FUNDAMENTAL STUDY OF LOW-NO_x COMBUSTION FLY ASH UTILIZATION

FINAL REPORT

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EXECUTIVE SUMMARY

Background

The Nation faces a serious question concerning what to do with fly ash from coal-fired power stations. Only about 15% are presently utilized in cement and concrete products, which is by far the largest single market for this material. This project was concerned with better characterization of the fly ash, in order to enable more effective use of the ash. The "organic" (carbon) portion of the ash is key to success in many new utilization schemes.

Project Overview

This project involved a collaborative effort between two universities (Brown and Princeton) and an electric utility (formerly New England Power, now part of US Generating Company). The goal was to provide a more basic understanding of the nature of the organic fractions of fly ash. The following specific tasks were defined as part of this program:

1. Characterization of the physical and chemical nature of ash organics. This task involved a) acquiring a suite of fly ash samples from utilities throughout the country and throughout the world, and b) characterizing this set of samples with respect to organic content, surface area and porosity. Also, the oxidation reactivity of the unburned carbon and the distribution of carbon in different ash particle size groups were characterized.
2. Development of new screening tests to evaluate the samples with respect to various applications. This included identification of a simple alternative to the foam index test, which can serve as a measure of suitability of the ash in concrete applications.
3. Characterization of the adsorption behavior of selected fly ashes relative to various organic and inorganic adsorbates. Also, the opportunity to beneficially alter the nature of the ash surface by selective oxidation was examined.

Key Results

The project results have highlighted the complexity of the problems facing those who need to assure acceptable performance of fly ash in concrete applications. The key is in reducing problems of poor air entrainment in ash-containing concrete. Screening of ashes for this problem involves the foam index test, a simple adsorption technique. It involves use of commercial air entraining admixtures (AEA), but it could be replaced by a more easily standardized test. The propensity of ashes to adsorb AEAs is dominated by the carbon portion of the ash, but depends strongly on a variety of factors such as surface area, surface accessibility and surface polarity of the carbon. It appears that several of these characteristics could have been altered by low-NO_x combustion modifications. Ash carbon ozonation offers a promising route for treating the problem ashes.

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2.0 INTRODUCTION

The Nation's electric utilities produce an enormous amount of coal ash - about 75 million tons per year (1997 data)¹. These utilities have long preferred recycling or reuse of the ash to landfill or pond disposal, but increasing landfill costs, liability concerns and other industry developments have shifted what was a mild preference for recycling to an imperative at many companies. At the present time, concrete products represent the major market for the ash, and consume about 1/6 of the total produced². Most of the remainder is presently landfilled. Many new market opportunities have been explored³, including lightweight aggregate, flowable fill, cement kiln feedstock, structural fill, alternate fuels, filtration media, ladle topping, fertilizer, casting sands and soil additives. To this list must be added sorbent applications, particularly for high carbon ashes from low-NO_x combustion.

The widespread application of low-NO_x combustion technologies has recently increased the carbon levels in fly ash at many utilities. In many instances, this has rendered the fly ash unsuitable for sale to the concrete industry³. Even in situations in which the carbon contents are within ASTM specifications, problems have still been reported with ashes from low-NO_x combustion systems.

In this project, Brown and Princeton Universities were teamed with New England Power to undertake a broad-based scientific investigation of the form, sorptive properties and behavior of the organic material in ash samples in order to help identify new commercial opportunities. A kickoff meeting of all main project participants was held on October 31 of 1996, at the Brayton Point Power Station of New England Power. Participants included the co-principal investigators from Brown, Professors Hurt and

Suuberg, the principal investigator from the Princeton group, Professor Wornat, and Mr. Peter Calvert of New England Power. The discussion centered on defining areas of responsibility, and the need to build up a reliable set of samples for study.

The objectives of this research were to 1) thoroughly characterize the organic matter in ash with respect to form (including char-derived carbon, soot, and extractables), structure and surface properties, 2) examine the sorptive properties of ashes in technologically significant situations, and 3) to define new applications opportunities.

2.1 Project Description

The project has been divided into different basic tasks. Project management was the responsibility of the team at Brown. The tasks have been described in some detail in several of the previous semi-annual reports. The tasks may be briefly summarized as follows:

Task 1- Physical and Chemical Characterization of Ash Organics

Sample acquisition

Commercially interesting fly ash samples, of both ASTM class C and class F types, were continually being solicited. It is important to note that these samples were characteristic of actual utility practice, with the majority having been collected during actual commercial operations. The sample bank now contains over 80 samples of different kinds.

Physical Characterization

All samples were characterized in-house at Brown with respect to organics content (Loss on Ignition, LOI), carbon form and morphology, surface area, and porosity. It is important to note that the “organic” matter in these ashes is actually a highly carbonaceous char that has been subjected to the actual, very severe conditions in utility boilers. This carbon cannot really be considered an “organic” material with respect to its chemistry, except insofar as its origin was in the organic matter of coal.

Selected samples were examined at Princeton, for their extractable organics content. In the case of these extractable materials, what was being sought were true organics, generally of a polycyclic organic nature. These can with certainty be characterized as “minor” or “trace” products, as their concentrations are low, again by virtue of the severe conditions to which they were subjected. The main reason for interest in these species derives from their potentially important health effects, even at very low concentrations.

As part of another program at Brown, this set of physical characterization data were supplemented by the results of the "Foam Index" test, which is one of the key assays for suitability in concrete applications (see next task).

Task 2- Analytical Technique Development

Samples of fly ash must typically be tested for performance with respect to specific key additives in the concrete, the so-called Air Entraining Admixtures (AEAs). The AEAs are used to ensure that the final concrete will contain sufficient numbers of

air bubbles, of the proper size, in order to impart good workability and freeze-thaw resistance to the concrete. The test used for this purpose is the "Foam Index" test, in which the required amount of AEA is measured in what is essentially a titration test. The endpoint of the test is determined by the stability of the foam created in a water solution of the AEA, which is a surfactant. The recent work^{5,6} at Brown has strongly suggested that the unburned carbon is acting as an adsorbent relative to the (organic) AEA surfactants. This work indicated that surface area of the unburned carbon in the fly ash is a key criterion in determining AEA requirements in the Foam Index test^{5,6}. An alternative to the traditional Foam Index Test was developed, as part of this task. Such an alternative is desired, because the Foam Index measurement is not in any sense a standardized or standardizable test. It is too dependent on the nature of the particular AEA chosen for the test, and on the particular technique employed by the individual performing the test.

In the course of this work, it also proved necessary to characterize the surface polarity of the carbons in the fly ash samples. For this purpose, a calorimetric assay was adapted from the activated carbon field, and applied to the carbons in fly ash. The extent of surface oxidation, and therefore possibly polarity, has been seen to be an important factor in determining the performance of the ash in the foam index test. This, in turn, is believed to be an important predictor of performance in actual concrete applications.

Finally, a specialized test was developed for characterizing the degree to which the carbon in the ash exists as a fine, soot-like particulate. The accessibility of the surfactant AEAs to the surfaces of the carbons in ash is a key factor in determining the foam index. Samples produced under conditions in which a great deal of carbon is

deposited in a very fine form appear to be much poorer candidates for concrete use than do samples whose carbon is in the form of large, non-porous particles. The so-called “fine particle index” is a test developed in the Brown University laboratories, in order to assess the amount of fine carbon.

Task 3- Adsorption Experiments Involving Strategic Compounds

Most of the earlier fundamental research on ash characterization has focused on the inorganic (majority) component of fly ash - its particle size, morphology, and chemical composition. It is, however, the organic portion of the ash, consisting mainly of carbon that could hold the key to success or failure in many new utilization schemes. This study involved investigating the sorptive behavior of ash organics (carbon), and the results allow some preliminary predictions of ash interactions with other adsorptives. The examination of different candidate materials for the foam index test has provided some insights into the nature of the porosity and how it can or cannot be used for adsorbing aqueous wastes. The calorimetric work has provided related insights.

As a result of interest in different areas, the present study involved an examination of the carbons in fly ash that was, in many respects, similar to the examination that candidate activated carbons undergo. In addition to the many different characterizations of the porosity and adsorptive behavior already described, a study was performed on how the nature of the carbon varies with different size fractions in the carbon. This would be of interest to those who are currently separating carbons from fly ashes, insofar as the properties of the carbons in one size range are not always the same as those of another range. In the case of the separation schemes, streams considerably

enriched in carbon (to tens of percent by mass) could become available. This may further expand the potential markets for application of the ash-derived materials to include some currently dominated by activated carbons, particularly powdered activated carbons.

2.0 PREVIOUS STUDIES RELATING TO THE SUITABILITY OF FLY ASHES FOR CONCRETE – THE FOAM INDEX PROBLEM

2.1 General Background

Today the most important commercial high value outlet for fly ashes is the concrete industry, in which they have been successfully used as a partial replacement for Portland cement. The production of Portland cement is resource intensive, as it consumes a great deal of energy and emits CO_2 , SO_2 and NO_x , which contribute to acid rain and to the greenhouse effect. At the same time Nation's electric utilities produce an enormous amount of coal fly ash - about 75 million tons per year¹, and the amount of ash produced increases every year. Coal fly ash is known to be an excellent artificial pozzolanic agent^{7,12}. Pozzolans are finely divided materials that react with calcium hydroxide and alkalies to form compounds possessing cementitious properties. The glassy spherical particles of coal fly ash are active pozzolans, and readily react with lime (produced when portland cement hydrates) and alkalies to form cementitious compounds. Partial replacement of the Portland cement by fly ash saves the cost of the replaced cement and improves certain concrete properties such as long term strength and permability¹². The addition of these pozzolans also slows the heat release of cement hydration. A sketch of a prototypical concrete making procedure, together with the components used, is shown in Figure 2.1 (see the end of this chapter)²¹.

Examples of where Portland cement-fly ash concrete has been successfully used, include Canyon Ferry Dam on the Missouri River (Montana), Palisades Dam on the Snake River (Idaho) (Figure 2.2), Hungry Horse Dam (Montana) (Figure 2.3) and Yellowtail Dam on the Bighorn River (Montana). Closer to home, the massive Boston

central artery project, the so-called “Big Dig”, has utilized enormous amounts of fly ash containing concrete, from the same Brayton Point power plant that has been a partner in this project.

It can be expected that the future will see even greater utilization of fly ash in concrete. Several factors suggest this. One factor is that landfill costs are steadily increasing, and landfiling is one of the main economically viable disposal methods for fly ash. In addition, pressure keeps mounting on the US Environmental Protection Agency to reclassify coal fly ash as hazardous waste (a change from its current RCRA exemption). Should this happen, there would be even greater pressure to dispose of fly ash in safe “beneficial use” technologies, such as concrete. Finally, the wave of utility deregulation and free market competition that is sweeping the Nation requires all coal plant operators to more seriously consider the ash as a potential revenue stream. Again, the use of the ash as a pozzolan offers the currently best option in this direction.

2.2 The Problem of Air Entrainment

Surfactants are used in concrete in order to provide needed air volume in order to impart freeze-thaw resistance to the mixture¹³. The typical amount of air during mixing and transportation to the job site is 3-6 vol.%⁶. The bubbles impart freeze-thaw cracking resistance via creation of void volume to accommodate the expansion of residual water upon freezing in the set concrete. Surfactants added to concrete mixtures for this purpose are called Air Entraining Admixtures (AEAs). They are carefully designed to stabilize the sub-millimeter air bubbles that are appropriate for imparting the freeze-thaw resistance. Today there are commercially available both natural and fully synthetic

AEAs for concrete application. The nature of the AEAs will be discussed more fully in the next chapter.

Solid carbon residues in fly ashes can adsorb these AEAs and therefore render them unable to fulfill their intended function as a bubble-forming surfactant^{6,13}. If the AEA exists as an adsorbed surface species on carbon, it can play no role in stabilizing bubbles in the liquid portion of the concrete mixture. The problem of residual carbon in fly ashes became more acute for the utility and concrete industries after the adoption of the Clean Air Act Amendments (CAAA) in 1990. The CAAA requirements prompted many power generating plants to retrofit their facilities with low-NO_x burners. Utilities were often not technologically prepared for the drastic changes in the ash that some of these retrofits caused. While quite successful at mitigating the NO_x problem, the changes brought with them some more subtle changes in the fly ash byproducts. Basically what introducing the low-NO_x burners involved (in combination with some other changes to the boiler) was a reduction in air fed to the primary combustion zone. This caused a reducing (oxygen deficient) environment in certain portions of the boiler. The remaining combustion air was fed at a later time, in order to complete combustion and ensure the required excess air stoichiometry. This strategy successfully reduced NO_x emissions, but was often accompanied by higher unburned carbon content in fly ash. At other times, the carbon content did not increase by very much, but the nature of the carbon appeared to change. The reasons for these changes are not fully understood, but they are clearly related to the somewhat poorer mixing of the air and fuel that delayed mixing strategies necessarily involve. This delayed mixing may additionally

lead to effectively reduced residence time for particles under actual combustion conditions.

Higher levels of carbon in fly ashes had a negative impact on the main market for the fly ash - the concrete industry. The problem with higher levels of carbon in fly ashes for concrete applications was related not only to the undesired darkening of the ash (and thus concrete), but more importantly to the fact that the carbon adversely affected the air-entraining properties of the concrete^{6,14}. This was related to the fact that higher levels of carbon in fly ash were responsible for higher adsorption uptakes of AEA. This problem could not be simply remedied by the addition of more AEA to the mix for a variety of reasons including economics, regulations and the general unreliability of performance of systems requiring high AEA dosing.

Even when markedly higher levels of carbon were not observed in the post-low NOx retrofit periods, there were similarly disturbing shifts in performance of the ashes. Ashes that would meet ASTM and state requirements for pozzolanic additives began failing in the field, for reasons of poor air entrainment. It seemed that the post-retrofit problem was not one of increased carbon content alone, but was also associated with subtle changes in the nature of the carbon as well

The subject of how air entrainment agents work in the presence of fly ash has not received a great deal of attention from the research community. There have been only a handful of studies that refer to the problem of adsorption of air entraining agents by fly ash carbons^{4-7, 14-22}. Many of these discuss the difficulty in finding a correlation between the Loss-On-Ignition (LOI) values and foam index values for the fly ashes.

The foam index test is a simple laboratory titration procedure, in which the degree of interaction between air entraining admixture and fly ash sample is characterized. The amount of AEA needed to support stable foam provides the foam index value (generally ml/2g ash)^{6,19,20,22} for the particular fly ash. Therefore foam index is a quick characterization of the suitability of a particular fly ash as a concrete additive. The higher the foam index of the fly ash, the less likely it is that it can be used as a concrete additive.

There are many factors that influence the numerical foam index results. Among them are the concentration and composition of the AEA, the time that the mix is allowed to sit, the proportions and compositions of the different non-AEA components (e.g. cement) and even the age of the AEA. For this reason, there is no standardized foam index test, as such. There are only a great many similar-looking procedures in use in a great many laboratories throughout the world. It is thus entirely inappropriate to compare the numerical results obtained in one laboratory with those obtained in another.

Although researchers have questioned the adequacy of a simple LOI criterion for determining the suitability of fly ash for concrete applications, it has often been regarded in practice as the best single criterion. Freeman et al.⁶ pointed out that foam index of a sample generally increased with carbon loading, but no unique trend was observed. The samples investigated by Freeman et al.⁶ included, in addition to fly ashes, activated carbon, pelletized carbon blacks and coal samples. These results showed that the carbons most active for adsorbing AEAs were activated carbons, followed by typical fly ash carbon, then carbon blacks and coal samples. An identical order was observed when the materials were ranked by surface area, suggesting that the AEA interaction was

primarily a surface area controlled phenomenon. In fact, a BET surface area-based correlation of foam index provided a somewhat better unification of the data set than did LOI, but the correlation was still far from perfect. The time dependency of the AEA-carbon interactions in the foam index test was also observed in this research⁶. The time needed to obtain true equilibrium behavior was quite high, exceeding 2 hours for some samples.

Gao et al.⁵ studied the effects of other factors on AEA adsorption on different carbon blacks and fly ashes. It was observed that the particle size of the sample greatly affected foam index value. Carbon blacks exhibited a wide range of specific activities, with activity increasing greatly as primary particle size decreased. A nearly linear relationship was observed between the foam index and the reciprocal of the primary particle size. This suggested that mass-specific external surface area of the carbon blacks played an important role in the AEA adsorption process. In addition, it is shown in Gao et al.⁵ that the specific activities (ml of AEA solution per gram of carbon) were higher for fine particles of carbon black as compared to the fly ash carbons. As in the study by Freeman et al.⁶, the materials were ranked by BET surface area. The results again suggested that the interaction of AEA with carbon blacks was primarily a surface phenomenon. The foam index values for fly ashes correlated quite well with BET surface area, but not as well as did the results for carbon blacks. At that time, the range of pore sizes that are accessible to the AEA molecules was not considered. This provided part of the impetus for the present study. It was also noted by Gao et al.⁵ that surface treatment of carbon blacks which introduced oxygen functionalities onto the

carbon surface, weakened the AEA interaction and lowered the foam index for any particular sample.

Hill et al.¹⁴ examined four class F fly ashes and also samples which were separated from these parent samples. Four of these were fractions with high carbon content, and four of them were low carbon content fractions. The AEAs used in that study were dodecylbenzylsulfonate (DDBS) and vinsol-based material. A slightly modified Dodson's foam index procedure²³ was applied in that study, and the cement to ash ratio was 3:1. The results of that research¹⁴ clearly showed that LOI is an inadequate predictor of fly ash performance in concrete mixtures. However specific BET surface area again correlated quite well with LOI. The AEA adsorption time was also investigated in that research¹⁴. For some fly ashes, AEA saturation was reached in approximately 500 seconds, while for some separated high carbon fly ash samples the saturation levels were reached only after 1500 seconds of adsorption. A method based on gasification reactivity was applied for characterizing the types of carbons present in the fly ashes. That study¹⁴ reported that isotropic carbon, the more disordered carbon, was more reactive than the anisotropic (ordered) coke. The optically isotropic carbon was also more active toward AEA adsorption than was anisotropic coke. This would make sense, insofar as the more isotropic, disordered material would be expected to have a more porous, higher surface area nature.

In addition, Hill et al.¹⁴ postulated that the higher demand for AEAs associated with the carbonaceous material in fly ashes was observable in samples which had relatively high oxygen content. Generally higher oxygen content is related to a higher oxygen functionality concentration on the carbon surface. Carbons with higher oxygen

group contents on their surfaces are known to be more polar compared to samples with relatively low oxygen content.

Hill et al.¹⁵ investigated the air entrainment in some of the poorest performing fly ashes delivered from two utilities. Commercial AEA, available from Boral Material Technologies Inc., was used as the air entrainment agent in foam index tests. The results of this study showed that the foam index (FI) to LOI ratio provided a good correlation with so-called mortar air present in actual test mixes. As the foam index value per constant amount of carbon for different fly ash samples increased, the percent of air held by a mortar test mix decreased. An unsatisfactory correlation was, however, obtained when percentage of air present in the test mix was plotted against LOI of the sample. A satisfactory correlation was obtained when the percentage of air in the test mixes (or LOI) was plotted against the specific BET surface area for the fly ash carbon. It was also noted that the nitrogen adsorption technique was insensitive to differences in carbon surface chemistry. These authors pointed out that the fly ash carbon surface chemistry could also influence its interactions with AEAs. In addition, these authors concluded that differential thermal analysis was not useful tool for predicting the performance of fly ash in air entrainment.

Sabanegh¹⁸ examined the influence of time and particle size on the results of the foam index test. In this research a spectrophotometric method was used to track Darex II AEA adsorption on selected fly ash samples. The results of that study showed that time had a significant effect on AEA adsorption. It took approximately 1 hour to saturate a high carbon fly ash sample with AEA. On the other hand, the simple foam index test, using the same amount of AEA, fly ash and water as in the UV absorption test, was

generally “complete” after 10 minutes. This implied that when the apparent end point was reached in the foam index test, the AEA was still actively adsorbing on the fly ash particles. However, it was noted that most of the AEA uptake occurred in the early stages, and the amount of AEA adsorbed after 10 minutes varied from sample-to-sample, depending on the fly ash carbon’s accessibility. In that study, it was postulated that the AEA molecules reached the carbon particles’ external surfaces essentially instantly and then as further adsorption occurred, the rate of uptake of AEA decreased, reflecting the loss of accessible carbon adsorption sites.

Sabanegh¹⁸ also investigated fly ash particle size dependence of the results of the foam index test. It was concluded that the amount of AEA adsorbed on the fly ash had an inverse relationship (d^{-1}) with the particle size. As the particle size decreased, the amount of AEA adsorbed on the fly ash increased. It was hypothesized that the smaller particles have higher external surface area, therefore providing more accessible sites for AEA uptake.

Sabanegh¹⁸ also determined the effect of fly ash oxidation at different temperature conditions on the foam index values. The results of this study showed that fly ash oxidation at around 450° C slightly reduced the AEA uptake. It was hypothesized that the beneficial effect of the oxidation was due to the polar oxygen functional groups introduced onto the carbon surface.

Maroto-Valer et al.¹⁷ investigated the characteristics of the unburned carbon present in fly ash samples. Three different types of carbon particles, inertinite, isotropic coke and anisotropic coke, have been identified microscopically. In order to isolate these

three types of carbon, a preliminary carbon enrichment, followed by the density gradient centrifugation was performed.

All of the above studies suffered from a common problem - namely that they involved use of only a limited number of fly ash samples. Previous work had already made sufficiently clear that there was a high degree of variability among different fly ashes and carbons. It became important to expand the studies to a broader range of samples.

To address this need, as one of the first tasks of this present project, Smith et al.¹⁹ performed work on an expanded sample bank. About 40 samples, both class F and class C fly ashes, were used in this part of the study. These early results showed the existence of a fair correlation between foam index and LOI, in seeming disagreement with some of the earlier conclusions. Results in this work¹⁹ also warned of using BET surface area as a predictor of performance of a particular fly ash in concrete applications. It was also concluded that the polarity of the fly ash carbon made a large difference in the ability of carbon to adsorb AEAs. It was hypothesized on the basis of this preliminary work that the low NO_x burner retrofits might also have modified the polar character of the unburned carbon surface.

A related study sought to examine the development of AEA adsorption capacity of ashes through an actual model combustion process. The AEA adsorption capacity of partially combusted coal char (derived from Pittsburgh #8 and Beulah lignite) samples, generated under carefully controlled and characterized laboratory conditions, was investigated by Hachmann et al.²¹. Pittsburgh #8 is a representative of high rank bituminous coals, which produce class F fly ash and Beulah lignite is a low rank lignite,

which generally produces class C fly ash. The experimental setup simulated high temperature pulverized coal combustor conditions. Runs were carried out on the two coals in a flame-supported, high-temperature flow reactor from which samples were taken at different residence times and rapidly quenched. The AEA interaction with the samples was measured using commercial Darex II, in a 10 wt.% solution, and the foam index procedure was the same as used in some of the above mentioned studies^{5,22}.

The results showed that the AEA adsorption activity of the parent coal and partially devolatilized chars is very low, but rises sharply near the end of devolatilization (see Figure 2.4). As the combustion of the char proceeds, the activity of the char towards AEA falls quickly. The BET surface area of the parent coals is very small and increases rapidly as the devolatilization occurs, reaching a maximum value (of around 180-200 m²/g of carbon) before the combustion of the char begins (see Figure 2.5). As the combustion of the char proceeds, the surface area drops. It was pointed out that samples passing out of the devolatilization zone possess high surface area, around 200 m²/g, but almost no measurable surfactant adsorption activity. The hypothesis was that the surfaces being identified in nitrogen adsorption for BET surface area are for some reason unavailable for AEA adsorption. Again, the time for AEA adsorption might have been an issue in that work. Nitrogen adsorption involves a long equilibration time, relative to the foam index test, which takes approximately 10 minutes. It was believed that the larger size of the surfactant molecules and liquid phase diffusion transport limitations are reasons why the two adsorptives might also give different behaviors. In particular, it was hypothesized that micropores were accessible to nitrogen molecules, but not to the surfactant molecules.

In addition, Hachmann et al.²¹ also discussed the role of carbon surface chemistry on AEA adsorption. It was hypothesized that the late development of surfactant adsorptivity (when surface area was already 200 m²/g) could be caused by the changes in surface oxygen functionality after devolatilization. The role of oxygen groups on carbons was also again noted in separate experiments in which high carbon content commercial fly ashes were oxidized at different temperature conditions. It was pointed out that following oxidation, AEA adsorptivity dropped to approximately half its initial value before measurable carbon loss was observed in the temperature range from 300 to 450° C. Again this was attributed to the formation of oxide surface groups on the carbon surface, which weakened the surface interactions with the AEA surfactant.

The main conclusion from the work by Hachmann et al. was again that LOI alone is not sufficient for predicting the AEA adsorption capacity of carbons. The AEA uptake also depends upon the surface area, its accessibility and its chemical nature.

Another closely related study was carried out by Yu et al.²⁰. This work involved a study of AEA adsorption on ashes derived from co-firing coal and petroleum coke. Petroleum coke is a byproduct from petroleum refining and it is characterized as being low-volatile, low ash, high sulfur and dense (~1.4 g/cm³) fuel. Pulverized petroleum coke combustion is possible in high volatile coal co-firing, for flame stability purposes²⁰. The samples examined were prepared in a commercial utility boiler. The AEA adsorption activity of the petroleum coke co-firing ash was reported to be zero, despite the unusually high carbon content (17 wt.%) of this ash. The extremely low surface area and non-porous structure of the unburned petroleum coke was believed to be the main reason why this ash did not show any activity towards AEA adsorption. This confirms

that an LOI criterion alone cannot properly predict AEA adsorption. A further aspect of the same study involved examination of AEA adsorption on coal fly ash and activated carbons. Adsorption again increased as the particle size decreased. The increase in AEA adsorption on activated carbons followed a d_p^{-1} law consistent with the variation of geometrical surface area with particle diameter (surface area/mass = $6d_p^2/\rho d_p^3$). Similarly with the results of other studies^{14,18} it was determined that the adsorption processes for some activated carbon samples were occurring over time scales of at least one hour. Again, it was hypothesized that the accessibility of the carbon particles and liquid phase diffusion limitations were responsible for such a long adsorption process time scale.

2.3 Summary of key unresolved issues

The preceding summary of previous work in this area has established that LOI is probably the best single predictor of foam index (and, thus, of concrete performance) for any series of fly ashes. On the other hand, it has been clearly shown to be a somewhat unreliable parameter, and surface area has shown itself repeatedly to be a somewhat better, though by no means perfect, correlative parameter. In many cases the surface area-based correlations have also proven to be inadequate.

Several studies have shown the importance of accessibility of carbon surface to be an important determining factor for foam index. There is little question that the short timescale of the foam index test almost assures that there will be a transport limitation within porous particles. The work with very fine carbons (ashes and carbon blacks) has shown that geometrical surface area is of prime importance, again confirming that transport and accessibility are important issues. This study involves examination of the

accessibility of the carbons in fly ash through a more careful characterization of the different size scales of porosity.

The role of surface polarity has also been suggested by the results of several studies. The earlier results from this laboratory strongly suggested that the more polar the surface, the less readily the AEA can be adsorbed. The actual mechanism by which oxidation influences AEA uptake remains unknown, however. Is the effect really tied to the creation of polar surface sites, which changes the physical nature of the surface in a general, non-specific way? Or does the oxidation create specific sites on the carbon surface, that reduce adsorption in a very particular way?

Whatever the actual mechanism involved in polar effects, there remains the need to resolve the discrepancy between our results and the results of Hill et al.¹⁴. In their work, Hill et al. postulated just the opposite effect of surface polarity on AEA adsorption potential. Namely, higher demand for AEA from the carbonaceous material in fly ashes was observed to be the case with the samples with relatively high oxygen content.

The foam index test itself has been pointed out to be a somewhat arbitrary procedure, whose standardization would be very difficult to accomplish using commercial materials. As part of this study, we have examined what alternatives exist for performing the foam index test, and how these might lend themselves to greater standardization.

A major problem in studies involving characterization of commercial materials derived from natural feedstocks (such as coals) is that work involving only a few samples might appear to define certain trends, which when viewed in the context of a larger sample base, are not statistically significant. One of the main aims of the present

study is to provide a sufficient base of data on enough different materials so that real trends and heretofore unrecognized variables may be identified. This is particularly important for the class C fly ashes (from low rank coals), that have not yet been adequately studied.

Finally, it is clear that a very large knowledge base on the characterization of activated carbons has not yet been brought to bear on the problem of characterization of fly ash carbons. This study will present results of various kinds that will show how this is relevant to the problem at hand.

FIGURES

Figure 2.1 Major components in cement-ash concrete making process²¹.

Figure 2.2 Palisades Dam on Snake River (Idaho). An example where Portland cement-fly ash concrete has been successfully used. Source internet.

Figure 2.3 Hungry Horse Dam (Montana). An example where Portland cement-fly ash concrete has been successfully used. Source internet.

Figure 2.4 Specific surfactant adsorptivity as a function of conversion during the high-temperature combustion of a high-rank and low-rank coal²¹.

Figure 2.5 The effect of conversion on specific surfactant adsorptivity and nitrogen BET surface area²¹.

3.0 EXPERIMENTAL TECHNIQUES

3.1 Loss-On-Ignition Test

The carbon contents of all of the fly ash samples were determined using the simple Loss-On-Ignition (LOI) test. The reported LOI values of all fly ashes, provided by their producers or providers, were double-checked, using a modified standard ASTM method (Standard No. C 311-96a and C 114-94)^{8,9}. The standard ASTM C 311-96a and C 114-94 methods involve the very simple procedures described below.

The LOI is calculated as the percentage weight loss from a dried, roughly one-gram sample of ash, after an initial determination of the moisture content of the as-received moist sample. The combustion of the dried sample to a constant weight in an uncovered porcelain crucible at $750 \pm 50^{\circ}\text{C}$ allows calculation of the percentage loss on ignition, to the nearest 0.1%, as

$$\text{LOI, [\%]} = (\text{Mass loss from dried sample} / \text{Mass of dried sample}) \times 100$$

The published ASTM procedure was slightly modified in our laboratory. The moisture in the fly ash sample was determined by pre-drying it for two hours in a laboratory oven at 120°C . After drying, samples were covered (to prevent re-absorption of moisture from the air) and then placed into a desiccator for cooling down to room temperature. Dried fly ash samples were then re-weighed. The moisture content of the fly ash was calculated from this dried, cooled sample mass loss relative to the initial mass. After complete drying, samples were placed into an air ventilated laboratory oven at 740°C for two hours. After complete burn-off, samples were cooled in a desiccator and

re-weighed. The mass loss relative to the dried basis was the reported LOI, and it is assumed to be the weight of unburned carbon in the original sample. This may or may not be exactly true, but it is certainly a good approximation for most samples, particularly those with LOI values of more than a few percent. This is basically the standard ASTM procedure, except for the duration of the LOI test. It was verified that two hours in the laboratory oven was more than enough to complete the burn-off of the test samples. Each fly ash sample was analyzed at least twice and an average percentage of weight loss was calculated. The typical variance in LOI values was quite small, and only in some cases did it get as high as 5% (relative basis). The higher variances were especially apparent in ashes with LOIs lower than 0.5% (absolute basis).

In most cases the value provided by the utilities or other sample donors was in good agreement with the value obtained in this laboratory. However some discrepancies were noted, especially with the fly ashes having LOI values lower than 2 wt.%. For fly ashes that have lower LOIs, a higher variance was noted, and therefore these samples were analyzed further. As the LOI of the sample drops below about 2 wt.%, the secondary reactions of the mineral part of the fly ash start to increase the uncertainty of the LOI measurements. This question was also examined by Brown and Dykstra¹⁰. They used pulverized Iowa bituminous coal fly ash with an original LOI of 1.7 wt.% and determined that the error in LOI is about 75% on a relative basis, as compared with the actual carbon content. The errors in LOI determinations for fluidized bed fly ash from the same bituminous coal were extremely high, ranging from 510 – 2780 %. In fact, this is not surprising, because fluidized bed fly ash samples can contain high levels of minerals like anhydrite (CaSO_4), lime (CaO), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3) and

Portlandite $[\text{Ca}(\text{OH})_2]$ ¹⁰. The low temperatures of fluidized bed combustion mean that not all decomposition reactions involving minerals have gone to completion, and this contributes to the uncertainty in the LOI measurement. On the other hand, the pulverized coal fly ash sample fly ash sample contains high levels of anhydrite (CaSO_4) but almost undetectable level of calcite (CaCO_3) and portlandite $[\text{Ca}(\text{OH})_2]$ ¹⁰, due to the higher temperatures that the ash experiences in the pulverized coal combustion process. Thus there is less opportunity for further mineral decomposition, as compared with the fluidized bed ash.

Thermogravimetric analysis (TGA) tests were also performed on the ash samples, using a TA Instruments TGA system. This was done in order to compare the "standard" LOI values with the nominally same values established in a TGA. The LOI results of the TGA analyses for the samples with LOI values above 2 wt.% were generally in good agreement with those obtained in the laboratory oven. The lowest LOI samples (less than 1 wt.%) did not, however, give very distinct endpoints even in the TGA, probably indicating the occurrence of secondary mineral reactions during the LOI testing. The mineral decomposition reactions would tend to have slow rates, even at high temperatures. It was also noted that class C fly ashes (which generally originate from sub-bituminous coals and lignites) give higher uncertainty than do similar LOI samples of the class F ashes, which originate from bituminous coals. This most likely has to do with the differences in mineral contents of the class F and C ashes.

A different method has been suggested for fly ash carbon content measurements when LOI values are less than 1 wt.% and also for the fly ash samples, which originate from fluidized beds¹¹. A photoacoustic response technique has been successfully applied

by Waller and Brown¹¹. The photoacoustic effect involves the conversion of modulated electromagnetic radiation, adsorbed by gaseous, liquid or solid media, into an acoustic wave, which can be detected by a sensitive microphone. In the reported research, the photoacoustic effect was generated by 1.315 μm infrared radiation from a 1.5 mW diode laser that was absorbed by the carbon in fly ash. The technique proved capable of measuring unburned carbon in fly ash in the range 0.1-7.0 wt.%. It was noted that fly ash sample compression and grinding prior to the measurement improved the correlation established between the photoacoustic signal and true carbon content. This technique was not available in this laboratory. The problem of LOI uncertainty was not considered significant enough in the present study, as to require turning to these more advanced techniques.

3.2 Foam Index Test

2.2.1 General Background

The surfactant adsorption capacity of the fly ash samples was determined by what amounts to a titration procedure^{5,6}. The role of surfactant in concrete mixtures is to provide the presence of small air bubbles (<0.25 mm), which will eventually increase the workability of the concrete mix, and also will improve the resistance of the set material to freeze/thaw cycles¹³. That is why these surfactants are often known as air entraining admixtures (AEAs). Commercial AEAs are typically aqueous solutions of ionic or nonionic surfactants, originating from natural sources (wood resins, tall oil) or from purely synthetic routes. It is not clear precisely how the AEAs “work”. In general, it is understood that these are behaving like surfactants in aqueous media. The foaming behavior of surfactant involves the partitioning of the surfactant molecules to the air –

water interface of a solution. The polar (ionic) end of the surfactant is readily soluble in water, while the non-polar (organic) end of the surfactant is not. The minimum energy configuration of a water surfactant system therefore involves a layer of surfactant at the air – water interface, with the non-polar tails pointing out towards the air. A foam is formed when the interface is disturbed, and pockets of water and air are interspersed (as by mixing). The same criteria still apply, as regards the desired (thermodynamic) position of the surfactant relative to an interface, but now the interface has become irregular with interspersed liquid and air pockets. It has been proposed¹³ that AEAs in concrete mixtures adsorb with their polar ends towards cement particle surfaces and their tails towards the aqueous phase. The hypothesis was that this imparts non-polar character to the cement particle surface, and that this surface collects air bubbles. This hypothesis is somewhat implausible as regards the sequence of events implied. It is more likely that the surfactant would partition to the rough surfaces of particles where air interfaces are available for accommodation of the non-polar end of the surfactant molecules.

The degree of interaction between an AEA and specific fly ash sample can be estimated using a simple laboratory titration procedure – the foam index test⁶.

2.2.2 Air Entraining Admixtures

As was earlier noted, air entraining admixtures are derived either from synthetic or natural sources. A commercial AEA Darex II (W.R. Grace & Co., Cambridge, MA) was extensively used in our research in order to determine the surfactant adsorption uptake of the fly ashes. Darex II is a complex mixture of organic acid salts in an aqueous solution specifically formulated for use as an AEA for concrete. It complies to ASTM C

260 Standard Specifications for Air Entraining Admixtures for Concrete. The main applications for Darex II are ready mix, block, and concrete products, in order to improve the air entraining stability of these products.

Another commercial AEA, Air 40TM from Boral Material Technologies, Inc, is also formulated to produce a stable air void/concrete mix system for transporting, placing and finishing. Air 40 is designed to perform with a wide range of concrete mixtures. Boral Material Technologies also states that the Air 40 AEA meets the requirements of ASTM C 260 and individual state DOT specifications. This AEA manufacturer has noted that the Air 40 reacts especially well with highly carbonaceous fly ashes. In our laboratory, it has been determined that the Air 40 AEA is more active, in terms of deactivating the carbon in fly ash with less AEA addition, relative to the Darex II. A simple laboratory test (a complete dry-off of aqueous AEA in vacuum oven), determined the dry mass of AEA in the aqueous AEA product. This showed that Boral Air 40 is more concentrated than Darex II by approximately 20 % (126 mg/ml, vs.100 mg/ml). However foam index tests showed that the difference in terms of amounts needed for deactivating the carbon in fly ashes was much more than 20%. Therefore there had to be a difference in the actual chemical characteristics of the two surfactants. More information on these relative efficacy of these AEAs will be provided in a later section.

Unfortunately both commercial AEAs, Darex II and Air 40, have poorly characterized molecular compositions, because they are natural products. Thus further effort was made to find inexpensive, common materials of known molecular structure to serve as models for commercial AEAs. These model materials would not be of commercial interest in concrete applications, due to their greater costs. Rather, we wanted

a material that would serve as a good model for commercial AEAs in the foam index testing procedure.

In order to find suitable replacement for the commonly used AEAs, sodium dodecyl sulfate (SDS) $[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}]$, dodecylbenzenesulfonic acid sodium salt (DBS) $[\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}]$ and abietic acid were checked as possibilities. Alkyl sulfates, such as sodium dodecyl sulfate (MW = 288) have been used mostly in production of the lightweight concrete and not typically for enhancing the freeze-thaw durability of normal concrete, for which purpose it would be rather expensive. This material is a basic surfactant, which is used in a variety industrial and domestic detergents¹³.

Abietic acid is also rarely used as a pure material in concrete mixtures. If this material is to be used as foaming agent for lightweight concrete, a proportion of animal glue is added to further stabilize the bubble structure¹³.

Abietic acid

(MW = 302)

Dodecylbenzenesulfonic acid sodium salt (DBS), is a fatty acid salt. This fatty acid is used as an AEA for concrete mainly in the form of its alkali metal salt. Again, pure DBS salt is actually rarely used as an AEA in concrete mixtures. The material is, however, compatible with certain lignosulfonates and hydroxycarboxylic acid salts as a part of an AEA mixture⁷.

3.2.3 The Foam Index Test for Fly Ash Samples

A simple laboratory titration procedure, called foam index test, can be applied in order to determine the degree of interaction between air entraining admixture and fly ash sample. The foam index test permits a quick characterization of the suitability of a particular fly ash as a concrete additive.

The test involves determining how much of a particular AEA must be added to a "standardized" hypothetical concrete mix, in order to obtain acceptable air void formation in the mix. In actuality, the test mix is very dilute in comparison to a real concrete mix. What is examined, as opposed to the air void volume, is the ability of the dilute mix to hold bubbles on its surface. The test itself gives a quantitative result, the so-called foam index value. It should, however, be recognized that this is only a qualitative guide to the problem of AEA adsorption in an actual concrete mix.

