Rapid Coal Ash & Air Entrainment Analysis with Automated Sample Transport

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A novel spectroscopy method and instrument is presented for accurately determining the levels of adsorption (or desorption) from a wide range of materials. The instrument is specifically designed to determine fly ash adsorption capacity and to provide comparative analysis for a wide range of commercial Air Entrainment Agents (AEAs). Comparing the effectiveness of different AEAs and the measurement of fly ash adsorption properties are important strategies for obtaining designated air entrainment in concrete. A robust and portable device for fly ash and AEA analysis can be an effective tool for delivering quick and accurate feedback in the field and during research and development activities. The new method can be used in evaluating the effects of the Loss on Ignition (LOI) of fly ash on AEA adsorption and can also be expanded/customized to any admixture or adsorbate/adsorbent system. Fifteen types of commercial AEAs have been evaluated and incorporated into a database to be used for quantifying ash adsorption and AEA precipitation behavior. The method has yielded accurate results with a low coefficient of variation (<5% COV) and high precision with good correlation when compared with the results from the ASTM foam index testing (FIT).

KEYWORDS: adsorption, fly ash, concrete, AEA loss, foam index

Introduction

Air Entrainment Agents (AEAs), important chemical admixtures in concrete, are surfactant-containing liquid reagents that are added to concrete for the purpose of inducing and stabilizing a certain amount of microscopic air void (Typically around 6% air content) in concrete during mixing. These stabilized air voids play an essential role in providing long-term freeze-thaw (F-T) durability and scaling resistance for concrete structures in cold regions. However, AEAs tend to interact with cementitious materials in concrete, especially fly ash. As a result, a certain amount of AEA "loss" will take place after it is added to mixing water in cementitious materials and/or concrete suspensions, even in the absence of fly ash. Supported by the Federal Highway Administration (FHWA) of the US Department of Transportation (DOT), an IDSpectra™ (IDS) device has been developed for such a purpose and is a spectroscopy-based analysis tool that has been tested and validated over the last several years to accurately determine the adsorption capacity of fly ash with AEAs [1]. In this paper, an updated IDS system (refer to Figure 1) with an expandable spectral database of AEAs and the latest data on the adsorption properties of various types of fly ash materials are being reported. The previously mentioned expandable database currently includes the 15 different commercial AEAs that are listed in Table 1. The primary goal of the final DOT project phase is to accelerate the commercialization of the IDS method and instrument and transform it into a market-ready product through expansion of its application capabilities as well as independent validation towards industry acceptance as a robust testing tool in concrete mixing laboratories and fly ash terminals.

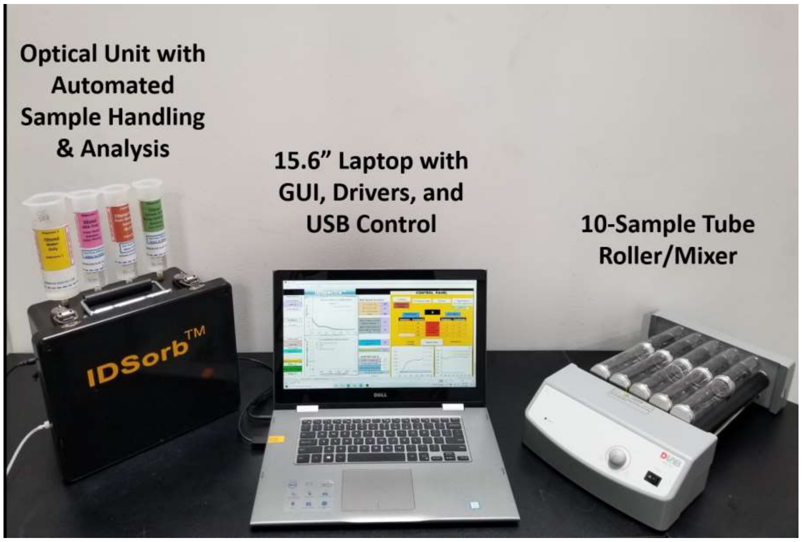

Figure 1. IDS System and Windows-based Graphical User Interface.

