

Development of a New Method to Replace the Foam Index Test

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FOAM INDEX TESTING

The foam index test is a relatively crude method used to predict the relative degree of adsorption of air-entraining admixtures (AEAs) that a fly ash sample's components, primarily carbon, will have in a concrete slurry. AEAs are surfactants that are added to concrete mixes to form fine, stable bubbles which are needed for void volume so that concretes do not crack when interstitial water freezes. Foam index tests are usually done by titrating an AEA solution into a mixture of fly ash and water until a stable foam forms on the surface after agitation. The number of drops of AEA that it takes to saturate the fly ash components so that some is available to form a foam denotes the sample's foam index (FI). Dividing the FI by the amount of carbon in the sample provides a Specific Foam Index (SFI).

Unfortunately, there is frequently significant variability and, sometimes, a lack of repeatability in performing foam index measurements. These are the result of significant operator discretion, the use of different and variable natural reagents, varying laboratory equipment and "drop" sizes, non-standardized procedures, and the dynamic, non-equilibrium nature of the test. And the foam index is specific to the AEA used in the particular measurement.

In its development of a concrete-friendly mercury sorbent, Sorbent Technologies Corporation needed a standard, repeatable method to gauge the effect that different powdered activated carbons (PACs) would have on AEAs in a concrete mix. PACs are similar to the unburned carbon found in fly ash, but they have significantly higher surface area and mercury capacity. When injected into a flue gas system, they become mixed in with the fly ash. The lack of reliability and precision encountered when trying to use foam index testing on PACs or PAC/fly ash blends proved unsatisfactory.

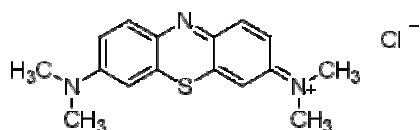
Consequently, a standardized and repeatable method for measuring the effect of fly ash carbon or mercury sorbent carbon on AEAs was developed to replace foam index test. The new method appears to be a more accurate, generalized, and robust indicator of AEA interference than the traditional foam index test. It uses a standard reagent, tests at an equilibrium condition, and eliminates operator discretion in determining when a sample begins to "foam" by utilizing instrumental measurements.

The development of this method and application results from some commercially available PACs, including Sorbent Technologies Corporation's B-PAC™ and C-PAC™ sorbents, together with a comparison with standard foam index tests, is presented in this paper.

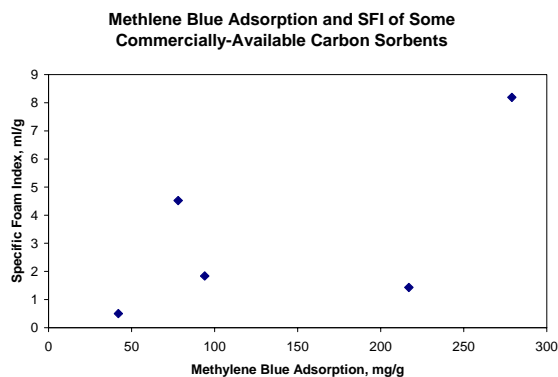
THE NEW METHOD

The new method is based on a standard reagent, acid blue 80 (AB80) (CAS 4474-24-2), rather than a non-standard AEA. Numerous dyes were evaluated for their correlations of adsorption with the foam indexes of various AEAs. AB80 provided the best results. Moreover, AB80 has a chemical structure and molecular size similar to some AEAs.

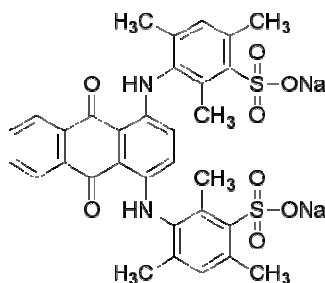
Among the other tested dyes, one was methylene blue (CAS 7220-79-3), with the following molecular structure:



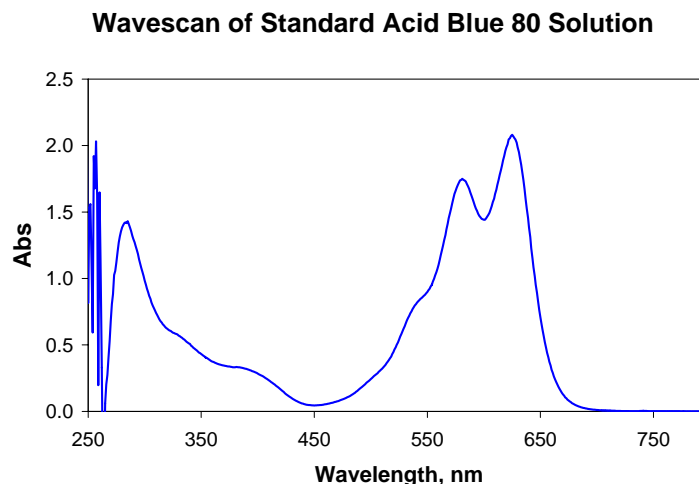
Methylene blue has been tried by other researchers for this role, however our results indicates that the methylene blue adsorption of several commercially-available PACs does not correlate well with their foam index values, as indicated in following figure, while acid blue 80 does.



Acid blue 80 is one of the anthraquinone type acid dyes, and has the following molecular structure:



The adsorption spectrum of an AB80 aqueous solution is shown below. It has three peaks at 626nm, 581nm, and 282nm, respectively. The appearance of several adsorption peaks for a given chromophore is common for a highly-conjugated system.



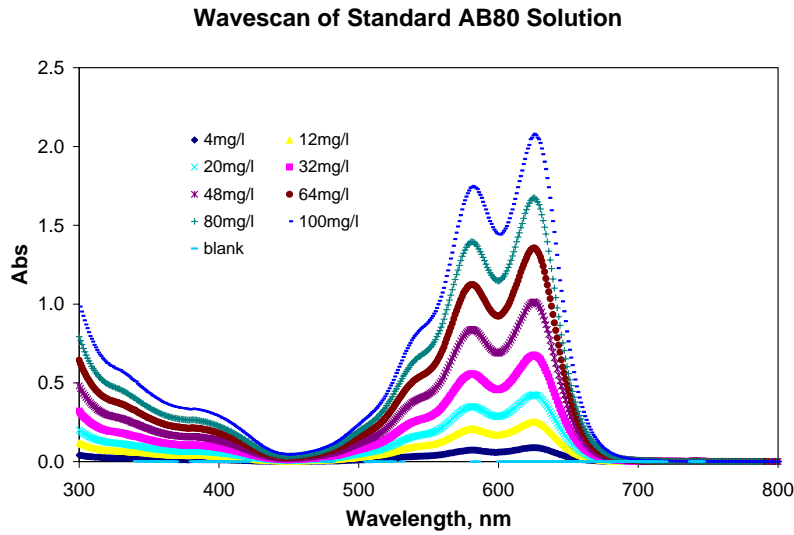
The overall procedure of AB80 adsorption that was developed is very similar to ASTM D 3860-98 Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique.

First, the PAC sample is oven-dried at 150°C for 3 hours prior to the test. Different dosages of dried carbon are then added to 50ml of 100 mg/l AB80 solution and well stirred. After the adsorption reaches an equilibrium, the carbon is separated from the AB80 solution by filtration. The concentration of the filtrate is determined, e.g. by using Perkin Elmer Lambda EZ201 Spectrophotometer. The amount of AB80 removed by the activated carbon is determined by the relative change of AB80 solution prior to and after contact with activated carbon. The AB80 adsorption of the dosage carbon is then plotted with the equilibrium concentration of AB80 solution. The adsorptive capacity is calculated from a Freundlich isotherm plot at the original concentration of the AB80 solution, which is defined as **Acid Blue Index (ABI)** in the present paper.