There are, of course, many factors that influence the foam index results. Among them are the time that the mix is allowed to sit, the proportions of the different components, and of course the type of AEA and even its age. The test is also sensitive to user technique (how vigorously the vial is shaken, what qualitative endpoint criterion is employed). For this reason, there is no standardized foam index test, as such. There are only a great many similar looking procedures in use in great many laboratories throughout the world. It is thus entirely inappropriate to compare the quantitative results

obtained in one laboratory with those obtained in another. This is why we began a search for an alternative test based on pure reagents. The search still involved a stable foam endpoint on similar mixtures as used for the normal foam index test. The results of this search for alternatives will be given in chapter 5.

Foam index measurements involve placing the mixtures for testing, which consist of 2 grams of fly ash, 8 grams of Portland cement and 25 ml of distilled or de-ionized water, into a 70 ml cylindrical jar with a 40 mm I.D., 80mm length. The jar is then capped and thoroughly shaken for one minute to completely wet the cement and fly ash. In the present work, a 10 vol-% aqueous solution of either Darex IITM or Air 40 was used as the AEA in the test. The 10 vol-% aqueous solution of AEA is added one drop at a time from a pipette gun with a 0.75 ml tube. The size of the drop is adjustable, and this is done on the basis of the expected value of the foam index. After each addition the jar is capped and shaken approximately 15 seconds, after which the lid is removed and liquid surface observed. Before the endpoint of the test, the foam on the liquid surface is unstable and breaks in the matter of a few seconds. The endpoint is taken to occur when a stable foam is established on the surface for at least 45 seconds. It is believed that the stable foam endpoint occurs at a relatively constant aqueous concentration of surfactant. To the extent that differing amounts of AEA must be added to the solution in order to achieve this particular concentration, this reflects different amounts of AEA being adsorbed onto the surfaces of the solids in the mixture. This is why the foam index is a measure of adsorption.

The entire procedure is repeated as above, using just 8 grams of cement and no fly ash. Subtraction of the two test results (the value for the sample with fly ash, less the

value for the sample without fly ash) gives the reported foam index for the fly ash, in ml per two gram of ash.

In this study, the foam index tests were carried out at least twice for all samples. Those which showed good agreement between the two results were reported as a simple average of the two tests. Otherwise an additional test was performed and the final foam index was calculated as the average of the three tests.

Foam indices for different fly ashes varied over a quite significant range. The lower the foam index value, the greater the uncertainty in its value. This is partly attributable to the drop-wise incremental titration involved in the test. For a sample with a low AEA capacity, addition of one drop can significantly overshoot the true endpoint of the test. At the same time, the lower foam index samples tend also to be those with quite low LOI values. The main factor determining foam index is the LOI of the sample, since as discussed above, it is the carbon that tends to adsorb the AEA. Low LOI samples also exhibit a larger uncertainty in the LOI values themselves. As a result, when the so-called specific foam index is calculated (as the ratio of foam index per carbon content) the low foam index and LOI samples show quite large variations. Nevertheless, reproducibility was quite good in the foam index tests themselves.

3.2.4 Studies on the Influence of Different Variables on Foam Index Results

As noted above, the foam index can hardly be considered a truly standardized test. To the extent that there are numerous reports of variability in results from different investigators, it was felt important to better characterize the test in other

ways. The previous chapter examined what has been previously concluded regarding the parameters that influence the foam index results.

As was noted above, Sabanegh¹⁸, Yu²⁰ and Hachmann²¹ examined the influence of time and particle size on foam index test. It was observed that time had a significant effect on apparent AEA adsorption capacity. In those studies^{18,20,21} the time required to achieve final, maximum uptake of the AEA by the fly ash was approximately 1 hour. However the simple foam index test described above is generally complete after 10 minutes. This implies that when an apparent endpoint is reached in the foam index test, the AEA is still being taken up by the fly ash particles^{15,17,18}. However, it was noted that most of the AEA uptake occurred in the early stages of the test, and the amount of AEA adsorbed after 10 minutes was somewhat variable. We did not pursue the issue of the time dependence any further in the present work, accepting that the adsorption capacity is not necessarily a true equilibrium capacity, but rather a fair approximation to it.

The earlier presented review also suggested that the size of the carbon particles could also make a difference in their AEA adsorption capacity. Again, apart from recognizing that this parameter can make a difference, there was little that could practically be done with particle size in order to influence the values of the test. There were some separate tests performed with fractionated fly ash samples, in which this might be more of a consideration. These will be discussed further below.

Surface polarity (or oxidation) was another factor that was observed to influence foam index values. This parameter was actually under experimental control, and many tests were performed with materials that had been deliberately oxidized. Generally speaking, the effect of oxidation was to generally decrease the foam index of a sample.

As noted above, the foam index results were obtained using two different surfactants whose efficacies were different. The comparison of the results obtained with the two different surfactants will be presented in Chapter 5.

It is also important to note that there are significant batch-to-batch variations in the same AEA, and that the AEAs tend to "age". These issues will also receive more attention in Chapter 5.

The foam index test is quite tedious, especially when used for examining a fly ash with significant carbon content. There is a strong incentive to reduce the time of the test by merely putting less of the fly ash adsorbent into the test mix. This raised a question regarding the sensitivity of the test to the absolute amounts of the components in the mixture. The results are shown in Figure 3.2.1.

Figure 3.2.1 The influence of the amount of fly ash on foam index value.

It was initially hoped that by simply decreasing the amount of ash in the sample from 2 gram to a lesser amount, the time of the test could be reduced because fewer drops would be needed to achieve an endpoint. Figure 3.2.1 shows the results of a test in which the ash loading was systematically varied, while keeping all other components constant. The foam index results have been recomputed to a constant 2 gram of ash basis. For example, the raw numerical value of the foam index (after correcting for the blank) for a 1 gram sample of ash was doubled for plotting in the figure. Unfortunately, as Figure 3.2.1 illustrates, while it is true that less AEA volume was required to reach the endpoint, with smaller samples, it was also the case that the results recalculated to the standard 2 gram basis were inconsistent with those from higher loadings of ash. Generally, higher apparent foam index values would result from smaller samples, until an asymptotic value was reached, beyond about half a gram of fly ash. The behavior was not uniform from sample – to – sample, as Figure 3.2.1 illustrates. As can be seen, lower LOI samples (e.g., FA 21) reached the asymptotic value earlier than did the higher carbon samples (e.g., FA 23).

A higher amount of AEA adsorption with smaller amounts of ash suggested that there might have been a competitive route for loss of AEA from solution (in addition to adsorption on the ash). Again, all of the experiments involved subtracting a blank obtained the same technique without the ash, and all of the actual test conditions remained the same regardless of the amount of added ash. The concern arose that the inorganic solution chemistry was somehow being influenced by the addition of ash, and that the ionic composition of the water, in turn, somehow influenced the formation and stability of the foam.

A separate set of experiments was conducted in which the Darex II AEA was added to the pure, deionized (DI) water. Even though the Darex II is a surfactant, it is a rather poorly foaming surfactant by itself. There was never a good stable foam endpoint achieved when adding Darex II drop-wise to DI water. It is clear that the inorganic components present in the actual foam index test in some way mediate the foaming behavior of the AEA. It initially appeared that as the ionic strength of the solution increased, the foaming action increased.

To examine the above point more carefully, experiments were then done in which different inorganic agents were added to DI water, and the foam index test performed on these solutions (generally involving no cement in the water). These results are shown in Table 3.2.1 (see Tables at the end of this chapter). The amount of water or buffer solution used in these foam index tests was 25 ml, just as in the normal foam index tests. The same 70 ml container was also used for these tests as in the actual foam index testing.

These results did not suggest a role of ionic strength per se in the AEA solution, as salt (NaCl) addition did not lead to a clear foam endpoint at whereas the cement blank does. Nor did pH appear to be a key issue; using a pH 10.4 buffer solution (close to the pH with cement in DI water) in place of deionized water, a good foam endpoint was again not obtained. Certain types of additives, however, markedly lowered foam index endpoint. Several carbonates showed this. The cement we used contains some calcium carbonate, as high temperature decomposition tests in the TGA-Plus showed (typically 1.4% by mass). The amount of added calcium carbonate (over the range from 0.5 to 2 grams) did not appear to significantly affect the endpoint. These tests also suggested that

the nature of the cation accompanying the carbonate played only a minor role in the results. Experiments were also performed with non-carbonate additives, and again these did not generally lead to a clear endpoint. A main component of cement, Ca(OH)_2 , was separately tested (results not shown) and also seen to be surprisingly ineffective.

Tests with pure fly ash 39 (2 grams of ash with LOI 0.8%) and calcium carbonate showed that the foam index was 4 times higher than the foam index for pure CaCO_3 in DI water. This is to be expected, insofar as the fly ash adsorbs the AEA. On the other hand, the actual foam index value for this sample (in the usual 2 gram of ash + 8 gram of cement test) is 0.10 ml/2g-ash. When corrected for a “cement blank”, calcium carbonate is seen to be just as effective as cement itself in promoting both the same foaming action and so apparently does not influence adsorption onto the fly ash. The lack of a distinct endpoint in the test with fly ash and sodium carbonate is presently not understood. A foam index test performed with pure ash (no cement) gives 0.16 ml/2g-ash (8 drops).

All of the above results suggest that the foaming ability of the AEA is influenced by the introduction of the cement and ash (and/or carbonates) into solution. Again this is not an ionic strength issue, but it depends somehow upon the nature of the anions. The way that the anions can affect the nature of the AEA is by determining its ionic form. Nor is this a pH effect alone. It should be noted that in the cases in which the solution was basic in pH (buffer solution), a clear foam endpoint was not necessarily achieved, unless carbonate was also present. At high basic strength, the presence of carbonate was not required in order to achieve a stable foam. Because of this, it is clear that inducing foaming probably does involve promoting ionization of the organic acids in the AEA. Still, there is a much more complicated equilibrium involved, and all components in the

foam index test- ash, cement and AEA are somehow involved. It is likely that the carbonate anion is involved in regulating some key equilibria in the mixtures. The decision was made in the context of this study to not pursue these questions any further, as this would have required some considerable investment of extra time in characterizing the aqueous phase chemistry of poorly- defined AEA materials.

It has been reported¹³ that the cation in ionic surfactant-type AEAs plays little role in determining its air entraining surfactant behavior. Indeed, as Table 3.2.1 suggests, it was the identity of the anion that made the most difference. Also the concentration of alkali cations has some effect on air entrainment, but the effect is only weak at high concentrations¹³.

The nature and amount of cement both make a difference in the air entrainment behavior of a mixture¹³. The reason may well be associated with the identity of cations that are added as part of the cement. The results of the foam index test were also sensitive to changes in the cement that was utilized in the test. Generally, the Portland cement used in our experiments was ordinary commercial cement obtained from the local “Home Depot” store. The Portland cement from different bags showed different activities in the foam index tests. It should be recalled that the foam index value for the standard amount of water containing the standard amount of Portland cement was used as a “blank” value. This value was subtracted from the value obtained with a mixture containing the 2 grams of fly ash in addition to the same amounts of water and cement. The amount of AEA needed to saturate Portland cement varied over quite a large range, $\pm 50 - 75\%$, on a relative basis, depending on the particular sample of cement. For many fly ash samples, the blank value was so small in comparison to the actual measured foam index that the

variation in cement blank made no difference. On the other hand, for low foam index samples, the variation in the blank could make a difference.

Therefore, to the extent possible, only one cement sample was used throughout any series of foam index tests. In each series of foam index tests, the blank Portland cement activity was measured many times. The foam indexes of the cement were measured, as a minimum, before and after each series of foam index tests, and the final blank result was an average of the two or more blank foam index values. Generally, when the same cement was used in a test series, the foam index value for the cement did not vary more than one drop (0.02 ml).

As Table 3.2.1 shows, the "typical" cement blank foam index is of the order of 5 drops (0.1 ml). Thus the cement is as effective at promoting the foaming action of the AEA as are the alkali carbonates. (which were added at somewhat lower concentrations). This, combined with the variability observed using different cements, suggests that there may be some small component in the cement that behaves as the AEA activator, and that the concentration of this agent in solution can be also influenced by the amount of ash addition in a foam index test. According to the results above, it can be hypothesized that this anion might be carbonate, though this issue was not examined in sufficient detail to allow the conclusion to be definitely drawn. Clearly, since cement is present in much larger quantity than the ash itself in the foam index tests, it is not likely to be a simple matter of pH change in the solution associated with using different amounts of ash. It appears as though it is an issue of small amounts of certain anions in solution.

3.3 Gas Adsorption

3.3.1 Apparatus and Experimental Procedure

Gas adsorption experiments were performed using an Autosorb-1 system from Quantachrome Corp. A picture of the front panel of the Autosorb-1 is shown in Figure 3.3.1 (at the end of this chapter). The Autosorb-1 provides adsorption isotherms in an automated manner. The machine operates by measuring the quantity of gas adsorbed (as an adsorbate) and/or desorbed from the surface of a solid (as an adsorbent) at a measured equilibrium vapor pressure, using the static volumetric method. The isotherm data are obtained by adding or removing a known quantity of known adsorbate gas into a sample cell containing a certain amount of solid adsorbent at a constant temperature. As adsorption occurs the pressure in the sample cell changes until equilibrium is established. The quantity of gas adsorbed at the equilibrium pressure is calculated as the difference between the amount of gas actually added (or removed during desorption), minus the amount of gas required to fill the void space in the sample cell at the final equilibrium pressure. The Autosorb-1 has the ability to measure volumes of adsorbed gas at pressures down to 10^{-7} atm. The adsorbed volumes (per mass of adsorbent) as a function of relative pressures of the adsorbate are the data that constitute the adsorption isotherms. These isotherm data can be used in order to calculate adsorbent surface areas, pore volumes and pore size distributions, as described below. In this research, nitrogen, carbon dioxide and ammonia were used as adsorbates in the study of adsorption on fly ash. In this report, only the results for nitrogen and carbon dioxide are considered.

A standard nitrogen adsorption technique was applied for determining the porosities and surface areas of the fly ash samples. Nitrogen adsorption experiments were

performed at the customary 77 K liquid nitrogen boiling temperature. Nitrogen gas adsorption experiments are convenient because of nitrogen's relatively low saturation pressure (1 bar) at 77 K.

The carbon dioxide adsorption experiments involved use of a dry ice-acetone bath, which provided a constant and stable temperature of 195 K. The saturation pressure for CO₂ gas at 195 K is about 1.8 bar. This is too high a pressure for the Autororb-1 instrument to establish and maintain, and thus only low relative pressure adsorption and desorption ($P/P_0 < 0.5$) experiments were performed with CO₂ as the adsorptive. Some workers prefer CO₂ adsorption because it occurs at higher temperature than does nitrogen adsorption, and thus problems associated with activated diffusion into the pores are minimized. On the other hand, carbon dioxide is not as good a choice for examining larger porosity. In general, fly ashes contain both macro- and micro-pores and, therefore, nitrogen is the best choice for general characterization.

Independent of the adsorptive used in the experiments, fly ash samples were outgassed for several hours at a constant temperature of 573 K, in vacuum, before each adsorption experiment was performed. Generally twenty adsorption and twenty desorption points were obtained in order to get complete isotherms. In some cases 60 additional adsorption data points (in the low relative pressure range [$P/P_0 < 0.1$]) were obtained in order to facilitate complete surface area and micropore analysis. From these isotherm data the surface areas of the fly ashes were calculated using Brunauer, Emmet and Teller (BET) theory²⁵. Dubinin-Radushkevitch (DR) theory²⁵ was applied in order to determine the microporosity of the fly ash samples. The main source of the micropores in

fly ashes is its carbon. The mineral part of the ash is largely nonporous, and what small amount of porosity it contains is mostly in macropores.

Fly ashes are rather low specific surface area powders. This meant that large masses of sample needed to be used in order to provide the requisite 10 m^2 of surface in the system's sample holder. In some cases, the 10m^2 surface requirement rendered analysis of samples available only in small amounts impossible.

3.3.2 Instrument Calibration Experiments with 8571 Alumina Reference Material

A reference material, 8571 Alumina, distributed by U.S. Department of Commerce, National Institute of Standards and Technology (NIST), Gaithersburg, MD, was used in order to check the performance of the Autosorb-1. The reference material is intended for use in calibrating instruments and evaluating the reliability of analytical methods used for determining the BET surface area of powders and catalysts. Reference material 8571 is prepared and analyzed through a cooperative program between NIST and ASTM Committee D32. NIST reports the mean BET specific surface area for 8571 Alumina to be $158\text{ m}^2/\text{g}$, but with a variation from 150 to $165\text{ m}^2/\text{g}$. The mean value is established from the surface area data provided by 18 test Laboratories in the US. Both Autosorb-1 instruments in our laboratory were tested and calibrated quite frequently in order to check their performance. The two separate instruments are referred to as the "physisorb" instrument and the "chemisorb" instrument. These names refer to the particular capabilities of the instruments, and the differences are not important here. A few measured surface areas are given in Table 3.3.1.

The difference between the mean NIST reported BET surface areas and our values is not fully understood, but it should be kept in mind that our values are in full accord with the range of values that NIST considers reliable. It is quite apparent that there is excellent reproducibility obtained when using one instrument, and also, in the surface area results from the two different instruments is small enough to be of no significance in this study.

It is worthwhile considering in a bit greater detail the raw data from which the calibration values are derived. Typically, 40 data point nitrogen isotherms were used for the instrument calibration runs. To check instrument reliability and reproducibility in another way, the mass of reference material 8571 Alumina was varied in different experiments (see Table 3.3.1). Figure 3.3.2 shows four different isotherms obtained for the reference material, superimposed onto one plot.

Figure 3.3.2 Physisorb and chemisorb instrument nitrogen isotherms for alumina reference material 8571 at 77 K.

The four isotherms of Figure 3.3.2 lay nicely on top of each other, demonstrating that there are no significant differences between the isotherms obtained from the chemisorb and physisorb instruments. In addition, as was expected, sample mass variation made no difference.

According to the Brunauer, Deming, Deming and Teller²⁵ (BDDT) isotherm classification system, the isotherms on Figure 3.3.2 could be classified as being type IV isotherms. The most characteristic feature of type IV isotherm is its hysteresis loop. The hysteresis loop is caused by the capillary condensation of the adsorbate in mesopores. In addition, the isotherms in Figure 3.3.2 have a steep slope at higher relative pressures, indicating a presence of mesopores.

The actual calculation of the surface areas presented above followed classical BET theory²⁵. The region of relative pressures at which this theory applies is 0.05 up to 0.3. The relevant portion of the isotherm for this region is shown in Figure 3.3.3.

Figure 3.3.3 N₂ isotherms obtained with Autosorb-1 instrument for Alumina reference material 8571 at 77 K, relative pressure region 0.05 to 0.3.

Again, the isotherms obtained from both instruments are seen to agree with each other quite well. In a relative pressures range of 0.05-0.3 there is no noticeable difference between the isotherms. However, in this relative pressures range, the chemisorb instrument isotherm shows a bit higher slope as compared to the physisorb instrument isotherm. This deviation is the origin of the slightly higher BET surface area calculated from the chemisorb instrument isotherm data. The reason for this slight instrument-to-

instrument variation is not clear, but again, the magnitude of the difference is so small as to be of no concern in the present study. The so-called BET plot, calculated from the isotherm data of Figure 3.3.3, is shown in Figure 3.3.4.

Figure 3.3.4 BET surface area plot for the physisorb and chemisorb instruments, reference material 8571 alumina.

An excellent linear correlation is seen in Figure 3.3.4. Of course, a good straight line on a BET plot is no assurance that the BET theory is being properly applied to a particular material. It is important to bear in mind that a BET calculation is inherently incorrect for a microporous material, on which multilayer sorption cannot possibly take place. Just as in all other studies of activated carbons and other microporous materials, the reporting of a BET area is not intended to convey the notion that the theory applies to these materials. Rather, it is only by convention that BET areas are reported for such materials to give a sense of the extent of their microporosity. In actual fact, the process of

adsorption on microporous materials involves mainly pore filling. It is for this reason that many workers advocate reporting micropore volume, as opposed to surface area.

Still, a question remains as to why our BET surface areas were smaller than the mean of the NIST values. Since the material is a carefully prepared standard, we must accept that it is the same material as has been studied elsewhere and that sample-to-sample variations are not responsible. We do not know, however, how other laboratories performed the BET surface calculations, and whether small differences in selection of the relative pressure range ($P/P_o = 0.05-0.3$)²⁵ contributes to the difference. Another possibility that received some attention was a small amount (<0.01 mg) of sample loss that accompanied outgassing of the samples. This amount appeared independent of the actual sample amount used in an experiment. The sample size in the calibration experiments ranged from about 0.12 to 0.24 g (see Table 3.3.1). The magnitude of this loss is such that it could possibly contribute an uncertainty of a few percent. With an active, high surface area material, this mass loss could be associated with loss of some moisture or adsorbed gases from the sample, but it could also include a small amount of material drawn up into the filters at the top of the sample tube. Since this material is outside of the cooled zone of the sample holder, it could not participate to any significant degree in adsorption experiments. Because of the small magnitude of the discrepancy from the published mean value and the fact that the present results were in the accepted range no further efforts were undertaken to resolve the issue. We would therefore caution against reading too much significance into small differences in any surface area reported in this work.

The fly ashes in our sample bank had an average surface area about 2 or 3 m²/g of ash. This very low surface area demanded that the sample amount in each experiment to be about 2 or 3 grams in order to satisfy the Autosorb-1 instrument minimum of 10 m² surface area in the sample holder. For those experiments in which 2 or 3 grams of fly ash was used, a possible 0.01 g of sample loss could only contribute an 0.33 % error to the surface area.

3.4 Flow Microcalorimetry

The flow microcalorimetry (FMC) technique was employed for determining the polarity of fly ash carbon surfaces. A Mark 3V Flow Microcalorimeter, manufactured by Microscal, Ltd. of London, was used for our fly ash polarity experiments. Experiments with the FMC involved a measurement of the heats of adsorption of liquid adsorbates such as n-butanol, t-butanol, methanol, and n-dotriacontane on the surfaces of the fly ash sample. From such heats, it is possible to infer the degree of surface polarity on carbon surfaces using a technique developed by Groszek^{26,27}. Groszek's original work involved only use of n-butanol for this purpose, but we have extended the method by measuring the heat effects using t-butanol and methanol as well. These other adsorptives were used to examine the effects of steric factors on the polarity determination.

The FMC sample cell, with a volume of 0.20 ml, was filled with approximately 0.15 ml of dry sample. Sample powders were washed into place with the carrier fluid (n-heptane). Thermistors in the sample cell provide a temperature difference related to the heat released during adsorption onto the fly ash sample of any compound (for example n-butanol) from the flowing heptane carrier solution. Heptane has historically been selected

as a carrier fluid because of its weak interaction with carbon^{26,27}. Measurements were made with the sample cell just above room temperature (generally 303 K). Perfusor VI syringe pumps were used to maintain a constant 6.6 ml/hour flow of the carrier fluid through the system. The calorimeter baseline was established over several hours by measuring the thermistor output when the sample was exposed to the pure carrier fluid. The adsorbate was then dissolved into the heptane carrier, and introduced from a second syringe pump to the sample. As the dissolved butanol adsorbate (flowing in heptane) reached fly ash carbon, a heat of adsorption was released as a result of its adsorption onto the sample. It has been suggested that the main reason why butanol would displace heptane from the surface is the thermodynamic favorability of the interaction of the polar OH group in n-butanol with polar groups on the solid surface. The heat of adsorption is comparable in magnitude to a hydrogen-bonding interaction involving hydroxyl groups. The nonpolar tail of the adsorbate is chemically indistinguishable from the heptane carrier, so that the interaction of this portion of the adsorbate with the surface would tend to be associated with no large heat effects.

The released heat of adsorption at a selected constant temperature is measured using the thermistors in the FMC sample cell. The signal from the thermistors is recorded using a Macintosh computer under Labview control. The FMC system is calibrated by feeding a known amount of power, for a controlled time, to a precision resistor embedded in the sample cell. Based on the adsorption peak size in the actual adsorption experiment, the calibration energy pulse is chosen to give a comparably sized peak. In this way, the response of the thermistors is related to an actual amount of heat release, with no need to assume anything concerning the nature of the heat transfer process in the cell. In most

experiments, a known amount of power of 100 μ W, delivered over 100 seconds, provided a suitable calibration. In this case, the total calibration energy would be 10 mJ. The effects of variation of carrier flowrate on the calibration peak size were experimentally explored. It was observed that over the entire range of practical operation (1-6.6 ml/hr), there was no influence of flowrate on the observed calibration peak area for a constant amount of heat supplied. What this means is that the technique is not sensitive to small flowrate fluctuations. This is logical, because at the low flowrates of interest in this method, the convective loss of heat with the carrier fluid would be negligible in comparison to the heat transfer through the sample cell wall to the thermistors.

The FMC technique involved stepwise increase of the concentration of the adsorbate in heptane, until surface saturation is achieved at some particular adsorbate concentration. This effectively traces out an adsorption isotherm for the system. Adsorption peaks generally become smaller with increasing concentration. At some particular concentration of adsorbate, no more heat was released upon further change in adsorbate concentration. It is assumed that at this stage of the experiment that all of the polar sites on the fly ash carbon have been completely saturated with adsorbate and the run is taken to be complete. Typically, a saturation endpoint is observed by the time the n-butanol concentration in the heptane reaches about 1% by volume.

Typical FMC results are shown in Figure 3.4.1 (at the end of the chapter). The characteristic adsorption voltage signal (from the thermistors) is displayed as a function of time, as the n-butanol concentration is increased in a stepwise manner. From these raw data, heats of adsorption were calculated using simple trapezoidal curve integration technique. The actual peak areas (in V-s) were converted into heats using the area of the

calibration peaks discussed above. The calculated heats of adsorption at each concentration step were added together, and a cumulative heat of adsorption determined (see Figure end of the chapter). Figure 3.4.2 presents the adsorption isotherm for a typical fly ash sample. It is clear that the asymptotic value has not quite been reached in this case, but it is quite close to the maximum value shown.

In order to determine heats of adsorption of n-butanol on a fly ash carbon, the contribution from the mineral portion of the fly ashes needs to be subtracted from the results on the whole fly ash. For this purpose, the heats of adsorption of n-butanol were measured on carbon-free fly ash. Taken as an average of many experiments, the heat of adsorption on the carbon-free samples was 0.088 J per gram of mineral for both class C and class F ashes.

Based upon the correction for the mineral contribution, equation 3.4.1 provides a formula for calculation of the heat of adsorption of fly ash carbon alone.

$$Q_{carbon} = \frac{Q_{ash} - (1 - \frac{LOI}{100}) \cdot Q_{min}}{\frac{LOI}{100}} \quad (\text{Eq. 3.4.1})$$

where Q_{ash} - heat of adsorption of fly ash per gram of ash,

Q_{min} - heat of adsorption of the mineral part per gram of mineral,

Q_{carbon} - is heat of the adsorption of carbon per gram of carbon.

From these heats of adsorption, the equivalent polar surface areas were calculated using a published conversion factor $6.7 \text{ m}^2/\text{J}$ of adsorption heat (for n-butanol on carbon)^{26,27}.

The experiments involving t-butanol and methanol were carried out in a similar manner. The same $6.7 \text{ m}^2/\text{J}$ was assumed for the heat of interaction of t-butanol with the surface. There is no basis in the literature for this value. It was assumed only on the basis that the strength of interaction of a hydroxyl group on t-butanol should be comparable to that of a hydroxyl on n-butanol. The t-butanol would be, by virtue of its large effective radius, excluded from many small pores that the n-butanol could access. Thus a drastic decline in polar surface fraction, using t-butanol as compared to n-butanol, would imply a molecular sieving on the size scale of a few Ångstroms. Methanol, on the other hand, should be able to access an even smaller range of the pore sizes than the somewhat larger n-butanol. The conversion factor from heat adsorption to surface area for methanol on carbons is $2.39 \text{ m}^2/\text{J}$ and was obtained from van Krevelen³⁰.

3.5 Fly Ash Fractionation

Most characterizations of the fly ash involved use of the whole as-received fly ash samples. A few tests involved sized sieve fractions prepared from these. Prior to sieving, all samples were carefully dried in air ventilated laboratory oven. The procedure involved placing approximately 150 gram batches of raw fly ash sample into flat, large diameter low height, crucibles, which were placed into a laboratory oven at 120°C . Fly ash samples were kept in the oven for 2 or 3 days. After drying, samples were cooled down in

a desiccator, in order to protect them from re-absorption of moisture from atmospheric air. Prior to sieving, the samples were re-weighed and moisture content determined.

U.S. standard testing sieves from Fisher Scientific were used to fractionate the pre-dried fly ash samples. A.S.T.M. E-11 specification sieves (Nos. 45, 75, 140, 325, with opening sizes of 355, 180, 106 and 45 micrometers, respectively) were chosen for separating the samples. In order to facilitate sieving of the samples, a portable sieve shaker from W.S.Tyler/Combustion Engineering, Inc. was used for 25 minutes. Each fraction obtained during sieving was weighed. The total mass before the sieving and the masses of the fractions obtained provided the raw data for calculating particle size distributions.

3.6 Microscopy

3.6.1 Optical Microscopy

In order to visualize structural (morphological) changes of fly ash and carbon samples, microscopy techniques were applied. Optical microscopy is a powerful tool in order to visualize surface features of scale $>0.5\mu\text{m}$ (for ordinary white light $0.4 < \lambda < 0.7\mu\text{m}$). It is quite obvious that using an optical microscope there is no chance to visualize particle micro- ($d < 20\text{\AA}$) or mesopores, ($20 < d < 500\text{\AA}$). However optical microscopy is a suitable and simple tool in order to examine macroscopic features of the carbon and ash particles.

Colored positive images were taken with an Olympus Vanox camera attached to the photomicrographic microscope. Kodak 400 film was used in order to record the

images. Film was developed and printed in local CVS store. Lenses designated 5x, 10x, 20x and 50x were used in order to get desired magnification levels when imaging fly ash particles (the numbers 5x, 10x, 20x and 50x do not really correspond to the final magnification, but they indicate the power of the main objective lenses). Pictures of a 1000 micrometer length calibrated ruler were taken with all of the objectives, in order to establish the true magnification. All pictures, shown in this report, have been electronically scanned from original photographs using a Color OneScanner 600/27 for the Macintosh, and then processed with Adobe Photoshope software.

3.6.2 Scanning Electron Microscopy

A JSM – 840 F Scanning Electron Microscope (SEM) was utilized in order to image samples of fly ash and to study their carbon morphology. Ted Pella Inc. 25.4 mm diameter carbon planchets were used as specimen holders. Before use, the planchets were ultrasonically cleaned in methanol in order to remove dust and dirt. The endpoint of the cleaning process was defined by when the methanol solution remained transparent and clean. Following this, the planchet's surface was divided into quadrants using copper tape. Establishing these four quadrants on the planchet allowed investigation of four different samples during the same SEM session. To assist in uniformly covering the planchet with the fly ash samples, each sample was first dispersed in methanol. An ordinary pipette was used to cover the appropriate section of the planchet with the fly ash-containing methanol solution. After this, the planchet was left to dry for several hours prior to microscopy.

All SEM experiments were performed with an electron accelerating voltage of 5 kV. The working distances were 8 and 15 mm, depending on the quality of the image. Polaroid 52 pictures were taken of the images.

3.1.1 Transmission Electron Microscopy

Fly ash and fly ash carbon features were examined with Philips EM420T transmission microscope with accelerating voltage 120kV. Bright Field (BF), Selected Area Diffraction (SAD) and Energy Dispersive Spectroscopy (EDS) techniques were applied in order to investigate fly ash features in TEM.

In order to form any image in TEM, it was necessary to use either a central transmitted spot of the diffraction pattern or some scattered electron spots. In the Bright Field imaging case, a direct beam (transmitted spot) was selected from diffraction pattern. A small aperture (5-70 μm diameter) was inserted in the back focal plane of the objective lens to intercept the diffracted beam. The only utilized radiation was the transmitted beam, which formed a BF image.

The Selected Area Diffraction mode was used to investigate a special area of the specimen. The SAD aperture was inserted into the image plane of the objective lens. The electron-stream, which hits the specimen outside the area defined by the aperture size, was excluded from contribution of the diffraction pattern. Changing SAD aperture size determined the area of the specimen that was under investigation. A larger SAD aperture means a larger area under examination on the specimen.

The EDS technique involves tilting the specimen towards to X-ray detector by 10° - 20° . The objective aperture was removed to prevent creation of spurious X-rays that would flood the detector. Beam intensity could be reduced using a smaller spot size,

which was important because a high intensity beam could flood the detector and result in bad counting statistics. The EDS X-ray detector had an ultra-thin window, which allowed us to see carbon (atomic number 6) and above in the periodic table.

3.6.3.1 Sample preparation for TEM analysis

One of the class F high carbon content fly ash samples (FA9) was picked for TEM analysis. Fly ash 9 is from the New England Power Brayton Point station. The carbon content of this fly ash was 66 wt-%, because it had been enriched in a separation process at the plant.

In order to make ash particles “transparent” for the beam in TEM, they were ground for a few minutes in a simple mortar with a pestle. Then a 10-ml volume Pyrex jar was used to mix fly ash sample with pure methyl alcohol. A Branson 2210 ultrasonic bath was used to ultrasonically suspend the fly ash with methyl alcohol for 20 minutes. After this, the ash in alcohol suspension was pipetted drop by drop onto a 3 mm diameter copper grid coated with a porous thin carbon film (Ted Pella, Inc.). The specimen was left to dry off for a couple days in a laboratory hood.

Surface Area & Pore Size Analyzers

Figure 3.3.1 A picture of the Autosorb-1 instrument from Quantachrome Corporation. Machine is designed to analyze surface areas and pore size distributions of powders and pellets.

Figure 3.4.1. Typical data set obtained by Mark 3V Flow Microcalorimeter, manufactured by Microscal, Ltd. of London. Data curve obtained with class F fly ash with LOI 33.6wt.%.

Figure 3.4.2. Typical Flow Microcalorimeter adsorption isotherm, for class F fly ash sample with LOI 33.6 wt.%.

TABLES

Table 3.2.1 Foam index results involving different inorganic agents

Experiment number	Components used in test	Foam index	
		# drops	[ml of 10 vol.% Darex II]
1	DI water + Cement	5	0.1
2	DI water	>75*	>1.5*
3	DI water + 2 g C-free mineral from FA	3	0.06
4	DI water + 2 gram NaCl	>35*	>0.7*
5	Buffer solution, pH=10.4	>38*	>0.76*
6	Buffer solution, pH=10.4 + 2 g CaCO ₃	1	0.02
7	Buffer solution, pH=10.4 + 1 g CaCO ₃	1	0.02
8	Buffer solution, pH=10.4 + 0.5 g CaCO ₃	2	0.04
9	Buffer solution, pH=10.4 + 0.7 g CaCO ₃	2	0.04
10	Buffer solution, pH=10.4 + 2 g Na ₂ CO ₃	2	0.04
11	Buffer solution, pH=10.4 + 1 g Ca (C ₂ H ₂ O ₃) ₂	> 34*	No endpoint
12	DI water + 2 g Na ₂ CO ₃	2	0.04
13	DI water + 2 g K ₂ CO ₃	2	0.04
14	DI water + 2 g CaCO ₃	2	0.04
15	DI water + 2 g Na ₂ SO ₄	No end	No endpoint
16	DI water + 2g FA 39 + 2g CaCO ₃	10	0.2
17	DI water + 2g FA 39 + 2g Na ₂ CO ₃	No end	No endpoint
18	DI water + 2g FA 39	8	0.16

19	DI water + 2 g FA 39 (with presence of cement), cement value subtracted	5	0.1
20	DI water + NaOH, pH = 13	4	0.08
21	DI water + NaOH, pH = 13 + 2 g CaCl ₂	No end	No endpoint
22	DI water + NaOH, pH = 13 + 2 g K ₂ CO ₃	4	0.08
23	DI water + NaOH, pH = 13 + 2 g CaCO ₃	1	0.02

***-no clear endpoint (foam) achieved on the surface of the vial**

All water experiments involved 25 ml DI water

Table 3.3.1 BET Surface areas for 8571 Alumina reference material.

Autosorb – 1 from Quantachrome Co.	Experiment 1	Experiment 2
	BET Surface area [m ² /g]	BET Surface area [m ² /g]
	Sample mass used in surface area experiment was about 0.24 g	Sample mass in used surface area experiment was about 0.12 g
Physisorb Instrument	152	152
Chemisorb Instrument	154	153

4.0 SAMPLE BANK

A fly ash sample bank was established in order to have access to a wide enough range of commercial samples to help both in defining trends as well as in identifying unusual behavior and its causes. Today the sample bank includes about 80 fly ash samples (Table 4.1, found at the end of this chapter), with samples from various US utilities and from international donors. The notes in Table 4.1 provide some information regarding the source of the samples and their nature. Most of fly ash samples in our sample bank originate from pulverized coal-firing boilers, though there are also fluidized bed and other types of ashes included in the bank. Depending on the type of coal used, the composition of the main part of the fly ash, the mineral portion, varies over quite a large range. Mineral matter in ashes has not been the focus of this study, since the interest is mainly in the carbon in the ash. It should be noted that most of the issues regarding the sorptive properties of the ash are connected with the carbon, even in ashes with relatively low carbon contents. This will be further discussed below.

Fly ashes are fine powder residues resulting from the combustion of solid fossil fuels (again in this study, mainly coals). The term "fly" refers to the fact that they are carried along with the flue gases, as they pass upward out of the boiler. This makes these materials distinct from ashes that are collected at the bottom of the boiler, the so-called bottom ashes. Fly ashes are captured from flue gases either by electrical precipitators or bag filters in commercial power plants. The main part of the coal fly ash by mass is its "inorganic" matter, typically in the range from 90-99 wt.%. This portion is derived from the mineral matter in raw coal, but is very different in composition and form from the original mineral matter, because it has gone through the very hot oxidizing environment

of a boiler. Strictly speaking, the carbon in fly ash is also "inorganic", as it really bears little resemblance to the organic matter from which it was derived. It is a very highly carbonaceous substance. Still, it is customary to treat it differently from the non-combustible ash residue.

Table 4.2 presents some typical “ash analyses” of coals. Such data are quite typically available for any coal of commercial significance, though the number of components presented will vary, depending upon how detailed an analysis was performed. The “ash” that is actually analyzed is the residue of combustion from an ASTM combustion procedure. These compositions are similar to, though not necessarily identical to, the compositions of fly ash from the same coal, because the preparation conditions are somewhat different. Again, this list does not represent the minerals in raw coal, but rather, what the minerals become after combustion.

In the example of Table 4.2 coals A and B are bituminous coals (high rank) and C is a sub-bituminous coal (low rank). The main constituents of the inorganic part of coal fly ash are silicon and aluminum oxides (up to 80 wt.%). The amounts of SiO_2 and Al_2O_3 are somewhat smaller in coal sample C (sub-bituminous). Lower rank coal ashes are known for their relatively higher calcium and alkali earth contents, and this is visible in Table 4.2. As will be explained below, these ash compositional differences are the basis for the main coal fly ash classification scheme.

A certain amount of unburned carbon is also always present in the fly ashes, usually in the range of 1 – 10 wt%. The main reason why this carbon is present in fly ash, is incomplete coal combustion in the utility boilers. Thus the carbon has the form of coal char particles. Ash analyses of the type shown in Table 4.2 rarely indicate unburned

carbon, because the nature of the test is such that the coal is burned to constant final mass. Consequently, all of the carbon has been removed. This is another important feature to take note of. The presence of unburned carbon in fly ash is only a consequence of the fact that the sample has not had the residence time required to complete the burnout of the carbon. Utility boilers can typically provide only a second or two of residence time in the hot zone of the boiler.

