

# Strategies and Technology for Managing High-Carbon Ash

Technical Progress

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## **ABSTRACT**

The overall objective of the present project is to identify and assess strategies and solutions for the management of industry problems related to carbon in ash. Specific research issues to be addressed include:

- the effect of parent fuel selection on ash properties and adsorptivity, including a first ever examination of the air entrainment behavior of ashes from alternative (non-coal) fuels.
- the effect of various low-NO<sub>x</sub> firing modes on ash properties and adsorptivity
- the kinetics and mechanism of ash ozonation. This data will provide scientific and engineering support of the ongoing process development activities.

During this fourth project period we completed the characterization of ozone-treated carbon surfaces and wrote a comprehensive report on the mechanism through which ozone suppresses the adsorption of concrete surfactants.

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## INTRODUCTION

Pulverized coal combustion produces over 75 million tons of fly ash and bottom ash in the U.S. every year. The most widespread and economically attractive option for utilizing fly ash is in concrete manufacture, where the fly ash serves as a partial replacement for Portland cement. In most concrete mixtures, specialty surfactants, or "air entraining admixtures" (AEAs), are added to stabilize sub-millimeter air bubbles, which improve resistance to freeze / thaw cycles (see Fig. i). The bubbles are believed to provide excess volume to accommodate the expansion of residual water upon freezing in the set concrete. Solid carbon residues, if present in fly ash in high concentration, can adsorb these surfactants and render them unable to fulfill their intended function (see Fig. ii). As a result the stable air volume is too low or the mean bubble separation (spacing factor) is too high to impart the desired freeze/thaw resistance.

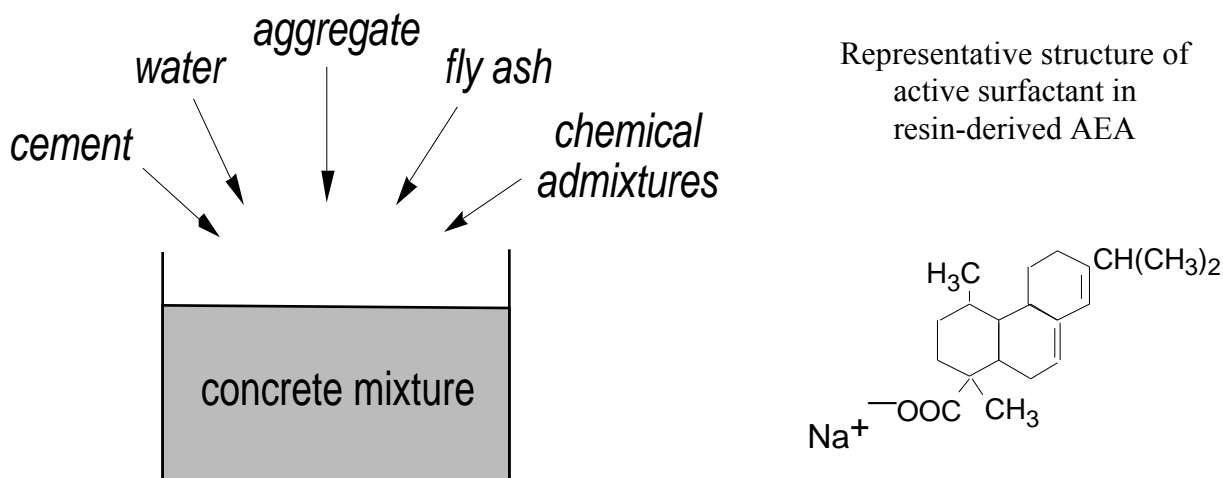


Figure i. Overview of the composition of fly ash concrete. One class of chemical admixtures are air entraining admixtures (AEA), for which a model structure is shown.

Although increasing surfactant dose may compensate for the adsorption loss, large surfactant doses in practice lead to large and intolerable variations in entrained air when normal variations in ash properties are encountered in the field. Current regulations in the U.S. limit the carbon content in ash streams for concrete applications to 2 to 6 weight-%, depending on region and regulatory body. Carbon content is typically measured by the ASTM Loss-on-Ignition (LOI) test, which reports the extent of weight loss during air oxidation at 700 °C. At high levels, carbon can discolor concrete, or lead to loss of strength, but the first problem encountered as carbon level rises is poor air entrainment behavior and this is the primary driving force for the current regulations. *If the air entrainment problem could be solved in some way, most ashes generated in the U.S. today would be utilized in concrete, even with current carbon levels.*

Almost without exception, combustion research focuses on the *amount* of char consumed and the mass of unburned carbon in ash. Recent studies, however have observed variations in the surfactant adsorptivity of commercial ash samples that cannot be explained by variations in the amount of carbon present, but are related to variations in specific carbon *properties* such as surface

## Surfactant adsorption sites



Figure ii. Surfactant adsorption on porous unburned carbon.

area, surface chemistry, and particle size. Very little is known about the effect of combustion conditions, coal type, and post-combustion treatment on carbon adsorptive properties. Several recent studies have measured the relevant adsorptive properties of commercial ash samples, but these samples come from complex and incompletely characterized combustion environments, and, as a result, it has not yet been possible to link surfactant adsorptivity to specific combustion conditions or fuel type.

A number of research and development groups are taking another approach to the carbon problem — they are developing technologies for the physical separation of carbon from the inorganic matter in ash, or for the burnout of carbon in dedicated combustion processes downstream of the boiler. These processes have not been widely adopted in the utility industry, largely due to capital cost and complexity. An alternative to these technologies is the use of ozone as described in the recent Brown University patent (US Patent 6136089). Ozonation at or near room temperature introduces oxygenated surface groups on the unburned carbon surfaces that increase the polarity of the carbon surfaces and reduce the surfactant adsorptivity, without removing significant carbon by full oxidation. In this respect the ozonation process is fundamentally different from all other proposed processes, including those in which carbon is burned out in a separate combustion process downstream of the primary coal-fired boiler. Potential advantages of ozonation include:

- simplicity of concept and operation
- operation under dry conditions, thus preserving the pozzolanic properties of ash.
- operation at ambient temperature, avoiding the need for a heat source.
- low estimated operating costs, consisting primarily of electricity.
- large-scale ozone generation is proven, off-the-shelf technology applied in water treatment, bleaching and disinfecting operations.

- ozonation does not generate a high-carbon waste stream (as do separation processes), which in most cases must be landfilled

Potential disadvantages of ozonation are:

- ozone is toxic and must be handled in sealed units (note however that ash is already handled in sealed units to prevent dust emissions)
- process leaves carbon in place, thus leaving regulatory hurdles based on LOI in some cases. Even after treatment, if the ash contains carbon above the governing local or federal limit (typically 3 or 4%), additional work is needed to verify its technical suitability for concrete, at least under current regulations.

The second cited disadvantage indicates that the most promising ash streams for initial demonstration are those that meet local LOI specifications, but still behavior poorly in concrete. We have identified a number of such field samples, typically class C ashes, and have focused early work on their treatment. It is anticipated, however, that successful with these low-carbon samples will allow even higher carbon-content ash streams to be considered in the second round of applications.

EPRI is funding the practical development of the ozone technology, but more laboratory work is needed on the kinetics and mechanism to provide the scientific and engineering data for intelligent scale-up and optimization.

### **Project Objective**

The overall objective of the present project is to identify and assess strategies and solutions for the management of industry problems related to carbon in ash. Options for improving or maintaining ash quality include:

- targeted fuel selection (or switching)
- modifications to combustion conditions or ash storage conditions
- post-combustion carbon surface modification by dry ozone

This project brings together a team of researchers from Brown University, the University of Utah, and Southern Company to address the problem of high carbon ash through a combination of bench scale experiments, pilot scale combustion trials with extensive analysis of collected ash samples, and the characterization of field ash samples. Specific scientific issues to be addressed include:

- the effect of parent fuel selection on ash properties and adsorptivity, including a first ever examination of the air entrainment behavior of ashes from alternative (non-coal) fuels.
- the effect of various low-NO<sub>x</sub> firing modes on ash properties and adsorptivity
- the kinetics and mechanism of ash ozonation. This data will provide scientific and engineering support of the ongoing process development activities.