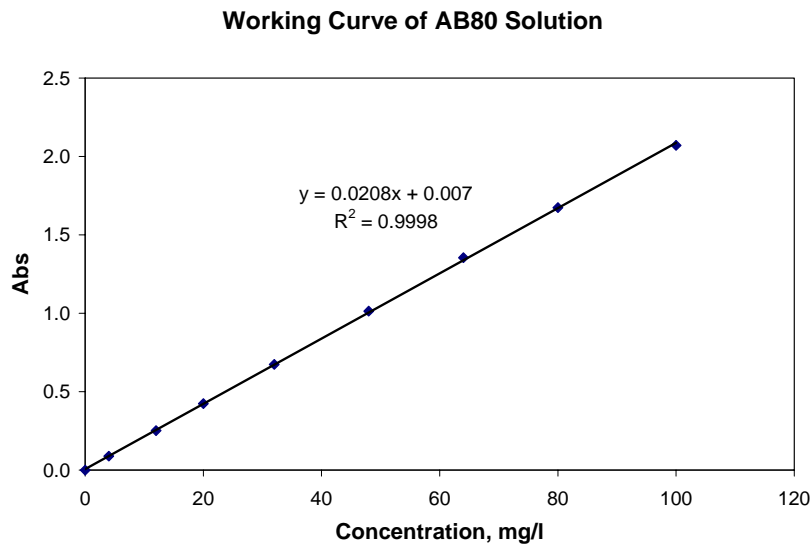
As discussed later, it was found that some chemically-treated carbons interfere with AB80 adsorption. In order to eliminate such interference, such samples should be pre-washed and extracted by deionized or distilled water until none of the impregnation chemicals is detected in the solution. For example, 5 gram of B-PAC™ was washed with 250 ml of water, then filtered and rinsed with 1 liter of water to properly prepare this brominated carbon for an ABI measurement.

The sample weights of the activated carbons used in the adsorption test may have to be adjusted depending on the adsorptive capacity of the activated carbon. A general guideline is that the concentration of the AB80 solution after contacting activated carbon should fit into the linear range of the AB80 working curve.

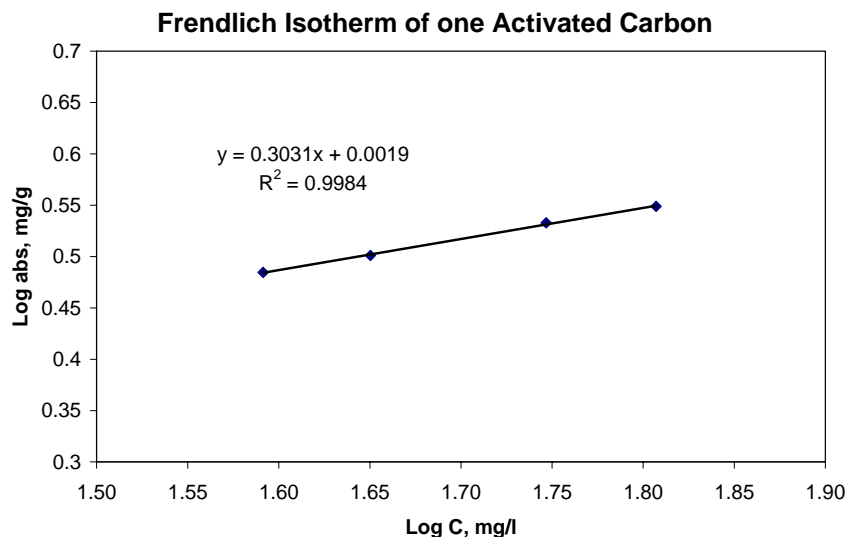
1. Working curve



AB80 solutions with different concentrations were measured and plotted in the graph above. Based on the absorbance at 626nm, the working curve for AB80 solutions was determined and is displayed in the following graph. It can be used to calculate AB80 concentrations in solutions after adsorption by various activated carbons at various dosages.

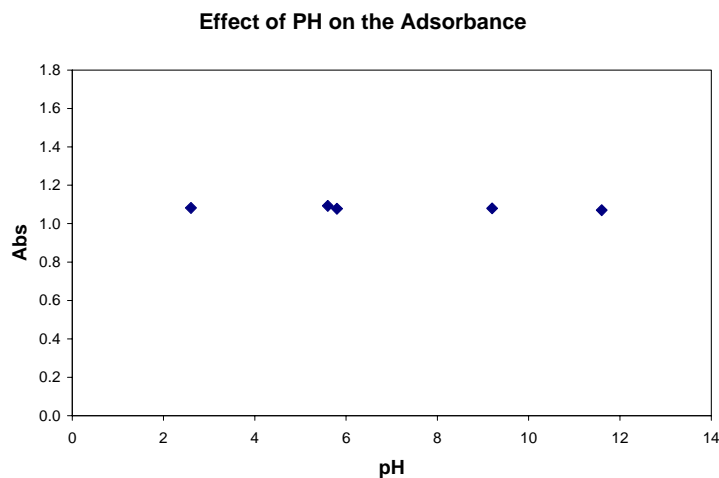


The adsorption of AB80 by activated carbon fits well into a Freundlich Adsorption Isotherm, as indicated below. The acid blue 80 adsorption of various activated carbons was determined based on Freundlich isotherms with the original AB solution concentration, 100mg/l in the present study, and the adsorption is defined as the acid blue index, ABI.