The chemical and physical requirements for fly ashes, which are intended for use as pozzolans are defined in ASTM C 618-85. The ashes have been classified into two main groups- class C and class F. Table 4.3 provides chemical and physical requirements for fly ashes defined by ASTM C618-85.

As may be noted from the Table 4.3, there are 5 so-called chemical requirements for both types of fly ash. They are all important for establishing their commercial value in the concrete industry. According to the chemical requirements, the bituminous coals A and B in Table 4.2 produce class F ash and the sub-bituminous coal C produces class C fly ash. This is typically the case. Class C fly ashes mostly originate from sub-bituminous coals or lignites, (which are collectively also known as "low rank coals"), while class F ashes come from bituminous coals or anthracite (known as a "high rank" coals). This means that in terms of the US market, most fly ashes produced in the eastern US are of the class F variety, while most ashes produced in the western US are of the class C variety. There are, naturally, exceptions to this general rule.

The fly ash fineness requirement specifies that more than 65 wt% of the fly ash sample particles must pass the 45 micron sieve in order to satisfy the physical requirements for concrete use. It is important to note this, in connection with the studies

on fractionated fly ashes presented later. It is certainly possible to have a significant amount of material larger than 45 μm in size. Additionally there are some other characterizations, specifically related to the effectiveness of the ash as a pozzolan, but these will not be discussed here

Fly ashes 1 – 13, and also 19-23, 30, 31, 46, 47 and 48 in our sample bank have been provided by New England Power Company (NEP), from their Brayton point and Salem Harbor Plants. They all are categorized as class F fly ash samples, and are the products of firing various bituminous coals. In many cases, these plants have used bituminous coals of foreign (mainly South American) origin. It is very difficult to say with any certainty which ash came from which coal, because of the manner in which the plants receive and stockpile coals. All that can be said is that these ashes are typical of the particular plants, under various kinds of conditions.

The LOI for these NEP samples varies over quite a large range. The majority of these samples exhibit LOI in a range of 1-10%, but there are also few very high LOI samples with carbon content all the way up to 65.5 wt.%. Most of the high LOI fly ash samples did not come directly from ash hoppers fed from the ESP's at these plants. Instead, they were produced in a separation process run by Separations Technology, Incorporated (STI) of Needham, Massachusetts. The separation process has a goal of providing fly ash that meets the above ASTM (and other specifications) for concrete, but produces a by-product stream of very high LOI ash. This is the source of the very high LOI ashes in our sample bank. These high LOI ashes are believed to contain carbon that is similar to the carbon in the whole ash - it is not believed that separation results in ash

samples that are markedly different in their carbon properties from the parent materials. This point will be examined further below.

As can be noted in Table 4.1 some of the NEP fly ashes were marked by the provider as “bad” or “good”. Those adjectives tell how this particular fly ash performed in actual concrete mixtures. Some of them are also marked to be as “problem” ashes, which also refers to the fact that this particular fly ash performed poorly in concrete mixtures. NEP mainly provided us with fly ash samples which were collected after the low-NO_x combustion retrofits were made to their boilers, but in one case (FA 5) the sample came from the pre-retrofit firing.

As noted above, following the recent changes in environmental regulations, power utilities were obliged to achieve mandated reductions of NO_x in flue gases. When the changes were made, undesired changes were observed in many fly ashes. Again, the changes have basically involved less air being fed into the primary combustion zone, resulting in regions of the combustor where there is not enough oxidizer present for complete combustion. These changes have sometimes made the combustion process less efficient in terms of carbon burnout, sometimes resulting in higher amounts of carbon in the combustion residues and higher LOI for the fly ash. Generally, though, the increase in LOI has been modest. There have been other changes in the unburned carbon which are of equal or greater concern. The concrete industry has experienced problems with some of the samples generated in the low NO_x units, even if the ashes have had LOI values well within ASTM C618-85 specified limits (6% or less). The pair of samples marked FA 5 and FA 6 in Table 4.1 show an example of what has been an often baffling problem for the utilities. The typical carbon content for the NEP samples prior to the low NO_x

retrofits was in the range from 1-2 wt. % (see Fly ash 5 in Table 4.1). After the changes were made, the LOI increased only slightly (see fly ashes 6 and 8, Table 4.1). The degradation in performance was more than what might have been expected from such a modest LOI increase. The nature of the carbon in the ash had also changed, so as to make it unacceptable for use in concrete, due to poor air entrainment. Nothing in the ASTM-type specifications had changed enough to flag a potential problem in advance.

Fly ashes 24 – 29 are sample from American Electric Power (AEP), from its Columbus Mountaineer and Rockport Plants. The Columbus Mountaineer plant used eastern bituminous coal, and therefore produced class F fly ash samples. The Rockport plant used Powder River Basin sub-bituminous coal, which produced class C fly ash. Again, as in the case of the NEP samples, fly ashes 24 and 25 in Table 4.1 have been classified by the utility as being “good” ashes and fly ash 26 as being “bad” in concrete performance, for reasons of air entrainment problems.

Fly ashes 36 to 45 in our sample bank could be categorized as fly ashes from bituminous or sub-bituminous coals, which have been provided by different utilities in central western part of the US (Colorado, Arizona) and in southern part of the US (Texas and Arkansas). It can be noted that the majority of these fly ashes have very low LOI content, ranging from 0.3 wt % to 1 wt %, except for fly ash 37. As has been explained earlier, this is a level of LOI in ash at which the measurement of LOI becomes quite cumbersome and potentially inaccurate, especially in sub-bituminous coals. For the most part, fly ashes 36 to 45 ashes have been categorized by their providers as being class C ashes, which is common for a sub-bituminous coal firing product. However fly ashes 37

and 39, both originating from sub-bituminous coals, are still classified according to the ASTM C618-85 as being type F ashes.

Fly ashes 49 to 60 in our sample bank were provided by Monex/Boral Corporation, a large ash marketing concern. Again, the majority of these samples have relatively low carbon contents, except the series of samples 49 to 51. These three samples were again processed (separated) samples. They are classified as being type F ashes. Unfortunately the company did not provide us with complete information regarding a few of their fly ashes. It is most likely that fly ashes 52 to 60 are class C type fly ashes based upon several considerations. These fly ashes all have very low LOI, which is quite common for class C ashes. Also they exhibit a yellowish color characteristic of the western class C ashes. Finally, they behave as do most other class C ashes in our sample bank, in the standard characterization tests we routinely perform.

Fly ashes 61 to 64 were purchased from the Southern Illinois University (SIU) fly ash sample bank. These SIU samples are class F type fly ashes from Illinois bituminous coal and have relatively high LOI values. The LOI for these fly ashes ranges from 1.6 to 7.4 wt.%. One of these fly ashes (FA 63) is produced by fluidized bed combustion (FBC), and is in fact the only such sample in our sample bank. It is quite interesting because it is the only example of the types of carbon that may be expected from that type of combustor. The LOI for this fly ash sample is 7.1 wt %, which is an unusually high LOI value for an FBC sample. Again, it offers an opportunity to examine the differences in the carbons produced by different firing technologies.

Dairyland Power provided us fly ashes 65 to 68, and also 73 to 75. Fly ashes 65 and 66 are from its Alma plant (J.P. Madgett Station) and are produced from Powder

River basin sub-bituminous coal. Fly ash 67 is a class F ash from another of its power plants. Fly ashes 73 and 75 are also from Dairyland's JPM station. These latter two fly ashes are classified as type C fly ashes. This is consistent with their very low LOI. However, fly ash number 75 has been particularly instructive. The significance of this fly ash comes from the fact that it is a class C fly ash but it has relatively high carbon content for class C ashes (an LOI of 1.3 wt %). As was discussed earlier, class C fly ashes typically have very low LOI values, to the point that there is a concern associated with the accuracy of calculation of properties on a mass of unburned carbon basis. This sample's higher LOI value minimizes significantly the uncertainty in some important carbon-specific properties.

Fly ashes 28 and 35 in our sample bank are classified as petroleum coke co-fired fly ash samples. The LOI of fly ash 35 is unusually high, 17.5 wt. %, despite its yellowish appearance (typical of class C ashes with much lower LOI values). This is because that the carbon particles in petroleum coke fly ash sample are relatively large, dense solid particles, uniformly mixed with the inorganic matter of the ash. Such particles do not provide much color to the ash. These carbon particles do not have almost any porosity, as compared with the carbon in most class C and class F fly ashes. Petroleum coke fly ashes have been studied in more detail by Yu²⁰.

Four samples, fly ashes 69 to 72 in Table 4.1, were provided by the Thermal Engineering Department, Tallinn Technical University, Estonia. These four fly ash samples originate from a very different type of solid fuel - oil shale. This oil shale has an ash content of about 50 wt. % on a dry basis²⁸. The lower heating value of the fuel is 9.6 MJ/kg for the dry oil shale²⁸. Another distinct feature of the raw oil shale is its very high

mineral carbonate content, which reaches 20 wt. %. This mineral carbonate is available in a raw oil shale mostly as limestone, CaCO_3 . The most distinct feature of the chemical composition of the typical oil shale fly ash is its lime CaO content, which is around 56 wt.%. The cumulative amount of the common fly ash minerals like SiO_2 , Al_2O_3 and Fe_2O_3 is only about 26 wt. %²⁸, compared to the 95 wt. % for typical class F fly ash. Few carbonates survive the high temperature pulverized firing conditions, about 1 wt.% on dry ash basis²⁸.

Another characteristic of oil shale fuel is its very high combustible volatile yield, in the organic part of the fuel (80-85 wt.%)²⁸. The high organic content of this fuel allows it to be directly burned in a pulverized firing-type of boiler. Thus, the combustion environment that these samples have seen is quite similar to that for pulverized combustion of coals. The origin of the unburned carbon is very different from coal. The shale oil kerogen is more similar to a petroleum than to a coal. Still, these samples provide an opportunity to gain insights from a very different type of material.

TABLES

Table 4.1 Fly Ash Sample Bank

Sample	LOI wt %	Sample Description
FA1	6.5	NEP - Brayton pt., Unit #3, #3E, unprocessed, problem ash
FA2	3.1	NEP - Brayton pt., Unit #3, from STI, unprocessed, problem ash
FA3	14.6	NEP - Brayton pt., Silo #2, #2D+E unprocessed, good ash
FA4	14.6	NEP - Brayton pt., Unit #2, unprocessed
FA5	1.9	NEP - Brayton pt., Unit #3, pre low-NOx conversion, good ash, CPI=0.14
FA6	3.4	NEP - Brayton pt., poor air entrainment (Tresca 5252)
FA7	2.6	NEP - Brayton pt., (BPP 50612-260, T24), problem ash, from STI
FA8	3.8	NEP - Brayton pt., (BPP 50612-261, T34), poor air entrainment, from STI, CPI=0.74
FA9	66.0	NEP - Brayton pt., black in color, from STI
FA10	2.6	NEP - Brayton pt., (BPM 50802-4) from STI
FA11	2.5	NEP - Brayton pt., (BPP 50612-262, T11), from STI, CPI=0.45
FA12	2.3	NEP - Brayton pt., (BPP 50610-258, T23), from STI
FA13	3.8	NEP - Brayton pt., (BPP 50612-261, T34), same as FA8, from STI
FA16	1.5	Helsinki (50703-136, E1), very bad ash, from STI, CPI=2.1
FA19	3.6	NEP - Brayton pt., Unit #3, ash with 5% Gas co-firing
FA20	2.0	NEP - Brayton pt., white-gray ash, problem ash, from STI, CPI=0.24
FA21	6.1	NEP - Brayton pt.
FA22	33.6	NEP - Salem Harbor ash, unprocessed, Surface area=18m ² /g
FA23	65.5	NEP - Salem Harbor ash, processed, Surface area=36m ² /g
FA24	2.7	AEP-Columbus, Silo #2, Unit #1, from Eastern Bituminous, good ash
FA25	2.5	AEP-Columbus, Silo #4, Unit #2, same as FA24
FA26	4.0	AEP- Columbus Mountaineer Plant, Silo #2, problem ash
FA27	0.16	AEP, Rockport Plant (R.#2) Reg. Ash, Powder River Basin Coal, good ash, Class C
FA28	2.4	same as FA27, except produced from a feed stream containing 5% Petroleum Coke
FA29	1.5	AEP, Clinch River Plant, Virginia Coal, 3% CaO but Class F
FA30	35.1	NEP - Brayton pt., High Carbon Fly Ash
FA31	0.88	NEP - Brayton pt., Low Carbon Fly Ash
FA32	44.7	HEL 60520 B-3-E-2, from STI
FA33	29.1	HEL 60517 B-6-E-2, from STI
FA34	4.9	BP 51103 B3 Feed, from STI
FA35	17.5	Petroleum Coke-western coal blended fuel

FA36	0.30	"NA" Salt River Project, Navajo Station, Page Arizona, Subbit. Coal from Black Mesa mine, Az, class F ash - acceptable (W.A. Co)
FA37	4.9	"CH" Public service of Colorado, Cherokke Station, either Subbit. or Bit., class F ash - not used because of high alkali content (W.A. Co)
FA38	0.2	"PAW" Public service of Colorado, Powder River Basin, class C ash-acceptable (W.A.Co)
FA39	0.82	"MO" Southern California Edison, Mojave Station, Nevada, subbit. coal from Black Mesa mine, Az, class F, acceptable but active (W.A. Co)
FA40	1.1	Welsh Power Plant, North-East Texas, 245620, class C Fly Ash, (G.-H. Co)
FA41	1.1	Welsh Power Plant, Texas, 245713, class C Fly Ash (G.-H. Co)
FA42	0.60	Welsh Power Plant, Texas, 245716, class C Fly Ash (G.-H. Co)
FA43	0.61	Flint Creek Plant, Arkansas, 213483, class C Fly Ash (G.-H. Co)
FA44	0.56	Flint Creek Plant, Arkansas, 213491, class C Fly Ash (G.-H. Co)
FA45	0.74	Flint Creek Plant, Arkansas, 22/4/97, class C Fly Ash (G.-H. Co)
FA46	11.1	NEP - Salem Harbor ash, Separated or no?, July 1997
FA47	41.5	NEP - Salem Harbor ash, Separated high Carbon, 1997
FA48	1.4	NEP - Brayton pt., Separated low Carbon, July 1997
FA49	19.9	Monex-Marshall, high Carbon, 19.5% LOI
FA50	22.2	Monex-Crystal River, high Carbon 20.3% LOI
FA51	20.9	Monex-Bowen, high Carbon 20.5% LOI
FA52	1.1	Monex-Craig Station, two bottles A and B, bad ash
FA53	4.0	Monex-Crystal River # 4, two bottles A and B
FA54	4.1	Monex-Crystal River # 5, two bottles A and B
FA55	0.68	Monex-Martin Drake, two bottles A and B, bad ash
FA56	1.2	Monex-Navajo, bad ash
FA57	0.80	Monex-Coleto Creek
FA58	1.9	Monex-Wansley
FA59	1.0	Monex-Mojave
FA60	6.0	Monex-Crystal River #2
FA61	1.6	Southern Illinois University at Carbondale - 1 PCF- Herrin III #6 PCC/cyclone
FA62	3.9	Southern Illinois University at Carbondale - 2 PPF - III #6 Herrin/Spring PCC/Scrubber
FA63	7.1	Southern Illinois University at Carbondale - 3 PF III#6 FBC Fly Ash
FA64	7.4	Southern Illinois University at Carbondale - 4 PPF, Springfield III #5 PCC/Cyclone
FA65	0.74	Dairyland Power, Wisconsin utility, class C, Powder River Basin - worst
FA66	0.92	Dairyland Power, Wisconsin utility, class C, Powder River Basin - better
FA67	0.79	Dairyland Power, Wisconsin utility, class F, Powder River Basin
FA68	0.84	J. P. Madgett Plant, Alma, Wisconsin, Dairyland Power, 12/3/98,

		class C, bad, LOI 0.97%
FA69	1.4	Estonian Oil Shale Fly Ash, Eesti Power Station, field one, 11/17/98
FA70	1.3	Estonian Oil Shale Fly Ash, Eesti Power Station, field two, 11/17/98
FA71	1.0	Estonian Oil Shale Fly Ash, Eesti Power Station, field three, 11/17/98
FA72	1.3	Estonian Oil Shale Fly Ash, Eesti Power Station, field four, 11/17/98
FA73	0.41	60 lb from Rick Larson, Dairyland Power Cooperative, JPM Station, 500 old STH 35, Alma, WI 54610 in July 1999.
FA74	9.8	60 lb from Peter Calvert on 08-04-99. (LOI ~ 10%, NH3~200ppm)
FA75	1.3	60 lb from Dairyland Power Cooperative, JPM Station, 3251 East Avenue South, LACROSSE, WI 54601, On 9-29-99 F. I. 325 1drop = 25
FA76	0.26	1100g good ash at normal operation 12-3-99 from Miller Plant, Alabama, Southern Company (Utility)
FA77	0.30	1200g "bad" Miller ash from < 12-99
FA78	0.47	940g from SRI (Southern Research Institute) pilot combustion LOI 0.16, 0.2 lb/106 BTU (bag house)
FA79	1.2	680g bad u3 miller A Side (older) 8/4/99
FA80	4.4	Russel Hill at Boral, sample #B, relatively bad, LOI ~4.5%, class F
FA81	1.4	Russel Hill at Boral, sample #BC, good ash, baseline material for sample M, LOI ~2%, class F
FA82	1.6	Russel Hill at Boral, sample #C, bad, LOI ~1.5%, class C
FA83	0.41	Russel Hill at Boral, sample #M, unusually bad (probably contains soot), LOI <0.5%, class F
FA84	10.9	Russel Hill at Boral, sample #MC, relatively bad, LOI 11-12%, class F

Table 4.2 ASTM properties of the some typical coals by *Singer*²⁹.

Coal*	A	B	C
ASTM RANK	h _v Ab	h _v Cb	Subbit C
Proximate Analysis			
Moisture	0.7	2.7	10.2
Volatile Matter	32.3	41.7	31.5
Fixed Carbon	54.4	46.4	42.8
Ash	12.6	9.2	11.9
Fusibility Temperatures (F)			
IT	2430	2080	2130
ST	2510	2140	2170
HT	2560	2170	2210
FT	2660	2300	2310
Ash Composition			
SiO₂	50.7	52.0	50.2
Al₂O₃	30.2	17.5	16.9
TiO₂	1.9	1.3	0.8
Fe₂O₃	9.5	15.5	8.9
CaO	1.6	4.5	11.5
MgO	0.9	1.1	3.5
Na₂O	1.0	0.6	1.8
K₂O	2.7	2.8	1.7
P₂O₅	<0.1	<0.1	...
SO₃	1.4	4.2	4.3

* - Reporting Basis: As-fired (pulverized)

**Table 4.3 Chemical and Physical requirements defined
in ASTM C618-85 for fly ashes for use in Portland
Cement Concrete.**

	Class F	Class C
A. Chemical requirements		
(SiO ₃ + Al ₂ O ₃ + Fe ₂ O ₃), min., %	70.0	50.0
SO ₃ , max., %	5.0	5.0
Moisture content, max., %	3.0	3.0
Loss on ignition, max., %	6.0*	6.0
Optional chemical requirements		
Available alkalies, as Na ₂ O, max., %	1.50	1.50
B. Physical requirements		
Fineness:		
Amount retained when wet-sieved on No. 325 (45 μm) sieve, max., %	34	34
Pozzolanic activity index:		
With portland cement, at 28 d, min., % of control	75	75
With lime, at 7 d, min., psi (kPa)	800(5500)	
Water requirement, max., % of control	105	105
Soundness:		
Autoclave expansion or contraction, max., %	0.8	0.8
Uniformity:		
Specific gravity, max. variation from average, %**	5	5
Percent retained on No. 325 (45 μm) sieve, max. variation, percentage points from average**	5	5
Optional physical requirements		
Multiple factor, product of LOI, %, and fineness, %, max.	255	—
Increase of drying shrinkage of mortar bars at 28 d, max., %	0.03	0.03
Uniformity requirements:		
When air-entraining concrete is specified, quantity of AE agent required to produce air content of 18.0 vol % shall not vary from the average of previous 10 by more than, %	20	20
Reactivity with cement alkalies:		
Mortar expansion at 14 d, max., %	0.020	0.020

*Reduced from 12.0% in 1984, with the provision that Class F pozzolan containing up to 12.0% loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.

**Average established by the ten preceding tests, or by all the preceding tests if the number is less than ten.

5.0 CHARACTERIZATION OF THE FLY ASH SAMPLES

5.1 Foam index – Basic Behavior

The so-called foam index test is a titration test, which measures the uptake of an Air Entraining Admixture (AEA) solution on a particular fly ash. Again, AEA is added to an actual concrete mix in order to provide the air volume in a concrete mix that, upon hardening, protects it during freeze/thaw cycles. The smaller the AEA uptake of an ash the better it will perform in concrete mixtures, because any AEA adsorbed on the ash is not available for producing the bubbles that provide void volume. As discussed earlier, AEA effectively partitions between the organic part of the fly ash (the carbon) and the water solution of the concrete mix. Generally the higher the carbon content of the fly ash the higher the uptake of AEA from solution. The foam index test is performed in a considerably more dilute mixture than that of the actual concrete, but the test serves as a semi-quantitative measure of how much uptake of AEA there will be in the actual mix.

In our research, foam index experiments were most often performed with a 10 vol.% Darex II™ AEA solution, obtained from Grace Construction Products. We diluted the original product with water to 10% of its original strength. Since the foam index is not a standardized test, users will often make such modifications that make the test more convenient for their particular application. As was noted in the previous chapter, the foam index value for a particular fly ash was highly sensitive to both the age and the concentration of the solution. Two shipments of nominally the same Darex II AEA were received during a two-year period. The first shipment of Darex II arrived in our laboratory in the spring of 1996, and the second one in the summer of 1997. The activity of these two solutions towards the same class F fly ash samples was observed to be

quantitatively different. Results of identical tests with both Darex II solutions are shown in Figure 5.1.1 (see the end of this chapter).

The “old” Darex II solution had a higher activity than the “new” Darex II solution shipped a year after first one (see Figure 5.1.1). If the AEA samples were identical, all points should fall on a 45° line, from the origin. There is a significant upward deviation from this trend. The error bars on both the x and y axes are 0.02 ml and indicate the degree of uncertainty present in our typical foam index test. As discussed in the previous chapter, the uncertainty in foam index tests is generally at least one drop (0.02 ml in our standard procedure). The activity differences between the two Darex II samples could possibly be due to concentration differences in the as-shipped materials, or be due to some chemical differences, because the materials are derived from natural materials and the nature of the feedstocks could be different at different times.

Foam index tests have been performed with both of the Darex II solutions over a long period of time (roughly 3 years). In addition to the differences in their initial activities, both AEA samples also tended to age. The activity of the 10% aqueous solutions decreased with time, and therefore each month a new 10 vol.% mixture was prepared. As a result, a “normalization” of the foam index values, obtained at different times, needed to be performed each time a set of tests were performed. The normalized foam index values were assumed to be comparable on an absolute basis. This normalization was performed using a selected “standard” ash. The properties of the ash itself were assumed not to vary with time. This is a fair assumption, insofar as the ash was stored in sealed containers and it contained no components that would be expected to be subject to air oxidation under such conditions. It should be recalled that the carbon in

the ash had seen much more severe oxidizing conditions and very high temperatures in the boiler.

One of the class F fly ashes, FA21 with LOI 6.1% (see Table 4.1 for more details of this ash), was used as the standard material for testing the activity of a particular batch of AEA solution. There were three main reasons why fly ash 21 was chosen from our sample bank for this purpose. First, the quantity of fly ash 21 available in our laboratory was large enough to allow a regular use of this sample over a long experimental program. Second, the foam index value for fly ash 21 was in a convenient range, about 0.3 ml per 2 gram of fly ash. The uncertainty in the value of foam index test was estimated to be about 7%. The reduction in uncertainty involved in use of higher carbon content samples was more than offset by the much longer time required to test those samples. Finally, fly ash 21 was not treated or enriched in any manner; it was provided by New England Power (NEP) directly from its Brayton Point plant. It was therefore considered as a good representative sample.

As was noted earlier, the results of the foam index test were also sensitive to changes in how the tests were performed, including the choice of cement additive. To the extent possible, each series of tests was carried out using the same cement, since each cement batch seemed to behave slightly differently in the tests.

All the fly ashes in our sample bank (Table 4.1) were subjected to the foam index test. The foam index values are generally presented on a basis of two gram of fly ash, which was the usual amount used in our tests. However, some of the high carbon fly ashes have been tested using lesser amounts of ash, and the results have then been recalculated back to a basis of 2 grams of ash. There is an incentive to use lesser amounts

of ash when carbon contents are high, because of the nature of the titration. High carbon samples require large amounts of AEA addition, which requires that many drops be added and that the samples be shaken many times. It proved unacceptable to try to shorten the procedure by adding a large initial aliquot of AEA. There is a time-dependence to the test, presumably associated with diffusion of the AEA into the pores of the carbon. The longer the test takes, the higher the apparent foam index.

The amount of ash used in foam index test was chosen based upon the results shown in Figure 3.2.4.1 (in Chapter 3). This figure showed the sample mass dependence of the test results. The amounts of ash used in the tests with highly carbonaceous fly ash were chosen to be high enough so as to be in the region on the Figure 3.2.4.1 where the foam index value was independent of the mass. This generally required more than 1 gram of ash in the test.

Traditionally, LOI has been the most important parameter for making predictions concerning the performance of fly ash in concrete. Again, the reason has to do with the efficacy of carbon in adsorbing AEAs. The higher the laboratory foam index, the worse the performance in the field was likely to be. All foam index values of samples in our sample bank are shown in Figure 5.1.2 versus LOI, and are also given in Table 5.1.1 at the end of this chapter.

The correlation of Figure 5.1.2 is deceptively good, as it tends to emphasize the contribution of fly ashes, which are far outside the realm of commercial acceptability. According to ASTM guidelines, fly ashes containing more than 6% LOI generally cannot be used in concrete, and even stricter standards have been developed by many state agencies. Thus the range of commercial interest is in the lower left corner of Figure 5.1.2.

It is within this subset of samples that most of the subtle commercial problems have been encountered.

Figure 5.1.3 shows the foam index values for the lower LOI portion of Figure 5.1.2. As can be seen, there is no clear relationship between foam index and LOI in this low LOI range. This indicates why there has been so much difficulty in predicting the actual concrete mixture performance of ashes, even if they have low LOI values. The origins of the fly ashes, presented together in Figure 5.1.3, are however so widely varying to the point that the presentation on the same plot can be criticized. The fly ash samples in our sample bank include some that are class C, some that are class F and a few of other types. To address this concern, the foam index values versus LOI for class F and class C ashes are shown separately in Figures 5.1.4 and 5.1.5, respectively. Clearly, both Figure 5.1.4 for class F and Figure 5.1.5 for class C show once again that it is difficult to predict foam index based upon LOI alone. There must be other factors, in addition to the absolute amount of carbon in the fly ash sample, that determine the AEA uptake by fly ash. This confirms the general belief that LOI by itself is an insufficient criterion for predicting suitability of fly ash for concrete applications. This is why it became necessary to search for other factors with which to correlate the foam index.

The inorganic (non-carbon) portion of the fly ash plays a minimal role in AEA adsorption. This was confirmed by direct experimentation. The foam index value for fly ash minerals has repeatedly been measured to be zero, indicating very little or no activity towards AEA adsorption. The representation of foam index as a specific foam index allows the elimination of the role of differing masses of inorganic material in the samples, making the comparison of materials of differing LOI easier. This is done by

defining the specific foam index as the uptake of AEA per unit mass of carbon in the ash. The specific foam index representation has the effect of emphasizing differences between the low LOI samples, which are otherwise crowded into the lower left-hand corners of the plots presented to now.

The high LOI samples fall at a relatively constant value of specific foam index, as indicated by the horizontal line in Figure 5.1.6. This could have been anticipated from the generally good correlation at high LOI values, seen in Figure 5.1.2. It can be seen from this plot that the nature of the carbon in the high carbon fly ash samples is quite similar to that in many of the fly ashes in the LOI range of commercial interest. On the other hand, the widely differing amounts of AEA adsorbed per unit mass of carbon in the fly ashes of the low LOI range confirms that other factors, in addition to the LOI, must play a role in AEA adsorption. Clearly these carbons in low LOI ashes must have very different characteristics.

5.2 Foam Index Results with Different AEA Materials

5.2.1 Foam Index Results with Air 40™ from Boral Material Technologies

Foam index tests with also performed using another commercial AEA. Air 40™ from Boral Material Technologies, Inc., was used in a series of experiments with the same set of fly ashes from our sample bank. As with the tests with the Darex II, these tests were performed using a 10 vol.% solution of the material provided by the manufacturer. The nature of the tests was identical to that described earlier. The results obtained using this material are shown in Figure 5.2.1. Again, the correlation between the values of foam index and LOI is discernible, but weak, indicating that factors besides the

LOI also play a role in this case. Thus there seems to be no difference in the conclusions drawn from the work on two different AEAs.

The foam indexes of both AEAs, Darex II and Air 40, are shown in Figure 5.2.2 for the same set of class F fly ashes. As can be seen in terms of the foam index results from Figure 5.2.2, the Air 40 is the more active of the two AEAs. In a simple laboratory test (a complete drying of the aqueous AEA in a vacuum oven), the dry mass of AEA in each aqueous AEA solution was determined. These results showed that Boral Air 40 had an approximately 25 wt.% higher concentration of non-aqueous, non volatile components (126 mg/ml, as compared to 100 mg/ml for Darex II). However the foam index tests showed a much greater difference between these two materials, in terms of foam index (almost a factor of three). Thus the chemical nature of an AEA will surely influence the numerical value of the foam index. It is little wonder, then, that results from different laboratories show widely differing values of foam index for the same fly ash. There have been few attempts to standardize the tests. Consequently, it is important to remember in examining foam index results that it is not absolute values that matter, but rather, the trends that are revealed.

5.2.2 Foam Index Results with Sodium Dodecyl Sulfate (SDS), Abietic Acid Sodium Salt and Dodecylbenzenesulfonic (DBS) Acid.

In an effort to begin to develop what might serve as a standard type of foam-index type test, various surfactant materials were tested in the same manner as the commercial AEAs. The intent was to eliminate the variability in the natural products-based AEAs,

and thus eliminate the batch-to-batch variations in foam index. Also, there would be better control on the aging process, when using pure materials. Finally, the use of pure materials, of known composition, would permit putting the highly empirical foam index test onto a more fundamental basis. For example, it becomes possible to calculate quantities such as fractional surface coverage on the carbon.

One of the most popular commercial surfactant materials is sodium dodecyl sulfate (SDS) $[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}]$. For the purposes of this test, SDS powder was mixed with de-ionized water to make a 1 wt.% concentration solution. The solution was agitated mechanically until the powder was completely dissolved. A representative set of fly ashes, namely FA21, FA26, FA 63, FA 74 and FA 75 (see Table 4.1 for more details) was chosen from our sample bank in order to measure the extent of adsorption of SDS onto typical samples. The results of these foam index tests with the SDS solution are shown in Figure 5.2.3.

The results on Figure 5.2.3 show that the correlation between two surfactants is good, but by no means perfect.

However, as can again be seen from the error bars, the uncertainty in the foam index test is quite high for this set of samples. It may be noted that the amounts of SDS required to provide a stable foam endpoint are quite low, in comparison to the amounts for the Darex II AEA. This is the reason that the error bars appear to be significantly larger with respect to the SDS foam index, than with respect to the Darex II.

Abietic acid sodium salt is a material that is regarded as a good molecular model for commercial AEAs. Since abietic acid salt was not readily available for purchase, the foam index type of test was initially attempted with pure abietic acid. It was noted that abietic acid dissolved to only a very limited degree in de-ionized water. In addition, the abietic acid-water

solution proved to have only weakly foaming characteristics. Therefore NaOH was added in order to produce the salt form, and to obtain foaming behavior in the solution.

Before the foam index tests, 1.5 g of abietic acid powder was mixed with 50 ml of de-ionized water. In addition, separately 0.2g of NaOH powder was mixed with the 50 ml of de-ionized water. The solutions were combined and diluted until no undissolved residues were left on the bottom of the vial. The final abietic acid salt concentration in the solution was 0.05 molar. The foam index test with 0.05 molar abietic acid salt solution surfactant was performed twice, and the average result recorded and plotted in Figure 5.2.4.

Figure 5.2.4 shows a near-linear relationship between the two surfactants. Fly ash 63 showed no adsorption activity towards abietic acid sodium salt, as was also the case in the tests with SDS. This fly ash is somewhat different than the others selected for testing, inasmuch as it came from a fluidized bed combustor. There is no other apparent basis for its low adsorption activity.

Dodecylbenzenesulfonic acid sodium salt (DBS) solution was tried as third pure surfactant. A 0.025 DBS molar solution was prepared before the foam index tests. The solution was prepared by adding a measured quantity of dry powder of DBS into a pre-measured volume of de-ionized water. Again, the mixture was agitated until all of the DBS powder was dissolved. Preliminary foam index test results with DBS surfactant, compared with the other model surfactant foam indexes, are shown in Figure 5.2.5.

As seen in Figure 5.2.5 DBS surfactant foam indexes show the same trends as seen with 10 vol.% commercial Darex II. Again, the foam index result for fly ash 63 did not line up with the Darex II foam index results. These results with DBS showed that the original solution was too strong. As seen from the results in Figure 5.2.5 only a few drops

of DBS solution were needed to saturate the surface of the ash. Lower surfactant concentrations give higher foam index values (more drops of added solution are required in the foam index test) and therefore lower concentrations reduce the effects of uncertainty in foam index test.

According to the preliminary results obtained with the three model surfactants, DBS surfactant was chosen to further investigate the possible correlation with commercial Darex II results. The use of abietic acid salt surfactant was ruled out, because it was not provide a good foam and it was tedious to prepare. DBS was preferred to SDS because it was less expensive and appeared to be more active on a mass basis.

The test sample bank was expanded for examination using DBS surfactant. A total of 9 fly ashes, 8 class F and 1 class C, were chosen to investigate further the behavior of DBS surfactant. The list of fly ashes tested includes FA3, FA 6, FA 21, FA 46, FA 51, FA 53, FA 64, FA 74 and FA 75 (see table 4.1 for more details). In order to avoid saturation at low foam index values, the DBS solution was further diluted to 0.00625 molar. The goal was to increase the number of drops required to form a stable foam on the liquid surface. Again, higher foam index values provide lower uncertainty in the foam index test (1 drop = 0.02 ml in all of these tests).

The results of the foam index tests with DBS were recorded and plotted against foam index obtained using 10 vol% Darex II solution (see Figure 5.2.6). An average of at least two foam index tests was used for each point. Although the correlation obtained in Figure 5.2.6 is not perfect, it still clearly shows that DBS acid salt could be a very reasonable surfactant surrogate for the commercial Darex II in foam index tests with fly ashes.

Another set of fly ashes were further chosen from our sample bank to check DBS surfactant effectiveness with mostly class C and low LOI fly ash samples. Fly ashes 25, FA 40, FA 41, FA 42, FA 43, FA 44, FA 45, FA 63, FA 65 and FA 68 (see details in Table 4.1), were chosen for this purpose. In order to get meaningful foam index values for low carbon-content fly ash samples both DBS and Darex II surfactant solutions were diluted to smaller concentrations. The concentration of the DBS was decreased to 0.001 molar, and that of Darex II was lowered to 4 vol. %. The foam index results with these surfactant concentrations are shown in Figure 5.2.7, for low carbon fly ashes.

Figure 5.2.7 exhibits a greater variance when compared to Figure 5.2.6 while still demonstrating a reasonable linear correlation. The reader should keep in mind that generally the foam index test reveals its limitations mostly in dealing with low-LOI fly ashes. Even at a lowered concentration level of 4 vol.%, Darex II required only few drops more than the five drops typically required for the cement blank in these tests. Hence, the uncertainty is apparently quite large for the Darex II solution.

Figure 5.2.8 shows a comparison of the molar uptakes of surfactants from all of the different tests described above. It is immediately apparent that the DBS salt and SDS give very comparable molar uptakes at the foam index endpoint. There is no reason to expect this a priori, since the endpoint is defined by the particular concentration required to give a stable foam. This concentration need not be the same in any of the different surfactants tested. Because this concentration is not necessarily the same for different surfactants, then the uptake at that concentration endpoint also need not be the same. The abietic acid salt illustrates the point - the

concentrations of abietic acid salt required for a foam endpoint is somewhat higher than that for the other two surfactants.

Figure 5.2.8 emphasizes another conclusion that could be reached in comparing Figures 5.2.6 and 5.2.7, namely that the DBS salt molar uptakes in the set of low LOI samples used in obtaining Figure 5.2.7 are generally higher than the molar uptakes in the higher LOI set shown in Figure 5.2.6. There is, moreover, a trend towards higher molar uptakes per mass of carbon as the LOI decreases. The trend is not as clear with the abietic acid salt, but there are not nearly as many data points in this set as in the DBS salt et. It is unclear from these data alone why there should be a sensitivity to LOI, since it is not expected that the carbon surfaces themselves are very different at different LOI values. It is again believed that other factors characterizing the carbon surface are showing themselves in these tests. These factors will be discussed below.

The conclusion is that DBS salt could be used in standardized laboratory tests as a model surfactant, in lieu of commercial AEA surfactants. This point is made most clearly in the comparisons of the high (Figure 5.2.6) and low (Figure 5.2.7) LOI fly ashes with the Darex II results. Bearing in mind that the Darex II results were seen to correlate reasonably well with the Air 40 results, it is believed that the result here can be regarded as reasonably general. The advantages of the DBS salt are its known molecular composition, the ease of preparing the solution, and its low cost.

5.3 Adsorption isotherms

5.3.1 General background. Analytical models for Adsorption

As was discussed earlier, fly ash carbon content (also known LOI) is a somewhat poor predictor of performance of a particular fly ash in concrete. It was concluded that factors beyond simply the amount of carbon in the ash must play a role in determining the amount of AEA uptake by a given ash. Of the additional factors, one of the most obvious candidates is the surface area of the carbon. Surface area and porosity are well established as primary variables affecting carbon adsorption capacity.

The standard gas adsorption technique is a powerful tool that can be used for characterizing the porous nature of solids. Nitrogen adsorption on pulverized solid samples is commonly employed for surface area and porosity determination. In this study, nitrogen adsorption experiments were performed using an Autosorb-1 system from Quantachrome Corp. The Autosorb-1 is a fully automatic instrument that provides complete adsorption isotherms for the materials under investigation.

The amount of gas that adsorbs (the so-called adsorbate) onto the solid surfaces (the adsorbent) depends upon the temperature, pressure and the composition of gas. In adsorption process the amount of gas adsorbed at different equilibrium partial pressures at constant temperature defines the adsorption isotherm. According to *Brunauer*³² physisorption of gases on solids can be grouped into six classes of solid behavior and character, based upon the observed isotherms (see Figure 5.3.1).

According to IUPAC classification, the porosity of solid powders is divided into three classes: micropores (pores smaller than 20 Å), mesopores (pore sizes between 20 and 500 Å) and macropores (pores larger than 500 Å). The Type I isotherm of Figure 5.3.1 is generally exhibited either by microporous solids with relatively small amounts of macroporosity and mesoporosity.

It is important to note at the outset that the isotherms can arise from both physisorption (in which the adsorbate is held on the surface by purely physical forces) and chemisorption (in which the adsorbate actually chemically reacts with the surface). For pure chemisorption, the Type I asymptotic approach to a limiting quantity adsorbed occurs when all reactive surface sites are fully occupied. For physisorption, the asymptote is defined by the physical filling of all adsorption sites (including micropores), but involving no formation of strong chemical bonding interactions. We believe that the isotherms observed with our fly ashes are all of a pure physisorption type, as there is no expectation that molecular nitrogen could ever react with carbon surfaces at these low temperatures. Thus chemisorption will not be further considered here.