Table 1. AEAs currently in the database of the IDS software

Number	AEA	Manufacturer
1	P10	Dow
2	Sika AIR	Sika
3	Darex AEA	GRACE
4	Daravair AT60	GRACE
5	MICRO AIR AE90	BASF
6	MasterAir AE90	BASF
7	MasterAir VR 10	Master Builders Solutions
8	Eucon AIR 40	Euclid Chemical
9	CHRYSO	CHRYSO
10	Eucon AEA 92S	Euclid Chemical
11	Eucon Airmac 12	Euclid Chemical
12	Darex II	GCP Applied Technologies
13	AE400	Master Builders Solutions
14	Sika air 160	Sika
15	Daravair 1000	GCP Applied Technologies

Results and Discussion

The IDS method can accurately determine the amount of AEA precipitation and soluble AEA loss due to fly ash and cementitious materials. For adsorption analysis of fly ash, the measured parameters are (1) the initial concentrations of AEA stock solutions (before AEA mixing with fly ash-water suspension); and (2) the final concentration of AEA solution following ash exposure and a filtration procedure to remove solid particles and AEA precipitates from the mixtures. The algorithm then automatically calculates AEA "loss" (ml/g) from the measured initial and final solution concentrations.

The analytical method is based on a broadband UV/Vis spectroscopy technique [1] capable of achieving high accuracy and precision for soluble chemical concentrations with detection sensitivity in the parts-per-million (ppm) range. To illustrate the system's capabilities, test results using various commercial AEAs are being reported in this paper. Figure 2 shows a calibration curve (R^2 value of 0.9966) of SikaControl® AIR-160 with a wide concentration range from 0 to 10000 ppm. According to the product data sheet [2], the recommended dosage range is from 7 to 400 ml/100 kg of cementitious materials. Assuming w/c (ratio of water to cementitious material) of 0.5, the recommended concentration of AIR-160 is then from 140 ppm to 8000 ppm. The calibration curve indicates the valid measurement range for AIR-160 with regards to dosage or AEA concentration when mixed with fly ash in typical conditions used for concrete production.

The testing accuracy has been demonstrated to be higher than 93% as the data in Figure 3(a) illustrates for AIR-160 with a concentration range from 1000 ppm to 10000 ppm. The IDS precision or coefficient of variation (COV) on measurement of AIR-160 solutions with concentrations of 1000 ppm and 5000 ppm were shown to be lower than 1% (Figure 3(b)). Precision estimates were conducted using measurement of soluble AEA loss due to fly ash (LOI of 0.11) from three independent experiments with each using 2g fly ash mixed with 25 ml 7400 ppm AEA solution. A COV of 0.72% was obtained (Table 2), which indicates high reliability on measurement of soluble AEA loss induced by fly ash addition to AEA solutions.

Table 2. Coefficient of variation (COV) on measurement of soluble AIR-160 loss (2g fly ash, LOI of 0.11) using 7400 ppm solution.

Exp.no.	**Q (ml AEA/100 kg)**
1	8222.37
2	8249.58
3	8336.56
Average	8269.50
SD	59.65
COV	0.72%