Data from the project will be transferred to industry through close interaction with EPRI and its member companies, the ozonation development team of PCI-Wedeco / Brown and selected ash marketing firms, and Southern Company.

## **PROGRESS THIS PERIOD**

The foam index test is widely used as a simple laboratory test to indicate the likely air entrainment performance of a test ash sample in concrete. It has been used extensively in the current project as a way of assessing the effectiveness of ozone-based surface treatment, and of understanding the behavior of carbon residues from alternative fuels. The underlying chemistry of the foam index procedure is poorly understood, however, and the test has been the subject of some controversy in the recent literature. Since air entrainment testing in concrete or mortar is time and labor intensive, it is essential for this field to establish a meaningful and reproducible laboratory test that accurately reflects the surfactant adsorption process in concrete solutions and the ultimate quality of the ash in applications. During this period, we carried out a special set of experiments designed to understand the complex chemistry in foam index solutions and the implications of various test condition choices (effect of cement, pH, calcium ions etc) on the ultimate usefulness and applicability of the index. The results are used to propose a standardized foam index test protocol. The sections below describe that work, which was co-funded by EPRI, and will form the basis for a future publication.

## **DETAILED REPORT ON PROGRESS**

### **1.0 Introduction**

At the present time, a large amount of coal fly ash is utilized worldwide as an additive to concrete. Not only does this use solve an ash disposal problem, but it also results in an improvement in concrete product properties (additives that serve this purpose are termed pozzolans). The suitability of a particular fly ash as a pozzolanic additive to concrete, however, depends upon several factors related to the unburned carbon content of the fly ash. It is the carbon's porous surface area which is important in determining the capacity of the carbon to adsorb air entrainment admixtures (AEAs) [1-3]. The AEAs are surfactants added to concrete in order to create fine air bubbles (<1 mm diameter) during the mixing of the concrete, hence the origin of the term "air entraining agent". These air bubbles impart freeze-thaw resistance to the concrete by providing void volume to accommodate expansion of residual water during freezing. When a fly ash contains a large amount of carbon, the adsorption of the AEA surfactant by the carbon destroys the ability of the concrete to hold the required air. It is this adsorption problem that dictates the rejection of large amounts of commercial utility ash. The ability of the carbon to adsorb AEA depends upon not only its surface area, but also the accessibility of that area and its polarity [3], factors that are well-known in activated carbon design. Recognition of this has led to the identification of ozonation as a tool for rendering ash carbon surfaces polar and thus of lower AEA adsorption capacity [4].

One of the key requirements for systematic design of activated carbons is that certain well-defined benchmark tests be available for evaluating the carbons. The same is true in evaluating the suitability of a fly ash as a pozzolan, or for designing AEA adsorption mitigation procedures. Historically, the well-known "foam index" test has served this purpose. Unfortunately, this is not a standardized test and different laboratories have used widely different procedures. Moreover, there are a great many candidate commercial AEAs that can be used for the test. Thus there has



never been good comparability of results from lab-to-lab, or even within a single lab, if the AEA supply is changed.

It has also been recommended by an ASTM task group that an improved foam index method be developed [5]. While this report does not touch upon all aspects of those recommendations, it offers some insights into some aspects of the problem, and provides what is a step in the desired direction.

In this report, we present research on several chemically pure candidate surfactants tested against commercial AEAs, utilizing many commercial utility ashes from the Brown University ash sample bank. These easily obtained pure chemical surfactants offer the opportunity for development of a standardized foam index test that can allow true inter-laboratory comparisons. Development of a standardized test using a spectroscopic assay of AEA adsorption, as has been recommended [5] would likewise benefit from use of a pure surfactant. While spectroscopic methods have already been utilized in examining adsorption of commercial AEA materials [6,7], there remains the concern that with the mixed commercial materials, there may be differences in how different fly ashes adsorb different components from the mixtures. If different components have different light absorbing characteristics, then there could develop uncertainties in calibration. For example, if an AEA were to contain one strongly and one weakly light absorbing component of comparable surfactant strength, and if one fly ash preferentially adsorbed mainly the first, while the second adsorbed mainly the second (as could happen for reasons of molecular accessibility of surface character), then the light absorption would characterize the AEA capacities as very different while the foaming behavior could be similar. To avoid any such issues, it would appear better to develop a spectroscopic test with a pure material that would at least serve as a reference for further testing with actual commercial mixtures.

## 2.0 Experimental

### 2.1 Air Entraining Admixture and Surfactant Materials

The commercial AEAs that were examined as part of this study were Darex II™ (provided by W.R. Grace and Co. of Cambridge, Massachusetts) and Air 40™ (from Boral Material Technologies, Inc.). Darex II is described by its manufacturer as a “complex mixture of organic acid salts”. It is a non-vinsol product, just as is the Air 40 which is formulated with a “stabilized modified resin surfactant”, according to its sales literature.

The candidate pure surfactant materials were sodium dodecyl sulfate (SDS), abietic acid sodium salt (AAS) and dodecyl benzenesulfonic acid sodium salt (DBS). All of these have either been used or considered for use as actual air entraining agents [8]. None of them, are however, in common commercial use in standard fly ash concrete, for reasons of performance and especially, expense. They do, however, closely mimic the behavior of the commercial anionic-type AEA compounds under the usual foam index-type test conditions, as will be presented below. The SDS (MW=288 g/mol) and DBS (MW = 348 g/mol) were purchased in commercial reagent grade, while the AAS (MW = 324 g/mol) was prepared in-house from commercial reagent grade abietic acid.

### 2.2 Fly Ash and Cement Samples

A total of 29 fly ashes, including both class F and class C samples, were selected for various aspects of the testing program. The samples were chosen from the Brown University coal fly ash sample bank of roughly 80 fly ashes. These samples have been obtained from utilities (or ash brokers) throughout the U.S. The class F ashes are formally characterized by an inorganics content of ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ) which is no less than 70%, whereas the class C ashes must

contain only more than 50% by weight of these components [9]. The difference between the two classes is associated with the higher alkali and alkaline earth contents of the class C ashes. This classification generally places the ashes from bituminous coals and anthracites into class F and those from lignites and subbituminous coals into class C.

The actual samples used in this study are shown in Table 1. The particular utilities and units that produced the samples are not specifically identified, because not all samples are fairly representative of their current “normal” practices. All samples were, however, produced in full scale boilers under actual load conditions.

The cements used in the foam index testing work were all standard commercial Portland cements, purchased from local hardware dealers. There was some variability in the results of foam index testing performed on different cements. For this reason, it was important to perform a “blank” experiment with each cement, as part of routine foam index testing. This will be discussed further below.

### *2.2 Loss-On-Ignition Measurements and Surface Area Determination*

The adsorption of surfactant is associated with the presence of unburned carbon in the ash. The test that is normally utilized for determining unburned carbon content is the “Loss-on-Ignition” (LOI) procedure. These tests were performed on 1 gram samples, pre-dried in a laboratory oven at 130°C for two hours. After drying, cooling and re-weighing, the samples were placed into an air ventilated laboratory oven at 740°C for two hours, in order to burn out the residual carbon. The loss in mass at 740°C was reported as the LOI, and this is assumed to be the weight of unburned carbon in the original sample (though there is a possibility of a small amount of contribution from some slow mineral phase decomposition reactions [10]).

Surface areas of the samples were determined using nitrogen in an automated Autosorb 1 gas adsorption device from Quantachrome, Inc. Standard BET analysis procedures were employed.

