Fly ash Adsorption Capacity as Measured by Spectroscopy Techniques

by

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Abstract: This 2-phased study examines the feasibility of using a fluorescence-based and related spectroscopy technologies in measuring the adsorption capacity of fly ash. Fly ash with high carbon contents or powder activated carbon (PAC) have the propensity for adsorbing Air-Entraining Admixture (AEAs) and potentially exposing the concrete to the adverse impact of freezing and thawing. To produce concrete resistant to freezing and thawing cycles, it is critical to adjust the dosage of AEAs to compensate for the portion that is adsorbed by fly ash. Foam index is the most prevalent method used for this purpose; however, this method relies on visual observation and is somewhat subjective with high degree of variability. In the first phase of this study, for the “proof of the concept”, FHWA’s concrete lab at Turner-Fairbank Highway Research Center (TFHRC) collaborated with Headwaters Resources, Inc. (now Boral Resources) in evaluating a new device called the “Sorbsensor™” that relies on fluorescence properties of a surrogate surfactant in quantifying the adsorption capacity of a fly ash. To further advance this technology, a Small Business Innovation Research (SBIR) proposal was advertised and a contract was awarded to PhosphorTech Corporation. The main objective of this SBIR project is to develop a more robust and semi-automated spectroscopy method (IDSpectra™) with a broader UV/Vis spectral range capable of measuring adsorption capacity of any combinations of fly ash and air-entraining agents. The new method has been shown to be more universal than the Sorbsensor™ method (current state-of-the-art), and once fully developed, it can rapidly and accurately identify and measure different surfactants (AEA’s) as well as quantify the amount of surfactant a given fly ash adsorbs.
INTRODUCTION:
One of the best ways to significantly improve concrete’s ability to resist the detrimental impact of freeze-thaw (F-T) action is through deliberately incorporating air-entraining agents (AEAs). When properly incorporated, air-entraining admixtures stabilize small bubbles of air that are produced in concrete during mixing. These well-distributed stabilized bubbles, in turn, play an essential role in providing long term F-T durability and scaling resistance for concrete infrastructures in cold regions. Depending on concrete’s degree of exposure and the nominal maximum size of the aggregate used, typically 4–8 percent total air is required to combat the F-T durability action in concrete. Many state department of transportation (DOTs) use fly ash as supplementary cementitious material (SCM) in their concrete mixtures. Typically, 20–30 percent of portland cement mass is substituted by fly ash. Proper incorporation of fly ash in concrete mixtures is environmentally friendly, reduces permeability, and improves durability. However, fly ash with high carbon content or powder activated carbon (PAC) when used as substitution for a portion of cement in concrete has the propensity for adsorbing AEAs and potentially exposing the concrete to the adverse impact of freezing and thawing. To produce concrete resistant to freezing and thawing cycles, it is critical to adjust the dosage of AEAs to compensate for the portion that is adsorbed by fly ash - determining the proper dosage of AEA is not a trivial task.

One of the most common methods of assessing the dosage rate of AEAs in mixtures containing fly ash has been the Foam Index (FI) test—a subjective test with a high degree of variability depending on the operator’s experience and the device used. A promising method developed by Boral Resources, Inc. was evaluated by the Concrete Laboratory at TFHRC for its potential in measuring the adsorption capacity of fly ashes. The method uses fluorescence to indirectly but quantitatively measure fly ash adsorption. A known amount of fly ash is mixed with a solution containing a surrogate surfactant called nonylphenol ethoxylate (or P10 for short). A portion of P10 is adsorbed by the fly ash, and the rest remains in the slurry (P10 solution and fly ash). After filtering the slurry, the concentration of P10 that remains in the solution is detected and quantified by fluorescence. While the Sorbsensor™ was found to be accurate and repeatable in measuring the adsorption capacity of fly ash,¹ it relies on the use of a specific surrogate surfactant. The method and instrument being developed by PhosphorTech and described here goes a step further by using variations in the UV/Vis spectral transmission of the fly ash solution, which enables the instrument to precisely measure the adsorption of any commercial AEA by fly ash.

Phase I Objectives:
The primary objectives of this study are to:
1- Examine the feasibility of using the fluorescence method to accurately quantify the adsorption capacity of fly ash.
2- Compare the results obtained from the fluorescence method with those obtained from the foam index test.