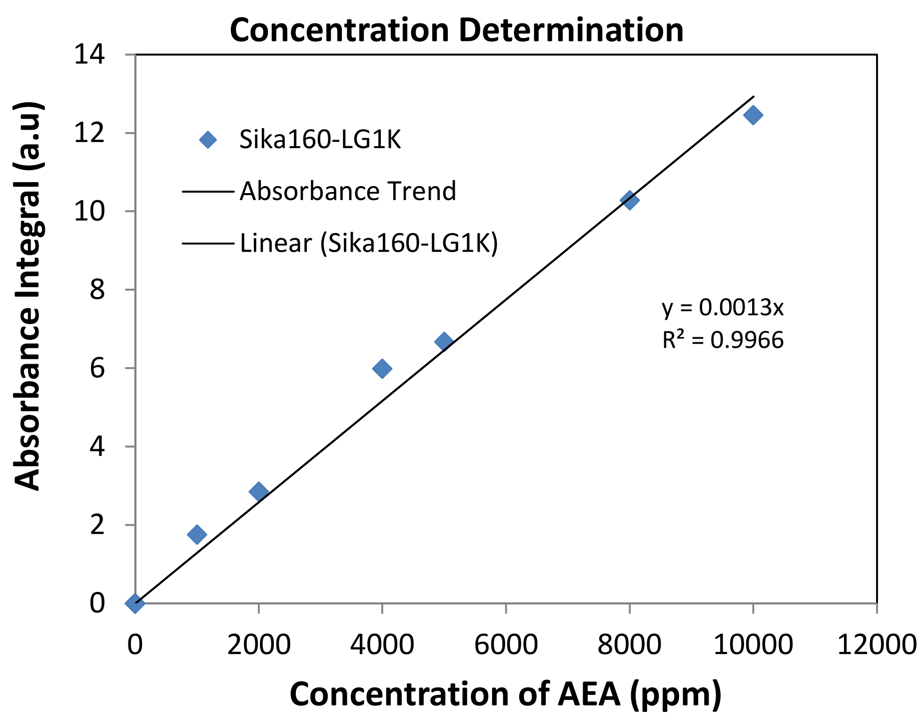

Figure 2. Calibration curve for SikaControl® AIR-160 solutions

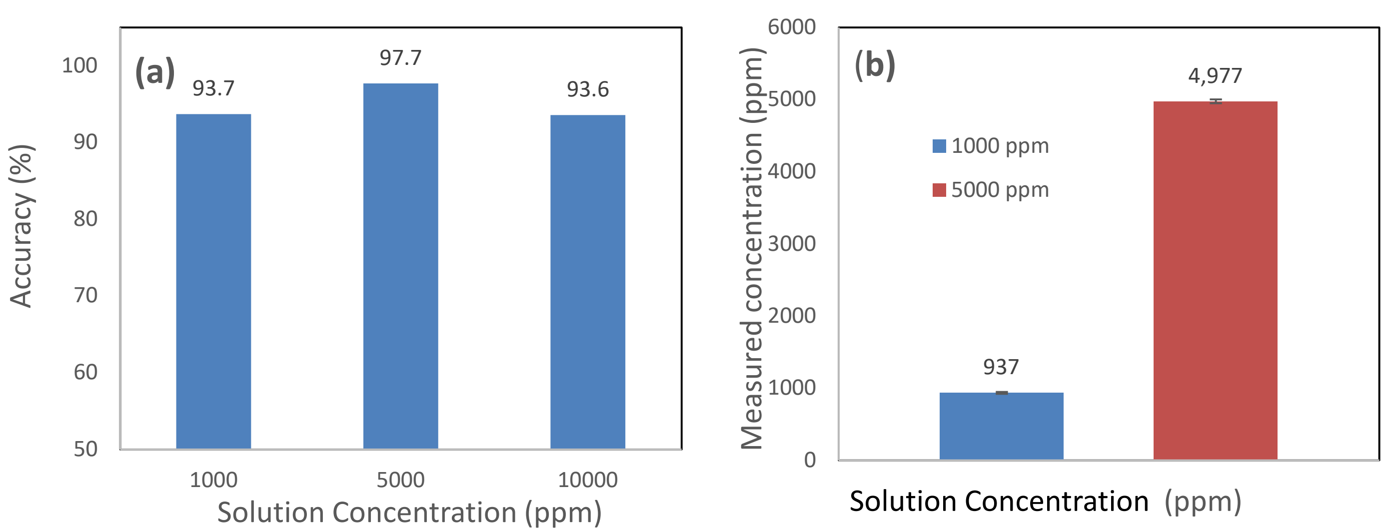

Figure 3. (a) accuracy and (b) precision of Air-160 measurement using IDS

The following concentration test accuracy data shown in Figure 4 illustrate the IDS analysis results from another commercial AEA, MasterAir AE90 with < 2% COV demonstrated on measurement of AE90 solution concentration.