### *2.3 Foam Index Test*

The foam index test is the commonly employed field test for determining the suitability of a particular fly ash as a concrete additive. Again, it is carried out in different ways by different groups, and there is no true standard methodology. The purpose of the test is to determine what is equivalent to a titration endpoint for adsorption of an AEA on a particular ash. The ash is contained in a simulated aqueous concrete mixture, which is somewhat thinner in consistency than an actual concrete mixture (in order to ensure good mixing). When the ash in the mixture has adsorbed an amount of AEA needed to fully saturate all *accessible* adsorption sites, “normal” surfactant behavior can be observed in the water phase, i.e., the test solution supports a stable foam on its surface. Generally speaking, the more surfactant that is needed for titration to the foam index endpoint, the poorer the performance of the ash is likely to be in the field. The test is very widely used because it can be performed in the field and involves no special equipment.

Different AEAs can give quite different values of the foam index, which is one reason why it is difficult to develop a truly standard test. The difference in performance has to do not only with the chemical nature of the AEAs (which may be derived from a variety of natural and synthetic sources), but also with their aqueous concentrations.

In the present work, the foam index tests were based upon commonly used procedures [11,12], but with details determined by local circumstances, as is generally the case. The testing involved placing two grams of fly ash, 8 grams of Portland cement and 25 ml of deionized water

into a 70 ml, 40 mm I.D. cylindrical jar. The jar was capped and thoroughly shaken for one minute to completely wet the cement and ash. A 10 vol.-% aqueous solution of commercial AEA was then added one drop (0.02 ml) at time from a pipette gun. Following addition of each drop the jar was capped and shaken for approximately 15 seconds, after which the lid was removed and the liquid surface observed. Before the endpoint of the test, the foam on the liquid surface was unstable, quickly breaking and disappearing from the free surface. The endpoint was taken to occur when foam remained stable on the surface at least 45 seconds. As noted above, a blank value was measured using only Portland cement in water. Subtraction of the blank value from the actual test results gave the reported foam index value for the fly ash (in ml, per two grams of ash). All foam index tests were replicated at least twice, and the reported values are averages of the replicates.

The same procedure was used with the pure surfactant materials, though the solution concentrations were varied so as to provide values in an easily measurable range. The actual concentration values will be given below.

It is important to note that the foam index test is a *dynamic* test, as opposed to an equilibrium measurement. It has been reported elsewhere [6] that the full equilibrium adsorption of surfactant by fly ash is characterized by timescales on the order of hours, as opposed to the timescale of the foam index test, which is minutes. Though this finding has recently been challenged, based upon results suggesting that the equilibration time might be ten minutes or less [7], it is believed that this could depend somewhat on the nature of the carbon in the ash. Regardless of which timescale is correct, there is general agreement that the dynamic nature of the commonly utilized foam index procedures could lead to an underestimate of actual long-time equilibrium uptake of AEA by fly ash carbon. This can help explain why in the field, it is observed that a load of concrete that appears to have proper dosing of AEA, based upon the foam index test, can sometimes go “flat” (lose its air content) during transport to a job site. This issue was not further considered in this work, except as noted below.

### 3.0 Results and Discussion

#### *3.1 Correlation of Foam Index Results Using Different Commercial AEAs*

Both the Darex II and Air 40 are widely used commercial AEAs, which are derived from natural materials, and as earlier noted, have complex and not easily characterized, compositions. One of the first issues addressed in this work was whether these different commercial AEA products behaved similarly, when tested under comparable conditions. If two common commercial materials do not show some degree of correlation in behavior, there would be little hope of developing a foam index test based upon pure surfactant models. Because of the wide variety of different types of materials used for preparation of commercial AEAs, a more extensive test matrix, comparing different agents under controlled conditions, would be useful for establishing the generality of the present results. Still, the results to be presented below, from work involving different kinds of model surfactants, provide confidence that a very wide range of commercial materials will behave in a similar manner.

An arbitrary choice was made to perform the foam index test using the commercial products at 10% volume dilution, in deionized water. Since the AEA products are aqueous solutions, as shipped, the addition of pure water is not expected to change their character. In any event, in actual use the solutions are diluted to an even greater degree in the concrete mixture. The dilution of the as-received AEA allowed a convenient number of drops to be utilized in the foam index test procedure described above.

The absolute concentrations of the surfactant compounds were probably not the same for the two commercial AEA solutions. In a test involving drying of the solutions in a vacuum oven, the Air 40 gave approximately 20% greater non-volatile residue than did the Darex II. No further effort was made to characterize the AEAs in detail, and this 20% difference in residues does not necessarily reflect the difference in actual surfactant concentrations in the two AEAs.

It was observed that the foam index results using Darex II and Air 40 were well correlated with one another, for the particular subset of ashes chosen for testing. The results are shown in Figure 1. It should be recalled that a difference of 0.02 ml is equivalent to a single drop uncertainty in determining the endpoint of the test. The results seemingly imply that the Air 40 solution is roughly three times “stronger” than the Darex II solution, but again, the concentrations used for this test are arbitrarily set. The results of Figure 1 gave confidence that the performance of commercial AEAs from different sources can be reasonably correlated with one another.

### *3.2 The Problem of AEA “Aging”*

There was a very obvious “aging” of the commercial AEAs. Over the course of several weeks, the foam index of a “standard” ash sample increased measurably, if the same batch of prepared 10% AEA was utilized. Both the Darex II and Air 40 showed the same qualitative trend. The trend could apparently be retarded by storing AEA solutions in a tightly stoppered vessel from which light was excluded. This was suggestive that the aging involved oxidation of the AEAs, but the question was not pursued further here.

A recent paper [7] has offered that there could be a role of carbon dioxide absorption in changing the character of an AEA solution. This was attributed to a change in the pH of the solution, and the formation of free acid from the original salt form, leading to surfactant precipitation. Oxidation processes can also lead to formation of additional organic acids, in addition to those from the carbon dioxide absorption route. Whatever the mechanism, the use of commercial AEA materials for routine foam index testing carries with it some danger of unanticipated change of composition.

Thus another advantage in the use of freshly prepared pure surfactants for foam index testing is that changes in the foam index obtained with the pure reagents will be more reliably indicative of changes in the fly ash, as opposed to an artifact of the change in the AEA itself.

### *3.3 The Role of Carbon in Adsorption*

It has recently been suggested that the carbon in fly ash might be unable to adsorb AEA on the timescale of the foam index test [7], and that this leads to greater importance of faster adsorption processes on mineral or inorganic fractions of the ash. The results of the present testing program do, however, support the key role that carbon plays in the present foam index testing program. Other papers have presented evidence of the important role of carbon [1-3], and it would be difficult to rationalize the effect of ozonation treatment on fly ash foam index [4], but for the role of carbon in adsorption.

Here, the results of two additional experiments directly supported the role of carbon adsorption in foam index testing. Samples of fly ashes 21 and 39 were subjected to foam index testing, following the LOI determination procedure described above. The samples tested in this way were therefore carbon free, but the inorganic portion should be essentially unchanged (the laboratory oven operates at a temperature much lower than the samples “saw” in the boilers). In the case of fly ash 39 (starting LOI = 0.8%), the foam index with Air 40 decreased from 0.06 to 0 and in the case of fly ash 21 (starting LOI = 6.1%), the foam index with Darex II decreased from

0.3 to 0. Thus in the foam index testing as performed here, the carbon is the primary variable that determines the foam index values.

### *3.4 Effects of Ash Sample Amount*

The foam index test can be quite tedious in the case of samples containing large amounts of unburned carbon (high LOI). If the drop size is kept small, in order to maintain accuracy at the endpoint, quite a large number of drops are required to reach the endpoint with a high LOI sample. Inasmuch as each drop addition is associated with 15 seconds of agitation, followed by examination of the foam, the testing time can become quite long for such high LOI samples.

As already noted, the foam index value is a result of a dynamic measurement, as opposed to an equilibrium measurement. If the procedure is changed so as to introduce a large initial aliquot of AEA (to quickly get near to the endpoint of the titration), the time of testing can be shortened. This, however, means that the time available for equilibration of the mixture is also shortened. The endpoint of the foam index test depends purely upon the aqueous concentration of the AEA, which can be taken as a constant value. A shorter test time means that adsorption on the solid is less complete when the required aqueous endpoint concentration is achieved, because of the finite kinetics of adsorption from solution (most likely dictated by diffusional kinetics). It was indeed observed that addition of a large initial aliquot of AEA gave lower foam index values than when the dropwise addition procedure was followed.