Type II isotherms are most frequently encountered when adsorption occurs on nonporous materials or microporous materials with macro- and mesopores³⁴. The inflection point (known as the "knee") of the Type II isotherm occurs near the completion of the adsorbed monolayer, in the case of the nonporous materials. As the relative pressure increases, other layers will be completed until the saturation pressure is reached³⁴. Unfortunately, the same isotherm shape may arise from other factors, such as micropore filling, when examining microporous materials.

Type III isotherms are relatively less common isotherms. It is believed that they are indicative of adsorbate-adsorbent interactions that are weak³² relative to adsorbate-adsorbate interactions in the adsorbed layer. Type III isotherms are characterized principally by heats of adsorption that are less than the adsorbate heat of liquefaction. The upturn of the isotherm at higher extents of surface coverage shows that the presence of adsorbate on the surface is itself actually helping to make the adsorption process progressively more favorable.

Isotherms of type IV and V show a hysteresis loop (see Figure 5.3.1), which means that the isotherm obtained during adsorption experiments sits below the isotherm obtained in desorption experiments, over at least part of the partial pressure range. This loop on both types of isotherms is believed related to capillary condensation in the adsorbent (solid) mesopores. The initial part of the type IV isotherm follows the same path as the type II isotherm, possibly indicating the absence of micropores in the sample. Again, the interpretation of this shape of isotherm is not straightforward, and micropores may actually be present. The initial part of the type V isotherm is basically that of the Type III isotherm, and shows that the capillary condensation processes can take place even when there are weak adsorbate-adsorbent interactions.

The stepped isotherm, type VI, is relatively rare and represents stepwise multilayer adsorption on a uniform non-porous solid³². All of the above types of idealized isotherms may in fact be considered as extreme cases of behaviors seen in real isotherms. The real isotherms may, in fact, exhibit characteristics of more than one of these model isotherms. Hence, these general isotherm shapes are to be used only as a guide to interpreting what we see in our isotherms.

The shapes of the hysteresis loops have often identified with specific pore structures. According to *Sing*³³ there are 4 types of hysteresis loops (H1-H4) depending on the structure of the macropores of the adsorbent (see Figure 5.3.2). Type H1 is often associated with porous materials known to consist of agglomerates or compacts of approximately uniform spheres in fairly regular array. These porous materials have narrow distribution of pore sizes³³. The type H2 hysteresis loop is quite difficult to interpret due to the fact that the sizes and shapes of pores are not well defined. The type H3 hysteresis loop is observed with aggregates of plate-like particles giving rise to slit-shaped pores. Similarly, type H4 loop appears to be associated with narrow slit-like pores, but in this case the isotherm character is indicative of microposity³³.

Interpretation of the adsorption isotherms and the application of different adsorption theories to explain them, is quite complicated and great care needs to be taken when examining actual isotherms. Many researchers have made an effort to model the shapes of different isotherms obtained from porous and non-porous solids, and used this to infer things about the structure of the solid. Langmuir's adsorption model²⁵ is a very simple example of such a model. It assumes that all adsorbent (surface) sites are identical and there are no surface complex- surface complex interactions occurring during the adsorption process. From this model, and the isotherm for the solid, the approximate extent of the surface of adsorption can be estimated. The Langmuir adsorption theory is useful because it is simple. However more often than not, it is an oversimplification of the real situation, and does not describe well the data obtained in real physisorption experiments. Many adsorbents have surface sites with varying degrees of affinity for the adsorbate, which effect is not taken into account in this model. Surface intrinsic

heterogeneity and complex-complex interactions present in real adsorption processes are the main reasons why Langmuir's theory does not generally correlate well with adsorption data.

The Brunauer, Emmet, and Teller (BET) model is the most commonly used adsorption theory for characterizing adsorbent surface areas. It represents an improvement beyond Langmuir theory because it assumes the possibility of surface multilayer coverage, by addressing the issue of adsorbed surface species interactions. BET theory accommodates the first five isotherm types quite well. However, BET theory rarely matches an experimental isotherm over its entire range of relative pressures. It has been noted that in the region of relative pressures $0.05 < P/P_0 < 0.35$, which is the relative pressure range near the completed monolayer³⁴, BET theory and experimental isotherms often agree very well. This means that BET theory is a powerful and extremely useful method of surface area determination, at least for non-microporous solids.

The validity of the BET theory for microporous solids is, however, questionable. The BET model does not take into account micropore wall potentials, which are important in adsorption into micropores. In addition, the multilayer coverage of adsorbate onto adsorbent is not generally possible in small micropores, which are not large enough to accommodate several layers of adsorption. Therefore BET theory is not recommended for detailed characterization of microporous samples, even though it is widely used for that purpose. When this is done, it is understood that this does not reflect the real physical situation.

The Dubinin-Radushkevich (DR) model is widely used for describing microporous samples. According to the DR model, micropore filling contributes to

adsorption on (or in) microporous solids more heavily than does layer to layer adsorption. The basis of the micropore filling mechanism is that every surface is characterized by a particular adsorption potential. Based on experimental data, and also assuming that the pore size distribution is Gaussian, Dubinin and Radushkevich derived an expression that relates the micropore filling (micropore volume) with the adsorption potential²⁵. The DR model provides an estimate of micropore volume, rather than surface area. A slight modification of DR model by Kaganer³⁵ provides an estimate of monolayer coverage, and therefore an alternative method for calculating surface area. The adsorption into micropores takes place at relatively low relative pressure, and therefore the DR equation is generally applied to isotherm data obtained at relative pressures below 0.1²⁵.

Fly ashes mainly consist of fairly non-porous mineral powders, containing mostly macroporosity, along with varying amounts of highly microporous carbon. Therefore use of the BET model in fly ash surface area calculations is as unreasonable as it is when characterizing any other carbon. The approach is, however, used here, because it is traditional to characterize carbons by BET area. At the same time, the DR micropore analysis is applied to these materials, in recognition of their microporous nature.

The total specific pore volume at a relative pressure of 0.95 is considered to involve the filling of pores of both micropore and mesopore sizes. This total meso- plus micro-porosity, less the DR micro-pore volume, is used to estimate the total mesoporosity of the particular sample. The total specific pore volume at relative pressure 0.99 less the total specific pore volume at relative pressure 0.95 provides an estimate of the macroporosity of the sample.

5.3.2 Interpretation of Nitrogen Isotherms

Nitrogen isotherms were determined for all fly ashes in our sample bank using an automated volumetric gas apparatus- the Autosorb 1 from Quantachrome Corp. Generally twenty adsorption and twenty desorption points were obtained in order to characterize the complete isotherm for a given fly ash. For some high carbon content fly ashes, an additional 60 adsorption data points were required (in the low relative pressure range, $P/P_0 < 0.1$) in order to get a full 80 point isotherm needed for accurate micropore analysis. Fly ashes are quite low specific surface area powders. This meant that large masses of sample needed to be used in order to provide the requisite 10 m^2 of surface in the Autosorb-1 sample holder. In some cases, the 10 m^2 surface requirement made analysis of samples that were available only in small amounts quite difficult. Detailed experimental procedures for the nitrogen gas adsorption experiments were given in Chapter 3.

BET theory was applied to all isotherms obtained in order to find surface areas for the fly ashes. In addition, the porosities of the fly ash samples were obtained from raw nitrogen isotherm data, as described above. The resulting fly ash BET surface areas and porosities are shown in Tables 5.3.1 and 5.3.2, respectively, at the end of this chapter.

Figure 5.3.3 shows standard nitrogen adsorption and desorption isotherms for some of NEP's Brayton Point class F fly ashes. These have relatively small carbon contents. Clearly the fact that generally greater extents of adsorption occur on the samples with higher LOIs suggests that the extent of nitrogen adsorption does depend on the amount of carbon in the fly ash sample. As can also be noted from Figure 5.3.3, factors beyond the amount of carbon must also play a role in adsorption process as well.

For example, comparing the results for fly ash 21 and fly ash 1, it is seen that the carbon content is smaller for fly ash 21 (LOI 6.1%; vs. 6.5% for fly ash 1), but nitrogen adsorption uptake is clearly higher for fly ash 21.

There are several further features of the isotherms on Figure 5.3.3 that warrant noting. The isotherms on Figure 5.3.3 appear to exhibit a mixture of Type I and Type II character³². Thus the isotherms for these samples exhibit some amounts of microporosity. The relative amounts may be crudely inferred from the height of the rise between relative pressures of 0 and 0.1. Also, the very slight hysteresis behavior between the adsorption and desorption curves is suggestive of a small amount of mesoporosity. Meanwhile, the sharp rise in the isotherms at near $P/P_0 = 1$ probably reflects capillary condensation between the fly ash spheres, though some macroporosity could also be involved..

Generally, higher uptakes of nitrogen lead to higher calculated BET surface areas (see results in Table 5.3.1). The fly ash isotherms presented in Figure 5.3.3 give rise to surface areas ranging from 1.7 m²/g to 3.8 m²/g. The fly ash BET surface areas generally increase with increased LOI (Figure 5.3.4). Again, this is not a surprising result, because the porous carbon provides more surface for adsorption than does the generally nonporous mineral part of the sample.

Figure 5.3.5 shows nitrogen isotherms for the high LOI class F fly samples obtained from NEP. Again, as can be seen from the isotherms of Figure 5.3.5 the uptake of nitrogen in the adsorption experiments is dependent on the amount of carbon in particular fly ash. The nitrogen uptake on fly ash 9 is roughly twice that for fly ash 22, very much in line with their LOI's. The adsorption isotherms in Figure 5.3.5 do not show as sharp a rise near a relative pressure of unity as do the results of Figure 5.3.3, probably

mostly because there was relatively more adsorption at lower P/P_0 values. In addition, the isotherms of Figure 5.3.5 show a sharp rise at small relative pressures (inferred but not drawn in, because the actual data points were not taken) indicating the presence of micropores. The fact that there is a slight hysteresis in the isotherms is suggestive of some amount of mesoporosity in the samples. Therefore, it can be concluded that there exist both micropores and mesopores in the samples. The isotherms on Figure 5.3.5 could again be classified as being a mixture of Type I and Type II isotherms³².

The BET surface areas for the high carbon fly ashes shown in Figure 5.3.5 have been tabulated in Table 5.3.1, and range from 10 m²/g to 43 m²/g of sample. Again, the surface area of the fly ashes is mainly contributed by the carbon part of the fly ash.

Other high LOI sample isotherms are shown on Figure 5.3.6. The same trends are observed in this figure as have been discussed previously. The BET surface areas calculated from these raw isotherms range from 6.9 m²/g to 43 m²/g (again, see Table 5.3.1).

Figure 5.3.7 presents the BET surface area calculated from raw isotherm data presented in Figure 5.3.6, as a function of LOI. The correlation between surface area and LOI is relatively good, despite the different origins of the fly ashes. Clearly carbons in these different fly ashes have similar adsorption behaviors towards nitrogen at 77 K. The similarity most likely has its origin in the fact that these samples were all high LOI class F samples.

Figure 5.3.8 shows a set of isotherms obtained in nitrogen adsorption experiments with class F fly ashes provided by NEP's Salem Harbor, and AEP's Columbus and Clinch River plants (see table 4.1 for detailed descriptions of the fly ashes). As seen in Figure 5.3.8, LOI differences on a scale of 1.5 % -

4% have an insignificant effect on nitrogen uptakes. The isotherms in this plot lie nicely on top of each other, exhibiting almost no variance. The isotherms on Figure 5.3.8 show modest amounts of microporosity, and significant mesoporosity. As expected from the similarity of the nitrogen isotherms, the BET surface areas for these fly ashes is in a very narrow range, 1.7 m²/g to 2.0 m²/g. These conclusions are similar to those drawn in connection with Figure 5.3.3, that is, LOI alone is not necessarily a particularly good predictor of surface area or porosity. Comparing this conclusion with the completely opposite one drawn from Figure 5.3.7 shows the danger inherent in drawing generalizations from any small sets of samples.

Figure 5.3.9 shows a set of nitrogen isotherms obtained from experiments with fly ashes supplied from various utilities by Monex/Boral, Co. The ASTM classification of the ashes (class C or F) was not clear, from the information supplied by the company. No tests were made in our laboratory in order to determine their chemical nature. Generally, samples with very low LOI are most likely class C fly ashes. Fly ash 52 (LOI 1.1 wt.%) shows an adsorption uptake which is much higher as compared to the uptake by fly ash 60 (LOI 6 wt.%). Therefore the carbon in these two fly ashes must be very different in nature. A comparison of BET surface areas obtained from the isotherms shown on Figure 5.3.9 shows that fly ash 52 has a much higher surface area than does fly ash 60 (3.8 m²/g as opposed to 2.2 m²/g).

Figure 5.3.10 shows a set of isotherms obtained from the adsorption experiments with class C fly ashes provided by Dairyland power. The results in Figure 5.3.10 strongly suggest that all the class C ashes have a similar nature (the shapes of the isotherms are similar). Again, as with class F ashes, nitrogen uptake is higher when the LOI is higher. The highest nitrogen uptake is observed with the fly ash 75 sample, which has the highest

carbon content of this series of samples. A slight hysteresis loop indicates a presence of mesopores in these class C fly ashes.

BET surface analysis of the isotherms in Figure 5.3.10 revealed that the class C surfaces are relatively high, compared to comparably low LOI class F fly ashes. The BET surface areas ranged from 1.1 m²/g to 5.7 m²/g.

Another set of class C ash isotherms is shown in Figure 5.3.11. As with the Dairyland fly ash isotherms, the amount of carbon seems to determine the uptake of adsorbate; the higher the LOI of the sample the higher the adsorption uptake. BET surface analyses of the isotherms shown in Figure 5.3.11 revealed that the surface areas are again relatively high, compared to comparable LOI class F ash surface areas. The surface areas ranged from 1.6 m²/g ash to 4 m²/g of ash. Thus, independently of the source of the class C ashes, their surface areas are higher relative to similar LOI class F ashes. From this, and the fact that the mineral portion contributes only a small amount of surface area regardless of class, it may be inferred that carbon in class C type of fly ash must be higher in surface area than the carbon in class F fly ash.

Figure 5.3.12 shows a set of isotherms obtained from the adsorption experiments with several “unusual” fly ash samples in our sample bank. The term “unusual” refers here to the fact that these samples were not produced in the usual manner, typical of class C and F fly ashes. All of these ashes were either products from slightly different combustion processes or they have been produced in processes with different additives to the normal coal feed. These samples are characterized in more detail in Table 4.1.

Fly ash 19 is a bituminous coal ash from a process with gas co-firing. Fly ash 28 is mostly class F ash together with some petroleum coke fly ash from a process in which

coal and coke were fed together. Fly ash 64 was collected from a cyclone, at an experimental combustor. Fly ash 16 has a very low LOI but is reported as being very “bad” for concrete purposes. This material was deliberately produced under simulated upset conditions, in a pulverized coal combustor.

Figure 5.3.12 shows that the highest adsorption uptake occurs with fly ash 64, which was also the highest carbon content sample (LOI 7.4 wt.%). BET surface area analysis gave surface areas for the samples shown on Figure 5.3.12 from 1.2 m²/g to 5.8 m²/g. Isotherms for another set of unusual fly ashes are shown in Figure 5.3.13. This figure compares some non-coal derived ashes with a typical class F ash (fly ash 5).

As discussed in chapter 4, fly ash 35 is mainly a petroleum coke fly ash and fly ash 70 is a representative of an Estonian oil shale fly ash produced by pulverized combustion of raw oil shale (see Table 4.1 for more details). These non-coal fly ash isotherms in Figure 5.3.13 have quite similar shapes to that for the low LOI class F fly ash 5. This indicates that a very wide range of feed materials will provide fly ashes with quite similar properties.

Adsorption uptake on the petroleum coke fly ash is quite modest, despite its very high carbon content (LOI 17.5 wt.%). Similarly, adsorption capacities on Estonian oil shale fly ash are relatively small compared with other similar LOI class F samples. The BET surface area for petroleum coke fly ash is only 1.3 m²/g. For comparison, class F fly ash 3 (with LOI 14.6%) has 8 times higher surface area, 10.6 m²/g. Therefore differences in the nature of the unburned carbon present in different fly ashes determine variations in adsorption capacities.

As further proof that the nitrogen adsorption capacity of fly ashes depends mostly upon the carbon part of the sample, a few samples of both class C and class F fly ash were fully burned in an air ventilated laboratory oven at 750°C in order to remove all the carbon present in samples. The carbon-free residue, the mineral part of the ash, was examined by nitrogen adsorption. Figure 5.3.14 shows the isotherms obtained with non-carbon (mineral) fly ashes compared with a typical class F fly ash isotherm for a sample that had carbon present. Clearly, the results on Figure 5.3.14 suggest that nitrogen adsorption mainly occurs on carbon site of the fly ash, particularly when it comes to the portion of the isotherm associated with micropores. The mineral part of the ash shows very little microporosity. The nitrogen uptakes are 4 times bigger for the as-received sample as compared to that which had been completely burned off. The BET surface area for fly ash 6 is 2.6 m²/g, compared to the non-carbon fly ash surface area of 0.75 m²/g. This strongly supports our previous contention that even a small amount of carbon in fly ashes provides the main surface for nitrogen adsorption.

In addition, the surface areas for the mineral part of the ash appeared to be independent of the type of the ash under investigation. Both class C and class F ash minerals provided quite similar BET surface areas, ranging from 0.7 – 0.8 m²/g. This is not surprising, because many minerals are observed to be glassy spherical particles with almost no porosity. However, carbon particles exhibit quite a large range of intrinsic surface areas, starting from a few square meters per gram and going up to a few hundred square meters per gram. This will be discussed further below.

Since it is the behavior of the carbon which has been concluded to be of greatest interest, the isotherm results presented above have been recalculated to a mass of carbon

basis. The raw isotherms, obtained on the as-received fly ash samples, have been recalculated by subtracting the contribution of the mineral part using isotherms such as those in Figure 5.3.14. Presenting the isotherms on gram of carbon basis helps to highlight the differences and similarities in fly ash carbons. The results of these recalculations are shown in Figure 5.3.15 for some class F fly ashes.

Four sets of carbon isotherms calculated from the data on the NEP Brayton Point class F fly ashes are shown on Figure 5.3.15. Similar isotherm comparisons of NEP Brayton Point as-received fly ashes (Figures 5.3.3 and 5.3.5) revealed significant adsorption uptake differences, clearly attributable to the differences in LOI. The isotherms of Figure 5.3.15 exhibit almost no differences at all, despite the very high carbon content differences in the as-received ashes (FA 8 has an LOI of 3.8%, FA 3 - 14.6%, FA 6-3.4%, and FA 21-6.1%). The results strongly suggest that there are no major differences in the nature of these fly ash carbons. The BET surface areas calculated from the isotherms shown in Figure 5.3.15 only ranges from 51 m²/g to 68 m²/g. This confirms the similarity of the carbons. Most likely all of these ashes have seen similar temperature and oxidizing conditions and have come from similar coals. All show very similar degrees of microporosity. The nitrogen uptake for these class F ash carbons is dominated by micropores, and the isotherms could be characterized as being Type I.

A similar comparison of isotherms calculated from class C as-received fly ash isotherms is shown in Figure 5.3.16. Class C ash carbon nitrogen adsorption uptake is much higher (by about 5.5 times on average) relative to the class F fly ash carbon nitrogen uptake. Most of this greater nitrogen uptake takes place at relative pressures below 0.1, indicating a significantly greater micropore content in the class C ashes. The

BET analysis supported this. The surface areas for the class C fly ash carbons shown in the isotherms of Figure 5.3.16 range from 210 to 370 m²/g. The surface areas for class C ash carbons are thus higher by a factor of 5 compared with the surface areas for the class F carbons. Again, similarly with NEP's Brayton Point class F samples, the adsorption uptakes were generally quite similar for all of these class C samples.

Finally, it should be noted that there are sometimes concerns expressed in the literature about the use of nitrogen isotherm data for characterization of surface area and porosity of carbons. This is particularly seen in the literature pertaining to characterizing porosity in coals themselves. Often, carbon dioxide has been recommended as a better characterization adsorbate, because of concerns about activated diffusional processes in small pores. Generally speaking, nitrogen is the better choice for characterizing microporosity in carbons, which have been burned off to a significant extent³¹. The reason has to do with the inability of the CO₂ to completely fill pores larger than medium-sized micropores. In order to understand better the nature of the microporosity in some fly ashes, the CO₂ gas adsorption technique was also employed.

5.3.3 Carbon Dioxide Isotherms

Despite its simple molecular structure, carbon dioxide has found relatively little use in surface area determination²⁵. Many researchers have suggested that the use of CO₂ as an adsorbate is preferred to use of nitrogen, because of the higher temperatures at which the adsorption process may be studied in the former case (generally 195 K or above, as compared to 77K). At higher temperatures the adsorption is expected to take place faster. Diffusion into the pores of a solid is proportional to (Temperature)^{3/2} in bulk

diffusion. In activated diffusion, as is more relevant for this concern, the temperature dependence is even stronger. There is still uncertainty about the state of the adsorbed CO₂ in micropores and thus there are still discussions about the cross sectional area of the CO₂ molecule. Carbon dioxide also has a high quadrupole moment, which means that its isotherm is more sensitive to the presence of polar groups or ions in the surface of the adsorbent²⁵. For this reason, carbon dioxide is not recommended for routine determinations of specific surface area. *Gregg*²⁵ proposes that the CO₂ adsorption technique should instead be particularly suitable for the study of the polarity of the surfaces.

Carbon dioxide isotherms were determined for selected class F fly ashes in our sample bank using the same automated volumetric gas apparatus described above. The Autosorb 1 user's manual provided a cross sectional area for the carbon dioxide molecule, which was taken to be 21 Å²/molecule and also a correction factor (gas non-ideality factor) which was 0.91*10⁻⁵ [mmHg⁻¹]. There are quite many other cross-sectional areas published in literature. For example *McClellan and Harnsberger*⁶⁵ cite CO₂ cross-sectional areas on solid carbon at 195 K varying from 20.4 to 22.08 Å²/molecule. These authors recommend for CO₂ adsorption at 195 K use of 21.8 Å²/molecule.

In the adsorption experiments involving CO₂ a bath temperature of 273 K was maintained using ice and water. At a temperature of 273 K, the generally accepted⁶³ saturation pressure for liquid CO₂ is 26144.1 torr (= 3484.8 kPa). The carbon dioxide saturation pressure calculated from the Clausius-Clapeyron equation is 26109.5 torr, which differs by 0.2% from the generally accepted value (see Table 5.3.3.1). There remains some controversy in the literature regarding the phase of the sorbed CO₂, both as

regards the density of the sorbed layer and the vapor pressure itself. At 195 K, if the carbon dioxide is taken to be in its normal solid phase, the vapor pressure would be very nearly 760 torr, which is almost a factor of two smaller than that offered by the extrapolation of liquid properties. This uncertainty also reflects itself in an enormous range of values being reported for its sorption cross-section⁶¹, a few examples of which were given above. Meanwhile, the very high value of saturation pressure, taken together with the operating limits of the available device (760 torr maximum pressure) suggests that CO₂ will only be useful for exploring microporosity. The critical temperature for CO₂ is 304.14 K.

As is standard in the literature, the convention used here involves calling any pores smaller than 20 Å in width “micropores”, any pores between 20 and 500 Å “mesopores” and pores larger than 500 Å “macropores”. The term “supermicropores” has recently come into use to describe the micropores between about 8 and 20 Å. This terminology has been adopted by some workers in recognition of what is thought to be an upper size limit of micropores that can be filled in a “standard” micropore filling process, in which the pore wall enhancement of gas-solid interactions plays a significant role. The 8 Å size roughly reflects twice the molecular diameter of typically employed molecular probes such as nitrogen and carbon dioxide. It may also be crudely estimated that the “primary” micropore filling process takes place at relative pressures between 10⁻⁵ and 10⁻² and secondary micropore filling in the supermicropores takes place between 10⁻² and 0.3. In this range of pore filling, some adsorbate-adsorbate interactions are also likely to play a role⁶⁴. This means that mesopore filling is also possible.

Sets of carbon dioxide adsorption experiments were performed with class F fly ashes provided by NEP. The results of those adsorption experiments are shown on Figure 5.3.17. As in the case of nitrogen adsorption, the extent of uptake of CO₂ by different class F fly ashes is dependent on their carbon content. Higher carbon content in ashes leads to higher uptake of CO₂ by the adsorbents. The isotherms on Figure 5.3.17 could be classified as being type I isotherms³². High CO₂ uptakes at low relative pressures is an indicator of high microporosity in these samples. Of course, the CO₂ cannot reveal anything but microporosity, as it is unable to fill large pores under these conditions. The BET analysis shows that the surface areas for those samples shown in Figure 5.3.17 are in a range from 3.8 to 59 m²/g per ash (see results in Table 5.3.3.2).

Table 5.3.3.2 BET surface areas with nitrogen and carbon dioxide.

Sample	Type of ash	LOI [wt. %]	BET Surface area Nitrogen, [m ² /g]	BET Surface area Carbon dioxide, [m ² /g]
FA 6	Class F	3.4	3.4	3.8
FA 21	Class F	6.1	3.8	5.0
FA 23	Class F	65.5	35.3	58.9
FA 40	Class C	1.1	4.0	7.3
FA 75	Class C	1.3	5.7	8.7

As with nitrogen surface areas, as the LOI of the fly ashes increases, the carbon dioxide BET surface area increases as well. In addition, BET surface areas obtained from

carbon dioxide isotherm data are all higher than the surface areas obtained from nitrogen isotherms. The higher uptake of carbon dioxide by these fly ash samples is attributed to the more favorable diffusion conditions available at higher (195 K) temperature. Some of the micropores could be accessible at 195 K carbon dioxide adsorption conditions, and not at 77 K nitrogen adsorption conditions.

Some class C fly ash carbon dioxide isotherms are shown in Figure 5.3.18. Again, as the LOI of a given type of ash increases, the uptake of the adsorbate increases. The BET surface areas for class C ashes (see Table 5.3.3.2), obtained from the raw carbon dioxide isotherms, are 7.3 and 8.7 m²/g respectively. The surface areas for class C ashes are almost twice as high as the surface areas obtained with nitrogen. This suggests that class C ash has more small, molecular-sieving type of microporosity than does the class F type of ash.

Figure 5.3.19 shows the comparison of the isotherms obtained with nitrogen and carbon dioxide. The nitrogen isotherm reveals only a very slightly smaller extent of microporosity than does the carbon dioxide isotherm. The agreement between the two adsorbates is otherwise remarkably good in the range of relative pressures that has been examined. It is expected that at higher relative pressures, the carbon dioxide isotherm would flatten out, and reveal little about mesopores and macropores, but this was not explored here. The main conclusion was that, at least for class F ashes, there is little difference between the micropore information provided by the two adsorbates.

Carbon dioxide experiments with fly ashes were also performed at higher than the usual 195 K temperature. In some cases CO₂ adsorption experiments were performed at 273 K and also at about 305 K temperatures. The critical temperature for CO₂ is 304 K.

An ice bath with water was used in order to maintain the 273 K temperature. A separate water bath with a pump for providing steady water circulation, was used to keep constant water temperature in the higher temperature adsorption experiments.

The comparative study of the adsorption behavior at different temperatures was performed using fly ash 21 (class F, LOI 6.1%). Fly ash 21 is a typical class F ash produced by pulverized combustion of bituminous coals at the Brayton Point Power Station. Its foam index behavior shows it to be very active towards AEA adsorption.

The carbon dioxide adsorption isotherms for fly ash 21 at temperatures 195 K, 273 K and 305 K are shown in Figure 5.3.20. As discussed earlier, the saturation pressure of CO₂ at 273 K is 26145 torr and at 305 K is 55906 torr, and the instrument cannot provide a carbon dioxide pressure in excess of 101 kPa. Hence, the results in Figure 5.3.20 do not reach very high relative pressures, only up to 0.03 for the 273 K adsorption experiment. Nevertheless, this is an important range of relative pressures for examining microporosity. The isotherms show a modest degree of hysteresis even in the very low relative pressure range involved. It is impossible to reliably determine a BET surface area from the data at such low relative pressures.

The adsorption uptakes for fly ash 21 are quite similar at temperatures of 305 K and 273 K. As seen in Figure 5.3.20 the adsorption uptake is slightly higher at 195 K. A small uncertainty in saturation pressure (P_o) could easily affect an adsorption isotherm, shifting it left or right relative to the other isotherms. On the other hand, the required shift of the 195 K isotherm would require that the saturation pressure of CO₂ at 195 K be a factor of approximately 2.6 too high. This would mean that the actual saturation pressure

would have to be roughly 530 torr at 195 K. This does not appear realistic, though a shift of a factor of two is entirely possible, given the uncertainty in the phase of the carbon dioxide. Still, it must be remembered that a change in the saturation pressure of CO₂ for this calculation must also be accompanied by a shift in the other calculations shown above. Thus, for example, the comparison in Figure 5.3.19 would no longer be nearly as good at the low end, but would improve in the midrange of relative pressures. At this point, all that may be said is that the issue of saturation pressure is unresolved. It can, however, be stated with confidence that since the 195 K isotherm lies above the 273 K and 305 K isotherms, activated diffusional limitations cannot be invoked to explain the difference. The rate of an activated diffusion process would increase with increasing temperature, and it would thus be expected that the higher temperature isotherms would lie above the lower temperature isotherm.

5.4 Flow Microcalorimetry Results

Fly ash carbon content was not by itself a particularly good predictor of the foam index behavior of fly ash. It is noted that the nature of carbon surface in ash can also determine its efficacy in adsorbing AEAs. Oxidized fly ash carbon surfaces adsorbed less AEA compared with unoxidized surfaces^{5,19,22}. This is not surprising, since AEAs are essentially detergent-like surfactants, containing polar endgroups and quite long non-polar chains. The non-polar parts of the AEAs are critical to stabilizing the bubbles in the otherwise polar medium of the concrete mix; these parts of the AEA molecules gather at the air-water interface. The inorganic ash components, cement, and water are all polar, while only the carbon surfaces, and in particular, unoxidized carbon surfaces, are non-

polar. The greater the amounts of non-polar carbon surface, the more effectively adsorption of the AEA by carbon will compete with the intended role of stabilizing bubbles.

Initially two fly ashes (FA5 and FA6) were picked from our sample bank in order to examine the surfaces of two otherwise quite similar fly ashes. Fly ash 5 was produced at the Brayton Point Power Station of New England Power prior to low-NO_x retrofit, while fly ash 6 was produced post-retrofit. Both are class F ashes from bituminous coal. There is a small but significant difference in LOI (FA5 is 1.9%, whereas FA6 gave 3.4%). The former sample proved to be quite acceptable in concrete applications, whereas the latter was entirely unacceptable. This led to an investigation of the differences between the samples.

There was a very large difference in foam indexes between the two samples. The unacceptable sample, FA6 had specific foam index 1.9 ml/g-carbon and FA5 0.34 ml/g-carbon respectively. Clearly in this case, neither the dramatic increase in foam index, nor the related strongly unacceptable decline in actual concrete performance was predictable from the less than factor of two increase in carbon content, as suggested by LOI. Since the foam index test is fundamentally a test of adsorption, the search for an explanation of the differences centered on a more complete characterization of the surface. Two possibilities existed. One was that the carbon that remained in FA6 was of a higher surface area per unit mass than the carbon in FA5. The second possibility relates to the discussion concerning the nature of the surfactant AEAs; there may be a difference in adsorption of the AEAs based on surface polarity of the carbons in FA5 and FA6. The effect of the surface area could easily be ruled out when the surface area results (see

Table 5.3.1, the end of chapter) are carefully examined. It may be seen that once again, the carbon surface areas differ by less than a factor of two, and that this does not offer an explanation for the much greater difference in foam index results. If the total surface areas offered by the carbons are divided by the mass fractions of carbon in the samples, this simply provides the specific surface areas per unit mass of carbon. Specific surface areas for samples FA5 and FA6 are 53 m²/g-carbon and 57 m²/g-carbon respectively. This small a difference in specific surface areas cannot explain a big difference in specific foam indexes. Again, fly ash 6 had specific foam index 1.9 ml/g-carbon and FA5 0.35 ml/g-carbon respectively. This reinforces the notion that differences in carbon porosity are not the basis for the major differences in AEA adsorption behavior.

This led to a search for methods to characterize more subtle differences in the surface chemistry of the unburned carbon fractions. Attention was turned to characterizing the surfaces in terms of polarity. For this purpose, adsorption calorimetry tests were performed with alcohols, using a flow microcalorimetry system (FMC). Polarity is determined by how many oxides (polar functional groups) are available on the carbon surface. The inorganic part of fly ash is expected to be mostly polar, and this was also verified experimentally. Thus the non-polar surface of an ash comes mostly from its non-oxidized carbon surface. Flow microcalorimetry, with alcohols like n-butanol, can be used to determine this area^{26,27}. The details of how these FMC experiments were performed are given in Chapter 3.

Briefly, these experiments involve placing a dry sample of fly ash into a calorimeter cell, and initially wetting it with a flow of pure n-heptane. The n-heptane does not adsorb strongly to polar sites. A solution of an alcohol in n-heptane is then

introduced into the cell, and the heat effect measured as the polar hydroxyl group in the alcohol interacts strongly with the polar surfaces on the material to be examined. The concentration of the alcohol is increased until no further heat effect is obtained, at which point the polar surface is assumed to reach complete saturation level.

For certain adsorbates, relationships have been developed between the sorption enthalpy and the extent of the polar (or non-polar) surface in the carbon sample under study^{26,27}. We have examined some alcohols for which such a relationship has not yet been reported. We have assumed that the proportionality constant for t-butanol is the same as that reported earlier for n-butanol²⁶, which was $6.7 \text{ m}^2/\text{J}$. In light of some of the results to be given below, we believe that this is reasonable. We have also tested methanol, which has been reported by van Krevelen³⁰ to involve a heat of wetting of approximately $2.39 \text{ m}^2/\text{J}$.

Table 5.4.1 reports the results of the calorimetry experiments performed on samples FA5 and FA6, as well as on a third sample, FA23. Fly ash 23 has been chosen for comparison because it is a carbon-enriched sample produced by the STI separation process from what was a very high LOI sample to begin with. The surface area of FA23 is approximately $54 \text{ m}^2/\text{g}$ carbon, which is not very different from the $53 \text{ m}^2/\text{g}$ and $57 \text{ m}^2/\text{g}$ determined for FA5 and FA6. Thus it is felt that FA23 has some similarity to the other two samples, even if there is much more carbon present.

The values of the surface areas from the alcohol adsorption experiments are reported on the basis of the carbon contribution alone (the small contribution of the heat of sorption on the inorganic components has been subtracted). It is immediately apparent in comparing the various surface area values for FA5, that the surface is highly polar in character. A very high fraction of the surface is accounted for by the polar adsorption methods. By way of contrast, in the case of

the FA6 sample much of the surface shows itself to have a non-polar character (about 50%). The FA23 sample has an even lower fraction of polar surface.

While these results do not in themselves constitute proof that it is the non-polar surface that is responsible for the high adsorption of AEA by sample FA6, it is clear that the explanation is consistent with the observation. Once again, the large differences in AEA adsorption behavior cannot be predicted on the basis of total surface areas, but an explanation based upon AEA adsorption on non-polar area appears more reasonable. The non-polar area of FA23 is a factor of 30 higher than the value of non-polar area in FA6, if the non-polar area in these samples is calculated based upon the difference between the total and t-butanol areas. The fact that the foam index result does not scale better with non-polar area could be attributable to accessibility limitations in the FA23 sample. Note that this sample shows a larger difference between the n-butanol and t-butanol results than do the other samples. This suggests considering further the possible role of accessibility limitations in fly ash carbons.

Preliminary fly ash polarity results above support the fact that the surface polar groups on fly ash carbons have a strong influence on the AEA uptake in concrete mixtures. However, the study of the fly ash polarity on AEA uptake for three samples from our sample bank was not enough to establish the validity of the characterization. Therefore a more complete study on fly ash polarity was performed. In this further work, only n-butanol was used in the FMC experiments.

Figure 5.4.1 shows the results of an extensive amount of characterization using the FMC device to measure the surface polarity of different fly ash samples. The plot shows the variation of specific foam index as a function of specific polarity index. The specific foam index is a measure of AEA uptake on a unit mass of carbon basis. It is

therefore independent of the absolute amount of carbon in a particular sample of fly ash. It is a measure of how “good” or “bad” the carbon itself is.

The specific polarity index is a ratio of the polar surface area determined using the n-butanol adsorption technique in comparison to the traditional BET surface area of the sample. In theory, this parameter should range in value between 0 and 1. The fact that two samples slightly exceed unity is of no major concern, considering the large number of assumptions that go into the different measurements. Generally speaking, the expected trend is observed in these results. The samples with very high surface polarity do not have very high specific foam index values, because these polar surfaces are not attractive adsorption sites for the surfactants. It is the samples with low surface polarity that are most likely to exhibit high AEA adsorption.

Within the class F ashes a quantitatively different trend is seen than that within the class C ashes (though qualitatively the trends are similar). Figures 5.4.2 and 5.4.3 show the specific foam index correlation with polar surface area separately for class F and class C ash carbons. The class F fly ash data again suggest that there is a trend of decreasing specific foam index with increasing polar surface area. At this point it should be recalled that specific BET surface area for class F ash carbons ranges from 40- 60 m²/g. Therefore fly ash carbons, which have polar surface areas above 30 m²/g on Figure 5.4.2 are mostly polar. Those polar fly ash carbons exhibit low AEA capacities.

Unfortunately only four class C samples were analyzed for polarity. It was almost impossible to measure AEA uptakes with 10 vol% Darex II solution with very low LOI class C ashes. The results in Figure 5.4.3 show that there appears to be a weak suggestion

of a trend of decreasing uptake of AEA when the polar surface of the class C ash carbon increases.

Surface polarity alone is not a good predictor of a particular ash's performance in concrete mixtures. Surface polarity would not, for one thing, explain the large difference between class C and class F ashes. This shows that factors other than surface polarity must clearly also play a role in determining the foam index. It is already clear that surface area is a key factor.

Tests in our laboratory proved that polarity can be influenced by surface oxidation. We have earlier shown that the surfaces of oxidized carbons have a lower foam index than un-oxidized. A sample of class F ash (FA21, 6.1% LOI) was deliberately oxidized. The specific foam index dropped from 2.475 to 0.66 (see Table 5.4.2). Further testing showed that the porosity was not affected by the oxidation, however a similar polarity analysis showed that what was affected was definitely surface polarity. This result confirms that polarity plays an important role in determining foam index.

Table 5.4.2 The role of surface polarity for oxidized fly ash 21 sample.

Sample	LOI, [wt%]	Specific FI, [ml 10% Darex II/g- carbon]	Specific volume of mesopores [ml/g- carbon]	BET carbon surface area, [m²/g- carbon]	Polar surface area [fraction]
FA21	6.1	2.48	0.027	51.2	0.21
FA21Ox*	6.2	0.66	0.020	39.0	0.32

* - oxidized sample

5.5 Microscopy

5.5.1 Optical Microscopy

Optical microscopy is a powerful tool for visualizing surface features of a scale $>0.5\ \mu\text{m}$. It is quite obvious that using an optical microscope there is no chance to observe micro- ($d < 20\ \text{\AA}$) or mesopores, ($20 < d < 500\ \text{\AA}$). However optical microscopy is a suitable and simple tool for examining macroscopic features of the carbon and ash particles. The main advantages of optical microscopy are the ease of sample preparation and ease of obtaining the images. The disadvantages of optical microscopy are generally poor image depth of field, and the inability to get information about the particle interior. Depending on the required depth of field of the image, sample preparation could require fine polishing of the sample (for higher magnifications fine polishing of the sample is required). Fine polishing of the sample requires that the sample to be first embedded in epoxy and after complete drying, the sample can be cut and polished to give a smooth surface. When higher magnifications are not needed, simple sample preparation techniques can be applied. Sample powders can be placed onto a glass plate as a single layer.