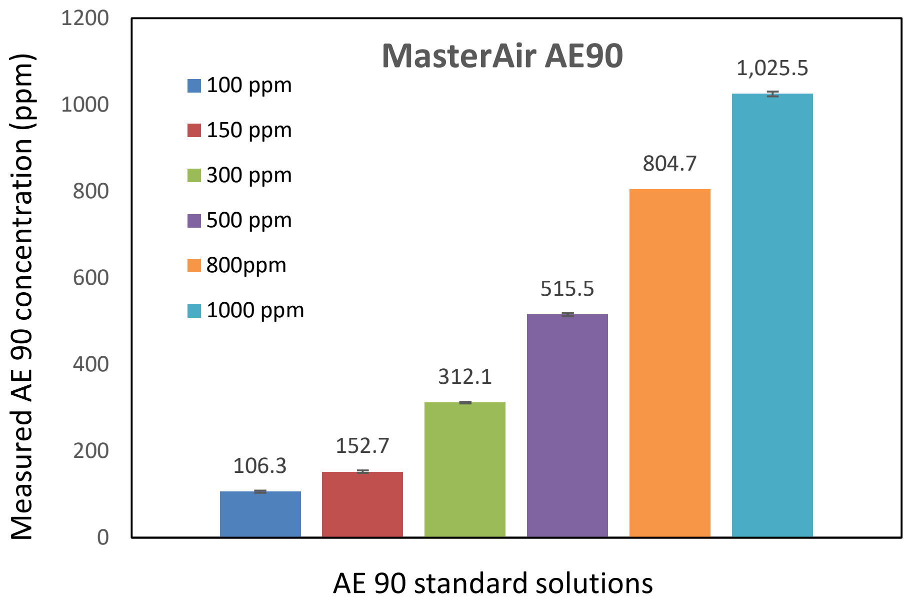

Figure 4. Accuracy of IDS on measurement of MasterAir AE90

Figure 5 below presents AEA analysis results for Daravair 1000 solutions with concentrations between 150 ppm and 1000 ppm with >90% accuracy in ppm measurements and less than 1% COV from repeated testing.