In certain types of AEA adsorption testing, gradual atmospheric carbon dioxide dissolution into the test solution can also influence results [7]. In the present study, this was of limited concern because there was always a high pH maintained in solution, due to the presence of a large amount of cement in the mix. This would easily overwhelm any small amount of carbon dioxide absorption that might occur during the test (the pH of saturated calcium hydroxide or carbonate solutions in equilibrium with atmospheric carbon dioxide is still basic). Because the procedure used in [7] did not include cement in the mix, there would have been a greater sensitivity to carbon dioxide absorption in that work. Thus we believe that the time dependence of foam index values in the present study does have to do with finite adsorption times of AEA onto carbon.

In an attempt to avoid use of a large number of drops during high LOI ash sample testing, another modified foam index procedure was developed. This simply involved reducing the amount of ash from the “standard” two gram amount to something lower, but then back-calculating the foam index results to an equivalent two gram of ash basis. The results of such experiments are shown in Figure 2. As the sample mass was reduced to small values the (back-calculated) foam index often became quite large. The behavior was not consistent from sample-to-sample. Ashes with higher LOI values seemed to require a greater amount of sample in order to achieve an asymptotic value, characteristic of the standard procedure.

The results of Figure 2 cannot be explained by the dynamic nature of the test, discussed above. The time for adsorption onto any particle of carbon should be independent of the total amount of ash sample that is tested. Since the time to reach the foam index endpoint is shorter the smaller the amount of sample, the time available for AEA adsorption onto the carbon decreases with sample amount. This should lead to a *lower* apparent foam index for small amounts of sample (when calculated to the two gram basis), opposite the observed trend. Consequently, the explanation for the dependence of foam index results on ash sample amount must instead be associated with changes in some mixture characteristics, related to the addition of differing amounts of ash to the testing mixture.

The most obvious possibility involves water-soluble inorganics in the ash. When a very high carbon ash (such as 23) is tested, adding a small amount of this ash adds very little mineral matter, and hence, soluble components. This is why the increase in foam index with decreased amount of sample is so notable in that case. Based upon present results, a minimum of at least 0.3 g of actual ash mineral had to be added to the test mixtures, in order to begin to see the asymptotic behavior.

The ash contributes soluble components to the testing mixture. It is possible that alkali components are responsible, since it is well established that increases in alkali content increase air entrainment [8,11,13,14]. An increase in foaming efficiency, as is associated with better air entrainment, would be correlated with a decrease in foam index. High concentrations of monovalent alkali cations assure good surfactant behavior whereas divalent alkaline earth cations reduce the efficiency of AEA surfactants by a precipitation mechanism, well known as the “hard water” problem [7, 11].

Because the introduction of ash to a testing mixture adds a number of soluble compounds, it is difficult to state with any certainty from these experiments which soluble components were the most critical. For this reason, a separate testing program was conducted, involving pure additives and commercial AEA solutions, in order to determine which soluble inorganic species might influence foam index values.

### *3.5 Influence of Solution Chemistry on Foam Index*

These tests were all carried out using 25 ml of deionized water, to which were added various salts. The foam index procedure was then followed, in this case without the addition of any cement or actual ash, except as noted. Both the Darex II and Air 40 were examined and always gave the same behavior, though the numbers of drops required for stable foam formation were always different. Darex II is a near-neutral water solution, whereas Air 40 is basic in character. This difference in starting characteristics had no apparent effect on the behavior observed in the following tests.

It should be noted at the outset that performing the foam index test with deionized water yielded no foam endpoint. This is presumably because the tested solutions became acidic, due to absorption of atmospheric  $\text{CO}_2$  [7]. The solutions had a cloudy character, as the surfactant precipitated in the expected manner.

Addition of just two grams of cement to deionized water reduced the AEA requirement for foaming to a few drops, just as in the case of the normal foam index “blank”. Addition of a few grams of carbon-free ash, prepared by completely burning out the carbon in a laboratory oven, also reduced the foam index “endpoint” to a few drops of 10% solution. Both these additions resulted in the solution becoming basic (the cement more so than the ash mineral). The solution pH was believed to be an important factor in foam development. This was explored using different alkali solutions.

Addition of NaOH to pure deionized water (pH =13) resulted in a foam endpoint comparable to that with mineral or cement, but if the NaOH was neutralized by addition of  $\text{CaCl}_2$ , again no stable foaming behavior was observed. Addition of neutral salts such as  $\text{Na}_2\text{SO}_4$  or NaCl, or acidic salts such as  $\text{CaCl}_2$  to deionized water did not yield any foaming behavior when tested with the AEA. Thus solution pH was shown to be important for developing the surfactant behavior, as expected, and the presence of monovalent alkali alone was not sufficient to create foaming action if the solution was not basic.

On the other hand, addition of 0.1 g of pure  $\text{Ca}(\text{OH})_2$  yielded a solution of high pH (12.8), but did not give a good, stable foam, even upon addition of a large number of droplets. This

is presumably a consequence of insoluble complexing behavior with the calcium ion, also in agreement with the results of another study [7]. Thus high pH alone does not necessarily lead to good foaming behavior. When the amount of  $\text{Ca}(\text{OH})_2$  was increased to 1 g, the solution was saturated and took on a milky white appearance, as opposed to the clear appearance of the true solution obtained with the lesser amount of  $\text{Ca}(\text{OH})_2$ . In this saturated solution case, a stable foam could be obtained, though only with a large number of drops.

Addition of alkali carbonates ( $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ) to deionized water led to stable foam formation upon addition of only a few drops. This is not surprising, in terms of the pH effect of the carbonate ions, and the fact that monovalent cations ( $\text{Na}^+$  and  $\text{K}^+$ ) were involved. These conditions together favor the usual foaming action of the surfactant. On the other hand, addition of divalent carbonate salts ( $\text{CaCO}_3$  and  $\text{MgCO}_3$ ) led to mixed results. The magnesium and calcium carbonate were expected to give poor foam formation and stability, because of the usual divalent cation effects. This was observed to be the case for magnesium, but surprisingly not for the calcium.

One particular sample of extremely finely divided  $\text{CaCO}_3$  gave a stable foam immediately upon mixing, whereas a solution prepared from a more coarse  $\text{CaCO}_3$  did not. The calcium carbonate has extremely low solubility, and in both cases the solutions were saturated. The more finely divided calcium carbonate provided an equilibrium (saturated) solution more quickly than could the coarser powder, based upon pH measurements of the solutions. Once the equilibrium pH (around 8.4, as expected for solutions in contact with air) was established, both calcium carbonate samples gave foam index endpoints that were very similar to those obtained with monovalent cation carbonates or cement. This result was not anticipated, as the usual “hard water” precipitation of surfactant had been expected. It has, however, been reported that the calcium surfactant salt precipitates can readily redissolve in such solutions, maintaining an equilibrium ionized surfactant concentration [15]. This is indeed why air entrainment is possible, despite the high dissolved calcium content of concrete mixtures.

In a separate experiment, a solution was again prepared with calcium hydroxide and tested with AEA (Air 40), yielding, as usual, no stable foam endpoint. This mixture of water,  $\text{Ca}(\text{OH})_2$  and AEA then had a few hundred milligrams of the finely divided calcium carbonate added, and was agitated. A stable foam was again immediately achieved with no further addition of AEA. In this experiment, the solution was always basic and always contained calcium ions. The difference in foaming behavior was associated with the introduction of the carbonate to the mixture. The earlier results with magnesium carbonate had demonstrated that improved foaming was not directly associated with addition of the carbonate ion, per se. In fact, the presence of a high concentration of calcium hydroxide would tend to greatly limit the solubility of the carbonate in solution, so it was unlikely that a solution equilibrium was being affected through dissolution of carbonate. These results, as well as the earlier described results with saturated  $\text{Ca}(\text{OH})_2$  solutions, suggested an alternative explanation. It appears that the presence of finely divided undissolved solids is beneficial to surfactant foaming behavior, possibly through a mechanism of adsorption of calcium surfactant species onto the surfaces of the solids [15]. This possibility received some support from the observation that there was an effect of the amount of finely divided calcium carbonate on foaming (addition of more of the finely divided carbonate induced foaming more readily). Because these amounts were always well above those needed for saturation of calcium carbonate solution, the effect could not be associated with contributions to solution from dissolution of the powder. The ability to produce a stable foam depends somehow on the available surface of undissolved carbonate or hydroxide particles. This is why the coarse calcium

carbonate powder was initially ineffective at inducing foaming action, and only slowly approached the finely divided powder in efficacy over time.