2. Effect of pH

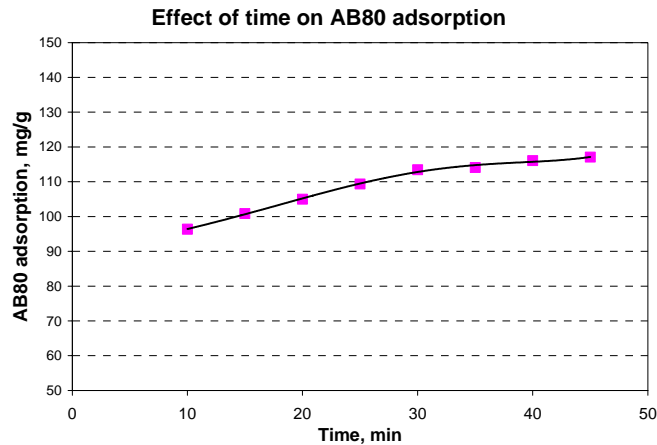
Depending on the different activation conditions the PACs encountered in its production, the pH of PACs can vary from very acidic to basic. Consequently, the effect of pH on the absorbance at 626nm of acid blue 80 solutions was investigated. The pH of the AB80 solutions was adjusted by H_2SO_4 or NaOH in order to obtain a series of AB80 solutions with different pHs. The resultant absorbances at 626nm of these AB80 solutions are indicated below.



Within the test pH range of 2-12, the absorbance of the AB solutions vary about $\pm 2\%$, which suggests that the absorbance of AB80 solution is independent of the pH of solution. Therefore, it was concluded that the plain PAC can be tested without pH adjustment.

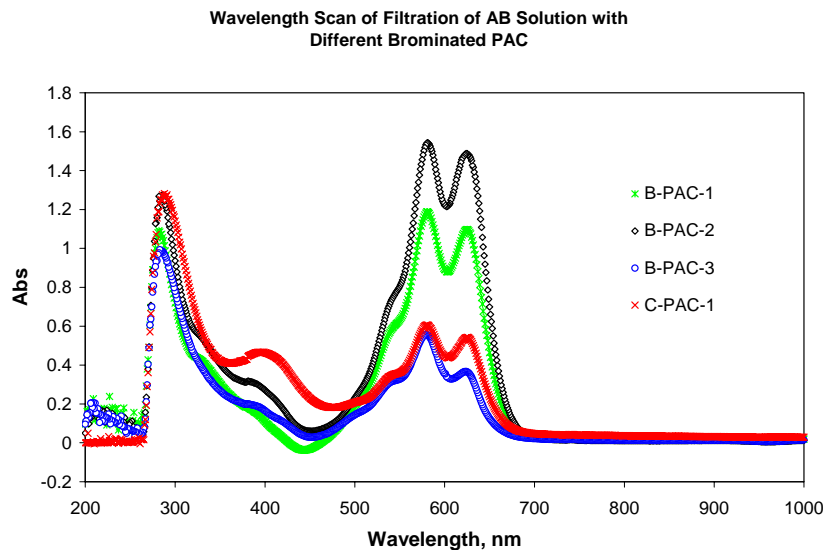
3. Effect of adsorption time

Tests were conducted to determine the amount of time needed for the adsorption to reach equilibrium. AB80 adsorption progresses relatively quickly, with the adsorption capacity reaching a plateau at about 30 minutes, as indicated below. Therefore, it was determined that 30 minutes would be sufficient as a minimum adsorption time for all subsequent AB80 tests.