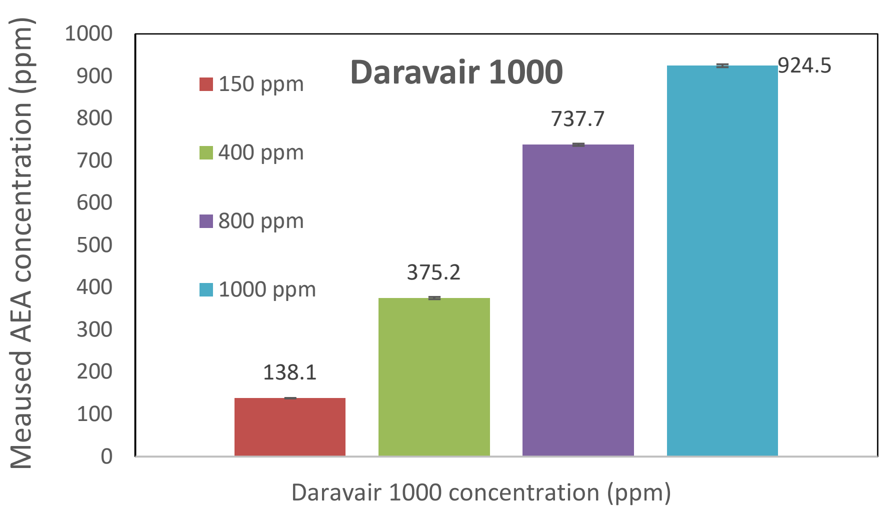

Figure 5. IDS analysis of Daravair 1000 solutions

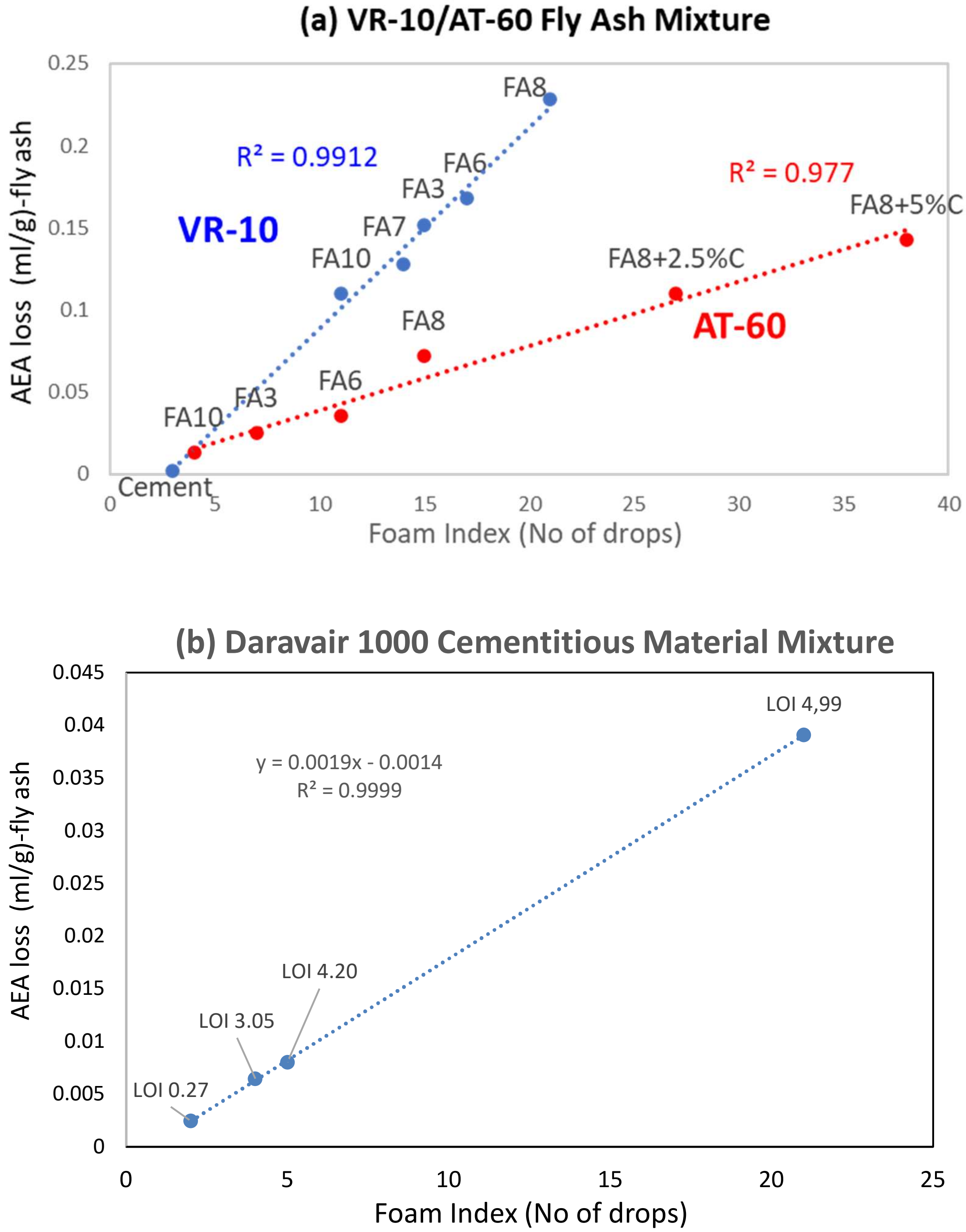

Figure 6. Correlation between ASTM foam index numbers and AEA loss due to various fly ash and cementitious material mixtures. (a) VR-10 & AT-60 AEAs with different fly ash materials (without cement) relative to adsorption by cement only. (b) Daravair 1000 AEA with fly ash and cementitious material mixture