Colored positive images were taken with an Olympus Vanox camera attached to the photomicrographic microscope. Objective lenses of 5X, 10X, 20X and 50X were used in order to get desired magnification levels when imaging fly ash particles. The objective lens values are actually multiplied by other magnification factors, which are not important at present. An actual visual scale was employed to scale the pictures that were taken. All pictures shown here have been electronically scanned from original

photographs using a Color OneScanner 600/27 for the Macintosh, and then processed with Adobe Photoshope software.

Selected fly ashes from our sample bank (Table 4.1) were investigated using the optical microscope. Colored pictures were taken at different magnification levels in order to visualize the specifics of the samples. Again, poor depth of field was the main problem at high magnification levels, due to the rough surfaces of the fly ashes.

Optical microscope images of class F fly ashes 5 (LOI 1.9%) and 6 (LOI 3.4%) are compared in Figures 5.5.1 and 5.5.1A (see the end of the Chapter). The images in Figures 5.5.1 and 5.5.1A are typical images obtained from bulk class F fly ashes at this magnification level. Fly ash 5 is a NEP Brayton Point fly ash, which was produced before the low-NO_x retrofits. As was discussed earlier, this ash was classified as being “good” ash (in terms of how it performed in concrete). Fly ash 6 is an ash produced in the same unit, but after low-NO_x retrofits were made. Fly ash 6 was classified as “bad” in terms of concrete performance.

The mineral particles in both fly ashes are mostly glassy spherical particles (they look like yellowish-white pearls) with an average diameter of 50 micrometers or less. Carbon particles are seen as dark spots in these figures. Carbon particles in these images have sizes starting from sub - micrometer all the way to 100 micrometer. They generally have irregular shapes, though some of the carbon particles have a regular well-defined spherical shape. However most of the carbon particles look like fragments, appearing as tiny dark specs on the surfaces of the minerals.

Qualitative examination of the bulk ash images shown in Figures 5.5.1 and 5.5.1A does not offer any real explanation as to why one fly ash performed poorly in concrete

mixtures and the other did not. It is not possible to see the differences in carbon particles that give rise to the differences in foam indexes. It can be speculated that the amount of carbon observed in the image of fly ash sample 6 is greater (more dark particles are seen than in the image of fly ash 5), but this was already known from LOI measurements. Perhaps more significantly, there appear to be more large unburned carbon particles in the case of fly ash 6. In order to gain more insights regarding the differences in carbon particles in these two samples, more higher magnification images of both samples were examined. These higher magnification images are shown in Figures 5.5.2 and 5.5.2A.

These more highly magnified images again suggest that the amount of carbon in fly ash 6 is higher (more dark particles in the image). In this case, the fly ash 6 carbon has an irregular shape and size (10 to about 100 micrometers) quite similar to the fly ash 5 carbon. This shows the danger inherent in concluding too much from single microscope images, because in the lower magnification image, fly ash 6 appeared to have more spherical particles. The apparent similarities and differences are a result of random variations through the samples selected for examination in this way. A truer picture of subtle differences can emerge only from techniques that integrate over a much larger sample.

Most of the images of both ashes show small amounts of very tiny carbon particles. It is difficult to say much about how these ashes compare in this regard, as these very fine particles go down in size to the point at which it is difficult to resolve them microscopically. Very fine carbon particles might well present a very active surface for AEA adsorption, since they have a high external (geometrical) surface to mass ratio, and accessibility to adsorption surfaces through pores is not an issue.

It is quite difficult to classify the carbon particles shown in Figure 5.5.2 optically. According to *Maroto – Valer*¹⁷ fly ash carbons can be classified as being inertinite, isotropic coke or anisotropic coke. The images support the existence of coke particles, since that would likely be the origin of the rounded particles. These particles would have softened during pyrolysis. The more irregular particles might be derived from inertinite, or they might be fragments of coke particles. It is difficult to conclude much from these images, without performing a petrographic type of analysis.

A higher magnification level (50X lens) optical microscope image of a typical fly ash 5 particle, presented first in Figure 5.5.2, is shown in Figure 5.5.3. Figure 5.5.3 shows that the carbon particle under investigation has a size of order 100 micrometers. This image shows the problem associated with depth of field at high magnification. Still enough detail is visible to say that it appears as though the carbon particle has its surface covered with minerals. It is unclear how or whether this inorganic ash coating might influence any carbon particle properties such as surface areas, reactivity or adsorption capacity.

A set of optical microscope images for class F fly ash 8 is shown in Figures 5.5.4 to 5.5.6. These images were quite similar to those presented above. Once again, the carbon particles are quite distinct from the mineral ash particles, and they come in a very broad range of sizes. The carbon particles show very distinct evidence of softening during pyrolysis. Many show the adherence of ash on their surfaces.

Because the mineral part of the ash was found to be relatively inactive towards AEA adsorption, interest during the course of this study was mainly focused on the nature of carbon particles in the ashes. It was concluded above that bulk fly ash images

are mainly useful for revealing the relatively high degree of segregation of ash and carbon, and the wide range of carbon morphology and size. This was not unexpected, as there are commercial separation processes that are based upon the fact that carbon and minerals are present in distinct phases. In an effort to understand better the nature of the carbon, some class F and class C fly ashes were separated, in order to remove a significant portion of their minerals. The separation procedure was described in the experimental section. Briefly, it took advantage of the differences in size distributions in the mineral and carbon fractions, as could be observed in the preceding images. For this purpose, simple dry screen sieving was appropriate.

Optical microscope images of separated (carbon-enriched) fly ash fractions were obtained on the separated fractions. Figure 5.5.7 shows an image of a fraction derived from what was originally a high-carbon ash, fly ash 21. The image is of a sieved particle size fraction of $180 < d < 355$ micrometers.

The particles in Figure 5.5.7 are mostly what appear to be carbon particles (they are of a dark color). A few yellowish particles on the lower right corner of the image appear to be carbon particles covered with minerals or large mineral particles containing carbon. The carbon particles have a somewhat irregular shape, with an average particle size about 200 micrometer. There are also a few carbon particles that have a size above 300 micrometers. Some of the particles look like pieces of what were originally larger particles, but some of them look like pieces of coke, showing rounded, vesicular structure. Figure 5.5.8 shows a higher magnification image of the same ash.

As is seen from the image of Figure 5.5.8, the carbon particles have an irregular shape, but have rounded edges indicative of having been through a softened period. This

would be expected with bituminous coals. The porosity on a micrometer scale is not great in these particles. In addition, these particles did not have a very high micro- and mesopore surface area; their carbon surface areas were in a range 40-60 m²/g. This is not unusual for bituminous coal chars.

Some carbon particles are quite large, about 300 micrometers diameter. The survival of such huge carbon particles in very high temperature conditions is quite intriguing. It is not believed that these particles are aggregates of several particles, based upon their appearance. These particles appear to have escaped the high temperature and oxidizing zones in the boiler, quite possibly due to aerodynamics. Another important aspect of these particles is their rather low LOI, despite their appearance. In the case of the material in Figure 5.5.8, the LOI is 19.4 wt %. What look to be pure char particles actually have quite a high mineral content. As seen from the image in Figure 5.5.8 all particles appear “shiny”, possibly indicating that the carbon surfaces were coated with minerals. These minerals, as appear to be present, seemed to be fused onto the carbon surface. What implications this has for the particle reactivity, or for surface adsorption processes, is not clear. Still, the coating of particles with a mineral layer could offer an explanation as to why these particular particles could indeed escape the boiler.

Other images of other fractionated class F ashes are shown in Figures 5.5.9 to 5.5.12. These images tend to confirm the picture that has been developed on the basis of the earlier discussed images. Figures 5.5.9 and 5.5.12 leave a distinct impression of particles that were partially eaten away. Others again show the mineral coating phenomenon (e.g., Figures 5.5.10 and 5.5.11). The similarities in the morphologies of the class F ashes were not surprising despite the fact that the ashes came from different

power plants. Many bituminous coal chars have similar appearances at comparable stages of burn out. Independent of class F ash carbon content, the specific BET area of the carbon in the ashes (per gram of carbon) also did not vary much, falling mostly in the range 40-60 m²/g of carbon.

The class C ashes present a somewhat different picture from that which the class F ashes showed. Figure 5.5.13 presents an image of the bulk class C fly ash 75 with an LOI of 1.3 wt.%. As can be seen from this image, most of the particles are minerals, which exhibit a yellowish color. Some of them, possibly iron oxides, have a reddish color. A very large portion of the mineral particles has a well-defined regular (spherical) shape. Most of these mineral particles are very small, of order 10 micrometers. The darker colored particles are presumably unburned carbon. Most of these carbon particles had a size of a micron and less. It may easily be observed that some of the carbon particles are quite large, having a size of about 30-40 micrometers. The number of these large black colored particles was small and therefore the parent class C ash generally exhibits a yellowish color, which is determined by the minerals.

A simple laboratory test was performed in order to verify that the large black particles were carbons. Some of the parent class C ash was immersed into water in a simple laboratory vial. Because of the density difference between carbon and minerals, these larger carbon particles did float on top of the water surface while the minerals immediately sank. Even if these large carbon particles had a high minerals content, this density check in water revealed that these particles are still very porous or low density. In order to obtain more information on these large carbon particles, a simple mechanical

sieving technique was again applied. Figure 5.5.14 shows an image of the $180 < d < 355 \mu\text{m}$ size range fraction of this ash.

As can already be guessed, no significant amount of pure mineral particulate is found in this fraction, relative to the parent ash. On the other hand, the LOI of this fraction is 12.8 wt %. Some carbon particles on Figure 5.5.14 seem to be heavily fused. The nature of these particles is unclear, unless chemical analysis is performed. They might be mostly mineral, or they might be carbonaceous. The extent of pyrolytic fusion that the organic matter of a low rank coal, such as the Powder River Basin coal that this ash came from, would normally not be expected to be very great.

Simple visual inspection reveals that the carbon particles in image 5.5.14 look significantly different than a similar cut of class F fly ash carbons. Class C ash carbons have more regular shape than do the class F carbon particles shown on Figure 5.5.8. This was quite unexpected, since it would normally be expected that in the process of softening, the class F particles would become more similarly rounded, while the non-softening class C particles would retain the more jagged appearance from the grinding process. What appears to dominate the impression of more or less uniformity is the fact that the class F ash coals softened and formed cenospheric-type char structures during combustion. It is probably the products of partial burnout of these that give highly irregularly shaped fragments observed in the class F images. On the other hand, it is quite possible that the high mineral content of the class C “chars” is what is responsible for their softened appearance. This rounded shape would presumably not disappear upon burnout of the carbon.

Figure 5.5.15 presents a magnified image of one of the very large class C carbon particles. The carbon particle shown in Figure 5.5.15 is almost 500 μm in size. It is not surprising that these particles stand out so clearly from the parent ash. The shape of this carbon particle is irregular, but smooth, and it looks like a piece of weathered rock. It contains what appears to be surface bands or internal veins of lighter-colored mineral matter. Figure 5.5.16 presents a magnified image of the particle surface shown in Figure 5.5.15. Examination of the particle shown in Figure 5.5.16, reveals that it is mostly covered with a mineral layer. Again, we believe that these mineral particles are adhered to the surface. The generally smooth surface of the particle image in Figure 5.5.15 suggests that the sharp carbon edges normally left after grinding have been reacted away. What is left is a carbon particle that might in some sense be protected by a mineral layer on its surface, with surface pits that are filled by fused minerals.

Still, there is no clear evidence how this mineral surface coverage affects the combustion or adsorption processes that the particle is subjected to. Are large carbon particle pores blocked or open? What species have access on what timescale to the interior of these particles if there are large micron-scale open pores, as it appears? Some of these questions are partially answered with the help of the surface area analysis performed on the parent fly ashes discussed above. It should be recalled that class C ash carbons had very high surface areas; about 250-400 m^2/g . Thus there is some significant accessibility to the particle interior under certain conditions (i.e., those of the nitrogen adsorption test). Again, there remains a question as to whether this surface is accessible on the timescales of combustion or the foam index test, both of which are shorter.

Other class C samples were also examined using optical microscopy. However no further new aspects of carbon morphology were revealed. These images are shown in Figures 5.5.17-5.5.20. A few show somewhat more jagged unburned carbon particles. Some show what appeared to be fused clusters of finer mineral particles. All show evidence of the inclusion of minerals in the carbon particles. The LOIs of these fractions were 9.9 - 10 wt. %, so it can be concluded that even though particles appear to be mostly unburned carbon, they are in fact mostly mineral by mass.

In conclusion, optical microscopy is a useful tool for examining the macroscopic features of the fly ashes and fly ash carbons. Class F fly ashes have carbon particles in various size ranges, starting from few microns all the way up to few hundred microns (the amount of these largest carbon particles was, however, not significant). The average size of the carbon particles was about 50 micrometers. The carbon particles in class F ash have very irregular shape, and they also seem to be very fragmented.

Class C ashes have two distinct groups of carbon particles available in their parent ashes. One of them is a fraction of carbon particles with very small particle size, less than a micron in some cases. The second group is a fraction with extremely large carbon particles in it. Those particles have well-defined smooth shapes, and contain little visible vesicular structure. All these large particles contain significant amounts of mineral matter.

Due to the fact that quite a large portion of the carbon particles was in a size range less than 1 micrometer, a more powerful microscopic technique needed to be applied in order to examine the morphology of those particles. Scanning Electron Microscopy was chosen for this purpose.

5.5.2 Scanning Electron Microscopy

Scanning Electron Microscopy is a powerful tool for examining surface features at a size scale above 10 nanometers. The SEM technique is thus able to image to about 50 times greater magnification than optical microscopy. The advantages of SEM imaging are high magnification, relatively simple sample preparation and a chance to investigate surface composition (with Energy Disperse Spectroscopy, EDS). The disadvantage of SEM imaging is that a sample must be stable in vacuum and also under an electron beam (e-beam). In addition, sample charging is likely to occur when proper care is not taken during sample preparation.

SEM was used to further investigate the nature of fly ash particles. The main focus was again the fly ash carbon - its particle sizes, shapes and structures. As has been shown earlier⁵, fly ash mineral components are often uniform spheres, containing hardly any porosity. This was also supported in our SEM studies. An image with a cluster of fly ash minerals is shown in Figure 5.5.21. As can be seen from the image in Figure 5.5.21, fly ash minerals can have a uniform spherical shape, with barely any porosity visible on this relatively high magnification scale. Of course, it would be mainly macroporosity that could be seen at this magnification.

The cause of the apparent damage to the mineral particle in the upper right part of this image is unclear; it could be from sample preparation for SEM, from prior handling, or it could have formed as such in the boiler. Fly ash particles in this image have diameters ranging from a few microns all the way up to 50 or 60 microns. A slight charging effect (seen as light white spots on the minerals) can also be seen on the image

in Figure 5.5.21. These come from the electron microscopy process itself, and are of no significance.

There were no significant differences observed in the morphologies of the mineral fractions of the class C and class F ashes. However fly ash carbons from class C and class F ashes exhibited noticeable differences both in their shape and structure. It was noted that the size of the carbon particles in class F fly ash varied over a quite significant range (from a few microns up to few hundred microns). Still, most of the carbon particles ranged in size range from 10 to 30 μm . Because of the low carbon content in class C fly ashes, it was quite difficult to observe many carbon particles in these samples using the SEM. Thus it was more difficult to obtain an impression of particle size distribution for these samples.

Figures 5.5.22 to 5.5.24 present images of a typical class F fly ash carbon (fly ash 22). Fly ash 22 is a representative of the ash from New England Power's Salem Harbor Unit (Table 4.1). It has a relatively high LOI, 33.6 wt%, which is unfortunately often encountered in that plant, particularly under upset conditions. The carbon particles in Figure 5.5.22 exhibit irregular shape and structure. Some of them are pieces; some of them are like spheres with lots of holes covering their surfaces. The average diameter of the particles in Figure 5.5.22, ranges from 30 to 80 micrometers. The carbon particles in this image are very porous, as compared to the common mineral particles seen in Figure 5.5.21. The pores seen in the carbon particles would be classified as being macropores with diameter ranging from 1 to 10 micrometers.

A higher magnification image of one of the particles seen in Figure 5.5.22 is shown in Figure 5.5.23. The carbon particle in the image has a size of approximately 50

microns. The particle seen in Figure 5.5.23 has a highly porous, skeletal form, very different from that seen in the minerals. This form suggests that the carbon particle went through a softened state during combustion. The large amount of porosity seen here is on a large size scale, and may be the result of blow-holes formed during the devolatilizing of the softened particle. There appears to be a mineral inclusion in the large interior cavity of the particle.

The relatively high LOI fly ash 22 allowed for investigation of the samples at higher magnification, due to carbon's high conductivity, and the smaller charging effects associated with this. Figure 5.5.24 shows an image of the magnified carbon particle. As can be seen from the image, this type of coked particle exhibits mostly 1 to 3 micron macropores, at least at this scale of magnification. No significant amount of larger mesoporosity could be observed. It is, of course, impossible to image micropores using this technique.

Figure 5.5.25 presents an image of another class F sample, fly ash 5. It is a sample from New England Power Brayton Point Station. Fly ash 5 has an LOI content of 1.9 wt % and is considered to be a “good” fly ash. An approximately 20-micrometer carbon particle is shown Figure 5.5.25. The general form of the particle is similar to what was seen in the other class F ash presented above. The particle is very porous and has a very open type of structure.

A higher magnification image of fly ash 5 carbon particle is shown in Figure 5.5.26. The size of the particle is about 12 micrometers and again, it is highly porous. The distinctive feature of this image, relative to the image in Figure 5.5.25 is the mineral matter, seen inside of the carbon particle. These minerals have a size about 1 micrometer

and less. This confirms the impressions obtained from the optical microscopy work, to the effect that there is a significant amount of mineral embedded in many of the larger unburned carbon particles.

Figure 5.5.27 shows an image of a similar class F fly ash carbon particle (fly ash number 8). Fly ash 8 originates from the same boiler (Brayton Point), but has a higher LOI, 3.8 wt %. Fly ash 8 was obtained from the boiler after the low NO_x retrofit was performed. As discussed in earlier, the retrofit decreased the NO_x emissions, but increased the LOI content of the fly ash from this plant. As can be seen from comparing the images in Figures 5.5.26 and 5.5.27, the pre- and post-retrofit samples (fly ashes 5 and 8, respectively) contain carbons that are generally quite similar to one another. Both show the same strong evidence of having gone through a softened period. Both have the same sort of lacy structure, implying that the development of pores was on the same large scale. The fly ash 5 carbon particle appears to have lost more pores during the combustion process relative to the fly ash 8 carbon particle, or viewed in other terms, fly ash 8 might have developed more pores during combustion than did fly ash 5 carbon.

A magnified image of the fly ash 8 carbon particle is shown in Figure 5.5.28. This image of the fly ash particles shows that the pores are mainly in micrometer size range (macropores). Some of them are about 10 micrometers, and then some of them around one micrometer. Unfortunately, due to charging effects, it was impossible to increase magnification, which might possibly have allowed observing mesopores, with a size of about 0.05 micrometers or less, though it is already apparent from Figure 5.5.28 that the surface is pockmarked with craters of just about that maximum size.

It is important to remember that the observed porosity is at a very large scale. These large pores can play a vital role in providing access into the particles, but themselves present fairly small amounts of surface area for adsorption.

A typical class C ash in our sample bank (Table 4.1) is fly ash 75. It was produced in the JP Madgett station of the Dairyland Power Cooperative and has an LOI of 1.3 wt%. Figure 5.5.29 presents the SEM image for what is believed to be a carbon particle from this fly ash. It was quit difficult to identify carbon particles in the large mass of minerals present in this class C fly ash. There were simply very few obvious large carbon particles. It took some time scanning to locate possible candidates. Minerals in this ash are responsible for most of the charging that occurred when the images were taken. Therefore, it was almost impossible to go up to very high magnification as was done with class F fly ash carbons. Even separation of the parent class C ash was not helpful. These very big carbon particles, seen clearly with the optical microscope because of their 300 to 400 micrometers sizes, proved quite difficult to get to stick onto the specimen holder. They were lost in most of the cases when the sample was placed into microscope. The SEM imaging occurs at high vacuum. It is believed that the very large particles were mainly lost during vacuum pumping. In addition, in spite of the separation of the parent ash, the smaller particle size fractions contained a lot of minerals. Those minerals prevented seeing the small particle carbons observed in class C ash with the optical microscope, due to heavy charging effects. As may be seen from the image in Figure 5.5.29, the carbon particle appears to have minerals adhering to its surface. This picture also allows noting the large size differences between mineral particles and carbon particles. This is typical in class C ashes. The carbon particle itself is relatively big,

having a size of approximately 80 microns. This image is therefore consistent with the optical microscope pictures that showed fine ash particles coating a large carbon particle.

Figure 5.5.29 also suggests how significant the interior surface of the carbon particle is, relative to its external surface area. The picture that is presented here suggests a much more porous structure than was seen with the class F carbons. Those tended to have a few large pores, which were well separated from one another. This carbon, on the other hand, shows a structure with many intersecting pores. Again, surface area and porosity both play a key role in adsorption. Unfortunately it was impossible to image this particle at a higher magnification because of mineral charging effects.

5.5.3 Transmission Electron Microscopy

Transmission Electron microscopy (TEM) is another powerful tool for determining the structure, shape and composition of solids. The advantage of the TEM is its ability to visualize sample morphology at scale of above 1-nanometer. Particle sizes on a microscale, and particle density variations are potentially available with TEM. The disadvantages of the TEM are the quite cumbersome sample preparation process and the high risk of damage the sample during measurement and preparation. The specimen has to be prepared thin enough to permit an electron beam to go through it. TEM Energy dispersive spectroscopy (EDS) provides elemental composition.

Bright field (BF) and EDS techniques were applied in examining class F fly ash 9 with a LOI 66 wt %. The BF imaging technique is good for specimen visualization and particle size and shape determination. In BF imaging, a direct beam (transmitted spot) is selected from the diffraction pattern.

Electron diffraction is by far the most important scattering phenomenon in the TEM machine. The diffraction pattern can be used to determine the spacing of planes in crystals. Interplanar spacings in crystal structure are characteristics of the material structure. The distances between diffracted beam spots determines the size and shape of the unit cell. The intensity of the beam governs the distribution, number and type of atoms in a specimen.

The EDS that is generally available on the TEM machine is a powerful technique for providing qualitative and quantitative information about elemental composition of the investigated specimen. The advantage of EDS is the relatively short time needed to record qualitative spectra that provide the elemental composition. EDS analysis is based on inelastic scattering phenomena, when incident electrons colliding with specimen atoms give off characteristic X-rays. Different X-rays, each of which corresponds to a certain element, provide the spectral data needed for composition determination.

The BF images of the high carbon fly ash sample 9 are shown in Figures 5.5.30 and 5.5.31. Fly ash 9 is also a Brayton Point sample, but it had been processed to a carbon content of about 66% before we received it. Thus it would be expected that this sample should exhibit carbon character similar to the other class F ashes described above. The only difference is in the fraction of sample that is made up of carbon particles.

The approximate particle size on the specimen is calculated based on the knowledge of the magnification constant. For Figure 5.5.30 the magnification was 10 500 and for Figure 5.5.31 it was 24 000. The image width, measured with a simple ruler, is divided by the magnification constant in order to get the actual width at the micro level. Both BF images suggest that the particle sizes in the fly ash 9 sample vary over quite a

large range. Quite a large fraction of relatively large dark irregularly shaped particles in Figure 5.5.31 corresponded to carbon or soot particles (this was verified later using EDS analysis). The size of these carbon particles ranged from 10 nm up to 500 nm. Thus the TEM imaging supports the small size of the carbon particles first noted in the optical imaging work. The irregular shapes of many of these particles strongly suggested that they were fragments formed from larger particles.

Minerals usually were a bit smaller in size, relative to the carbon particles in the images. The uniform circles on the BF images (Figure 5.5.31, at eight a clock position and Figure 5.5.30 at one a clock position) are most likely minerals. The specimen was tilted in order to verify that these 2-dimensional circle images were actually spheres. It should be recalled that from the other images, a spherical shape is more common for minerals.

The TEM/EDS analysis provided qualitative information about the elemental composition of the material under investigation. Unfortunately the fly ash specimen did not have any regions with known composition and therefore a quantitative Cliff-Lorimer analysis³⁸ cannot be performed.

The EDS X-ray spectra are shown in Figures 5.5.32 to 5.5.42. All the spectra were processed using the DeskTop Spectrum Analyzer (DTSA) program for the Power Macintosh. The fly ash spectra showed quite a broad range of elements present in the parent ash. This is expected, because the fly ash is known to have a complicated chemical composition. The main elements were indexed using KLM notation, indicating the orbit of the emitted X-ray. Regions A, B, C, D in the BF image Figure 5.5.31 were analyzed using the EDS technique.

The EDS spectrum in Figure 5.5.32 is a spectrum of the specific area “A” on the BF image of Figure 5.5.31. The particle in area “A” has a size of approximately 250 nm. The EDS spectrum showed that the main elements present in this area were Si, Al and O. According to the elemental data obtained from the spectrum, it could be speculated that the particle under investigation is an aluminosilicate ash. All three Cu peaks in the spectrum corresponded to the specimen holder, which is a copper grid. In Figure 5.5.33, an expanded version of the previous spectrum is shown. Clearly the main elements in area “A” of Figure 5.5.31 are Al, Si and O.

In Figure 5.5.34 a spectrum of area “B” in the BF image Figure 5.5.31 is shown. The particle (size approximately 0.5 μm) under investigation in area “B” is most likely a carbon particle. Carbon dominates in this area of interest, and this was verified by looking at the expanded spectrum in Figure 5.5.35. The particle right above this carbon particle, at the two o'clock position in Figure 5.5.31, is also a carbon particle, with approximately the same size and shape. There are many similarly shaped and sized carbon particles seen in the BF image in Figure 5.5.31. The origin of this fine carbon particle “B” is unclear. It could be either soot or fragments of the char. It is believed that the latter is more likely, given its shape.

The spectrum for area “C” (9 o'clock position in Figure 5.5.31) is shown in Figure 5.5.36. The main elements in this spectrum are Si, Al, O, C and Mg. As with area “A”, it can be surmised that the main minerals in area “C” are fly ash aluminosilicates.

Figure 5.5.37 shows a spectrum of area “D” at a 6 o'clock position in the BF image of Figure 5.5.31. The elements present in this area are Ca, S, Si, Al, Mg, O and C. All these elements are quite common in a typical fly ash. In Figures 5.5.38 and 5.5.39

spectra taken in what is believed to be a region of a minerals are shown. Again, the main elements were Si, Al, O, Fe, Ca and Mg. Fe is mostly present in fly ash as Fe_2O_3 .

In Figures 5.5.40 and 5.5.41 a spectrum of a region of possible CaSO_4 is shown. The main elements present are Ca, S, O.

In Figure 5.5.42 the spectrum of the particle with a spherical shape in the BF image of Figure 5.5.31 (at the 8 o'clock position) is shown. The spectrum of this sphere suggests that it is most likely another aluminosilicate.

The TEM and EDS analyses tended to confirm the general impressions obtained using optical microscopy. It did not really offer too many surprises, in this regard. The mineral particles were mainly aluminosilicates, and they appear quite often as fused glassy spheres. Carbon particles, on the other hand, are present at sizes down to well below sub-micron range. They tend to appear as fragments formed from larger bulk material. It is of course unclear from this imaging work whether the fragments were formed before or during combustion. It would appear, however, that most of the particles show evidence of high temperature exposure. Thus it would only be reasonable to believe that they are combustion fragments.

TABLES

Table 5.1.1 Foam index results with Darex II and Air 40.

Fly Ash	Fly Ash	LOI	Foam Index	Foam Index	Specific Foam Index
	Type	[wt %]	Air 40 [ml/2g FA]	Darex II [ml/2 g FA]	Darex II [ml/g-C]
1	class F	6.5	0.081	0.213	1.637
2	class F	3.1		0.058	0.951
3	class F	14.6		0.486	1.666
4	class F	14.6	0.203	0.476	1.628
5	class F	1.9		0.013	0.348
6	class F	3.4		0.131	1.945
7	class F	2.6		0.052	1.009
8	class F	3.8		0.087	1.162
9	class F	66.0		2.562	1.941
10	class F	2.6	0.041	0.051	0.994
11	class F	2.5		0.074	1.505
12	class F	2.3		0.065	1.427
13	class F	3.8		0.078	1.032
16	possibly class F	1.5		0.264	8.812
19	gas co- firing	3.6		0.131	1.815
20	class F	2.0		0.023	0.582
21	class F	6.1	0.101	0.300	2.475
22	class F	33.6		1.203	1.788
23	class F	65.5		2.418	1.847
24	class F	2.7		0.026	0.476
25	class F	2.5		0.016	0.335
26	possibly class F	4.0		0.052	0.660
27	class C	0.16		0.000	0.000
28	co-fired Pet. Coke	2.4		0.000	0.000
29	class F	1.5		0.026	0.860
30A	class F	35.2		1.464	2.082
31	class F	0.9		0.047	2.646
32	possibly class F	44.7		1.503	1.681
33	class F	29.1		0.863	1.482

34	class F	4.9		0.118	1.203
35	Pet Coke	17.5		0.000	0.000
36	class F	0.3		0.013	2.178
37	class F	4.9		0.078	0.807
38	class C	0.2		0.013	2.841
39	class F	0.8	0.071	0.101	6.180
40	class C	1.1		0.011	0.508
41	class C	1.1		0.011	0.495
42	class C	0.6		0.000	0.000
43	class C	0.6		0.000	0.000
44	class C	0.6		0.000	0.000
45	class C	0.7		0.012	0.814
46	class F	11.1		0.373	1.674
47	class F	41.5		1.650	1.987
48	class F	1.4		0.060	2.136
49	class F	19.9	0.122	0.368	0.927
50	class F	22.2	0.182	0.556	1.251
51	class F	20.9	0.243	0.688	1.646
52	class F	1.1		0.182	8.426
53	class F	4.0	0.041	0.128	1.621
54	class F	4.1		0.079	0.968
55	class F	0.7		0.020	1.500
56	class F	1.2		0.101	4.153
57	class F	0.8	0.040	0.000	0.000
58	class F	1.9		0.000	0.000
59	class F	1.0		0.020	1.024
60	class F	6.0		0.061	0.505
61	class F	1.6	0.063	0.142	4.173
62	class F	3.9		0.140	1.801
63	class F	7.1	0.020	0.061	0.428
64	class F	7.4	0.122	0.263	1.778
65	class C	0.74		0.081	5.459
66	class C	0.9		0.081	4.396
67	class F	0.8		0.000	0.000
68	class C	0.8		0.057	3.393
69	Est. oil shale FA	1.4		0	0.000
70	Est. oil shale FA	1.3		0	0.000
71	Est.O.S.	1.0		0	0.000

72	Est. oil shale FA	1.3		0	0.000
73	class C	0.4		0.023	2.817
74	class F	9.8		0.485	2.485
75	class C	1.3		0.096	3.683
76	class C	0.3		0	0.000
77	class C	0.3		0.034	5.637
78	class C	0.5		0.020	2.132
79	class C	1.2		0.074	3.072
80	class F	4.4		0.191	2.190
81	class F	1.4		0.014	0.476
82	class C	1.6		0.082	2.544
83	class F	0.4		0.014	1.682
84	class F	10.9		0.150	0.688

Table 5.3.1 BET surface areas for all sample bank ashes.

Sample	Fly Ash Type	LOI [wt %]	Ash Surface Area [m²/g-ash]	Carbon Surface Area [m²/g-carbon]
FA1	class F	6.5	3.4	42.6
FA2	class F	3.1	2.5	60.5
FA3	class F	14.6	10.6	68.4
FA4	class F	14.6	10.1	64.9
FA5	class F	1.9	1.7	53.4
FA6	class F	3.4	2.6	56.7
FA7	class F	2.6	2.5	69.8
FA8	class F	3.8	3.1	63.6
FA9	class F	66.0	43.3	65.3
FA10	class F	2.6	2.4	66.2
FA11	class F	2.5	2.3	64.5
FA12	class F	2.3	2.4	76.3
FA13	class F	3.8	3.2	66.9
FA16	possibly class F	1.5	2.6	126.7
FA19	gas co-firing	3.6	4.6	108.5
FA20	class F	2.0	2.1	69.2
FA21	class F	6.1	3.8	51.2
FA22	class F	33.6	17.7	51.2
FA23	class F	65.5	35.3	53.6
FA24	class F	2.7	1.8	42.0
FA25	class F	2.5	1.7	39.3
FA26	possibly class F	4.0	2.0	32.8
FA27	class C	0.2	0.9	97.6
FA28	co-fired Pet. Coke	2.4	1.2	20.2
FA29	class F	1.5	1.8	67.8
FA30A	class F	35.2	15.2	42.0
FA31	class F	0.9	1.3	69.4
FA32	possibly class F	44.7	21.5	47.2
FA33	possibly class F	29.1	12.7	41.8
FA34	class F	4.9	3.1	50.2
FA35	Pet Coke	17.5	1.3	4.6
FA36	class F	0.3	1.0	110.0
FA37	class F	4.9	2.6	39.6
FA38	class C	0.2	1.6	304.8
FA39	class F	0.8	3.3	311.8
FA40	class C	1.1	4.0	281.8

FA41	class C	1.1	4.2	308.9
FA42	class C	0.6	2.1	238.2
FA43	class C	0.6	3.0	364.7
FA44	class C	0.6	2.7	325.9
FA45	class C	0.7	3.2	335.2
FA46	class F	11.2	6.9	56.0
FA47	class F	41.5	26.9	63.8
FA48	class F	1.4	1.7	79.3
FA49	class F	19.9	4.5	20.3
FA50	class F	22.2	6.7	28.0
FA51	class F	20.9	9.1	41.1
FA52	class F	1.1	3.8	282.3
FA53	class F	4.0	2.7	50.2
FA54	class F	4.1	2.2	37.1
FA55	class F	0.7	2.1	212.3
FA56	class F	1.2	3.0	178.8
FA 57	class F	0.8	1.5	101.9
FA58	class F	1.9	1.4	36.1
FA59	class F	1.0	1.3	60.5
FA60	class F	6.0	2.2	24.9
FA61	class F	1.6	1.3	37.6
FA62	class F	3.9	2.2	38.8
FA63	class F	7.1	3.9	45.3
FA64	class F	7.4	5.8	69.1
FA65	class C	0.7	3.1	326.4
FA66	class C	0.9	4.3	392.9
FA67	class F	0.8	1.1	55.5
FA68	class C	0.8	3.5	325.7
FA73	class C	0.4	2.3	366.3
FA74	class F	9.8	6.8	62.8
FA75	class C	1.3	5.7	376.9
FA76	class C	0.3	1.1	108.5
FA77	class C	0.3	1.5	220.8
FA78	class C	0.5	1.8	210.1
FA79	class C	1.2	4.1	274.3
FA80	class F	4.4	2.7	45.5
FA81	class F	1.4	1.1	20.3
FA82	class C	1.6	5.7	303.7
FA83	class F	0.4	2.4	388.0
FA84	class F	10.9	3.2	23.1

Table 5.3.2 Micro-, meso- and macropore volumes for fly ash carbons.

Sample	LOI	Micro- pore Volume	Meso- pore Volume	Meso and macropore Volume	Macro- pore Volume	Total Pore Volume
	w-%	cc/g-C	cc/g-C	cc/g-C	cc/g-C	cc/g-C
FA1	6.5	0.020	0.022	0.034	0.012	0.054
FA2	3.1	0.029	0.018	0.018	0.000	0.047
FA3	14.6	0.034	0.030	0.054	0.024	0.088
FA4	14.6	0.036	0.044	0.069	0.025	0.105
FA5	1.9	0.026	0.010	0.010	0.000	0.036
FA6	3.4	0.028	0.028	0.049	0.021	0.077
FA7	2.6	0.034	0.038	0.062	0.024	0.096
FA8	3.8	0.031	0.029	0.077	0.048	0.108
FA9	66.0	0.031	0.018	0.027	0.009	0.057
FA10	2.6	0.031	0.033	0.074	0.041	0.105
FA11	2.5	0.031	0.018	0.018	0.000	0.049
FA12	2.3	0.037	0.035	0.083	0.048	0.120
FA13	3.8	0.033	0.029	0.058	0.029	0.091
FA16	1.5	0.062	0.089	0.278	0.189	0.340
FA19	3.6	0.054	0.058	0.175	0.117	0.228
FA20	2.0	0.033	0.045	0.102	0.057	0.135
FA21	6.1	0.025	0.027	0.041	0.014	0.066
FA22	33.6	0.026	0.016	0.027	0.010	0.052
FA23	65.5	0.025	0.015	0.023	0.008	0.048
FA24	2.7	0.020	0.023	0.029	0.006	0.049
FA25	2.5	0.018	0.019	0.057	0.038	0.076
FA26	4.0	0.016	0.016	0.047	0.031	0.063
FA27	0.2	0.018	0.023	0.087	0.064	0.104
FA28	2.4	0.020	0.038	0.088	0.051	0.109
FA29	1.5	0.035	0.027	0.027	0.000	0.062
FA30A	35.2	0.020	0.024	0.045	0.021	0.066
FA31	0.9	0.034	0.031	0.039	0.008	0.073
FA32	44.7	0.023	0.020	0.035	0.015	0.058
FA33	29.1	0.020	0.016	0.021	0.005	0.042
FA34	4.9	0.024	0.025	0.058	0.033	0.082
FA35	17.5	0.002	0.002	0.008	0.007	0.011
FA36	0.3	0.101	0.217	0.708	0.492	0.810
FA37	4.9	0.019	0.031	0.141	0.111	0.160
FA38	0.2	0.169	0.168	0.168	0.000	0.336
FA39	0.8	0.142	0.109	0.186	0.077	0.328
FA40	1.1	0.141	0.066	0.118	0.052	0.259

FA41	1.1	0.159	0.068	0.095	0.027	0.254
FA42	0.6	0.107	0.053	0.189	0.136	0.296
FA43	0.6	0.171	0.061	0.061	0.000	0.232
FA44	0.6	0.148	0.053	0.053	0.000	0.201
FA45	0.7	0.171	0.078	0.130	0.052	0.301
FA46	11.2	0.027	0.022	0.033	0.011	0.061
FA47	41.5	0.031	0.017	0.020	0.002	0.051
FA48	1.4	0.040	0.035	0.106	0.071	0.145
FA49	19.9	0.009	0.016	0.026	0.010	0.035
FA50	22.2	0.013	0.017	0.034	0.017	0.047
FA51	20.9	0.020	0.018	0.027	0.009	0.047
FA52	1.1	0.142	0.138	0.446	0.308	0.588
FA53	4.0	0.023	0.027	0.044	0.018	0.068
FA54	4.1	0.018	0.015	0.021	0.006	0.039
FA55	0.7	0.107	0.085	0.190	0.106	0.297
FA56	1.2	0.092	0.070	0.070	0.000	0.161
FA57	0.8	0.045	0.053	0.074	0.021	0.119
FA58	1.9	0.017	0.020	0.039	0.019	0.056
FA59	1.0	0.029	0.041	0.041	0.000	0.070
FA60	6.0	0.011	0.011	0.011	-0.000	0.023
FA61	1.6	0.016	0.026	0.076	0.051	0.092
FA62	3.9	0.018	0.022	0.032	0.009	0.050
FA63	7.1	0.022	0.054	0.150	0.095	0.171
FA64	7.4	0.034	0.089	0.089	0.000	0.123
FA65	0.7	0.177	0.091	0.137	0.046	0.314
FA66	0.9	0.197	0.091	0.186	0.095	0.383
FA67	0.8	0.025	0.026	0.171	0.145	0.196
FA68	0.8	0.171	0.117	0.199	0.082	0.370
FA73	0.4	0.183	0.159	0.498	0.339	0.681
FA74	9.8	0.030	0.024	0.024	0.000	0.054
FA75	1.30	0.187	0.100	0.149	0.049	0.336
FA76	0.3	0.047	0.108	0.196	0.088	0.243
FA77	0.3	0.100	0.122	0.464	0.343	0.564
FA78	0.5	0.095	0.167	0.612	0.445	0.706
FA79	1.2	0.135	0.086	0.168	0.082	0.303
FA80	4.4	0.018	0.030	0.038	0.008	0.056
FA81	1.4	0.007	0.012	0.012	0.000	0.019
FA82	1.6	0.123	0.156	0.500	0.344	0.623
FA83	0.4	0.142	0.430	0.591	0.162	0.734
FA84	10.9	0.009	0.014	0.025	0.010	0.033

Table 5.3.3.1 Saturation pressures for CO₂ at 195 K, at 273.2 K and at 305 K obtained from different sources.