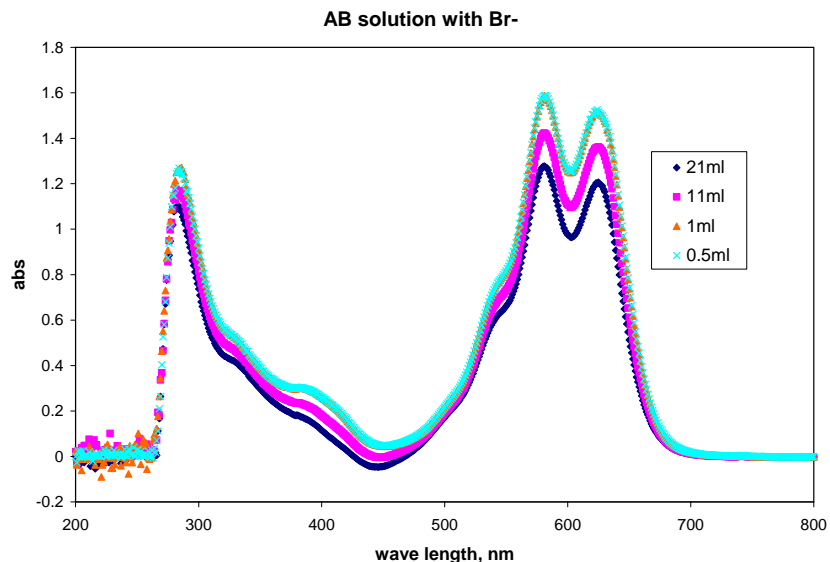


4. Effect of chemical treatment of PAC

The standardized AB80 adsorption method described above applies well to plain activated carbons with various pore structures. However, when it is applied to chemically treated carbons, the AB80 molecular structure can apparently change, which is illustrated by the following spectral analyses using brominated PAC, B-PAC™, as an example. The color of the AB80 solution changed from blue to orange after contact with these treated activated carbons.

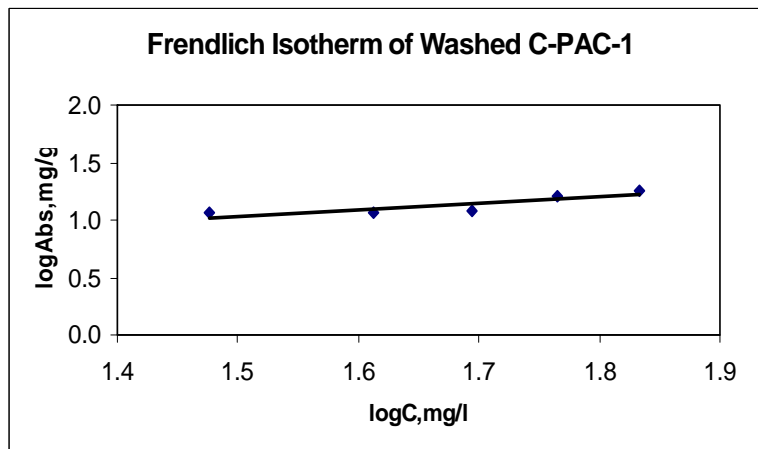
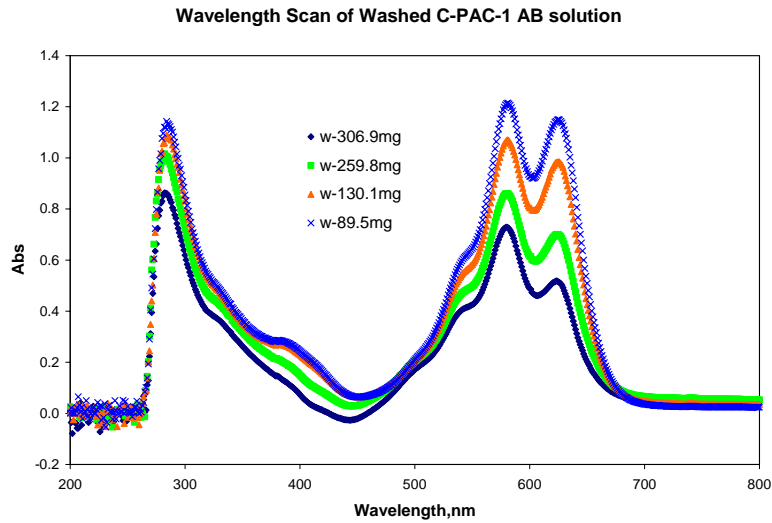


There were two possible reasons for this change: one was that the AB80 reacted with bromide anion in solution; the other was that the AB80 reacted with bromine (hypobromide) in solution. In order to explore this problem, different amounts of 0.1M bromide standard solution were added to a plain AB80 solution and the color of the solutions was monitored. The resultant spectra are shown below.