The foam index of an ash tested in solution together with pure finely divided  $\text{CaCO}_3$  was the same as that when the ash was tested with the normal amount of cement. The behavior was no different than when the ash or calcium carbonate were tested alone. Addition of  $\text{Ca}(\text{CO}_3)$  to a solution of  $\text{Mg}(\text{CO}_3)$  again very quickly provided the latter the ability to develop a stable foam, despite the fact that the  $\text{Mg}(\text{CO}_3)$  solution was by itself completely unable to support a foam.

The above results have made a strong case for the importance of finely divided calcium powders in providing foaming action, in solutions that might otherwise be unable to support foaming action. In the normal foam index test, the cement powder clearly provides this function. To the extent that related behavior has been observed before, in different kinds of experiments [15], the result is not surprising.

The above results, together with others recently published [7], thus confirm the importance of aqueous medium in the foam index test. Different choices have been made by us and by others [7], with regard to the addition of cement to the test mixtures; we have chosen to add cement to the mixtures. Addition of cement of course makes the performance of spectroscopic measurements, such as have been of recent interest [6,7] very difficult. On the other hand, the presence of cement assures the existence of an aqueous medium much more representative of the actual concrete mix. The presence of a high concentration of cement in the mixture eliminates concerns about the effect of  $\text{CO}_2$  dissolution during testing [7], as it serves as an excellent alkaline “buffer”. It also provides the finely divided calcium solids that appear to be important. The question of the mechanism by which finely divided calcium solids influence the foaming behavior was not pursued further here. It can, however, be noted that the testing work with pure surfactant materials proved much less sensitive to such additive effects (see below).

### *3.6 Alternative Surfactants for Foam Index Testing*

Three alternate surfactants were examined, SDS, DBS and AAS. The foam index test procedure with all three of these surfactants was the same as it was for the commercial AEA materials.

In the case of the SDS, the surfactant was prepared into a 1 wt. % solution (approx. 0.035 M), using deionized water. Results for a series of typical ashes are shown in Figure 3, in comparison with the results using Darex II on the same ashes. It should be noted that the actual mass of Darex II in solution was quite comparable to the mass of SDS in solution. The SDS is quite clearly a much stronger surfactant, as less SDS is required to reach a stable foam endpoint, compared to Darex II.

An AAS solution was prepared by dissolving pure abietic acid into water, and then reacting with a stoichiometric amount of sodium hydroxide. The resulting solution was 0.05 M. The behavior of AAS against Darex II was qualitatively similar to that already reported for SDS, but the required volume to reach the endpoint was quite a bit higher (see Figure 3).

A fundamentally more appealing comparison of the surfactants involves showing actual molar uptake at the endpoint. This comparison is shown for SDS, AAS and DBS in Figure 4. The DBS solution was initially prepared at 0.025 M concentration. The molar uptake of AAS at the foam endpoint is over five times greater than the molar uptake of SDS, but the different surfactants are clearly well correlated with one another. The molar uptakes of SDS and DBS are much closer to one another at the endpoint. It should be kept in mind what the endpoints actually mean. They are not true equilibrium values, though it would be expected that they should be related to equilibrium uptakes. Also, the endpoint is a function of the particular foaming efficacy



of the surfactant in water. It would be expected that the lower the required aqueous phase concentration at the foam endpoint, the lower the molar uptake of surfactant on the carbon surface.

From the preliminary data above, it appeared as though the DBS might be a good choice for a pure surfactant-based standardized foam index test. Figure 5 shows the comparison of the performance of this surfactant against the Darex II data for a larger set of ashes. In this case, the DBS concentration had been reduced to 0.00625 M. There is a very good linear correlation. There, however, remained a concern that the initial testing had been performed using a set of fly ashes with a biasing towards high LOI values. Consequently, a second round of testing was performed using a set of ashes with much lower LOI values. Because the adsorption capacities of a low LOI set were much lower, the DBS solution was further diluted to 0.001 M, so as to permit a larger number of drops to be used in determining the endpoint. These results were compared with the results from a series of tests with Darex II solution likewise diluted to 4%, from the normal 10%. The results are shown in Figure 6. A reasonable linear correlation is again observed.

Experiments were also performed with DBS in which the apparent foam index of various salt solutions were explored in the absence of ash and cement, just as they had been with the commercial AEAs. There was somewhat less sensitivity of the results to differences in additives—potassium carbonate added to the deionized water gave foam index results that were similar to those for sodium sulfate or calcium hydroxide. Calcium and sodium carbonate gave only slightly lower effective foam index values than those for the above compounds (differing by only one drop). Calcium chloride again gave unstable foams. These results imply that the use of pure surfactants will tend to make the results of foam index testing somewhat less sensitive to the effects of soluble components in the ash, and to the presence of finely divided calcium solids, than in the case of commercial AEAs.

### *3.7 Surface Capacities of the Fly Ash Carbons*

The nitrogen BET surface areas for the ashes tested in this study are shown in Table 1. The equivalent surface coverage of DBS on the carbons in the ashes may be estimated using the LOI and BET values in Table 1. The results are shown in Figure 7. The capacities range from roughly 0.05 to 0.35  $\mu\text{mol}/\text{m}^2$ , but there is a cluster of low LOI points near 0.1  $\mu\text{mol}/\text{m}^2$  whereas many high LOI points fall at around 0.2  $\mu\text{mol}/\text{m}^2$ . What this seems to suggest is that the higher surface area in the lower LOI samples is not equally accessible to DBS as is the surface areas in higher LOI samples. It has already been noted that accessibility issues do play a role in foam index testing, in connection with the effect of time on the results. Surface area, its accessibility, and other factors determining AEA capacity have been more generally discussed elsewhere [3].

As a frame of reference for the above coverage values, it may be noted that a monolayer coverage of nitrogen on carbon would involve roughly 10  $\mu\text{mol}/\text{m}^2$  (using the generally accepted value of 16.2  $\text{\AA}^2$  for nitrogen [16]). The DBS is a much larger molecule than is  $\text{N}_2$ , so the fact that the molar capacity for  $\text{N}_2$  is higher is not surprising. For example, the surface coverage of pure dodecane has been estimated to be 82.8  $\text{\AA}^2$  and that of benzene about 43  $\text{\AA}^2$  [16]. A very crude estimate of surface coverage for DBS would be provided by adding together these two values (assuming that the polar sulfate endgroup would not lie upon the nonpolar carbon surface). In the case of 0.2  $\mu\text{mol}/\text{m}^2$  DBS coverage, it can then be estimated that roughly 15% of a monolayer coverage is achieved on the ash carbon at the foam index endpoint. A less than monolayer coverage might be anticipated for several reasons. One reason is that DBS might be subject to carbon porosity accessibility limitations not important to the much smaller  $\text{N}_2$ . Of course, the BET

model is of questionable theoretical validity in highly microporous materials, and thus comparison of the DBS coverage to a BET surface area is only qualitative.

#### 4.0 Summary

There appears to be a good possibility of standardizing the widely used foam index through the use of pure surfactant materials. The present study has shown that there is a good correlation between the adsorption behavior of two commercial anionic AEA materials and three pure surfactant compounds. Apart from the advantage of avoiding issues related to uncontrolled and difficult to characterize “aging” of the commercial materials, the use of pure surfactant materials permits the examination of adsorption effects on a more fundamental basis.