Temperature [K]	Source		
	Calculated from Clausius Clapeyron Eq.	Extrapolated from Perry's Handbook data, [temperatures 273–305 K, Table 3-209, page 3-151]	Published value in <i>Bridgeman</i> ⁶³
	[torr]	[torr]	[torr]
195	1380		
273.2	26110	26145	26144
305	55748	55906	

Table 5.4.1 Total nitrogen BET surface areas and polar surface areas of class F fly shes 5, 6 and 23.

Sample	FA5	FA6	FA23
LOI [wt.%]	1.9	3.4	65.5
N ₂ -BET Total ash surface area, [m ² /g ash]	1.7	2.6	35.3
N ₂ -BET Carbon surface area, [m ² /g carbon]	53.4	56.7	53.6
Specific foam index [ml of 10 vol. % Darex II/ g-carbon]	0.35	1.95	1.85
Polar surface area, n-butanol, [m ² /g-ash]	1.1	1.1	6.9
Polar surface area, t-butanol, [m ² /g ash]	1.0	0.9	4.0
Polar surface area, methanol, [m ² /g ash]	1.2	1.3	ND

FIGURES

Figure 5.1.1 Darex II activity comparison for two different batches of Darex II. All tests were performed on class F fly ashes with LOI values in the range 0.8% - 4 %.

Figure 5.1.2 Relationship between foam index and LOI for all of the fly ashes in our sample bank.

Figure 5.1.3 Relationship between the foam index and LOI for fly ashes near the range of commercial interest (LOI less than 8 wt. %).

Figure 5.1.4 Relationship between foam index and LOI for class F fly ashes in our sample bank. Again, only the range of LOI near those of commercial interest, are shown.

Figure 5.1.5 Relationship between foam index and LOI for class C fly ashes in our sample bank. Virtually all class C ashes have LOI values within the ASTM-designated acceptable range.

Figure 5.1.6 Specific foam index as a function of carbon content for class F fly ashes from our sample bank.

Figure 5.2.1 The relationship between foam index and LOI for class F fly ashes, using Air 40 AEA.

Figure 5.2.2 A comparison of foam index values obtained with Darex II and Air 40 surfactants, using class F fly ashes.

Figure 5.2.3 A comparison of foam index values obtained with Sodium Dodecyl Sulfate (SDS) and 10 vol.% Darex II surfactants using a selected set of fly ashes from the sample bank.

Figure 5.2.4 A comparison of foam index values obtained with 0.05 molar abietic acid sodium salt solution and with 10 vol.% Darex II surfactant using a set of test fly ashes from our sample bank.

Figure 5.2.5 A comparison of foam index values obtained with Sodium Dodecyl Sulfate (SDS), abietic acid sodium salt, dodecylbenzenesulfonic (DBS) acid sodium salt and with 10 vol.% Darex II surfactant using a set of fly ashes from our sample bank.

Figure 5.2.6 A comparison of foam index values obtained with DBS acid salt and 10 vol.% Darex II surfactant, using a set of fly ashes from our sample bank.

Figure 5.2.7 A comparison of foam index values obtained with DBS and 4 vol.% Darex II surfactants using a set of low LOI fly ashes .

Figure 5.2.8 A comparison of the molar uptakes of different surfactants, per mass of carbon, in fly ashes.

Figure 5.3.1 Physisorption Isotherm types classified by *Brunauer*³²

Figure 5.3.2 Hysteresis loops defined by *Sing*³³

Figure 5.3.3 Nitrogen isotherms obtained at 77 K on class F fly ash samples, in an as-received condition from the NEP Brayton point.

Figure 5.3.4 A comparison of NEP's Brayton point class F fly ash BET surface area with LOI.

Figure 5.3.5 Nitrogen isotherms obtained at 77 K on high LOI class F fly ash samples from NEP.

Figure 5.3.6 Nitrogen isotherms obtained at 77 K on high LOI class F fly ash samples from NEP and other sources.

Figure 5.3.7 Class F fly ash BET surface areas as a function of their LOIs.

Figure 5.3.8 Nitrogen isotherms obtained at 77 K on class F fly ash samples from NEP's Salem Harbor, and AEP's Columbus and Clinch River plants.

Figure 5.3.9 Nitrogen isotherms obtained at 77 K on ash samples from Monex/Boral Co.

5.3.10 Nitrogen isotherms obtained at 77 K on class C ash samples provided by Dairyland power.

Figure 5.3.11 Nitrogen isotherms obtained at 77 K on class C ash samples provided by the Welsh power plant (Texas) and by Flint Creek plant (Arkansas).

Figure 5.3.12 Nitrogen isotherms obtained at 77 K on so called "unusual" condition and origin fly ash samples.

Figure 5.3.13 Nitrogen isotherms obtained at 77 K on non-coal fly ash samples, compared to a class F coal fly ash.

Figure 5.3.14 A comparison of nitrogen isotherms obtained at 77 K on the non-carbon containing fly ash samples and a class F fly ash sample containing carbon.

Figure 5.3.15 Nitrogen sorption isotherms obtained at 77 K on three different fly ash carbons. All are calculated on the basis of nitrogen sorption volume per mass of carbon present in sample.

Figure 5.3.16 Nitrogen sorption isotherms obtained at 77 K on four different class C fly ash carbons. All are calculated on the basis of nitrogen sorption volume per mass of carbon present in sample.

Figure 5.3.17 A comparison of carbon dioxide isotherms (at 195 K) obtained on class F fly ashes.

Figure 5.3.18 A comparison of carbon dioxide isotherms (at 195 K) obtained with class C fly ashes.

Figure 5.3.19 A comparison of nitrogen (77 K) and carbon dioxide (195 K) isotherms on class F fly ash 6 with LOI 3.4%.

Figure 5.3.20 Carbon dioxide isotherms at 195 K, 273 K and 305 K for class F fly ash 21 with LOI 6.1%.

Figure 5.4.1 The specific foam index as a function of carbon surface polarity and the total surface area presented by the carbon.

Figure 5.4.2 Specific foam index versus polar surface area for class F ash carbons.

Figure 5.4.3 Specific foam index versus polar surface area for class C ash carbons.

OPTICAL-, SCANNING- AND TRANSMISSION MICROSCOPY IMAGES, TEM
EDS SPECTRA, Figures 5.5.1 – 5.5.41

Figure 5.5.1 Optical microscope image of bulk class F fly ash 5 with LOI 1.9 wt.%. Ash is considered as “good” in concrete applications. Units on the ruler are in micrometers, 200 up to 1000 μm .

Figure 5.5.1A Optical microscope image of bulk class F fly ash 6 with LOI 3.4 wt.%. Ash is considered as “bad” in concrete applications. Units on the ruler are in micrometers, 200 up to 1000 μm .

Figure 5.5.2 Optical microscope images of bulk class F fly ash 5 LOI 1.9 wt.% at a higher magnification level. Ash is considered as “good” in concrete applications. Units on the ruler are in micrometers, 100 up to 500 μm .

Figure 5.5.2A Optical microscope images of bulk class F fly ash 6 LOI 3.4 wt.% at a higher magnification level. Ash is considered as “bad” in concrete applications. Units on the ruler are in micrometers, 100 up to 500 μm .

Figure 5.5.3 Optical microscope image of bulk class F fly ash 5 with LOI 1.9 wt.%, maximum magnification with microscope, 50X objective, units on the ruler are in micrometers.

Figure 5.5.4 Optical microscope image of bulk class F fly ash 8, LOI 3.8 wt.%.

Units are in micrometers.

Figure 5.5.5 Magnified optical microscope image of bulk class F fly ash 8, LOI 3.8 wt.%. Units are in micrometers.

Figure 5.5.6 Magnified optical microscope image of bulk class F fly ash 8, LOI 3.8 wt.%. Units are in micrometers.

Figure 5.5.7 Optical microscope image of fly ash 21 (Class F), a separated fraction of particle size $180 < d < 355 \mu\text{m}$.

Figure 5.5.8 Optical microscope image of class F fly ash 21, a size classified fraction of $180 < d < 355 \mu\text{m}$.

Figure 5.5.9 Optical microscope image of class F fly ash 26,
fraction $180 < d < 355 \mu\text{m}$.

Figure 5.5.10 Optical microscope image of class F fly ash 26,
fraction $180 < d < 355 \mu\text{m}$.

Figure 5.5.11 Optical microscope image of class F fly ash 24,
fraction $180 < d < 355 \mu\text{m}$.

Figure 5.5.12 Optical microscope image of class F fly ash 24,
fraction $180 < d < 355 \mu\text{m}$.

Figure 5.5.13 Optical microscope image of the bulk class C fly ash 75, with LOI 1.3 wt.%.

Figure 5.5.14 Optical microscope image of class C fly ash 41,
fraction of $180 < d < 355 \mu\text{m}$ size.

Figure 5.5.15 Optical microscope image of the class C fly ash 75, fraction $d > 355 \mu\text{m}$.

5.5.16 Optical microscope image of the class C fly ash 75, fraction $d > 355 \mu\text{m}$.

Figure 5.5.17 Optical microscope image of the class C fly ash 66,
fraction $180 < d < 355 \mu\text{m}$.

Figure 5.5.18 Optical microscope image of the class C fly ash 65,
fraction $180 < d < 355 \mu\text{m}$.

Figure 5.5.19 Optical microscope image of the class C fly ash 65,
fraction $180 < d < 355 \mu\text{m}$.

Figure 5.5.20 Optical microscope image of the class C fly ash 65, fraction $180 < d < 355 \mu\text{m}$.

Figure 5.5.21 SEM image of fly ash minerals from a typical class F fly ash, $V_{\text{elect.}} = 5\text{kV}$, magnified 800 times.

Figure 5.5.22 SEM image of class F fly ash 22 carbon particles. Electron accelerating voltage $V_{\text{elect.}} = 5\text{kV}$, magnified 800 times.

Figure 5.5.23 SEM image of class F fly ash 22 carbon. Electron accelerating voltage $V_{\text{elect.}}$ = 5kV, magnified 1800 times.

Figure 5.5.24 SEM image of class F fly ash 22 carbon. Electron accelerating voltage $V_{\text{elect.}}$ = 5kV, magnified 7500 times.

Figure 5.2.25 SEM image of class F fly ash 5 carbon. Electron accelerating voltage $V_{\text{elect.}}$ = 5kV, magnified 3500 times.

Figure 5.5.26 SEM image of class F fly ash 5 carbon. Electron accelerating voltage $V_{\text{elect.}}$ = 5kV, magnified 6000 times.

Figure 5.5.27 SEM image of class F fly ash 8 carbon. Electron accelerating voltage $V_{\text{elect.}}$ = 5kV, magnified 1600 times.

Figure 5.5.28 SEM image of class F fly ash 8 carbon. Electron accelerating voltage $V_{\text{elect.}}$ = 5kV, magnified 6500 times.

Figure 5.5.29 SEM image of a class C fly ash 75 carbon. Electron accelerating voltage $V_{\text{elect.}} = 5\text{kV}$, magnified 1400 times.

Figure 5.5.30 Bright filed image of the fly ash 9 particles, magnification 10 500, exposure time 0.5 seconds, image is positive.

Figure 5.5.31 Bright filed image of the fly ash 9 particles, magnification 24 000, image is positive. Regions A, B, C and D have been analyzed with EDS.

spectrum of 8541A. Fly Ash major elements Si and Al. Both are represented as SiO₂ and Al₂O₃ in F
ly Ash.
Analyst: keV: 120.00 Current: 0.00 Live Time: 100.00 eV/Channel= 10.00
Detector Resolution: 142.80 eV Take-off angle= 10.00

Figure 5.5.32 EDS spectrum of the area A in BF image Figure 5.5.31. Major peaks associated with elements Si, Al and O.

Expanded spectrum of 8541A. Fly Ash major elements Si and Al. Both are represented as SiO₂ and Al₂O₃ in Fly Ash.
 Analyst: keV: 120.00 Current: 0.00 Live Time: 100.00 eV/Channel= 10.00
 Detector Resolution: 142.80 eV Take-off angle= 10.00

Figure 5.5.33 Expanded EDS spectrum of the area A in BF image Figure 5.5.31 Major peaks associated with elements Si, Al and O.

Spectrum of 8541B. Mostly Carbon.
 Analyst: keV: 120.00 Current: 0.00 Live Time: 100.00 eV/Channel= 10.00
 Detector Resolution: 142.80 eV Take-off angle= 10.00 Spectrum # 1 From the file: 8541B

Figure 5.5.34 EDS spectrum of the area B in BF image Figure 5.5.31. Major element C.

Expanded spectrum of 8541B. Mostly Carbon.
Analyst: keV: 120.00 Current: 0.00 Live Time: 100.00 eV/Channel: 10.00
Detector Resolution: 142.80 eV Take-off angle= 10.00 Spectrum # 1 From the file: 8541B

Figure 5.5.35 Expanded EDS spectrum of the area B in BF image Figure 5.5.31. Major element C.

Figure 5.5.36 EDS spectrum of the area C in BF image Figure 5.5.31. Major elements Si, Al, O and C.

Figure 5.5.37 EDS spectrum of the area D in BF image Figure 5.5.31. Major elements Ca, S, O, Si and Al.

Al₂O₃ and SiO₂ spectrum. Mainly Al, Si, O present.
 Analyst: keV: 120.00 Current: 0.00 Live Time: 100.00 eV/Channel= 10.00
 Detector Resolution: 142.80 eV Take-off angle= 10.00 Spectrum # 1 From the file: AlSiO
 Markers for C, 6

Figure 5.5.38 EDS spectrum of the area of minerals in BF image Figure 5.5.31. Major elements Si, Al, O, Fe, Ca.

Figure 5.5.39 Expanded EDS spectrum of the area of minerals in BF image Figure 5.5.31. Major elements Si, Al, O, Fe, Ca.

Figure 5.5.40 EDS spectrum of the possible CaSO_4 area in BF image Figure 5.5.31. Major elements Ca, S and O. Cu peaks are from specimen Cu grid.

Figure 5.5.41 Expanded EDS spectrum of the possible CaSO_4 area in BF image Figure 5.5.31. Major elements Ca, S and O.

Perfect circle on BF images are pure minerals like Al₂O₃ and SiO₂.
 Analyst: keV: 120.00 Current: 0.00 Live Time: 100.00 eV/Channel= 10.00
 Detector Resolution: 142.80 eV Take-off angle= 10.00 Spectrum # 1 From the file: perfect sphere

Figure 5.5.42 EDS spectrum of the particle with shape of the perfect sphere in BF image in Figure 5.5.31. Major elements are Si, Al and O.

6.0 UNDERSTANDING THE FOAM INDEX PROBLEM

6.1 The Relationship between Foam Index, Surface Area, Porosity and Polarity

It is generally accepted that it is the “organic” matter of fly ash, i.e., the unburned elemental carbon, which is responsible for the undesired adsorption of organic admixtures from concrete mixtures^{5,6,12,13,14}. As discussed earlier, in the case of adsorption of AEAs, this adsorption leads to problems with loss of entrained air. What is less well established is which characteristics of carbon are critical in determining the extent of adsorption. It has often been suggested that there is a correlation between LOI and foam index^{6,14,18}. It is logical that the extent of adsorption of organics from a generally very polar concrete mixture should depend upon the presence of an organic carbon phase in an otherwise polar fly ash.

As shown earlier (Chapter 5), fly ash LOI is not a satisfactory predictor either of how a particular fly ash will perform in concrete mixtures or how it will behave in the foam index test. Of course, LOI is the main factor that determines the foam index, since it is mainly the carbon that adsorbs the AEA. As noted before, though, some very low LOI samples (containing much less than the allowed ASTM 6 wt% specification of carbon) performed poorly in concrete mixtures. Therefore there is reason to believe that it is some further characteristics of the carbons that must determine their behaviors. As has already been suggested, it is believed that besides the LOI of the ash, its surface area, surface area accessibility, and surface polarity must all affect the AEA uptake.

6.1.1 The Role of Carbon Surface Area

It was earlier suggested that rather than the total amount of carbon itself, it is the surface area which the carbon offers for adsorption that is key in determining how high an AEA capacity of a particular fly ash^{5,6,19}. There is little doubt that surface area can be the basis of some gross differences in observed behavior. Table 6.1.1 compares the foam index of pairs of fly ashes of comparable LOI, in which one of the samples in each pair is a “normal” coal-derived sample and the other comes from co-firing of petroleum coke with coal. In the case of the petroleum coke co-fired samples, the residual carbon content is dominated (96 wt.%) by carbon which came from the petroleum coke in the fuel feed.

Table 6.1.1 Foam index and surface area for different types of fly ash in our sample bank.

Sample	Final LOI	Foam index	Carbon Surface Area	Surface Area contribution of carbon from coal
	[wt. %]	[ml of 10 vol.%Darex II per 2 g-ash]	[m ² /g-C]	[m ² /g-C]
class C fly ash	0.9	0.081	392.6	392.6
class F fly ash	2.6	0.052	69.8	69.8
co-fired Pet. Coke fly ash*	2.4	0	20.2	380
Pet. Coke fly ash	17.5	0	4.6	0

* containing 3.8 wt.% class C fly ash carbon

The foam index values of the petroleum coke samples are much lower than the foam index values for the coal-derived samples. This is mainly attributed to the very low

intrinsic surface area of the petroleum coke samples compared with the coal-derived samples, as seen from Table 6.1.1. The differences in morphology of these different carbons have been the subject of a recent paper²⁰.

The variation of carbon BET surface area with LOI is represented in Figure 6.1.1 (see the end of this chapter). The values in this figure were calculated from measurements of the surface areas of the original ash, less the surface area measured for the same ash with the carbon completely burned out. This difference is attributable to the carbon in the ash, and was divided by the LOI of the sample to give an estimate of the surface area per mass of carbon. Figure 6.1.1 shows that class C and class F ashes show generally distinct characteristics in the carbon phase, in addition to the differences in their inorganic compositions. Relatively high carbon surface areas and low LOI values characterize the class C ashes. The range of their carbon surface areas is 250 to 400 m²/g. Such values are not unusual for combustion chars of low rank coals; a study of the development of porosity under such conditions has recently been presented⁷⁰.

The surface areas of carbons in class F ashes are, on the other hand, all somewhat lower, and in most cases fall into a range from 20 to 80 m²/g. A single class F ash from a boiler in which gas was co-fired with coal, with an LOI of about 3.6 %, appears outside of the band of normal class F surface areas. There are also few low LOI samples (<2%) among the class F ashes that have higher surface areas. These have all been identified to us as “bad” ashes, and our own foam index characterizations confirm this.

Bituminous coals soften during pyrolysis and lose all or most porosity when they do. They also often tend to form somewhat ordered structures that resist the development of high surface area during combustion. The limited way in which this carbon can form

porosity is thus imprinted on it from the earliest stages of the burning process. As high carbon burnoffs are achieved, a decrease in surface area can actually be observed, perhaps as a consequence of pore coalescence, but perhaps also due to further thermal annealing of the structure²¹.

It is unclear exactly what factors dictated the higher surface areas in what may be termed the unusual class F ashes. In one case, we know that the sample contained a large amount of soot-like material⁵. This sample (fly ash 16 in our sample bank, see more details in Table 4.1) came from what may be termed “upset” firing conditions, and was black in color, despite an LOI of only 1.5%. In contrast, the petroleum coke co-fired ash sample (fly ash 35 in our sample bank) which has an LOI of 17.5% was light tan in color. The difference in the colors of these samples is attributable to the large difference in carbon particle sizes that they contain. Fly ash 16 has finer particles that are much more effective at coloring a sample. These fine soot particles also offer very large external surface areas per unit mass. Thus ash color may be a much more sensitive indicator of carbon fineness than of total carbon content, and the fineness itself may correlate somewhat with available surface area for adsorption⁵.

The class F ashes that gave higher surface areas at low values of LOI (see Fig. 6.1.1) do not necessarily contain unusual carbon. In separate burnout experiments described in a later chapter, it will be seen that the 20 to 80 m²/g range does not represent an inherent property of bituminous coal chars. Rather, it is dictated by a combination of carbon properties as well as by the nature of the combustion process in the boiler. Higher surface areas can indeed be achieved during oxidation of these carbons.

Figure 6.1.2 shows a plot of foam index as a function of total BET surface area (per gram of ash) for all ashes in our sample bank. The correlation seen in Figure 6.1.2 appears reasonably good, suggesting that as the surface area increases, the AEA uptake increases as well. We have earlier discussed the fact that higher fly ash surface areas are strongly related to higher carbon content in ashes. The surface area of the mineral part is essentially independent of the type of ash, and is about $0.8 \text{ m}^2/\text{g}$ of mineral. Therefore the result seen in Figure 6.1.2 is expected, because it is really a correlation of foam index with carbon surface area. However, just as in the case of the correlation of foam index with LOI, there are many cases that do not fit the general pattern. These are not visible in Figure 6.1.2 because of the choice of how the data were plotted. The very high surface area ashes are also generally very high LOI ashes, and therefore of no commercial interest. Figure 6.1.3 shows the lower left corner of Figure 6.1.2, which contains most of the commercially interesting ashes.

The data points in Figure 6.1.3 show a much higher degree of scatter, suggesting that there is not a good correlation between foam index and total ash surface area for this subset of samples. Therefore, other parameters beside the surface area must help determine the AEA uptake. In passing, it might be noted that the intercept with the abscissa, at about $1 \text{ m}^2/\text{g}$, is to be expected since this is the surface area obtained with the mineral part of the ash. The foam index for the mineral components of the ashes have been repeatedly measured to be zero.

Figures 6.1.2 and 6.1.3 are drawn for ashes having many different origins and types. Some of the ashes are of class C and some of them class F type. As already discussed, the carbons in these different types of ashes are dissimilar. Therefore Figure

6.1.3 has been redrawn as Figure 6.1.4, which shows separately the class C and class F ashes. At this point, it must be cautioned that all of the ashes in the bank were not re-checked as to their type, so the classification is based upon donor information only, or in a few cases, upon some guesses based upon the information provided.

The results in Figure 6.1.4 show that class C and class F ashes show markedly different trends in foam index as a function of total BET surface area. Class F ashes have higher AEA uptake at a given surface area as compared to class C ashes. As seen from Figure 6.1.4, fly ash foam indexes for similar surface area class C and class F ashes can differ by a factor of 8 to 10 times. This suggests that a large part of the class C ash surface area may not be effective in adsorbing AEAs. There is, of course, no guarantee that the surface area is fully utilized in class F ashes. It is simply the case that it must be less effectively utilized in class C ashes.

There is a significant amount of scatter visible in both data sets. This is not likely to be attributable to foam index or surface area measurement uncertainties in the case of the class F ashes. The class F ashes have relatively high foam index values, and these can be measured with a high degree of reproducibility. The surface area analyses are quite straightforward and reproducible. However, it must be recalled that class C ashes have extremely low foam index values for many samples in the bank, so some of the scatter in that data set could be due to measurement uncertainties. For example, one of the highest LOI class C ash in our sample bank had a foam index 0.096 ml per two grams of ash. As discussed earlier, each foam index test has an uncertainty of about 1 drop, which equals 0.02 ml. This shows that the foam index test itself has an uncertainty of about 20%. On the other hand, this uncertainty is not large enough to say that the class C ashes are

statistically indistinguishable from the class F ashes. There is no question that these two types of ashes are taken from populations with very different properties. As regards the class C ashes, it should also be recalled that in spite of the high uncertainty associated with some of the values, a high degree of measurement reproducibility is generally obtained, and the reported values are averages of several trials. Consequently it is believed that the scatter in the class F case, which has its origin in material property variations, must have a parallel in the class C ashes. It is unlikely that all of the class C ashes are identical in property, and that all that is being reported in Figure 6.1.4 is data scatter.

Since surface areas and foam indexes for both types of minerals (class C and F) are essentially constant, there is an opportunity to recalculate the same data to show properties on a mineral-free carbon basis. Specific foam index is calculated from foam index data obtained separately for the ash and mineral. Subtraction of the mineral part from the whole ash value should leave only the value attributable to carbon. In fact, the mineral part of the fly ash is repeatedly measured to have constant zero uptake capacity for the AEA. Therefore it is believed that the AEA uptake by fly ashes depends only upon the amount of carbon and its nature. Thus specific foam index is calculated as milliliters of AEA per gram of carbon.

The specific BET surface area of a particular fly ash carbon is also calculated by subtracting the mineral contribution from the total ash surface area, and dividing by the carbon content of the ash. Specific BET surface area is given as m^2 (of carbon surface) per gram of carbon. Figure 6.1.5 shows the correlation between specific surface area and specific foam index for both class C and class F ashes.

Figure 6.1.5 shows a large cluster of points at low specific surface area and low specific foam index. The majority of class F fly ashes fall into this tight cluster near the origin. In contrast to this, the class C ashes are observed to be characterized by high specific carbon surface area, but this does not necessarily lead to high specific foam index, as might be expected. This again implies that there exists a significant difference in how effectively the carbon surface area can be utilized in class C and class F ashes. There are a few class F fly ash samples shown in Figure 6.1.5, which have very high specific surface areas, that are more typical of those found in class C ashes. These class F fly ash carbons, three of which had a surface area greater than $200 \text{ m}^2/\text{g}$ of carbon, are FA 39, FA 52 and FA 55. While the coals that gave ashes 52 and 55 were not identified by the sample donor, fly ash 39 was specified to originate from a sub-bituminous coal. It is perfectly reasonable that sub-bituminous coals give behavior that is one the one hand like that of other low rank coals (i.e., high surface area), but on the other hand have ash compositions comparable to those of some higher ranks coals.

There are several other class F ashes that do not follow the general pattern established by the majority of class F ashes. A few are characterized by somewhat higher than usual surface areas (for class F) but they are all characterized by high specific foam index. In a sense these few samples do confirm that high surface areas are related to high foam index, but the points are so widely scattered that it is impossible to say that they establish a clear trend.

Again, it must be recalled that class C ashes have extremely low LOI and foam index values. Once again, the small LOI and foam index values lead to a very high uncertainty in specific foam index. For example, class C fly **ash 75 has an LOI of about**

1.3 wt %. As discussed earlier, secondary reactions in the LOI test can lead to significant uncertainty in this value. Together with simple mass measurement uncertainty, the LOI uncertainty for class C ash 75 can be estimated to be as high as 0.45 wt%, or about a 36% error, on a relative basis. The uncertainties in both tests (foam index and LOI) are thus quite high. This is why care should be taken in drawing quantitative conclusions from the class C data set. Still, there can be no question that the specific BET surface areas for class C ashes are much higher than those for class F ashes. This is because if there is an error in the standard LOI determination, it will generally be in the direction of overestimation of carbon content (due to the previously discussed mineral decomposition reactions). The same overestimate of carbon content would tend to lead to an underestimate in the specific foam index, but again, this would not alter the conclusions drawn from Figure 6.1.5.

Therefore it may be seen that surface area-based trends can be used to explain AEA uptake behavior in a limited subset of samples, but not across the full range of samples of commercial interest. There must be other factors that at least partly determine AEA adsorption behavior.

6.1.2 The Role of Accessibility

Full nitrogen isotherms were used to determine the BET surface areas of all of the fly ash samples. There is, however, a great deal more information available from the full adsorption isotherm, and this has been utilized in examining further the issue of differences in adsorption capacities of carbons from different ashes. Figure 6.1.6 shows the isotherms for typical class F and class C ashes, as well as an isotherm for a sample

from which the carbon has all been burned out. The isotherm for the class F ash shows a steep rise at low values of P/P_0 . This is characteristic of microporosity, and the volume is given in this figure in terms of STP cm^3 of sorption capacity for the nitrogen gas adsorptive (this value is, of course, converted to actual condensed phase volume, in order to describe the true pore volume). Above about $P/P_0 = 0.3$, there is a gentle upward slope in both the adsorption and desorption isotherms, up to very near P/P_0 of unity. This, together with the small hysteresis loop that closes at about $P/P_0=0.4$, is indicative of mesoporosity in the sample. The relative volumes of these two contributions to porosity may be seen to be comparable. Examining the same features of the isotherm for class C ash, it is apparent how the microporosity is relatively much more significant in this case. In the sample of pure mineral matter, it is notable how little microporosity is present, and how the porosity is actually dominated by the upswing very near a P/P_0 of unity. This means that large capillary openings dominate in this sample, and in fact, this is probably attributable to the spaces between the glassy, often spherical, close-packed inorganic particles themselves. This is consistent with the character of the fly ashes as revealed by electron microscopy (see Chapter 5 and references 5 and 20).

A more formal and quantitative analysis of the porosity present in the ash particles is possible, using methods which are well described by Rodriguez-Reinoso et al.³¹. The procedure, as adapted for present purposes, involves the following steps. First, the contribution of the pure inorganic mineral components is subtracted from the fly ash isotherm of interest. Then, the contribution of the microporosity is subtracted from the residual carbon isotherm, assuming that the micropores contribute as described by the Dubinin-Radushkevich analysis. The result is an isotherm which describes only the meso-

and macroporosity in the carbon. The corrected isotherm is displayed in Figure 6.1.7. This corrected isotherm can then be analyzed by the method developed by Barrett, Joyner and Halenda⁷¹ in order to yield the size distribution of the meso- and macropores. The size distributions are displayed in Figure 6.1.7 for typical class F and class C ashes. The size distributions themselves are of very similar shape, but there is a much smaller amount of porosity in the class F sample chosen for this comparison. This difference is not always seen, though a large fraction of class C ashes do have significant mesoporosity (see Table 5.3.2, presented earlier). A few class F ashes also appear to have high mesoporosity, but most of these are derived from non-softening subbituminous coals.

These calculated pore size distributions reveal an important feature of the carbons. It must be remembered that the constituents of the AEA, are large surfactant molecules. Boral/Monex Co has suggested that abietic acid (or its salt) is reasonable model for many of the constituents of the AEAs; its structure was presented in an earlier chapter. In order for the surface of carbon to be effective for adsorption of the AEAs, it must be accessible to such large molecules. The problem is familiar to designers of activated carbon systems used for wastewater treatment. The carbons useful for such treatment systems are those with significant mesoporosity; microporosity alone cannot provide enough access to the interior of the particle to make use of adsorptive capacity which may be located in those pores. Such water treatment carbons are different from those of interest in gas adsorption, in which premium is placed on high surface area in micropores. It would appear as though the carbon in class C fly ash is both more microporous, and also more mesoporous (see examples in Table 5.3.2, fly ashes 65, 66, FA 75 – FA78), and should

therefore exhibit higher adsorption capacity than class F carbons. The fact that class C carbons do not always exhibit higher specific foam indices again suggests that yet other factors play a role in determining AEA capacity.

To explore further the issues surrounding accessibility differences in class F and class C ashes, the influence of meso- plus macro-porosity on specific foam index has been presented in Figures 6.1.8 and 6.1.9. The data in Figures 6.1.8 and 6.1.9 confirm that class C ashes have generally higher meso- plus macropore volume than class F ashes. Most of the class F ash fly ash carbon data cluster (in Figure 6.1.9) below 0.1 ml/g-carbon, whereas most of the class C carbons fall above this value (Figure 6.1.8). The data in Figures 6.1.8 and 6.1.9 thus support the conclusion from Figure 6.1.7 that class C ashes have more large porosity, but the differences are not always as large as that comparison suggested. Also, the scanning electron and optical microscopy analyses had suggested that class F ash carbons did not show as much large porosity as did the class C ash carbons. This is likewise confirmed by the present results.

For neither class F nor class C fly ash carbons is there any clear relationship between large pore volume and AEA uptake. Some of the fly ash carbons have meso- and macropore volumes above 0.1 ml/g-carbon, but their activity towards AEAs is measured to be zero. On the contrary, some of the very low porosity samples have high AEA uptake. Clearly these data suggest that large porosity is not by itself a primary factor in determining AEA uptake in fly ash carbons.

Figure 6.1.10 shows specific foam index as a function of mesoporosity alone for the class C ashes. As seen in this plot, class C ashes have been differentiated according to their parent coal origin. The first group included 8 class C ashes, which originated from

Powder River Basin (PRB) coals. Dairyland Power provided most of these PRB coal ashes (FA 65, FA 66, FA 68, FA 73 and FA 75). We were not sure from which parent coal other class C ashes in our sample bank originated therefore they were classified as “other class C ashes”. Most of this second group ashes were provided by Welsh Power Plant (FA 40, FA 41 and FA 42, see details in Table 4.1) in Texas and by Flint Creek Plant (FA 43, FA 44 and FA 45) in Arkansas. This group also included samples from Miller Plant, Southern Company in Alabama (FA 76, FA 77, FA 78 and FA 79). There was also one class C sample (FA82 with extremely high LOI for class C ashes 1.6 wt%) provided by Russell Hill of Boral. This ash was grouped with the “others” because the origin of the parent coal was unknown.

The results of Figure 6.1.10 suggest that the Powder River Basin (PRB) coal ashes are not unique, when compared to “other class C ashes”. The only PRB sample that did not follow the trend established by the other PRB samples was fly ash 27 from AEP (lower-left corner of Figure 6.1.10). This ash was specified as “good” in terms of how it performed in concrete mixtures. The reason for the difference from the other PRB samples is unknown. Another data point (at mesoporosity above 0.1 ml/g carbon, with zero specific foam index) is Southern Company's ash 76. Southern Co has also specified that ash 76 is a “good” sample in terms of concrete applications. Thus the specific foam index appears to be correctly picking out the good and problem ashes.

Fly ash 77 is a "problem" ash from the same Southern Company plant. Our foam index test results confirm the difference between ashes 76 and 77. The mesopore volumes of these two ashes are, however, quite similar. The carbon surface area of the "bad ash" is almost twice that of the "good ash". Also, the macropore volume of the "bad ash" is much

higher than that of the "good ash". Which of these factors is the more important cannot be concluded from the present results. All that may be concluded from this comparison is that mesoporosity alone cannot explain the difference in ash quality.

The interplay between surface area (which provides capacity) and accessibility is addressed in several further plots. Figure 6.1.11 displays the porosity analysis results for the carbons in class C ashes in surface area/microporosity space. Figure 6.1.12 shows the results of the analyses in surface area/mesoporosity space and Figure 6.1.13 in surface area/meso-and macroporosity space. The groupings in Figures 6.1.11 through 6.1.13 are made according to specific foam indexes (SFI); very high ($3 < \text{SFI} < 6$), high ($2 < \text{SFI} < 3$) and low ($\text{SFI} < 0.8$) SFI.

Figure 6.1.11 shows the expected good correlation between micropore volume and BET surface area for class C ash carbons. This confirms that surface area is dominated by micropore contributions. Clearly specific foam index plays no role in the main correlation that is being displayed in the plot. Low SFI samples may be found equally at low and high surface areas.

The results in Figure 6.1.12 show that there is no particular correlation between the surface area and mesopore volume in carbons from class C ashes. As discussed earlier, it seems from the results in Figure 6.1.12 that high surface area together with high mesoporosity leads to higher AEA uptake (the data cluster in top-right corner of the plot). Clearly, though, there is not the expected trend seen with the high and very high SFI samples. There must be other factors that play a role in completing the picture of AEA uptake capacity. These factors might include accessibility that is determined on a size scale larger than that defined by mesopores or the chemical nature of the surface.

Figure 6.1.13 suggests that the inclusion of macropores with the mesopore volumes does not significantly alter the conclusions drawn above. There must be other factors that determine the AEA uptake in class C ashes.

Figure 6.1.14 shows the relationship between surface area, porosity and specific foam index for class F ashes. The results in Figure 6.1.14 demonstrate that samples with both high specific surface area and porosity are unlikely to exhibit low AEA uptake. However, there are samples which have very high specific foam indexes ($SFI > 2$), but at the same time relatively small surface area and porosity. In fact, most of the samples in Figure 6.1.14 cluster in the lower-left corner of the plot. Again, this all confirms that other factors beside the surface area and porosity must play a role in determining AEA uptake for class F ashes in this range of specific surface area and porosity.

Thus it appears as though simple, general explanations of the AEA sorption capacity of different fly ashes cannot come from routine porosity analyses. One reason why this is the case is already clear - the nature of the carbon surface can influence its suitability for adsorption. This will be explored in greater depth in a later part of this chapter. It is also the basis for the very successful use of ozone for mitigation of the AEA adsorption phenomenon. The other reason is more difficult to quantitatively characterize. The fact that the foam index test is a very rapid measure of AEA uptake means that the full extent of accessible porosity will not necessarily be utilized by the AEA. This has already been observed in previous studies^{5,18,20}. This means that there should be a biasing of foam index results due to the existence of a large fraction of very fine carbon

particulate in an ash. The influence of different sizes of carbon particulate is explored below.

6.1.3 The Role of Carbon Surface Polarity

There appears to be general agreement in the literature that the chemical nature of the carbon surface should in some way determine the ability of a fly ash to adsorb AEA^{5,14,19}. It remains unclear, however, whether the adsorption of AEA is enhanced¹⁹ or decreased^{5,14} in the presence of a more polar carbon surface. It is logical that surface polarity should play some role in determining the adsorptive capacity of the carbon, since it is well known from the carbon adsorption literature that this aspect of carbon surface can play a key role in this regard. Since the wet concrete mix environment is highly polar (both due to the water environment as well as the polar nature of the mineral components), then there is a thermodynamic driving force for adsorption of the strongly nonpolar “tails” of the AEA molecules onto the relatively nonpolar carbon surfaces. The same principal applies to use of activated carbon for removal of organic material from wastewater. By making the surface of the carbon more polar, this adsorptive driving force is diminished, and with it, the adsorption capacity of the carbon. It is, on the other hand, unlikely that the surface of the carbon could ever be made so polar as to favor preferential adsorption of the polar “head” of the AEA molecule onto its surface; the surrounding environment will remain far more polar.

It is difficult to obtain “clean” examples of the effects of polarity from the sample bank. Table 6.1.2 provides data on two sets of samples that suggest a role of polarity. In the first set, data are compared for two fly ashes obtained from the same boiler, one pre-

low-NO_x retrofit, and the other post-retrofit. The LOI of the post-retrofit sample is higher, but this can be discounted if the samples are compared on the basis of specific foam index and specific surface area. It is seen that the carbon surface areas of the two samples are quite comparable. What is different is both the polarity of the samples' surfaces and the mesoporosity of the samples.

Table 6.1.2 The role of surface polarity in AEA uptake for class F fly ashes 5 and 6.

Sample	LOI, [wt.%]	Specific FI, [ml 10% Darex II/g- carbon]	Specific volume of Mesopores [ml/g- carbon]	BET carbon surface area, [m²/g-carbon]	Polar surface area [fraction]
FA5	1.9	0.35	0.010	53.4	0.95
FA6	3.4	1.95	0.028	56.7	0.20

In the case of the sample FA6 which yields the much higher specific foam index, the surface is considerably less polar than in the case of sample FA5. This was revealed by the results obtained by flow microcalorimetry from which the polar surface area was calculated as described in the experimental section (and is here given as a fraction of total surface area). It cannot, however, be concluded from this pair of samples alone that polarity is the main factor determining AEA adsorption. It is clear that at the same time as polarity changed, so too did the nature of the sample porosity. The higher mesoporosity present in sample FA6 could also contribute to its greater ability to adsorb AEA, though the results of the previous section would tend to discount the importance of this factor. Still, it is often difficult to draw unequivocal conclusions regarding the main determining factor, when commercial samples are examined. It is quite plausible that the

extensive mixing changes that took place in the boiler as a result of the low-NO_x retrofit influenced both the way in which the char formed and burned, and the degree to which it could develop and hold a surface oxide film before quenching.