Correlation with Foam Index Test

In order to demonstrate the practical application of this new tool, correlation studies were conducted between the standard foam index test (FIT) (ASTM method [3]) and corresponding AEA loss (ml/g) as measured by the IDS instrument and sample processing method. It is well understood in the industry that a higher foam index number translates into a higher amount of AEA "loss" due to fly ash adsorption and interactions with cementitious material suspensions. Therefore, a good correlation between the ASTM foam index numbers and soluble AEA loss measurement is an important indicator to the reliability of the new method. In order to achieve a good correlation, it is crucial that the sample preparation method be designed to reduce or eliminate variables that might affect AEA loss. Such variables include AEA stock solution properties (including shelf life), mixing speed/time, temperature, and sources of reactive ions such as those present in hard water or released by fly ash and cementitious material mixtures. The best way to control for all the different variables is to use the same solution and mixture to conduct both the ASTM FIT experiments as well as the IDS testing. Correlation studies conducted using AEAs such as VR10, Daravair AT60, and Daravair 1000 are presented in Figure 6, where a strong correlation (R^2=0.98-0.99) is observed between the foam index number and soluble AEA loss due to fly ash over a wide range of LOI values.

The system provides accurate information on the initial AEA concentration in the mix (C_i), the remaining AEA concentration (C_T and/or C_e), and the AEA loss due to adsorption and/or precipitation (Q_e and/or Q_T) in the cementitious materials. These are important parameters for determining air content of concrete mixtures. Whenever an experiment is conducted with a fly ash and an AEA, the IDS instrument essentially captures the adsorption amount by the fly ash at a particular AEA concentration and processing conditions. This is not necessarily the same as the adsorption capacity since the fly ash can continue to adsorb more by changing the conditions such as initial concentration or even the mixing process. This behavior is illustrated in the graphs shown in Figure 7 for 3 different types of samples containing low carbon, medium carbon, and high carbon ash. Plotted in the figure are the cumulative Qe/Ce values versus Ci, which can be thought of as a visual chart for recreating what happens during a typical foam index experiment where the initial concentration is gradually increased (by adding more drops of an AEA). As more drops are added, the fly ash adsorption increases initially at a fast rate but then the rate slows down after reaching a "breakthrough-point". When the IDS data is overlapped with the foam index points represented by large squares, it becomes obvious that the foam index experiment is trying to capture each breakthrough point but it doesn't always hit the target because the FIT accuracy depends not just on the specific operator/user, but also on the type of fly ash being used. When a low carbon ash is used, different operators seem to capture the breakthrough point reasonably well with a small deviation. However, as the amount of carbon in a fly ash increases, the discrepancy between different individuals increases and the FIT predictions seem to move away from the breakthrough point. For high carbon ash, the discrepancy can be off by a factor of 2 or 3 so the FIT method becomes very unreliable. Therefore, while the FIT method is attempting to capture each breakthrough point, the IDS method provides the complete evolution of the sample mixture and enables the user to capture what is happening in details under basically any condition for a wide range of fly ash and AEA mixtures.