Materials:

Boral Resources identified and provided 10 sources of fly ash from 8 different States for this study. Table 1 shows source State, classification, calcium oxide (CaO) content, carbon content, and LOI for these fly ashes.

<table>
<thead>
<tr>
<th>ID</th>
<th>State</th>
<th>Class (ASTM C618)</th>
<th>CaO (%)</th>
<th>Carbon (%)</th>
<th>LOI (%)</th>
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<tbody>
<tr>
<td>16045</td>
<td>Alabama</td>
<td>Class C</td>
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<td>0.33</td>
<td>0.45</td>
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<td>16046</td>
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<td>1.96</td>
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<tr>
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<td>Florida</td>
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<td>1.93</td>
<td>3.03</td>
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<tr>
<td>16050</td>
<td>Mississippi</td>
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<td>1.01</td>
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<td>16052</td>
<td>Arkansas</td>
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<td>16053</td>
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<tr>
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<td>16066</td>
<td>Georgia</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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</table>

**Testing Approach**

The adsorption capacity of all the fly ashes were obtained using the device and the procedure developed by Boral Resources. Figure 2 shows the components of the device used in this study.

The test methodology involves mixing distilled water with the P10 solution to create a 150 ppm of P10 solution. Then, 20 grams of fly ash is mixed into 400 mL of this solution and stirred for 10 minutes, creating a slurry. During this process, a portion of P10 is adsorbed
by the fly ash, and a portion remains in solution. The slurry rests for 2 minutes to allow the suspended fly ash particles to settle, so that a solid-free slurry can be filtered into the measuring chamber. An attached fluorescence probe is used to determine the concentration of the surfactant remaining in the filtered solution. The remaining P10 in the solution fluoresces when excited by UV light and the fluorescence intensity is proportional to concentration of the P10 in the solution. As shown in Figure 3 there is an excellent correlation between the P10 concentration and the emitted light.

**Figure 3. Correlation of P10 concentration in the solution and the fluorescence intensity**

The adsorption capacity of the same 10 fly ashes was also measured with 3 different air-entraining agents using the foam index test. The AEAs included the following:

**Figure 4. Adsorption capacity results with a typical standard deviation bar based on four replicate tests**

Figure 4 shows the adsorption capacity results of 10 fly ashes obtained by the Sorbsensor with typical standard deviation bar based on four replicates in each test. The measured adsorption capacities ranged from 0.26 mg/g to 1.52 mg/g.
- Vinsol resin AEA.
- Alpha olefin sulfonate AEA.
- Resin/Rosin and fatty acid AEA.

Figure 5 shows the foam index test results with the three air-entraining agents and the same fly ashes that were used with Sorbsensor™.

Figure 6 compares the adsorption capacity measured with Sorbsensor with those of the foam index. As shown the correlation between the two methods looks good with different air-entraining agents exhibiting different correlation curve.
UV/Vis Spectroscopy Method using IDspectra™

The IDspectra™ (IDS) system by PhosphorTech (Figure 7) is designed as a compact and portable low power unit that can be used both in the laboratory, inside a processing plant, as well as outdoors in the field powered by a portable or car battery.

The apparatus is modular by design and currently employs four small dispensers: two for adding analyte and two for adding reference solutions. A drain line at the bottom enables draining of the solution following spectral analysis. The instrument is connected through a USB port to a PC and uses a proprietary software with a simple graphical user interface (GUI) and fluid processing system for collecting samples from each dispenser and for recording/analyzing spectral data (See Figure 9). The collected data is then processed through a built-in database and used for the determination of fly ash adsorption capacity. In addition to the apparatus shown in Figure 7, two 1000mL conical flasks (Flask A for AEA solution and Flask B for reference solution) placed on top of small magnetic stirrers are used for preparing the analyte and reference solutions.

**Experimental Methods:**

Once an AEA is selected and the “Calculate” button is pressed, the built-in algorithm provides details on the concentration of AEA solution and how the analyte and reference solutions should be prepared for accurate analysis and high precision. For example, if VR10 is chosen from the dropdown list, the details involving preparation of 250ppm AEA solution would be as follows: (1) 250 microliters of the VR10 AEA is pipetted and mixed...
into flask A, which contains 1000mL of water. On the other hand, flask B is filled with 800mL of water while 200mL is added into dispenser 1 (D1) and used for rinsing the lines and as one of the reference solutions. After thoroughly mixing the contents in flask A, 200mL of that solution is drawn out and a sample of which is added into dispenser 2 (D2). Finally, the same quantity of fly ash is added to each of the two flasks and the contents are then stirred for several minutes. Once stirring is completed, fly ash particles are allowed to settle down to the bottom of the flasks before removing about 100mL from each one. The untreated fly ash solution is removed from flask B and added to dispenser 3 (D3) while the AEA-treated fly ash solution is removed from flask A and added to dispenser 4 (D4). Automated spectral testing is then initiated by pressing the “Run” button which withdraws and compares the various samples against their respective reference solutions. At the end of the analysis and subsequent calculation, the algorithm reports the AEA adsorption capacity of the fly ash in mL/g or in mg/g.