More definitive proof of the hypothesis that polarity affects AEA adsorption comes from tests in which fly ashes are deliberately oxidized, in order to increase the oxide content on the surfaces of their carbons. Table 6.1.3 shows the results of an experiment in which the surface of a particular fly ash was deliberately oxidized, using hydrogen peroxide solution for this purpose. In this work, the sample was simply immersed in a 50% peroxide solution for 24 hours, vacuum dried, and then tested. The specific foam index decreased markedly, and the polar surface area increased as a result of this treatment. The nature of the porosity was largely unaffected. The surprising thing about these results was how a fairly modest extent of oxidation could so strongly influence the foam index. A number of different oxidation procedures have been performed, and will be described further below. The general conclusion from all those tests is that oxidation increases the polarity and decreases the foam index.

Table 6.1.3 The role of surface polarity for oxidized class F fly ash 22 sample.

Sample	LOI [wt.%]	Specific FI, [ml 10% Darex II/g- carbon]	Specific volume of Mesopores [ml/g- carbon]	BET carbon surface area, [m²/g-carbon]	Polar surface area [fraction]
FA22	33.6	1.8	0.016	51.2	0.21
FA22Ox.	32	0.6	0.020	53.4	0.32

Recognizing the caveat concerning the possibility of correlated changes in the nature of the surface and polarity of commercial samples, Figure 6.1.15 shows results for a broad range of samples in our sample bank.

These results suggest (albeit weakly) that the specific foam index per BET nitrogen surface area decreases as the surface polarity index increases for both types of ashes. The scatter in the figure may certainly be attributable to not taking into account factors such as total LOI, porosity, accessible surfaces and particle size. Class C ashes have generally lower polar surface fractions than do class F ashes. In fact, this figure also emphasizes how ineffectively the surface area in class C ashes is used, as compared to that in class F ashes. Since micropores are the same in both types of carbons, then the ability to utilize the micropores is what must differ. The fact that the class C ashes are also more porous on the scale of large porosity, as discussed above, would lead one to believe that they should have higher ability to utilize the surface area. This figure also makes clear that the class C ashes have surfaces that are more favorable for sorption than the surfaces of the average class F ashes, because they are less polar. All of these factors together make it surprising how ineffective the class C ashes are, compared to the average class F ashes. This very strongly suggests that it is the accessibility on the scale of the particle diameter that must be the final factor in explaining the differences between ashes. If particles are large, they do not represent available surface on the timescale of the foam index test. This point will be discussed further below.

Class F ash polarities follow the same generic trend as class C ashes. The specific AEA uptake per surface area decreases as the surface polarity index increases. Again, the role of accessibility is expected to be the main factor contributing to the scatter in these results.

6.2 Behavior of Fractions

The previous section has suggested how important accessibility of carbon surface must be in determining AEA uptake capacity in the foam index test. No other measures of porosity and surface area or polarity can otherwise explain the data that were obtained. Consequently, the examination of different size fractions of carbons in fly ash became essential to understanding the nature of the problem.

The fly ashes in our sample bank are highly heterogeneous in terms of particle sizes. Both class C and F ashes exhibit particle sizes in a range from submicron up to 500 micrometers (see Chapter 5, in which the micrographs were presented). It is quite possible that particles exhibiting a large range of sizes, could also exhibit a range of adsorptive properties, associated with size. This would be expected on the basis of surface accessibility arguments alone. In addition, it is not clear that all of the different size carbon particles would necessarily have the same porous and surface properties. For this reason, it was felt important to examine this question in some detail.

As has been discussed previously, the mineral portions of the fly ashes are expected to exhibit similar adsorptive properties, mainly because they are all poor AEA adsorption surfaces. Moreover, differences associated with particle size differences in the mineral portions of the ash are also expected to be minimal. This is because the adsorptive surface is mostly located on the outside of the particles (minerals have an extremely low surface area in small pores), and therefore accessibility and pore structure are not issues.

In previous foam index studies^{6,15,17,18} and in the work presented above, it was concluded that factors besides fly ash surface area, porosity and polarity must play a role in AEA adsorption. It was observed that different particle size fractions had slightly

different AEA adsorption characteristics. Generally a trend of d^{-1} was observed in AEA activity towards fly ashes^{18,20}. In other words, as the particle diameter decreased in an ash fraction, the AEA interaction with particular sample increased. This was not a surprising result in one respect. It is known that smaller particle sizes provide bigger external surfaces per unit mass for AEA adsorption. On the other hand, those earlier results suggested that the internal porosity might play a less important role than had been earlier believed. This might help explain why the attempts at correlating specific foam index with accessibility measures based on carbon porosity have been only partially successful. If the external surface of the particles plays a disproportionate role in adsorption, the role of internal porosity is decreased.

An expanded investigation of the characteristics of different fly ash fractions was thus conducted. The aim of the study was to examine the carbon particle size distributions in both type C and type F fly ashes as well as to investigate the nature of the carbon in each size fraction. As was already clearly established above, the carbon portion of the ash is mainly responsible for AEA uptake.

In order to characterize the adsorptive properties of different size fractions of fly ash a total of nine fly ashes, five class F and four class C samples, have been selected from our sample bank (Table 4.1). The fly ash samples chosen for fractionation are shown in Table 6.2.1, at the end of this chapter.

Fly ashes were mechanically sieved according to the procedure previously described in the experimental section. The usual characterizations, such as LOI, foam index, microscopy, BET surface area and porosity were performed on different size fractions separated from the same parent ash.

Fly ashes exhibit broad particle size distributions. Figures 6.2.1 and 6.2.2 show typical particle size distributions for the class C and class F fly ashes, based upon the sieve separation of the whole ashes. These distributions are plotted to show the percentage mass in each fraction, irrespective of composition (carbon or mineral). The results of Figure 6.2.1 emphasize the fact that most of the class F ash is smaller than about 106 μm in diameter, consistent with what is known about ESP collection.

Figure 6.2.1 shows that there are differences between the relative amounts collected in the particle size fractions $d < 45$ micrometers and $45 < d < 106$ micrometers, from the different class F samples. It should be recalled that these ashes came from entirely different power plants, burning different coals, so the fact that differences do exist is not surprising. Still, the main conclusion is that all of the samples are similar in terms of having little material larger than 106 micrometers in size.

Figure 6.2.2 shows a similar particle size distribution for class C ashes. Again, there are clearly differences in the size distributions of these ashes, but similarity in that the majority of particles are smaller than 106 micrometers in size. Approximately 90 wt.-% of both the class C and class F fly ashes are contained in particles smaller than 106 μm .

The amounts in the smaller fractions of the size distributions were sensitive to subtle differences in the experimental conditions. The same separations, repeated on different days, could show variations of ± 40 wt.-% (relative) in the < 45 μm and 45 to 106 μm cuts. It is believed that this could be attributed to the extent of agglomeration of the finer particles in different experiments (larger particle fractions did not show such variation). Factors such as moisture and electrostatic charging (which would be sensitive

to daily variations in the relative humidity of the air) would influence the agglomeration. The uncertainty introduced by this variation in separations would not be expected to have a significant impact on the general conclusions of this study.

The possible “mis-classification” of particles into the wrong size fractions must thus always be considered a possibility. It should, however, be remembered that very fine surface-adhered particles could not contribute very much to the mass distribution of large size fractions shown in Figures 6.2.1 and 6.2.2. There was not nearly enough such matter observed under the microscope to influence the particle size distribution. What can be influenced is the apparent relative ability of different size fractions to adsorb AEA, since very fine carbon particulate matter can offer both high geometrical surface area and high accessibility. With respect to this it should be kept in mind that the external surface area of the smallest easily observable particles ($0.1\mu\text{m}$) is roughly $50\text{ m}^2/\text{g}$:

$$A = \frac{6}{D\rho} = \frac{6}{0.1 \cdot 10^{-6}(\text{m}) \cdot 1.3 \cdot 10^6(\text{g} / \text{m}^3)} \approx 50 \quad [\text{m}^2/\text{g}] \quad (\text{Eq. 6.2.1})$$

As was observed using optical microscopy (discussed in Chapter 5), some of the fine carbon particles appeared as though they may have been "melted" onto the surface of other bigger particles. Some other particles appeared to have just loosely adhered onto the surface of larger particles, possibly due to electrostatic forces.

The simple LOI test was used in order to determine the carbon content of each separated fly ash fraction. The results are shown in Table 6.2.2. These results clearly show that the larger particle size fly ash fractions always have higher carbon contents than the smaller particle fractions. This conclusion is independent of the class of fly ash.

Our earlier optical microscope and SEM analysis had suggested that fly ash carbon particles are relatively larger in size when compared to fly ash mineral particles. An optical microscopic analysis of the fly ash fractions confirmed that the larger particles in the fly ash are carbon particles.

The contribution (C) of each particle size fraction to the total carbon content of the sample could be calculated from the data of Table 6.2.2 as follows:

$$C = \frac{M \cdot F}{LOI} \quad \text{Eq. (6.2.2)}$$

where M is fractional mass contained in the particular fly ash fraction (wt. %),

F is carbon content for the particular fly ash fraction (wt. %), and

LOI is the overall whole fly ash carbon content (wt. %).

The contributions of the different size fractions to the total carbon content are shown in Table 6.2.3 and in Figures 6.2.3 and 6.2.4.

Though the earlier comparison of fly ash size particle size distributions did not reveal any major differences between class C and class F fly ashes, a similar comparison of carbon size distributions showed differences between the ash types. All the class F fly ashes have most of their carbon in fractions smaller than $180 \mu\text{m}$, though fly ash 24 also had a significant amount of larger carbon particles. In contrast to this, all of the four class C ashes had very large amounts of carbons in large particles (see Figure 6.2.4). It might be concluded that the differences are due mainly to the type of coal from which the ash came, but it could also reflect the particular grinding and firing conditions in use at the different plants using the different coals.

The differences between class F and class C ash carbons were also examined using optical microscopy. The optical microscope images of the $106 < d < 180$ micron size fractions from class F ashes 21 and 22 (Figures 6.2.5 and 6.2.6) showed that the carbon particles in these ashes look quite similar in their size and shape. More minerals could be seen in the image of Figure 6.2.5 relative to that in Figure 6.2.6, due to the lower carbon content for the fly ash 21 sample (see Table 6.2.1). As can be seen from Figures 6.2.5 and 6.2.6, many of the carbon particles were very irregularly shaped. It could be surmised that at the time when the solid reactions were quenched, the carbon was in a final stage of burn-off. There is some adherence of minerals on the carbon particle surface. This mineral coverage on the carbon particles is easily noted in both Figures 6.2.5 and 6.2.6.

The similarities in the morphologies of the class F ashes were not surprising despite the fact that the ashes came from different power plants. Many bituminous coal chars have similar appearances at comparable stages of burn out. In addition, independent of class F ash carbon content, the specific BET areas of carbons in the ashes (per gram of carbon) did not vary much, falling mostly in the range 40-60 m²/g of carbon.

It was also observed that a great many small carbon particles, which should theoretically have passed the 106 micron sieve, were carried on the larger particle size fractions perhaps due to the electrostatic forces present in the ash powder, as noted above. It is, however, abundantly clear from the microscopic images that the overwhelming majority of carbon in these fractions is in the large particles, and thus these must therefore dominate the surface area.

Class C fly ashes 41, 65, 66 and 75 (Figure 6.2.4) show roughly a bimodal distribution of carbon particle sizes. Roughly half the mass is in particles smaller than

180 μm , and half in larger particles. Thus, as has been already discussed Chapter 5, class C ashes contain at least two distinct groups of carbon particles. Optical microscope analysis confirmed this.

Figure 6.2.7 presents an optical microscope image of the class C fly ash 75 fraction of $d < 45$ micron. Little black spots on the image indicate the presence of quite small diameter carbon particles in this fly ash fraction. Most of these carbon particles had a size of a micron and less. Because of the non-uniformity of the sample it was quite difficult to obtain a higher resolution and clearer image. Quite a significant number of carbon particles in class C fly ash are very big in size relative to the carbon particles in class F fly ash. Figure 6.2.8 shows an image of the class C fly ash fraction in the $180 < d < 355$ μm size range. As is already known, no significant amount of pure mineral is found in this fraction. It appears as though most large carbon particles are in the 180-355 μm and > 355 μm cuts. Of course it is clear that these particles must contain a large fraction of mineral, since the LOI for these fractions is only 20 to 25%. As it is known that the parent coals would typically contain only 10-15% by mass of mineral and lose about half their weight during pyrolysis, the large “carbon” particles of Figure 6.2.8 can hardly be regarded as “typical” of unburned fuel. The degree of mineral enrichment in these particles is unexpected. The reasons for this are not clear. It could be reflection of the inherently low reactivity of carbon in high mineral content particles. Alternatively, it might suggest a segregation of these particles, possibly due to density differences and their influence on aerodynamics, into low reactivity zones of the boiler. It is still also possible that segregation during preparation for optical microscopy is an issue, as smaller more dense mineral particles would tend to fall through the larger carbon particles. It

must, however, be remembered that what is being examined in Figure 6.2.8 is already a sieved cut, so there would have to be visible separation of large minerals to the bottom of the sample vial. This is not seen.

Foam index testing was performed on the sieved fly ash fractions. The amount of AEA adsorbed by fly ash is generally correlated with the amount of carbon in the ash^{5,6,8-22}, and the same would be expected of the fractions. There was an interest in establishing whether correlations similar to those presented above would apply for the different size fractions of the same fly ash. It was reasoned that such a correlation with carbon content should be very good for all of the fractions produced from one ash, if all of the fractions had the same physical characteristics. A d^{-1} trend of decreasing foam index with particle size was observed by other researchers^{5,18,20}. Our results of AEA uptake versus particle diameter are shown in Figure 6.2.9. The class F ashes generally follow what looks to be crudely a d^{-1} relationship. This is an important result, in that again it suggests that accessibility to the particle interior is not purely a question of pore size distributions. A generally similar correlation seems to hold for class C ash fractions, though it seems to break down at the largest particle size. The reason for this breakdown is unclear.

There was interest in whether the fractions would allow any better correlation of foam index with LOI than was previously possible. The results of examining these data in this way are shown in Figures 6.2.10, 6.2.11 and 6.2.12. Figures 6.2.10, 6.2.11 and 6.2.12 show that a trend of foam index with LOI is generally observed, but a good correlation is not obtained with either the whole data set or with the fractions of a single fly ash. However, fractionated class C ashes show (Figure 6.2.10) a better correlation of foam index with LOI compared to the class F fly ash samples (Figure 6.2.12). For

example, fractionated fly ashes 41 and 75 show a reasonable correlation between foam index and LOI in the high LOI range, suggesting that the carbons in different size fractions of these ashes must be quite similar in their nature. Figure 6.2.10 also shows a similar slope for the correlations of most class C fly ash samples, indicating that the carbons in the ash fractions were somehow similar in different ashes.

What is notable is the non-zero foam index intercept that is seen for FA 75 and FA 66 (Figure 6.2.10). Since mineral components give zero foam index, it is clear that the lowest LOI fractions, generally from the smallest size cuts, contain carbons which are considerably more active than that in the largest size cuts. This will be discussed below. In addition, as Figure 6.2.11 shows, the FA 65, FA 66 and FA 41 results show that the curves of foam index vs. LOI curve towards to the origin, also suggesting that the high LOI correlation no longer holds as the LOI values fall below 1 wt %. This kind of curvature towards to the origin has also been seen in our earlier work²². It is noted that the results of Figure 6.2.11 have much greater uncertainty than the results of Figure 6.2.10. This is attributable to the considerable difficulties in measuring both LOI and foam index in low LOI samples. Still, it is clear that uncertainties in LOI and foam index cannot explain the curvature towards the origin, noted on Figures 6.2.10 and 6.2.11. This suggests that there are also actual property differences between low and high LOI samples. Again, low and high LOI samples also reflect small and large particle fractions, respectively. Thus the difference in foam index behavior with LOI could, again, reflect a difference related to particle size effects.

The correlation of foam index with LOI is quite poor in the case of class F ashes (Figure 6.2.12). The inability to find a good correlation involving the whole set of ashes

came as no surprise, as already noted above. The failure to see a correlation when using fractions from a single ash was, however, a bit surprising. Within a series of fractions from a single fly ash, some portions of the data suggest a fair correlation (e.g., fly ash 21), but even in cases in which some correlation could be seen, it held over only a portion of the data. Once again, these data confirm our earlier conclusion regarding the inadequacy of LOI alone for predicting the suitability of a particular ash.

It was also earlier concluded that the failure of simple LOI-based characterizations could be partially traced to differences in surface areas of carbons in different ashes. The variation of total ash surface area with LOI is shown in Figure 6.2.13. Present results confirmed the conclusions offered previously. Generally speaking, there are quite distinctly different relationships between surface area and LOI in class C and class F ashes. Class C ashes have significantly higher surface areas for a given value of LOI, compared to the class F ashes (Figure 6.2.13). This has already been discussed.

At this point it should be recalled that the contribution of the inorganic part of the fly ash fractions is relatively small in comparison to the total fly ash BET surface area. This is especially the case for those fly ash samples that have LOI values greater than 2 wt %. The BET surface area for the inorganic part is only about 0.8 m² per gram of mineral.

Figure 6.2.13 shows that several of the fractionated fly ash samples do show a good correlation between BET surface area and LOI, indicating that the carbon in the different fractions varies in size and amount, but not in terms of nitrogen adsorption capacity per unit mass. However class F fly ash 22 did not show a good correlation between surface area and LOI. The absence of a correlation is seen where it might be

least expected - at high LOI values (Figure 6.2.13). At high LOI values, the total ash surface area is clearly dominated by the carbon content of the ash. It would be expected that in this region the clearest correlation of surface area and LOI would emerge. Instead, the relationship between LOI and surface area for FA 22 appears to break down at high LOI. There is a similar trend to be seen in the results for FA 74, though it is not as distinct. The results for FA 24 show low surface areas at high LOI, but the trend with LOI is less clear from this figure.

Re-examining the results as specific carbon surface areas, using Table 6.2.4, confirms that all three of these ashes (FA 22, FA 24, FA 74) show a trend towards lower carbon surface area with increasing particle size. In Table 6.2.4, an entry listed as “not determined” (ND) indicates that the quantity of the sample available for the particular test was too small to be measured reliably (either there was no or very little sample collected for this particular sieve size range).

The carbon BET surface areas of the fly ash fractions in Table 6.2.1 were calculated as is shown in Equation 6.2.3:

$$SA_{\text{carbon}} = \frac{SA_{\text{ash}} - (1 - \frac{LOI}{100}) \cdot SA_{\text{min}}}{\frac{LOI}{100}} \quad (\text{Eq. 6.2.3})$$

where SA_{ash} – BET surface of the whole fly ash sample,

SA_{min} – BET surface of the mineral part of the sample,

SA_{carbon} - BET surface of the fly ash carbon, per gram of carbon.

The data in Table 6.2.4 help to explain why the correlation of absolute BET area with LOI breaks down, even for fractions from a single ash. The reason is that different size fractions sometimes show different specific carbon BET areas. The class C ashes (41, 65, 66 and 75) show consistently smaller specific areas in the smaller size fractions compared to the bigger size fractions of the same ash. In contrast to this it can be seen from Table 6.2.4 that small particle size fractions of class F ashes often have bigger specific BET areas compared to the larger size fractions.

It has been previously suggested that surface area must be considered together with porosity, in order to understand AEA uptake. For porosity calculations, just as for the BET surface area calculations, nitrogen isotherm data obtained on the fly ash fractions were used. The fractionated fly ash carbon porosities are shown in Table 6.2.5.

Dubinin-Radushkevitch (DR) theory²⁵ was applied in order to determine the microporosity of the fly ash carbon. The total specific pore volume at a relative pressure of 0.95 less the DR micro-pore volume gives the total mesoporosity of the particular sample. The total specific pore volume at relative pressure 0.99 less the total specific pore volume at relative pressure 0.95 provides the macroporosity of the sample. Most of the specific BET surface area of the fly ash carbons is contributed by its micropores. The external surface area contribution to the specific BET surface area is usually less than 1 %. For an external surface area of 50 m²/g, the earlier presented calculation suggested that particles of 0.1 μ m diameter are required. Clearly geometrical area is negligible for the large size fractions, but it could offer some contribution in small size fractions in which the low LOI is contributed mainly by small fragments.

Fractionated fly ash carbon porosity analysis showed that as the specific BET area for class C ashes increased with the particle size, the microporosity of the same sample increased as well (Figure 6.2.14). This is to be expected, as microporosity contributes most surface area in these porous solids. The class F ash samples followed the same trend in terms of BET area and microporosity. As the specific BET of the class F ash fractions decreased the microporosity of the same sample decreased as well (see Table 6.2.5). Thus it appears as though when there is a trend towards lower surface areas with increasing particle size, this is associated with a trend towards lower microporosity with increasing size. There is however, no general trend of microporosity with particle size. In some class F ashes, microporosity decreases with size. The implication is that in these samples the larger particles had perhaps not been activated by combustion. Microporosity is often opened up during burn out. The difference between different class F ashes can thus perhaps be attributed to differences in combustion conditions in the boiler, leading to the different burnout histories. Again it should be recalled that large class F size fractions have high LOI values, but contain only a very small fraction of total unburned carbon. Thus such unactivated large particles are quite rare.

The class C ashes present a different picture. Optical microscope imaging of the class C ashes (Figures 6.2.7 and 6.2.8) provided some clues to the origin of the differences observed in the surface areas of different size fractions of these ashes. This examination revealed that while the larger fractions of the class C ashes contain a large amount of what is known (from separate analysis) to be microporous unburned char (Figure 6.2.8), the smallest fractions contained very few distinct char particles near the upper size limit (Figure 6.2.7). In these smallest fractions, the carbon was instead widely

distributed as very fine particles, much smaller than the sieve size would suggest. These particles were observed both as free particles and adhering to the surface of mineral particles. These carbon particles ranged in size from the order of micrometers down to hundredths of micrometers (essentially down to the ability of the microscope to resolve them). These fine particles appeared to be more like char fragments, as opposed to the soot particulate that is sometimes also observed in ashes.

In the class C ashes the smaller fractions contained much more macroporous and less microporous carbon than did the larger fractions. For example, the class C fly ash 75 small particle fraction ($d < 45$ micron) is mostly meso- and macroporous (0.509 cc/g-carbon) compared to the $180 < d < 355$ micrometer size fraction which has the largest amount of its porosity in micropores. This could imply that during the process of burnout and fragmentation in the boiler, there is a loss of microporous volume. Alternatively, it is possible that the fragments in the small size fractions have survived because they were not microporous (and therefore less reactive, for some reason, such as not offering as much reactive surface).

The results in Table 6.2.5 provide a clue as to why smaller particle class C ash samples had high AEA uptake compared to the bigger particle size fractions. It was earlier hypothesized²² that the small micropores are not accessible to the relatively large AEA molecules. Thus the existence of microporous surface area is not adequate to assure a high capacity for AEA. It was hypothesized that the meso- and macropores, present in the smaller size samples provide greater accessibility to AEA-s. On the other hand, high surface area is important, in terms of providing adsorption sites. Still, the explanation in terms of the quantities reported in Table 6.2.5 is incomplete. For example, there is only a

modest difference in total surface area between the $106 < d < 180 \mu\text{m}$ and $180 < d < 355 \mu\text{m}$ fractions of FA 66 (374 and $470 \text{ m}^2/\text{g-carbon}$). Additionally, there is almost no difference between both fractions' meso- plus macroporosity. As reported in Table 6.2.5 the above larger fraction of FA 66 has a total meso- and macroporosity of $0.146 \text{ cc/g-carbon}$ and the smaller fraction $0.181 \text{ cc/g-carbon}$. However, there is a large difference in the specific foam index of the two fractions (2.40 and 0.97 ml/g-carbon respectively). Similarly, the relatively modest meso- plus macropore volume in the $45 < d < 106 \mu\text{m}$ fraction of FA 75, combined with its low surface area, appears inconsistent with the high specific foam index of this sample in comparison with the $180 < d < 355 \mu\text{m}$ fraction.

Results in Figure 6.2.15 and Table 6.2.6 clearly suggest that smaller particle size fractions adsorb AEAs more effectively than large particle size fraction carbon. The two smallest fractions ($d < 45 \mu\text{m}$ and $45 < d < 106 \mu\text{m}$) are responsible for 90% of the total specific foam index value. As seen from Figure 6.2.15 this result is independent of the type of ash carbon. In both class C and class F fly ashes, it is the smallest particles that contribute most to the foam index, and this suggests that AEA interactions in ashes occur mostly with small carbon particles rather than big microporous carbon particles.

It is unlikely that surface polarity can be very different for different size fractions of the same ash. This is because it would not be expected that the different size fractions would see much different chemical environments, as would be required. Thus it is believed that the key in this series of experiments is the accessibility of the carbon surface to AEA. Accessibility cannot be reliably characterized by meso-plus macroporosity alone, but must somehow take into account particle size. We believe that the existence of network of large pores is a necessary, but not sufficient, criterion for

determining whether the surface area of the carbon can be reached by the AEA solution. The foam index test is a dynamic test. Even if at long times mesoporosity can be penetrated by liquid solution, this might not happen on the time scale of the foam index test. Our previously presented results already showed that the time scale of the test has an effect on the values obtained.

This is presumably why the finest particles show highest uptake of AEA. They have the highest fraction available surface area near their geometric surfaces. Recall that a $1\mu\text{m}$ diameter particle has a geometrical (external) surface area of about $5\text{ m}^2/\text{g}$, all of which is accessible. Considering also porosity within an arbitrary $1\mu\text{m}$ distance of the particle surface, obviously a $1\mu\text{m}$ diameter or smaller particle would have 100% of its volume at that distance from the surface, whereas a $180\mu\text{m}$ particle would have only 1.7% of its volume at that distance. The existence of macropores and mesopores in the interior of a $180\mu\text{m}$ (or any) large particles cannot alone assure that a large fraction of particle volume has access to the liquid.

Class F fractionated fly ash samples show relatively low porosity values in comparison to the fractionated class C ashes (Table 6.2.5). Despite this, Table 6.2.4 shows that they have comparable specific foam indices to those for class C ashes. This confirms that neither surface area nor porosity alone can predict AEA capacity in foam index tests. It can also be noted from Table 6.2.5 how class F carbon porosities do not follow any specific trend with fraction size, but instead vary in a narrow range. The porosities of the carbon particles in different fractions are rather similar. Similarity in porosity (mostly at the micropore level) suggests similarity in BET specific surface area for the different size fractions, which is confirmed (see Tables 6.2.4 and 6.2.5).

The BET surface area of FA 22 decreases with an increase in particle size because both microporosity and mesoporosity decrease with an increase in particle size (Tables 6.2.4 and 6.2.5). The other class F ashes show less clear trends, though both FA 74 and FA 24 show lowest microporosity in the largest size fraction.

Foam index data and specific foam index data were both presented in Table 6.2.4. The specific foam index was calculated from the whole sample foam index, taking into account the small contribution of the mineral portion of the ash, and dividing the part of the foam index attributable to carbon alone by the LOI value. The specific foam index data are plotted as a function of carbon BET area for both class F and class C ashes (Figure 6.2.16). Since both specific foam index and carbon BET area are functions of the carbon portion of the ash alone, to the extent that carbon surface dominates AEA adsorption, a good correlation would be expected. Consistent with the above discussion, the actual correlation was only fair to poor. The class F ashes showed the expected trend, though with a fair amount of scatter. The fact that the largest particles showed lower foam index values must be taken as further evidence of the effect that has been discussed – that of transport limitations on the particle level. Only FA 26 appeared to not follow the trend, for reasons that are not clear yet.

The class C ashes provide results that are also suggestive of transport limitations. They show no clear trend with surface area or even a trend with surface area opposite that which would be expected. The unusually high specific foam indices exhibited by the low surface area fractions of fly ashes 75 and 66 again suggest very strongly that these fractions have high accessibility which more than compensates for low surface area. These are the fine particle fraction samples with high external surface area and porosity

near the surface. The trend in the other class C fly ashes, 65 and 41, are not as distinct, but are in the same direction. Crudely speaking, the class C ash fractions therefore show behavior that suggests a mixture of two distinct populations of carbon in the ash. There are very large, highly microporous char particles that are seemingly quite far from final burnout. These have only a modest tendency to adsorb AEA (note that their specific foam indices are comparable to those of class F carbons, despite their much higher BET surface areas, see Figure 6.2.15). There is a second fraction of carbon that appears to be the product of fragmentation of larger particles, and which are extremely effective at adsorbing AEA-s, due to the high availability of the surface.

6.3 The Dynamics of Sorption on Fly Ash

The results obtained before strongly suggested that foam index test had significant mass transfer limitations which could play a key role in AEA uptake. In addition, it was observed in our microscopy analysis that most of the carbon particles in ashes (mostly in class C) were heavily covered with minerals. There is still uncertainty about whether these mineral particles were adhering or whether these minerals were fused onto the carbon surface. Nitrogen gas adsorption analysis supports the idea that these carbons had high active internal surface. This is a clear indication that the pores in carbon particles were accessible despite of their heavy coverage with minerals. However our foam index results suggest that most of these carbons were not active in adsorbing AEA molecules. As was discussed earlier, one reason could be the size of the AEA molecule, which cannot penetrate into relatively small micropores on a foam index test time scale. As discussed in detail in Chapters 3 and 4, the foam index test is characterized by a relatively

short time scale, of up to 10 minutes. A previous study¹⁸ has examined the influence of time on the results of the foam index test. In that work a spectrophotometric method (UV radiation absorption by the AEA solution) was used to track Darex II adsorption onto selected fly ash samples. A Perkin Elmer UV/VIS Spectrophotometer was used to track the absorption in time. The experimental procedure is given in more detail in Sabanegh¹⁸. As the results showed (Table 6.3.1, and Figure 6.3.1) time had a significant effect on AEA adsorption. For example, it took approximately 1 hour to saturate a high carbon (LOI 74 wt.%)¹⁸ fly ash sample with AEA. The results in Figure 6.3.1 strongly suggest that the rate of adsorption of AEA onto carbon surfaces is limited by diffusion into small carbon pores. These tests involved using the same amount of AEA, fly ash and water as in the actual foam index test. This implied that when the apparent end point was reached in the foam index test, the AEA was still actively adsorbing onto the fly ash particles. According to these results, it is hard to believe that our standard foam index test was “complete” at its nominal endpoint. This is the reason why often, internal porosity and surface area could not play a role in AEA uptake. These results support the model of the phenomena given in section 6.2, which suggested that small carbon particles play an important role in AEA uptake. The relatively large carbon particles are not accessible on the foam index test time scale.

The results in Figure 6.3.1 also confirmed that very little AEA is adsorbed by the fly ash mineral in the same time scale one hour.

TABLES

Table 6.2.1. Fly ashes selected for fractionation.

Sample	Type	LOI	Remarks
No.		(mass %)	
FA21	class F	6.1	NEP – Brayton Point
FA22	class F	33.6	NEP – Salem Harbor ash, unprocessed
FA24	class F	2.7	AEP – Columbus, Silo #2, Unit #1, from Eastern Bituminous, “good” ash
FA26	class F	4.0	AEP- Columbus Mountaineer Plant, Silo #2
FA74	class F	9.8	Sample from Peter Calvert on 08-04-99. (LOI ~10%, NH ₃ ~200 ppm)
FA41	class C	1.1	Welsh Power Plant, Texas, 245713
FA65	class C	0.74	Dairyland Power, Wisconsin utility, Powder River Basin - worst
FA66	class C	0.92	Dairyland Power, Wisconsin utility, Powder River Basin - better
FA75	class C	1.3	Dairyland Power Cooperative, JPM Station, on 9-29-99

Table 6.2.2 LOI values for fly ash fractions.

Sample	Fly ash type	LOI [wt %]	Sample	Fly ash type	LOI [wt.%]
<i>FA21, d<45µm</i>	class F	3.41	<i>FA24, d<45µm</i>	class F	1.31
FA21,45µm<d<106µm	class F	7.24	FA24,45µm<d<106µm	class F	2.45
FA21,106µm<d<180µm	class F	13.79	FA24,106µm<d<180µm	class F	6.91
FA21,180µm<d<355µm	class F	19.38	FA24,180µm<d<355µm	class F	28.93
FA21, d>355µm	class F	N/D	FA24, d>355µm	class F	62.25
FA22,d<45µm	class F	18.15	FA26,d<45µm	class F	1.87
FA22,45µm<d<106µm	class F	40.96	FA26,45µm<d<106µm	class F	4.23
FA22,106µm<d<180µm	class F	50.33	FA26,106µm<d<180µm	class F	8.27
FA22,180µm<d<355µm	class F	67.31	FA26,180µm<d<355µm	class F	25.77
FA22,d>355µm	class F	N/D	FA26,d>355µm	class F	N/D
FA74, d<45µm	class F	4.55	FA41,d<45µm	class C	0.79
FA74,45µm<d<106µm	class F	13.85	FA41,45µm<d<106µm	class C	0.68
FA74,106µm<d<180µm	class F	24.99	FA41,106µm<d<180µm	class C	1.39
FA74,180µm<d<355µm	class F	46.01	FA41,180µm<d<355µm	class C	12.79
FA74,d>355µm	class F	50.2	FA41,d>355µm	class C	37.84
FA65, d<45µm	class C	0.42	FA66,d<45µm	class C	0.44
FA65,45µm<d<106µm	class C	0.35	FA66,45µm<d<106µm	class C	0.53
FA65,106µm<d<180µm	class C	0.85	FA66,106µm<d<180µm	class C	1.76
FA65,180µm<d<355µm	class C	10.03	FA66,180µm<d<355µm	class C	9.91
FA65,d>355µm	class C	33.69	FA66,d>355µm	class C	19.53
FA75, d<45µm	class C	0.65	FA75,180µm<d<355µm	class C	16.91
FA75,45µm<d<106µm	class C	0.68	FA75,d>355µm	class C	44.97
FA75,106µm<d<180µm	class C	2.72			

Table 6.2.3 Contributions of the different size fractions to the carbon contents of the whole ashes.

Ash Fractions	FA22 (class F)	FA24 (class F)	FA21 (class F)	FA26 (class F)	FA74 (class F)
	Carbon [wt %]	Carbon [wt %]	Carbon [wt %]	Carbon [wt %]	Carbon [wt %]
d<45 µm	16.9	26.5	26.6	22.5	29.8
45µm<d<106µm	60.0	30.3	56.7	38.5	33.82
106µm<d<180µm	21.8	18.9	14.6	31.6	26.46
180µm<d<355µm	1.3	8.5	2.0	6.8	9.3
d>355µm	0	12.4	0	0	0.46
Total carbon accounted for	100.0	96.6	100.0	99.4	99.9
Ash Fractions	FA41 (class C)	FA65 (class C)	FA66 (class C)	FA75 (class C)	
	Carbon wt %	Carbon wt %	Carbon wt %	Carbon wt %	
d<45 µm	23.4	29.54	31.21	14.79	
45µm<d<106µm	24.4	11.76	17.05	21.02	
106µm<d<180µm	6.8	9.39	8.16	10.08	
180µm<d<355µm	13.0	22.19	23.43	24.09	
d>355µm	33.1	31.87	19.92	30.19	
Total carbon accounted for	100.7	104.7	99.8	100.2	

Table 6.2.4 LOI, foam index, specific foam index and BET surface areas for fractionated fly ash samples.

Sample	Type	LOI	Foam index	Specific Foam Index	BET Surface Area	BET Surface Area
		w-%	ml/2g ash	ml/g carbon	m ² /g ash	m ² /g carbon
<i>FA21, d<45µm</i>	F	3.4	0.222	3.25	2.3	48
FA21,45<d<106	F	7.2	0.427	2.95	4.2	49
FA21,106<d<180	F	13.8	0.820	2.97	8.2	55
FA21,180<d<355	F	19.4	0.281	0.72	10.9	53
FA22,d<45µm	F	18.1	1.082	2.98	14.2	75
FA22,45µm<d<106µm	F	41.0	1.55	1.89	22.4	54
FA22,106µm<d<180µm	F	50.3	1	0.99	21.4	42
FA22,180µm<d<355µm	F	67.3	0.548	0.41	19.3	28
FA24, d<45µm	F	1.3	0.045	1.72	1.23	35
FA24,45<d<106	F	2.5	0.045	0.92	1.62	35
FA24,106µm<d<180µm	F	6.9	0.105	0.76	3.16	35
FA24,180µm<d<355µm	F	28.9	0.105	0.18	9.67	32
FA24,d>355µm	F	62.3	0.093	0.08	16.72	26
FA26, d<45µm	F	1.9	0.073	0.87	1.2	23
FA26,45<d<106	F	4.2	0.125	0.75	2.0	28
FA26,106µm<d<180µm	F	8.3	0.230	0.45	3.6	35
FA26,180µm<d<355µm	F	25.8	0.072	1.07	8.1	29
FA74, d<45µm	F	4.6	0.192	2.11	3.7	65
FA74,45<d<106	F	13.9	0.352	1.27	9.25	62
FA74,106µm<d<180µm	F	25.0	0.623	1.25	14.66	56
FA74,180µm<d<355µm	F	46.0	0.467	0.51	21.74	46
FA74,d>355µm	F	50.2	N/D	N/D	14.91	29
FA41,d<45µm	C	0.8	0.027	1.69	1.9	166
FA41,45µm<d<106µm	C	0.7	0.020	1.47	1.9	137
FA41,106µm<d<180µm	C	1.4	0.033	1.20	5.5	337
FA41,180µm<d<355µm	C	12.8	0.171	0.67	54.0	416
FA41,d>355µm	C	37.8	ND	ND	ND	ND
FA65, d<45µm	C	0.4	0.023	2.77	1.42	153
FA65,45<d<106	C	0.4	0.015	2.19	1.43	182
FA65,106µm<d<180µm	C	0.9	0.031	1.82	3.12	277
FA65,180µm<d<355µm	C	10.0	0.164	0.82	32.65	318
FA65,d>355µm	C	33.7	1.297	1.93	104.72	309
FA66, d<45µm	C	0.4	0.069	7.84	2.05	287
FA66,45<d<106	C	0.5	0.084	7.96	2.03	234
FA66,106µm<d<180µm	C	1.8	0.084	2.40	7.36	374
FA66,180µm<d<355µm	C	9.9	0.192	0.97	47.33	470
FA66,d>355µm	C	19.5	N/D	N/D	89.07	453
FA75, d<45µm	C	0.6	0.092	7.08	2.3	225

FA75,45<d<106	C	0.7	0.078	5.75	2.3	230
FA75,106<d<180	C	2.7	0.168	3.10	11.6	399
FA75,180<d<355	C	16.9	0.753	2.23	77.6	455
FA75,d>355µm	C	45.0	ND	ND	ND	ND

Table 6.2.5 BET surface area, micro-, meso-, macro- and total porosities for fractionated fly ashes.