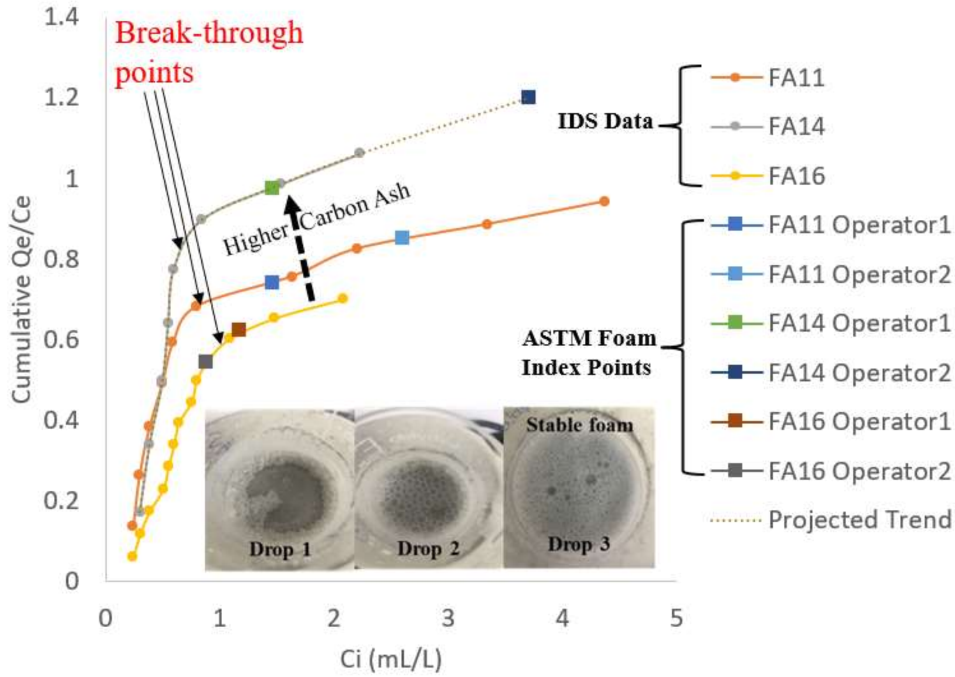

Figure 7. Relationship between cumulative Qe/Ce and initial concentration (Ci) of VR-10 AEA solutions in the presence of cementitious materials and fly ash with different carbon content. ASTM foam index points (large squares) collected by two different operators overlap the IDS data curves.

Adsorption Isotherms & Kinetics

The IDS method is effective for determining adsorption isotherms of fly ash with various AEAs. Table 3 lists the adsorption of fly ash with different AEA dosage with less than 2% COV demonstrated. By studying the behavior of fly ash with AEAs at different concentration, adsorption isotherms and mathematical modeling of fly ash and AEA performance can be established, which helps achieve a fundamental understanding on the adsorption properties of various materials. Adsorption models (Figure 8) can also be used for predicting AEA dosage in practical applications involving concrete manufacturing.

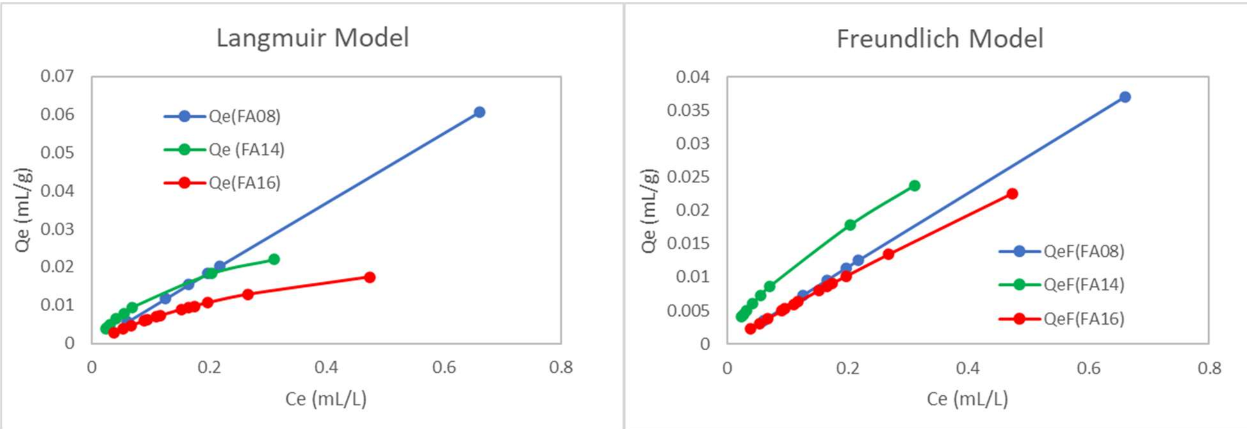

Figure 8. Adsorption isotherms using both Langmuir and Freundlich models of different fly ash materials used with a commercial AEA.

Table 3. Precision of IDS system on measurement of VR10 adsorption capacity of flyash 15 (50 ml AEA solution and 4g flyash 15)