The absorbance of the three peaks changed systematically following the dilution of AB80 concentration due to the addition of bromide solution, however the relative heights of the peaks remain constant. Therefore, the bromide hypothesis was discarded and the cause of the chemical changes was determined to be due to a reaction of AB80 with bromine (hypobromide). In order to eliminate the effect of bromine (hypobromide) on AB80 molecules, pre-washing the chemically-treated samples to remove weakly-attached bromine species was added to the procedure in the standardized AB80 measurement method.

For example, concrete-friendly C-PACTM mercury sorbent, which was described in the previous figure, was pre-washed with adequate DI water and then dried and tested for its ABI. The spectrum of the AB80 filtrate solution after adsorption by different dosages of pre-washed C-PACTM is shown below. The adsorption of the sample again well follows the Freundlich isotherm.

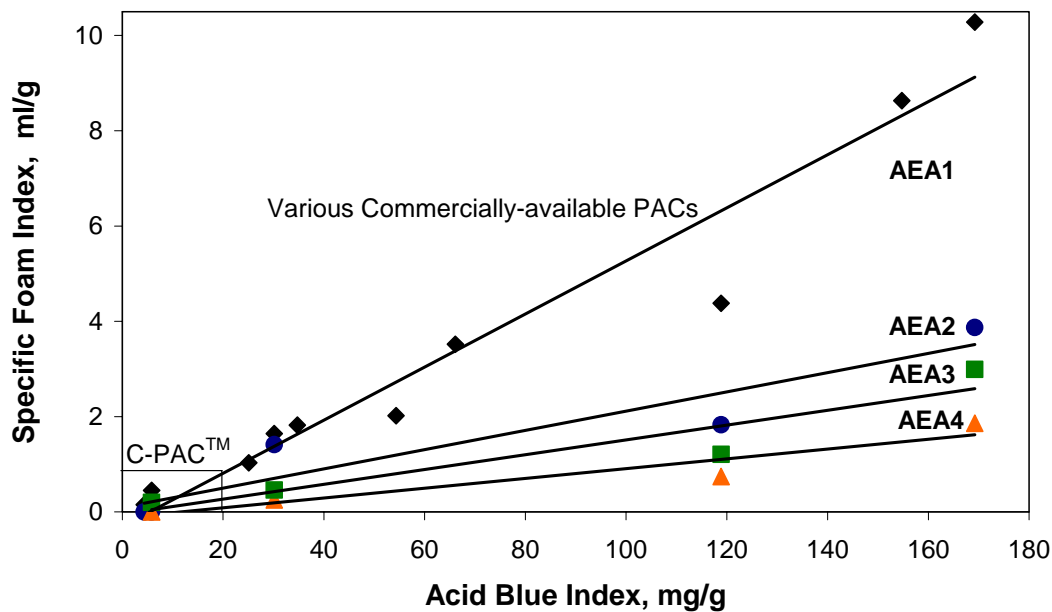


Therefore, whenever chemically-treated PACs are tested for AB80 adsorption, pre-washing procedures should be followed.

5. *The ABIs of various samples, including activated carbon and brominated activated carbon, compared with foam index measurements*

The ABI method has been extensively tested using a broad variety of carbon-containing materials. These include a series of laboratory-made activated carbons, a range of commercially-available activated carbons from different precursors, and different chemically treated activated carbons, including Sorbent Technologies' B-PAC™ and C-PAC™. A comparison of the ABIs and SFIs of some of these activated carbons using various commercially-available AEAs is shown in the following figure.

ABI & SFI of Some Commercially-Available Carbon Sorbents and C-PAC™



As previously reported, Sorbent Technologies has developed a brominated activated-carbon-based mercury sorbent with a very low SFI value, called C-PAC™. The ABI of this material is less than 10mg/g, as indicated in above figure.

CONCLUSIONS

The ACI method appears to be a better method than the foam index test for quantifying the relative interference of carbons on air-entraining admixtures. It uses a standard reagent, tests at an equilibrium condition, and eliminates operator discretion in determining when a sample begins to “foam” by using instrumental measurements. The method appears particularly applicable in examining effects of activated carbon in fly ash on AEAs in concrete compositions, an increasingly important issue as power plants install mercury controls over the coming years.