We recommend, as a candidate “standard” procedure our technique based upon use of DBS. This method seems to work as a good surrogate for commercial anionic AEA materials, and the results appear to be well correlated with those obtained using common model anionic surfactants. We also recommend performing the test with addition of cement to the test mixture, in order to create solution conditions most closely resembling those in the actual air entrainment application. It needs to be emphasized that the numerical values of foam index so obtained will, as always, have greatest value when they are correlated with actual air content measurements on a similar set of ash-containing concretes.

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**Table 1. The Fly Ash Samples Examined**

<u>Sample Number</u>	<u>Class</u>	<u>LOI (%)</u>	<u>BET Area (m<sup>2</sup>/g-C)</u>
1	F	6.5	43
3	F	14.6	65
4	F	14.6	65
6	F	3.4	57
10	F	2.6	66
21	F	6.1	51
23	F	65.5	54
25	F	2.5	39
26	F	4.0	33
39	F	0.8	312
40	C	1.1	282
41	C	1.1	309
42	C	0.6	238
43	C	0.6	365
44	C	0.6	326
45	C	0.7	335
46	F	11.2	56
49	F	19.9	20
50	F	22.2	28
51	F	20.9	41
53	F	4.0	50
57	F	0.8	102
61	F	1.6	38
63	F	7.1	45
64	F	7.4	69
65	C	0.7	326
68	C	0.8	326
74	F	9.8	63
75	C	1.3	377

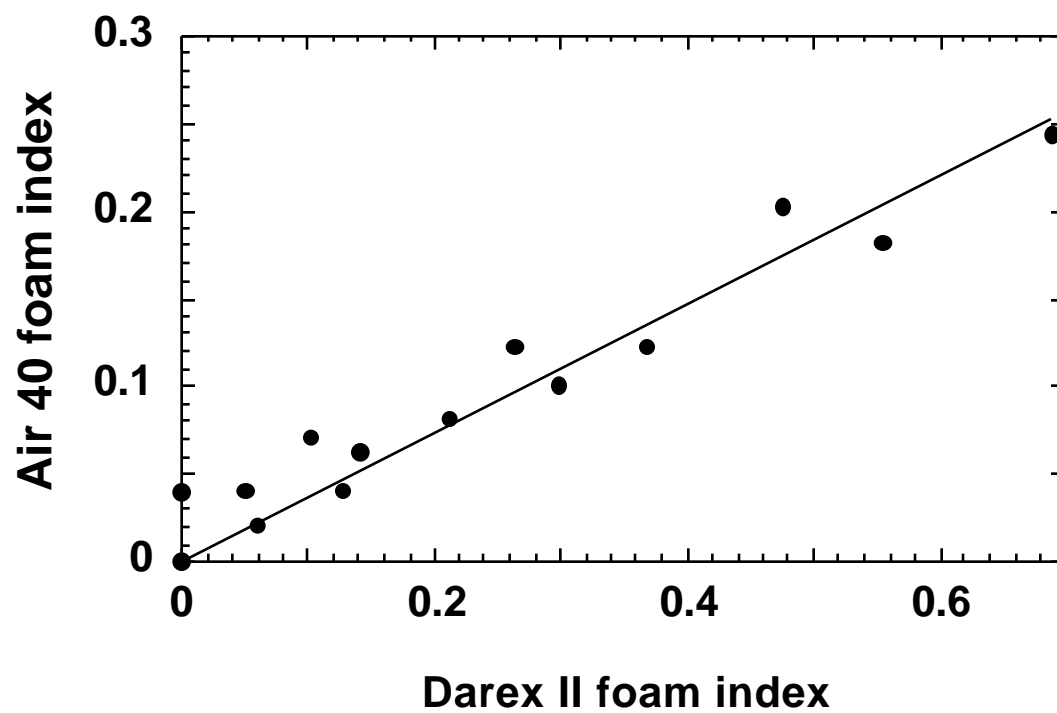


Figure 1. Comparison of foam index measured with Darex II 10% solution vs. that measured with Air 40, 10% solution. The fly ashes used in this comparison were numbers 1, 4, 10, 21, 39, 49, 50, 51, 53 57, 61, 63 and 64.

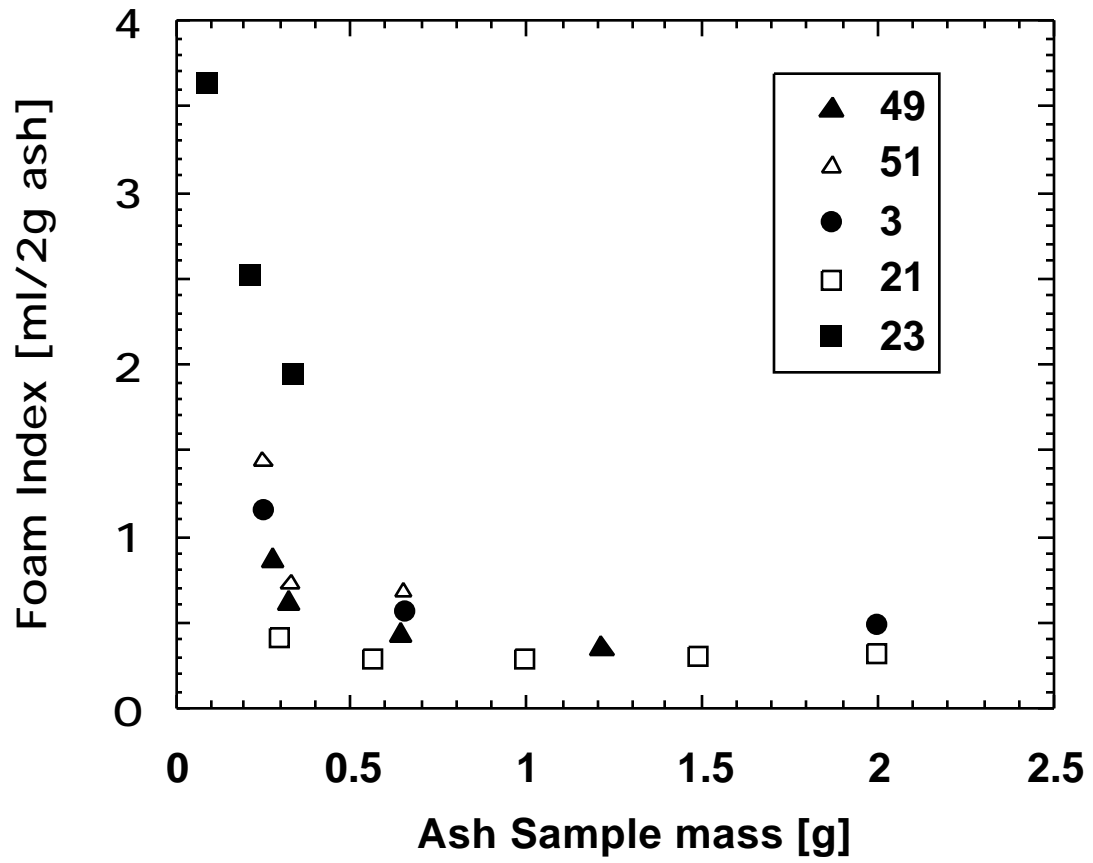


Figure 2. The influence of amount of fly ash on apparent foam index, for Darex II. The amount of cement and water were kept constant for all of the tests.

