 57, 385–470.

(38) 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.

(39) Pinova, Inc. Product data sheet of Vinsol resin; Document number 4340. www.pinovasolutions.com/docs/Vinsol.pdf (accessed November 30, 2012).

(40) BASF The Chemical Company. Micro Air Material Safety Datasheet version 2.2. Beachwood, OH, MSDS ID Number: 10075, 2006.

(41) Chemecaland21.com. Sodium alpha olefin sulfonate. http://www.chemicalland21.com/specialtychem/perchem/ SODIUM%20ALPHA%20OLEFIN%20SULFONATE.htm (accessed April 29, 2014).

(42) W. R. Grace & Co. Daravair AT60 Material Safety Datasheet; MSDS ID No. D-06544; GRACE: Cambridge, MA, 2009.

(43) 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.