![Spectral Data from Dispensers D1-D4](image)

**Figure 9:** Example of the wavelength-dependent spectral intensity data used to determine AEA concentration and fly ash adsorption capacity.

PhosphorTech is currently in the process of developing a database for various AEAs that correlates the characteristic spectrum of an AEA to its concentration in solution. The spectral database, which currently contains data for 6 different types of AEAs, is used for the determination of AEA adsorption capacity of fly ash. The IDSpectra™ system is currently undergoing Beta testing while work continues to further expand the spectral database to include virtually all commercial AEA and other admixtures.

The current database has so far been successful in testing the AEA adsorption capacity of various types of fly ash materials (provided by Boral Resources). The AEA adsorption capacities of Flyash 1223, Flyash 1, Flyash 2, Flyash 3, and Flyash 9 were studied. The AEAs used in these studies were P10, VR10 and AT60, as illustrated below.

**Results and Discussion**

Figure 10 shows the adsorption capacity results of Flyash 1 for three different AEAs (P10, VR10, and AT60), which were measured using the IDSpectra™ (IDS) system. All measurements were repeated 3 times (using the same liquid samples) in order to determine the standard deviations with regards to liquid processing and spectral data acquisition and analysis. The extremely low standard deviation (RSD ≤1.89%) in Figure 10 is indicative of the instrument precision in measuring fly ash adsorption capacity of
different AEAs. Such a precision can be achieved provided the fly ash sample solutions are carefully prepared using a large stock AEA solution in order to minimize variations (due to operator error) in AEA and relative fly ash concentrations between experiments.

Figure 10: Adsorption capacity of Fly ash 1 with different types of AEAs, specifically P10, VR10, and Daravair AT60. (Assuming 5% surfactant composition in VR10 and 10% surfactant composition in Daravair AT60).

Figure 11: Fly ash adsorption capacity with standard deviation from 3 different AEA/fly ash mixtures (3 experiments per mixture with each mixture prepared independently for each experiment). P10/flyash 1, VR10/flyash 1, and AT60/fly ash3 (Assuming 5% surfactant concentration in VR10 and 10% surfactant concentration in AT60).

Figure 11 shows the results of repeated experiments (3 experiments in each case) used for determining the adsorption capacity of different AEA/flyash mixtures. During these
experiments, fresh analytical solutions were repeatedly prepared, so the larger standard deviations (compared to Figure 10) include operator error. Figure 12 shows results obtained using Daravair AT60 with different types of fly ash materials.

![Graph showing adsorption capacity of different types of fly ash with Daravair AT60.](image)

**Figure 12: Adsorption capacity of different types of fly ash with Daravair AT60.**

**Summary:**
- This study examined the feasibility of using a fluorescence-based technology to quantitatively measure the adsorption capacity of different fly ashes. The Sorbsensor device uses a surrogate surfactant called nonylphenol ethoxylate (P10 for short) at a specific starting concentration of 150 ppm.
- The results from Sorbsensor compared well against the results from foam index test with an average correlation factor $R^2 > 0.88$.
- The value of adsorption is different for different fly ashes and different air-entraining agents.
- Currently, the fluorescence-based device for measuring adsorption capacity is based on the P10 standard solution; other commercial air-entraining admixtures could potentially be used with different optic filters.
- The study also examined the potential of a new compact and portable instrument (IDSpectra™) currently under development by PhosphorTech in Kennesaw, Georgia.
- The IDS system (currently undergoing Beta testing) uses broadband UV/Vis spectral analysis to measure adsorption capacity of fly ash with any commercial AEA material within a built-in database currently under development.

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**DISCLAIMER**

Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement or recommendation by the Federal Highway Administration nor does it indicate that the products are necessarily the best available for the purpose.

**References**