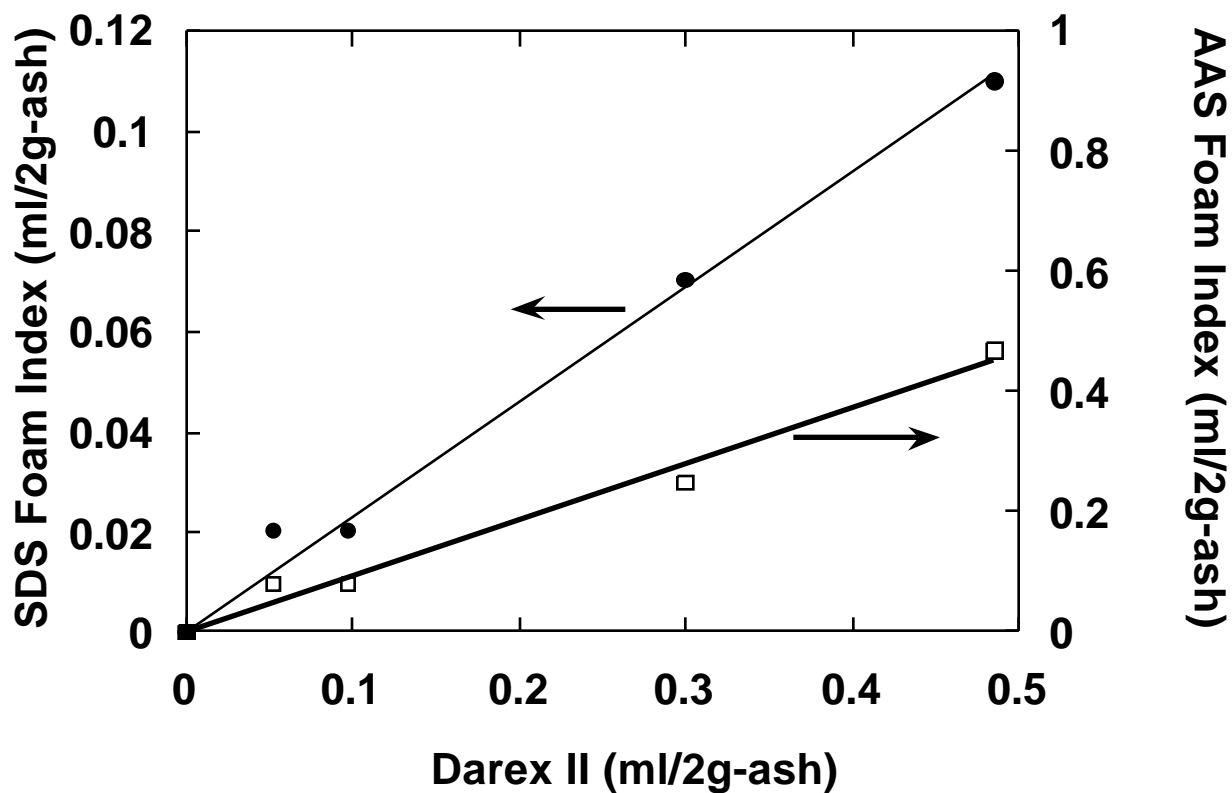


Figure 3. A comparison of the foam index determined using SDS and AAS, versus the foam index using the Darex II standard. The ashes used in this comparison were 21, 26, 63, 74, 75. Open points- AAS, closed points, SDS.

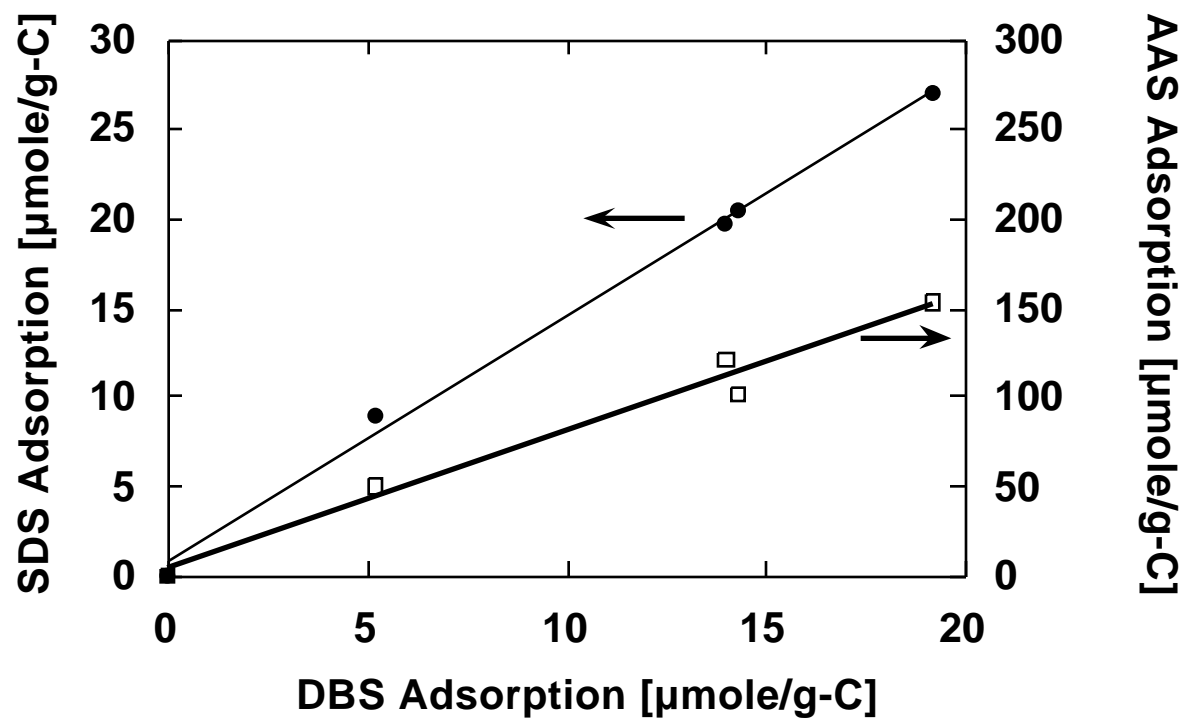


Figure 4. Comparison of the relative amounts of adsorption of AAS, SDS and DBS, on a molar basis. The ashes shown are the same as for Fig. 3.