Experiment no	Ci (ppm)	Ce (ppm)	Qe (ml/100kg)	Qe (ml/g)	Average Ci	Average Ce	Average Qe (ml/g)	SD of Qe	COV % of Qe
No.1	168.65	11.39	196.58	0.001966	168.29	7.81	0.002006	3.486E-05	1.74
No.2	168.18	6.14	202.55	0.002026					
No.3	168.03	5.89	202.68	0.002027					
No.1	326.96	26.99	374.96	0.003750	326.76	28.34	0.003730208	2.575E-05	0.69
No.2	325.54	29.46	370.10	0.003701					
No.3	327.78	28.58	374.00	0.003740					
No.1	474.36	58.03	520.41	0.005204	473.63	55.54	0.005226125	2.472E-05	0.47
No.2	474.04	56.33	522.14	0.005221					
No.3	472.49	52.26	525.29	0.005253					
No.1	654.89	71.32	729.46	0.007295	655.00	84.24	0.007134542	0.0001388	1.95
No.2	655.6	90.7	706.13	0.007061					
No.3	654.52	90.7	704.78	0.007048					
No.1	843.08	114.46	910.78	0.009108	843.16	124.56	0.008982417	0.0001627	1.81
No.2	843.97	120.69	904.10	0.009041					
No.3	842.42	138.54	879.85	0.008799					
No.1	1017.14	181.66	1044.35	0.010444	1016.39	184.10	0.010403625	3.798E-05	0.37
No.2	1018.06	186.1	1039.95	0.010400					
No.3	1013.97	184.54	1036.79	0.010368					

In addition, information about adsorption kinetics of fly ash can also be derived, which can help determine the optimal mixing time for cementitious materials that can vary depending on the type and amount of fly ash and surfactants being used. Figure igure 9 shows an example of adsorption kinetic graphs of fly ash with VR10 having different initial concentrations. At low AEA concentrations (<300 ppm), a 5 minute mixing time can generally achieve equilibrium but at higher concentrations (>1000 ppm) such as the one shown in Figure 9, a minimum of 10 minute mixing time is needed to obtain equilibrium concentration of AEA in AEA-fly ash mixtures.

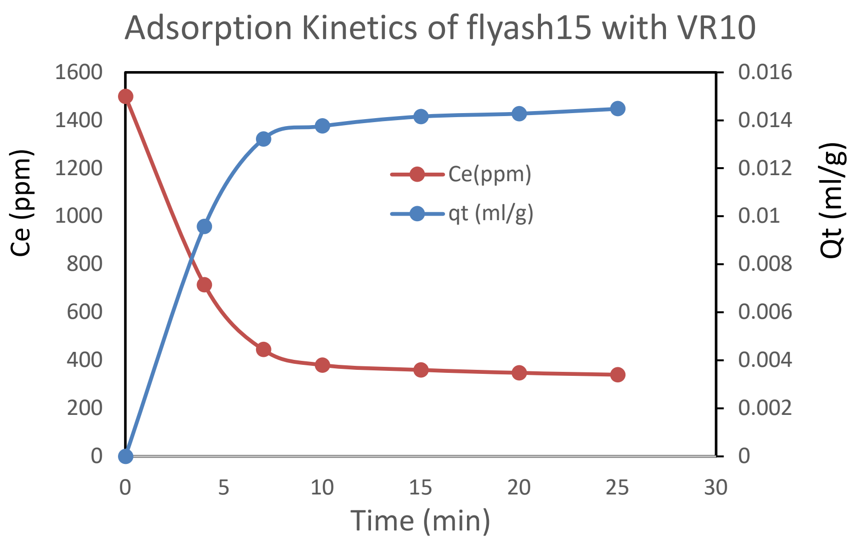

Figure 9. Adsorption kinetic modeling of fly ash with VR10

Conclusions:

The IDSpectraTM device and corresponding sample preparation method have been shown to deliver robust performance with useful and accurate quantitative information for evaluating and analyzing the properties of fly ash materials and of commercial air entrainment agents. The unit is controlled by an intuitive interface and employs an expandable AEA database that currently includes 15 commercial AEAs and offers semi-automated sample handling & analysis. The IDS system has been shown to deliver high precision with low standard deviation (<5% of COV) and high accuracy (>90 %) on AEA concentration measurements. Additionally, the ability to generate adsorption isotherms and kinetics of fly ash make it possible to use the instrument for predicting the adsorption capacity using any combination of fly ash and admixtures over a wide range of concentrations or dosage in cement materials. The IDS method has been shown to exhibit high correlation (R^2 > 0.97) with the ASTM foam index test method provided sample preparation variables can be controlled with a proper experimental procedure.

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