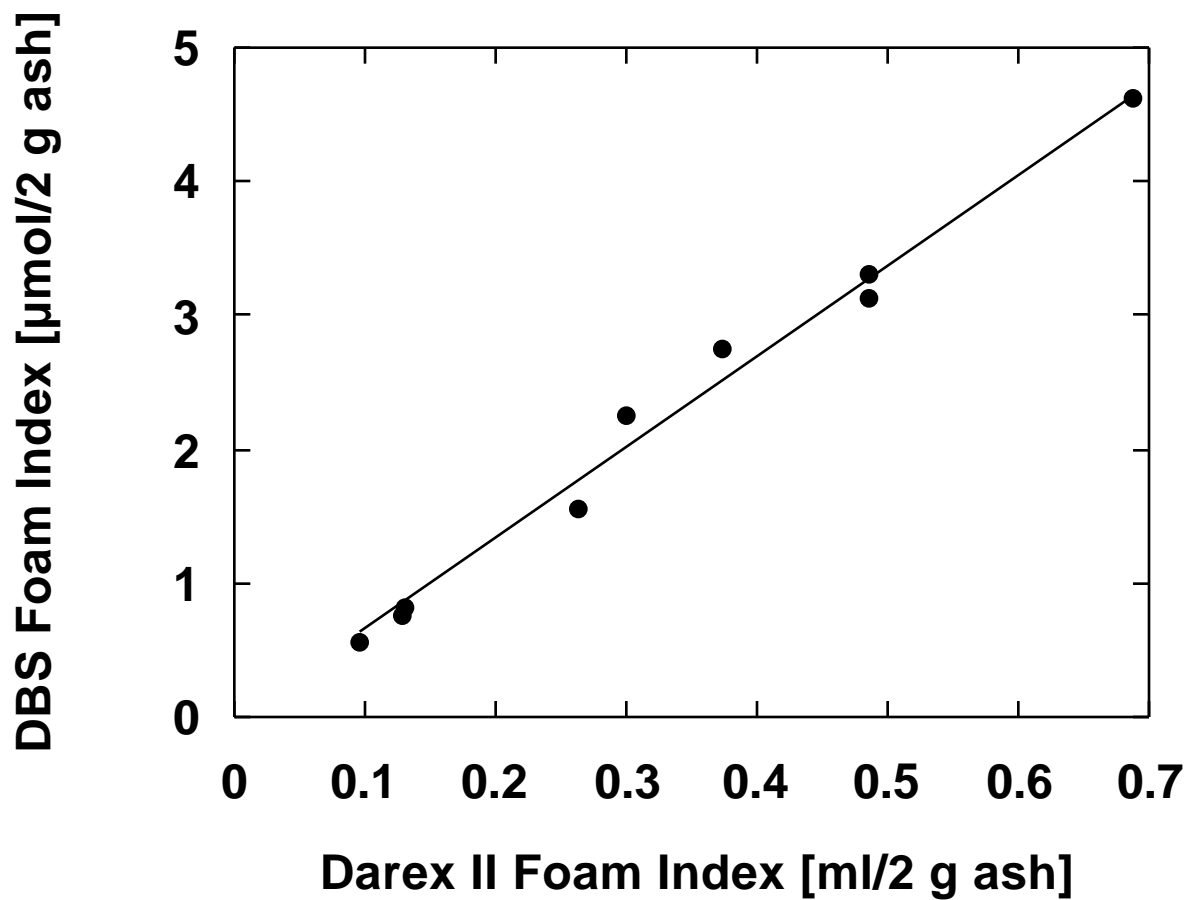


Figure 5. Comparison of DBS Foam Index with Darex II foam index, for high LOI ashes. The DBS concentration was 0.00625 M. The ash test set consisted of samples 3, 6, 21, 46, 51, 53, 64, 74, 75.

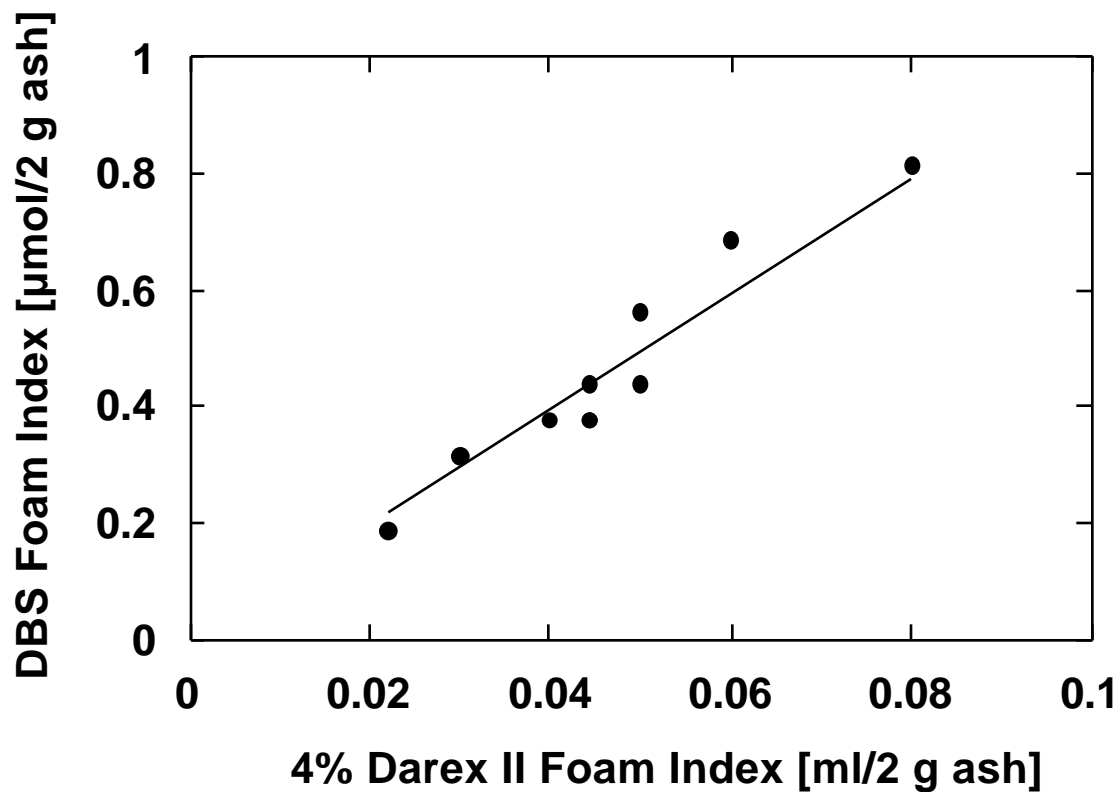


Figure 6. Comparison of DBS Foam Index with Darex II foam index, for low LOI ashes. The DBS concentration was 0.001 M. In this test, the Darex II was used in 4% solution. The ash test set consisted of samples 25, 40, 41, 42, 43, 44, 45, 63, 65, 68.

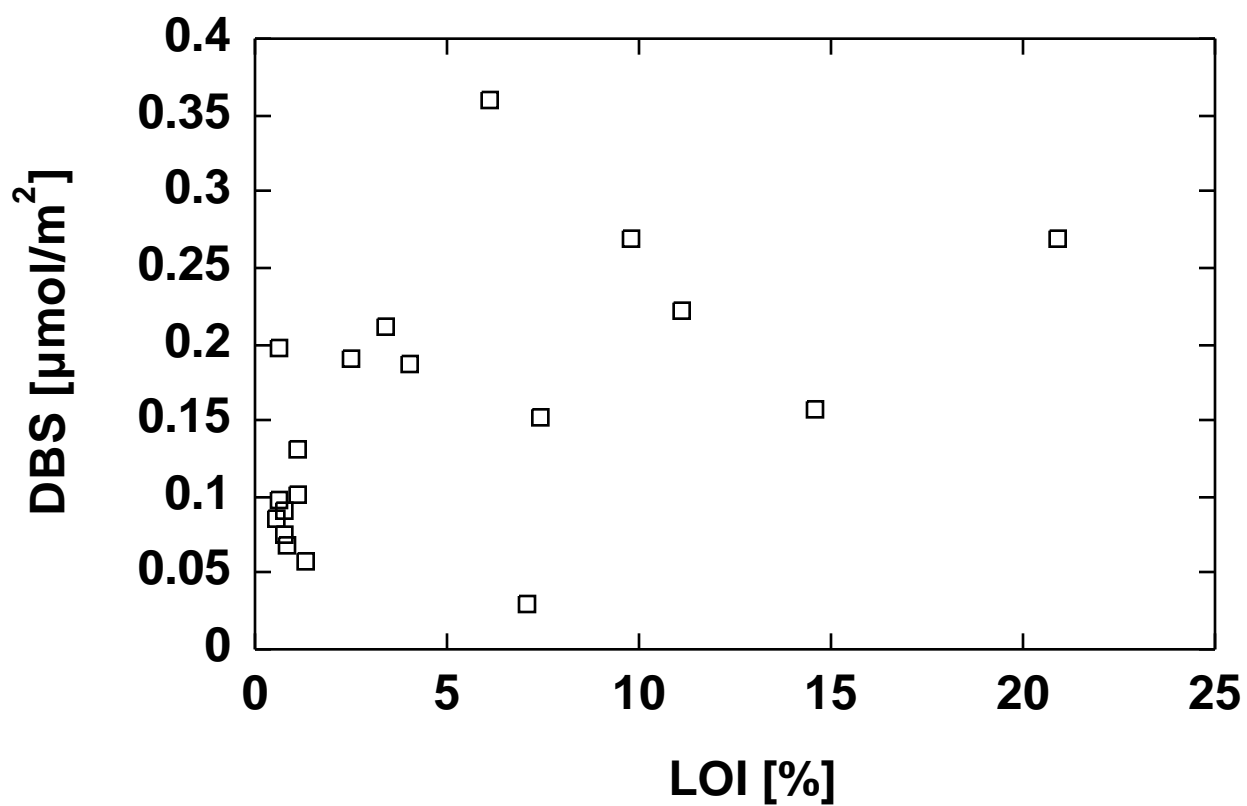


Figure 7. Molar uptake of DBS per gram of unburned carbon for the combined sample sets of Figs. 5 and 6, as a function of unburned carbon content.