Sample	Type	Micropore Vol.	Mesopore Vol.	Macropore Vol.	Total pore Vol.	BET Surf.Area
		cc/g-Carbon	cc/g-Carbon	cc/g-Carbon	cc/g-Carbon	m ² /g-Carbon
FA21, d<45µm	F	0.019	0.03	0.027	0.076	48
FA21,45<d<106	F	0.018	0.039	0.041	0.098	49
FA21,106<d<180	F	0.021	0.042	0.025	0.088	55
FA21,180<d<355	F	0.019	0.047	0.033	0.099	53
FA22,d<45µm	F	0.029	0.027	0.012	0.068	75
FA22,45µm<d<106µm	F	0.022	0.026	0.011	0.059	54
FA22,106µm<d<180µm	F	0.016	0.02	0.012	0.048	42
FA22,180µm<d<355µm	F	0.011	0.016	0.014	0.041	28
FA24, d<45µm	F	0.014	0.009	0	0.023	35
FA24,45<d<106	F	0.013	0.014	0	0.027	35
FA24,106<d<180	F	0.015	0.026	0.0045	0.0455	35
FA24,180<d<355	F	0.012	0.022	0.0127	0.0467	32
FA24,d>355µm	F	0.009	0.02	0.0128	0.0418	26
FA26, d<45µm	F	0.008	0.008	0	0.016	23
FA26,45<d<106	F	0.018	0.025	0	0.043	28
FA26,106<d<180	F	0.012	0.026	0.0094	0.0474	35
FA26,180<d<355	F	0.011	0.023	0.0123	0.0463	29
FA74, d<45µm	F	0.025	0.028	0	0.053	65
FA74,45<d<106	F	0.024	0.038	0.0135	0.0755	62
FA74,106<d<180	F	0.02	0.039	0.0191	0.0781	56
FA74,180<d<355	F	0.018	0.032	0.0172	0.0672	46
FA74,d>355µm	F	0.01	0.024	0.019	0.053	29
FA41,d<45µm	C	0.049	0.118	0.317	0.484	166
FA41,45µm<d<106µm	C	0.061	0.137	0.416	0.614	137
FA41,106µm<d<180µm	C	0.139	0.142	0.153	0.434	337
FA41,180µm<d<355µm	C	0.184	0.116	0.027	0.327	416
FA65, d<45µm	C	0.066	0.123	0.4493	0.6383	153
FA65,45<d<106	C	0.068	0.098	0.2465	0.4125	182
FA65,106<d<180	C	0.11	0.116	0.1223	0.3483	277
FA65,180<d<355	C	0.089	0.077	0.0242	0.1902	318
FA65,d>355µm	C	0.133	0.089	0.026	0.248	309
FA66, d<45µm	C	0.103	0.22	0.5552	0.8782	287
FA66,45<d<106	C	0.089	0.149	0.2744	0.5124	234
FA66,106<d<180	C	0.151	0.137	0.0087	0.2967	374
FA66,180<d<355	C	0.199	0.143	0.0383	0.3803	470
FA66,d>355µm	C	0.199	0.111	0.0238	0.3338	453
FA75, d<45µm	C	0.093	0.182	0.327	0.602	225
FA75,45<d<106	C	0.095	0.108	0.07	0.273	230
FA75,106<d<180	C	0.163	0.154	0.113	0.43	399
FA75,180<d<355	C	0.249	0.174	0.044	0.467	455

Table 6.2.6 Specific foam index distribution between fractions.

	Specific Foam indexes [ml/g-carbon]				
Sample	FA21	FA22	FA24	FA26	FA74
Parent ash	2.48	1.79	0.48	0.66	2.49
d<45µm	0.86	0.50	0.46	0.20	0.63
45<d<106µm	1.67	1.13	0.28	0.29	0.43
106<d<180µm	0.43	0.22	0.14	0.14	0.33
180<d<355µm	0.01	0.01	0.02	0.07	0.05
d>355µm			0.01		
Sum of all fractions	2.99	1.86	0.90	0.70	1.43
	FA65	FA66	FA75	FA41	
Parent ash	5.46	4.40	3.68	0.50	
d<45µm	0.82	2.45	1.05	0.40	
45<d<106µm	0.26	1.36	1.21	0.36	
106<d<180µm	0.17	0.20	0.31	0.08	
180<d<355µm	0.18	0.23	0.54	0.09	
d>355µm	0.61	0.38	0.58	0.00	
Sum of all fractions	2.04	4.61	3.69	0.92	

Table 6.3.1 Fraction absorbed by UV /VIS Perkin Elmer spectrophotometer per mg of carbon versus time¹⁸.

Sample	Time [minutes]	Absorbance	Relative Absorbance	Fraction Adsorbed per mg of carbon
Class F ash 150<d<212μm, with LOI 74 wt%	0	2.022	1	0
	1	1.877	0.9283	0.00097
	15	1.535	0.7591	0.00326
	30	1.243	0.6147	0.00521
	60	0.724	0.3581	0.00867
Class F ash 38<d<45μm, with LOI 80 wt%	0	1.897	1	0
	1	1.713	0.9030	0.00121
	15	1.457	0.7681	0.00289
	30	1.216	0.6410	0.00449
	60	0.923	0.4855	0.00642
Carbon free class F Mineral, 150<d<212μm	0	2.001	1	0
	1	1.912	0.9555	0.0006
	15	1.72	0.8595	0.00189
	30	1.654	0.8266	0.00234
	60	1.601	0.8000	0.0027

FIGURES

Figure 6.1.1 BET surface areas versus LOI for all ashes from our sample bank.

Figure 6.1.2 Foam index as a function of the total BET surface area of the ash (all ashes in the sample bank).

Figure 6.1.3 Foam index correlation with total BET surface area, low BET surface area ashes (mainly low LOI ashes in the sample bank).

Figure 6.1.4 Correlation between foam index and surface area for class C and class F type ashes.

Figure 6.1.5 Specific foam index as a function of specific BET surface area for class F and class C fly ash carbons.

Figure 6.1.6 Typical nitrogen adsorption and desorption isotherms for class C and F ashes.

Figure 6.1.7 Results of the fly ash pore size distributions in class C and class F ash determined according to the Barret, Joyner and Halenda (BJH) method⁷¹.

Figure 6.1.8 Fly ash carbon specific foam index as a function of meso- and macro-porosity for all class C ashes.

Figure 6.1.9 Specific foam index as a function of meso- and macro-porosity for class F ash carbons.

Figure 6.1.10 Specific foam index versus mesoporosity for class C ash carbons in our sample bank.

Figure 6.1.11 BET surface area versus microporosity for class C ash carbons with varying specific foam indexes.

Figure 6.1.12 BET surface area versus mesoporosity for class C ashes with varying specific foam indexes.

Figure 6.1.13 A correlation between specific BET surface areas and meso plus macroporosities for class C ashes with varying specific foam indexes.

Figure 6.1.14 BET surface area versus meso- and macropores for class F fly ashes with varying specific foam indexes.

Figure 6.1.15 Specific foam index and BET nitrogen specific surface area ratio versus specific polarity index. Specific polarity index is defined as a ratio of the carbon polar surface area and BET nitrogen specific surface area.

Figure 6.2.1 Class F fly ash particle size distribution. Loss refers to material unaccounted for after sieving. Diameters (d) are in μm .

Figure 6.2.2 Class C fly ash particle size distribution. Loss refers to material unaccounted for after sieving. Diameters (d) are in μm .

Figure 6.2.3 Carbon particle size distribution in class F fly ashes. Diameters (d) are in μm .

Figure 6.2.4 Carbon particle size distribution in class C fly ashes. Diameters (d) are in μm .

Figure 6.2.5 Optical microscope image of the class F fly ash 21, fraction $106 < d < 180$ μm .

Figure 6.2.6 Optical microscope image of class F fly ash 22, fraction $106 < d < 180 \mu\text{m}$.

Figure 6.2.7 Optical microscope image of the class C fly ash 75 fraction $d < 45$ micron.

0 80 160 240 320 400 microns

Figure 6.2.8 Optical microscope image of the class C fly ash 75 fraction $180 < d < 355$ microns.

Figure 6.2.9 A correlation between specific foam index versus particle diameter for class C and F fly ashes.

Figure 6.2.10 Foam Index versus LOI for fractionated class C fly ashes.

Figure 6.2.11 Foam Index versus LOI for fractionated class C fly ashes, low LOI corner.

Figure 6.2.12 Foam Index versus LOI for fractionated class F fly ashes.

Figure 6.2.13 Ash BET surface area versus carbon content, for different fly ash fractions. The solid line shows a general trend for class C ashes and the dashed line for class F ashes.

Figure 6.2.14 Fly ash carbon microporosity vs. specific BET surface area for class C ash fractions.

Figure 6.2.15 Fractional specific foam index distribution between different fractions.

Figure 6.2.16 Specific foam index vs. fly ash carbon BET surface area for fractionated fly ashes.

Figure 6.3.1 Fraction absorbed by UV /VIS Perkin Elmer spectrophotometer per mg of carbon versus time¹⁸.

7.0 EFFECT OF OZONATION ON FLY ASH ACTIVITY TOWARDS SURFACTANTS

Fly ash can serve as an inexpensive artificial pozzolan in concrete mixtures. Its ability to react with calcium hydroxide supports a formation of a strong cementitious matrix. Carbon in fly ash has been repeatedly reported^{6,14,18,20,22} to be a problematic component, as it is involved in surfactant uptakes. The basis for this has been explored in the earlier chapters. Now attention is turned to what may be done to mitigate the harmful effects of the carbon. Bearing in mind that one of the very attractive features of use of fly ash in concrete is the low cost of the fly ash additive. This means that whatever is done towards mitigation of the problem cannot be very costly.

As noted above, even small amounts of carbon in ash (a few percent) can be harmful for concrete mixtures^{14,18,20,22}. As was shown earlier, fly ash carbon surface chemistry plays a key role in AEA uptake by ashes. The more polar the surface, the less AEA is adsorbed. In this chapter, it will be shown that a certain type of selective oxidation has a significant, beneficial effect on AEA adsorption. Other results have been presented in previous chapters, showing that other types of oxidations also have a beneficial effect. The accumulated suite of results will be examined in an effort to resolve the apparent controversy as regards effects of surface polarity.

7.1 Relevant Previous Studies in Surface Oxidation Chemistry

The role of the surface chemistry vis-a-vis AEA uptake was examined in this research by deliberately oxidizing the fly ash carbons. Clearly fly ash surface treatment with oxygen has an impact on AEA uptake in the foam index test (see Tables 5.4.2, 6.3.1). Generally speaking, the more severe the surface treatment, the greater the decrease

in the foam index value. The effect of surface oxidation was also investigated by Hachmann et al.²¹. In that work, sample surfaces were treated using air oxidation at about 350° - 450°C. The results clearly suggested that the introduction of the surface oxides significantly reduced AEA adsorption without consuming any measurable amount of carbon. Hachmann et al.²¹ also measured the impact of removing surface oxides, on the results of the foam index test. Oxidized samples were treated in inert gas at about 900°C in order to remove most or all of the oxide groups from the carbon surface. As a result of this treatment, the AEA uptake increased back to same levels as before oxidative surface treatment. It was concluded that surface chemistry, involving oxide groups, must play a role in AEA uptake.

Gao et al.,⁵ investigated the impact of the carbon black surface treatment on surfactant adsorptivity. Treated carbon blacks had slightly smaller AEA uptake relative to the non-treated samples⁵ again supporting the idea that oxidized surfaces tend to adsorb less AEA, relative to non-oxidized surfaces. They also showed that the surface area of the treated samples did not change, supporting the idea that only surface chemistry was responsible for the smaller uptakes of AEA.

All these investigations strongly suggested that the non-polar portion of the sample is problematic in the surfactant adsorption test. The addition of oxide groups to a carbon surface is normally associated with changes in the polarity of the surface. By making the surfaces more polar, the strong thermodynamic driving force for adsorption of the non-polar tails of the surfactants onto the non-polar carbons would be reduced. Any surface treatment by oxygen has been observed to have significant effect on the

foam index test value. The AEA uptake following treatment was dependent on the sample mass used in the test, the oxidizer concentration and type, and the total treatment time.

There are many techniques available for carbon surface oxidation. Some of these techniques involve wet treatment of the surfaces, some of them dry treatment. One example of wet treatment, oxidation in hydrogen peroxide solution, was presented above. Wet surface treatment is not practical for commercial fly ash carbon surface treatment. One problem with wet surface treatment is the possibility of self-cementation of the ash or a loss of pozzolanic activity. Also, ash users generally prefer to receive a dry powder product. It is quite expensive to re-dry wet-treated ashes.

One dry treatment method was also already discussed above, namely, surface oxidation in air at 300 - 400°C. Oxygen treatment at such high temperatures does not provide any practical advantage over a combustion process for total carbon removal, since the temperatures required to burn off all of the carbon are only modestly higher. A commercial carbon burnoff process is presently being tested by Progress Materials Company, but there are serious concerns regarding the complexity and economics of such a process. Thus, the air oxidation method was used in this study only as a laboratory method for preparing ashes with surface oxides.

Fly ash ozonation is another dry method suggested by Gao et al.⁷⁴. The method involves reacting fly ash surface with ozone gas at ambient temperatures. It is clear that O_3 is a more powerful oxidant than air, as it can attack carbon surfaces in ash at ambient temperature. There have been many other investigations of ozone treatment of carbonaceous samples.

The impact of ozonation on carbon fibers has been studied by Xu et al.⁷⁶, by Fu et al.,^{77,79} and Rakitskaya et al.⁷⁸. The primary goal of these investigations was to find ways to improve surface adhesion of carbons in reinforced cementitious mixtures. These workers reported that ozone treated carbon significantly improved the properties of carbon-reinforced cements or concretes, specifically their tensile strengths, modulus and ductility parameters. The fiber ozonation experiments involved^{77,79} an exposure of the fibers to 0.3-0.6 vol.% O₃ gas (in air) for 10 minutes at 160° C. The results clearly showed that the surfaces that were treated with ozone had increased surface oxygen concentrations. These workers also reported a change in surface oxygen functionalities from C-O to C=O^{77,79}. These newly formed oxygen functionalities on the carbon surface effectively improved the wettability of the carbon fiber by water (they made the carbon more hydrophilic). A more hydrophilic sample has slightly smaller contact angle with water. The increased wettability was believed to lead to increased tensile strength, modulus and ductility by improving the fiber-matrix bond.

Another carbon fiber study⁷⁸ focused on ozone destruction kinetics. The results suggested that the ozone decomposition rate at low ozone concentration (less 0.5 vol.%) proceeds via a catalytic pathway, whereas at higher concentrations ozone-surface oxygen group interactions must determine the rate⁷⁸.

The characteristics of oxygen plasma-treated carbon black was investigated by the Cascarini de Torre et al.⁸⁰. Sterling FT carbon black was oxidized in a cool oxygen plasma to various (6-84%) degrees of burn-off. Basic nitrogen BET surface area and standard SEM analyses were performed. In addition, the water contact angles of the surfaces were measured. The results of this study showed that there were neither

significant morphology changes (via SEM analysis) nor surface area changes⁸⁰ in the treated carbon black samples. Similarly with other surface treated carbon materials, the contact angles of carbon black with water were reported to decrease⁸⁰ already at low degrees of burnoff. The major surface functionalities⁸⁰ detected by C1s XPS spectra were C=O, O-C-O and O-C=O.

Magne et al.⁸² investigated ozone treated crystalline graphite. This research mainly focused on the determination of the surface functionalities created and destroyed by ozone treatment. It was reported that most of the ozone was chemisorbed on the graphite surfaces without a-priori dissociation. After this, these complexes decomposed to give new surface complexes below 400°C. Oxygen release and the usual graphite-oxygen complexes were detected following decomposition of the ozone-carbon complexes.

Interaction of the ozone with charcoals was investigated by Deitz et al.⁸¹. This research mostly focused on the study of the reaction mechanism of the ozone-charcoal reaction at ambient temperatures. Reaction of ozone with the charcoal surface was reported to increase the weight of the sample. Catalytic decomposition of the ozone by the charcoal was not observed. Simple BET surface area analysis revealed changes in surface area following ozonation.

Another kinetic study on the reaction of irregular agglomerate structure soot (aerosol) with ozone was conducted by Kamm et al.⁷⁵. Ozone did initially decompose relatively quickly on the carbon aerosol, followed by a much slower catalytic decomposition, which ceased after a characteristic time of 12 hours.

7.2 Ozone Treatment of Fly Ashes

The most recent study of ozone treatment of fly ash surfaces was performed by Gao et al.⁷⁴. The results of that reaction study were combined with the normal analyses of this present study, in order to gain a better understanding of the effects of ozone treatment.

While the actual ozonation treatment of the samples was performed by others in this laboratory, the characterization of the products was the subject of the work described here.

Figure 7.2.1. shows a sketch of the laboratory apparatus used for ash ozonation in these experiments. Compressed air was introduced to the small or large capacity ozone generator (500 ppm to 2 vol.% output ozone concentration) and passed upward through the fixed beds of ash samples (generally 50-200g). Both class C and class F fly ashes were examined in these experiments. The ozone-ash contact time was varied from about 1 min to 20 hours. The outlet ozone concentration was monitored in real time, using an ozone analyzer. Any ozone left after ash ozonation was destroyed in a device designed for this purpose. After the treatment, ash samples were removed from the reactor and their activity towards AEA (Darex II) adsorption measured. Details of the simple titration procedure for measuring the AEA uptake were given previously.

The results of the study (Figures 7.2.2 and 7.2.3) clearly show the beneficial effect of the ash surface treatment with ozone. These two figures show the same data set expressed on a total ash mass basis and on a carbon mass basis, respectively. Depending on ozone concentration, bed mass and contact time, the fly ashes had slightly to significantly smaller activity for AEA uptake. The results in Figure 7.2.2 suggest that the

AEA uptake decreased by a factor of two or more, very near the start of the ozonation. Sharp reductions in surfactant adsorptivity were observed at between 0-3 gm of ozone fed, per kg-ash.

In addition, the ozone exit concentration was monitored while the ozonation experiments were performed. These monitoring results showed that depending on the ozone inlet concentration, flow rate and ash bed mass, the ozone outlet concentration was initially zero, followed by a rapid asymptotic rise to the ozone inlet concentration value. This clearly reflected a situation in which easily accessible fly ash surfaces were first saturated and then no significant reaction occurred thereafter. Based on the shapes of these ozone concentration curves, it was suggested that ozonation involved relatively rapid kinetics. The initial portion of the curve in Fig 7.2.2 (the region below 3 g-O₃/kg-ash) was regarded as indicating the intrinsic relation between ozone reactive uptake and the decrease in surfactant adsorptive capacity. The data beyond 3 g-O₃/kg-ash probably begins to involve loss of ozone via other parasitic pathways⁷⁴.

Figure 7.2.3 shows the results⁷⁴ of the ozonation experiments as ash AEA uptake capacity versus ozone input per gram of carbon. The data in Figure 7.2.3 strongly suggest that class C ashes consume more ozone than class F ashes, for a particular extent of decrease in surfactant capacity. This may be related to the differences in class C and class F ash surface areas. As was discussed in Chapter 6, class C ashes have higher surface areas due to the higher porosity of their carbons. If ozone consumption is related to the surface area of carbon, then the high surface area of the class C could serve as a sink for ozone, while at the same time not really being involved in the adsorption of surfactant.

The effect of ozone treatment on Loss-On-Ignition (LOI) was also examined. Results of this analysis are shown in Figure 7.2.4. The results suggest that no significant LOI change occurred when ozone input increased from 0 to 25 g per kilogram of ash, and, therefore, no carbon gasification or combustion loss occurred during the early stages of ozonation. The slight weight gain that was detected is believed to be real, and due to the addition of chemisorbed (or reacted) oxygen species onto the carbon surfaces.

There was no clear trend noted in surface area following ozonation. One class F ash sample (LOI 6.1 wt.%) showed a significant area reduction, similar to the behavior obtained by Deitz at el.⁸¹ with charcoal. Another sample (with LOI 33 wt%) did not show any change in BET surface area at all. To the extent that it is not believed that micropore penetration is significant in the foam index test, loss of surface area is probably secondary to change in polarity, as an explanation of AEA capacity.

Figure 7.2.5 presents data obtained from Gao at el.⁷⁴, in which the ash ozone input requirement was normalized with the carbon's BET surface area. The plot suggests that the ozone needed to achieve a particular AEA reduction effect is directly proportional to the amount of carbon surface present in ash. The more available surface, the more ozone required for a particular degree of AEA capacity reduction. As noted above, the higher surface area Class C ashes consume more ozone per mass of carbon than do the lower surface area class F ashes. On the other hand, when plotted as in Figure 7.2.5, the class C and class F ashes are indistinguishable, at least early during the ozonation process. This may be understood in terms of where the initially ozonated sites are located. They are most likely quite near the geometrical surfaces of the particles. It has been argued that these are the most important (accessible) sites for AEA uptake.

The results of this research⁷⁴ strongly suggest that fly ash ozonation has potential as a post-combustion treatment process for utilities. Such a process could significantly improve ash surface chemistry and therefore qualify ashes that were previously unusable, for reasons of poor air entrainment. A simple preliminary cost analysis showed that the main cost for such a process is associated with ozone generation. The ozone generator electricity requirements were estimated from equipment vendor data to be about 7 kW-h/lb ozone. At an electricity cost of 1-2 cents/kWh this suggests that the cost for electrical power for ozonation to be about \$ 0.3-1.2/ ton-ash. This is much less than is paid now in order to landfill unsalable ash.

7.3 The Effect of Ozonation on Surfactant Activity

The effect of ozonation on ash surfactant capacity is clearly seen in Figure 7.3.1. The experiments in Figure 7.3.1 differ from those shown in Figure 7.2.2 insofar as they were all conducted at one particular value of ozone concentration. In addition, the experiments were all terminated using the same ozone breakthrough criterion. The input ozone concentration in all these experiments was 2 vol% at a corresponding carrier flow rate of about 1.5 L/min. The experiments were quenched when ozone concentration at the exit reached the level of the input ozone concentration. The ozone input and output concentrations allowed calculation of the amount of ozone chemisorbed or reacted onto the surface on ash. The results in Figure 7.3.1 again clearly suggest that ozone treated samples had smaller surfactant capacities than the original samples. Note that the scale in this figure emphasizes the low ozone uptake range previously examined in Figure 7.1.2.

The class F ash samples (FA80, FA81, FA83 and FA 84), shown in Figure 7.3.1 had LOIs from 0.4 up to 10.9 wt%. The class C ash sample (FA 82) shown on same plot had an LOI of 1.6 wt%. These results strongly suggest that class F ashes lose their capacity for AEAs, either totally or at least by a factor of two, at around 0.6 g-O₃/kg-ash. Class C ash appeared to need about twice as much ozone (~1.3 g-O₃/kg-ash) in order to reach a similar relative adsorptivity level (though the sparsity of data make drawing firm conclusions on this point somewhat difficult). These data also support the previous conclusion⁷⁴ that it is not the amount of carbon is the primary factor that determines the required ozone uptake, but rather, the nature of the surface that is the key factor in deciding required uptake.

Figure 7.3.2 presents the same data shown in Figure 7.3.1, but recalculated onto a basis of ozone requirement per mass of carbon. Ozone uptake by ash mineral matter is believed to be unimportant, since minerals are generally in fully oxidized states. As seen in Figure 7.3.2, most class F ashes achieve almost complete foam index reduction at around 25 g-O₃/kg-carbon. However there are two class F data points (both data from FA 83, only different ozone concentrations) indicating much higher ozone uptakes of more than about 100 g-O₃/kg-carbon. This ash is classified in our sample bank as a class F ash, with very low LOI 0.4%. Its specific BET surface area is around 380 m²/g-carbon, which is more like a surface area observed with class C ashes. Both LOI and surface area suggest that this sample could originate from sub-bituminous coal and this is why it behaves more like a class C ash.

Class C ash data reach similar relative surfactant adsorptivity levels at somewhat higher (about 4-7 times) ozone uptake values. This result is not surprising, since class C

ash specific BET surface areas are on average about 5-8 times higher. Class F ashes, excluding the high surface area sample, have specific surface areas of about 20 - 60 m²/g-carbon. The class C ash has a surface area about 305 m²/g-carbon.

These results again strongly confirm that ozonation significantly reduces the surfactant capacity of these fly ashes. There is, however, an enormous variability in the ozone uptake at breakthrough, which is not related to the degree of decrease in the foam index. This is unexplained, but might well be again attributed to accessibility issues, and the differences in accessibility for AEA and ozone.

7.3.1 The surface area reduction effect in ozonated fly ashes

It was already inferred above that it is unlikely that ozonation could decrease AEA capacity through a micropore blockage mechanism, because it is not clear that the AEA can even enter micropores. To explore this point further, three class F ashes and one carbon black sample were ozonated under identical conditions (contact time, ozone concentration, bed mass) and their surface areas and porosities determined. The results of these analyses are given in Table 7.3.1 and on Figures 7.3.3-7.3.7. Figure 7.3.3 presents the nitrogen isotherm data for ozonated and non-ozonated class F fly ash 21 (LOI 6.1 wt.%). These results clearly suggest, as previously reported^{74, 81}, that nitrogen uptake is reduced in the ozonated sample. The isotherms reveal that the ozonated sample has lost about half of its microporosity, relative to the non-ozonated sample. The loss in nitrogen adsorption uptake at low relative pressures is directly related to the loss of surface area. As the data in Table 7.3.1 show, the surface area for ash 21 decreased by a factor of two, from 52 m²/g-carbon to about 26 m²/g-carbon.

A similar comparison of the isotherms for another ozonated class F ash, FA 23 (LOI 66 wt.%), is shown in Figure 7.3.4. The highest nitrogen uptake occurred with the raw (non-ozonated) fly ash. It has been observed that sample outgassing conditions (temperature and strong vacuum) strongly influence the measured isotherms for the ozonated samples. Our generic procedure required outgassing at 573 K. This was the case with all non-treated samples in our sample bank. However, as the results in Figure 7.3.4 showed, outgassing at a lower temperature of 453 K had a significant impact on the nitrogen isotherms. These results support the hypothesis that some oxide complexes, formed during ash ozonation, were lost at temperatures of 573 K. Since the ashes that are tested for foam index are never outgassed, these results suggest that the processes involved in loss of porosity might be even more important than the data obtained with the normal outgassing might suggest. On the other hand, certain types of oxides can also be decomposed in water solution, so it is not clear exactly how different the conditions really are.

The results in Table 7.3.1 and Figures 7.3.4-7.3.6 show that the nitrogen surface area and porosity can be strongly affected by the outgassing conditions. We believe that this is the reason why there are reports in literature of varying surface area behavior with treated porous carbonaceous samples.

Figure 7.3.7 shows a comparison of ozonated and non-ozonated isotherms for carbon black (M120). Clearly the results in this figure suggest that the nitrogen isotherm for this non-porous carbon black is not affected by the ozonation at all. This is not unexpected, as this material does not contain much microporosity or mesoporosity. Still, there is a decrease in surfactant adsorption capacity from 7 ml/g-carbon to 1 ml/g-carbon

as a result of ozonation. This is powerful evidence that changes in surface chemistry can and do influence AEA capacity, independent of any changes in porosity.

A further set of experiments was conducted to explore the relative importance of surface chemistry and pore blockage effects. Ozonated fly ash 21 was examined using the Flow Microcalorimetry (FMC) device. The experimental details regarding the FMC were given in chapter 3. The polarity analysis for ozonated class F ash 21 revealed that in addition to the surface area reduction that this sample experiences, the surface polarity changed as well (see Table 7.3.2). The surface polarity index (SPI) is an index of the polar surface area, and is computed as the ratio of the polar to total BET surface area. The value of this index increased to almost 1, indicating that the surface of this ash had become almost completely polar.

The assay that is used for surface polarity measurement is in many respects the mirror image of the foam index test. Whereas the adsorption that takes place in the foam index test involves the non-polar portion of the AEA molecule adsorbing onto the non-polar surface, the FMC test involves the adsorption of the polar endgroup of n-butanol adsorbing onto polar sites on the carbon surface. It is no surprise that the beneficial effects of ozonation on foam index would show themselves strongly in the polarity test.

The steric effects of surface oxidation, reflected in the decreased access to microporosity, are difficult to separate out from the effects of polarity. Both will tend to decrease the ability of the AEA to find adsorption sites. It must, however, be remembered from the earlier comparison of specific foam index and carbon surface area that not all surface area is usable in AEA adsorption. The class C carbons clearly had much micropore area that was not utilized, and one would have to conclude that the class F

carbons would therefore likewise contain such unusable micropore volume. It is this smallest micropore area that is being blocked by the ozonation processes, as the isotherm comparisons have shown.

The earlier presented results using different alcohols for interrogating the surface polarity (Chapter 5) showed some small differences between n-butanol, t-butanol, and methanol, at least in the class F carbons examined in this manner. This supports the notion that the surfaces of the micropores are only partially accessible to these reagents. These alcohols are likely to be smaller than the AEAs involved in the foam index testing, again suggesting that the micropores cannot all be utilized for AEA adsorption.

It is therefore still a matter of debate whether ozone-induced micropore blockage plays a significant role in decreasing the AEA capacity of ashes. The nitrogen molecule used for surface area and porosity characterization is much smaller than the AEA species, and would tend to get into porosity that those species could not. Even if the AEA molecules can penetrate to some level of microporosity, the earlier questions regarding diffusion rates still remain. For example, the adsorbed AEA species themselves can block the mouths of micropores effectively sealing them against further AEA uptake, in much the same way that the ozonation products block the pore mouths to entry by nitrogen. The times for diffusion to occur into the pores under these circumstances could well be quite long, compared with the time of the foam index test.

Finally, it can be noted in connection with Figure 7.3.2 that there is no simple monotonic relationship between the extent of foam index decrease and the amount of ozone uptake at breakthrough. What this means is that some ashes continue to react for a long time, longer than needed to significantly reduce their AEA adsorbing capacity. This

means that the ozone may be reacting with the interior of pores that cannot be reached by AEA. Figure 7.2.5 already showed that in many cases much smaller than monolayer capacities were needed in order to see significant AEA capacity decreases. This could again have to do with the fact that it is not necessary to react all surfaces with ozone, as many are inaccessible to AEA in any case.

In conclusion, the tests involving ozonation have confirmed that changing the chemical nature of the carbon surfaces, as is associated with the polarity change accompanying oxidation, has a definite effect on the ability of the surface to adsorb AEAs. The effect appears to always be in the direction of decreased adsorption of AEA with increased polarity, in contrast to the conclusion offered earlier by Hill et al.¹⁴. The influence of micropore blockage, which unquestionably also occurs during ozonation, is much less clear, because of the previously established inability of the AEA to fully utilize micropore area.

Whatever its mechanism, the influence of ozonation on improving the quality of fly ash, as revealed by foam index testing, is clear and always positive. Thus this technique shows some considerable commercial potential for treating fly ashes.

TABLES

Table 7.3.1 Surface area and porosity analyses results for ozonated samples.

Samples	LOI [wt.%]	Out. Temp [°C]	Total BET surface area [m²/g- ash]	Specific BET surface area [m ² /g- carbon]	Micro- porosity [ml/g- ash]	Meso- porosity [ml/g- ash]	Macro- porosity [ml/g- ash]
FA21	6.1	300	3.8	51.9	0.0019	0.0023	0.0017
FA21Oz	6.2	200	2.27	25.9	0.0011	0.0017	0.0023
FA21Oz	6.2	300	2.32	26.6	0.0011	0.0017	0.0025
FA23	65.5	300	37.0	56.2	0.0154	0.0165	0.0074
FA23Oz	67	180	14.5	21.4	0.0043	0.0134	0.0183
FA23Oz	67	300	25.0	36.5	0.0093	0.0149	0.0154
FA22	33.6	300	17.6	51.1	0.0088	0.0058	0.0054
FA22Oz	34.0	300	13.9	39.5	0.0069	0.0057	0.0036
Carbon Black	100	300		38.5	0.0156	0.0554	0.3240
Oz Carbon Black	100	180		36.7	0.0166	0.0435	0.1856

Table 7.3.2 Ozonated and non-ozonated fly ash 21 polarity comparison.

Sample	SPI [Fraction]	LOI [wt.%]	Polar Surface area [m ² /g-carbon]
FA21	0.52	6.1	25.7
FA21 Ozonated 32 min.	0.95	6.2	46.5

FIGURES

Figure 7.2.1 Sketch of the laboratory apparatus for ash ozonation experiments⁷⁴.

Figure 7.2.2 The effect of ozone treatment on surfactant capacity of commercial fly ash samples. Data were collected at different ozone input concentrations (500ppm-2 vol.%), contact times and bed masses (50-400 gm). Ozone usage is expressed per kilo of ash⁷⁴.

B

Figure 7.2.3 The effect of ozone treatment on surfactant adsorptivity of commercial fly ash samples. Data were collected at different ozone input concentrations (500ppm-2 vol.%), contact times and bed masses (50-400 gm). Ozone usage is expressed per kilo of carbon⁷⁴. The abscissa is again the ratio of final to initial foam index.

Figure 7.2.4 The effect ozonation on Loss-On-Ignition (LOI).

Figure 7.2.5 Relative AEA adsorptivity as a function of ozone input, expressed per unit carbon surface area (N_2 BET surface area). Ozone feed also expressed as number of monolayer equivalents (top axis) calculated assuming one chemisorbed oxygen atom (0.28 nm Van der Waals diameter) per molecule of ozone reacted⁷⁴.

Figure 7.3.1 Relative surfactant adsorptivity as a function of the amount of O₃ absorbed per kilo of ash by (reacted with) the class F and class C fly ash samples.

Figure 7.3.2 Relative surfactant adsorptivity as a function of the amount of O₃ absorbed per kilo of carbon by the class F and class C fly ash samples.

Figure 7.3.3 Ozonated and non-ozonated class F ash 21 N₂ isotherms. Sample LOIs 6.1-6.2 wt.% respectively.

Figure 7.3.4 Ozonated and non-ozonated class F ash 23 nitrogen isotherms. Sample LOIs about 66 wt.% respectively. Two ozonated ash isotherms were taken on the same ozonated sample batch, but the samples were outgassed, prior to isotherm measurement, at slightly different temperatures (300 °C and 180 °C).

Figure 7.3.5 Specific BET surface areas of the ozonated fly ash samples as a function of sample outgassing temperature. Identically ozonated ash samples were outgassed at different temperatures, and values for these samples are compared with the surface areas obtained from raw (non-ozonated) ash samples.

Figure 7.3.6 Total BET surface area change with DR microporosity for ozonated and non-ozonated class F ash 23.

Figure 7.3.7 Ozonated and non-ozonated carbon black (M120) N_2 isotherms.

8.0 FLY ASH CARBON REACTIVITY AND BURN OFF BEHAVIOR

8.1 Fly Ash Carbon Reactivity

Unfortunately it is practically impossible to avoid loss of carbon in the fly ash produced from any commercial coal combustor. The amount of carbon in typical fly ashes varies in the range 1-10 wt%, and the amount depends on the coal itself, as well as on the temperature and oxidation conditions in the combustor. As discussed earlier, low rank sub-bituminous coals generally burn off to a greater extent than do the high rank bituminous coals. This suggests that sub-bituminous coals are more reactive towards oxygen, relative to bituminous coals. Because the inherent mineral contents of the two ranks are, in very broad terms, similar, the Loss-On-Ignition (LOI) values for class F ashes are generally somewhat higher than those for class C ashes. For example, there is only two class C ashes with an LOI's as high as 1.3 wt.% and 1.6 wt.% in our sample bank (see Table 4.1).

The content of carbon in ashes from any particular boiler generally becomes slightly higher after a so called "low-NO_x" burner retrofit. In current commercial practice, this carbon loss is of concern mainly because of its effects on ash reuse, as opposed to fuel heating value loss. The consequences of carbon in fly ash have been discussed at length in the previous chapters. Here, attention is turned to the nature of the carbon, as it relates to combustion properties and development of porosity in the carbons. This part of the study indirectly relates to the use of the ash, but could be important in terms of how the ash develops certain characteristics, and perhaps even in deciding how to process the ash in post-combustion applications. There is no obvious direct tie between the carbon

oxidation reactivity and suitability of the fly ash as a pozzolanic agent (attempts to find any correlation have, not surprisingly, yielded nothing).

The previously described work has concluded that the amount of carbon (LOI) is not the only parameter that determines the suitability of fly ash for concrete applications. In addition, the accessibility, surface area and polarity of the fly ash carbon all played key roles. The porosity is clearly influenced by the nature of the burnout process, as well as by the parent coal material. The accessibility of the carbon for AEA adsorption is determined not only by the development of porosity, but also by the fragmentation that accompanies the burnout of the particles. The polarity of the carbon surfaces can be determined by the last few fractions of a second that the fly ash spends in the hot boiler environment, and what the temperature and oxygen contact history of that time is. The hope is that some of these results might be of use in considering some subtle aspects of boiler design, so that perhaps some degree of improvement may be made to the ash before it ever leaves the boiler.

Fly ash post-processing is another way to deal with problematic carbonaceous fly ash samples. The main goal is to make possible their use in concrete mixtures. The main problem in ash post-processing is related to the question of how to deactivate the problematic carbons. Oxidation is clearly one possible post-combustion treatment. This chapter also aims at providing information that could guide the search for suitable conditions. As discussed in a separate chapter, ozonation is another particular technology that can accomplish this task.

Fly ash oxidation reactivity is an easily measurable characteristic. In addition, the existence of an extensive sample bank of commercial fly ash samples provided a unique opportunity to study the reactivity characteristics of unburned carbons produced under actual boiler conditions (rapid heat-up, high temperatures). Thus, the objective of the current work was to investigate the oxidation reactivity of fly ash carbons, using simple thermogravimetric analysis techniques. Thermogravimetric analysis (TGA) has been employed widely in coal and carbon science to perform numerous types of characterizations, including carbon oxidation reactivity determinations.

A simple approach for characterizing carbon oxidation reactivities has been developed at Advanced Fuel Research, Inc. (AFR) and described in their publications^{71,72}. Their approach is based on the concept of critical (T_{cr}) and late temperatures (T_{late}), which are the indexes of carbon reactivities related to the concentration of accessible active sites. The determination of the T_{crit} and T_{late} relies on a TGA measurement, in which sample weight loss is tracked while the sample is heated at a constant rate in the presence of an oxidizing gas. Critical and late temperatures are defined as the temperatures at which the rate of the weight loss reaches to $0.065 \text{ [mg]/[mg}\cdot\text{min]}$ ^{71,72}. The choice of this particular reaction rate for performing characterizations was based on a careful empirical study of the combustion behavior of many chars. This rate is high enough to be easily measurable in a TGA device, but still low enough to ensure that reaction is occurring in a kinetically controlled regime.

Generally speaking, the lower the critical temperature of any carbon, the more reactive the sample. By contrast, the higher the value of T_{late} , the less reactive the carbon.

The difference between T_{cr} and T_{late} can provide information about the reactivity distribution, but in our case was mainly dependent on fly ash carbon content.

8.1.1 Experimental Techniques for Fly Ash Reactivity

Over 50 fly ashes from different commercial boilers, located throughout the US, were examined in this research. These fly ashes had LOI values in the range from 0.2 wt % to 66 wt %. Both class C and class F fly ashes were examined.

A TA Instruments 951 Thermogravimetric Analyzer (TGA) was used for the examination of the fly ash samples under low temperature, air oxidation conditions. The mass loss associated with oxidative loss of carbon was tracked as a function of temperature and time. In order to keep mass and heat transfer conditions approximately the same in different experiments, more or less constant volumes of fly ash sample were used on the sample pan. The sample mass was about 20 mg for most experiments and decreased to 8-9 mg for high carbon content samples (LOI 66 wt %).

Thermogravimetric analysis requires care in the positioning of the sample temperature measurement thermocouple above the sample pan. This requirement stems from the quite high (up to 50 degrees) radial and axial temperature differences, which exist in the TGA furnace. Small thermocouple positioning differences can significantly affect the temperature readings. In order to get consistent results care was taken before each run to install the thermocouple as close as possible to the sample pan. After a set of four tests with different fly ash samples, a calibration test was performed to establish reproducibility. Two calibration materials, a selected fly ash and calcium oxalate hydrate ($\text{CaC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$) were used in order to check the performance of the thermocouple and TGA balance. The results of typical calibration tests are given in Table 8.1.1. In the case

of the fly ash standard, the critical and late temperatures should all be constant from run-to-run. Likewise, the three decomposition temperatures for the calcium oxalate hydrate should all be the same. These results suggest that the temperature measurements have an uncertainty of just few degrees at low temperatures, increasing to 16°C at the highest temperatures. Generally speaking, it is unwise to ascribe too much significance to differences of (10°C in T_{cr} or T_{late} values) based upon single experiments. In many cases, replicate experiments were performed. In this case, differences of a few degrees in mean values of T_{cr} and T_{late} could be significant. In this study, no use needed to be made of results involving only small differences in T_{cr} and T_{late} .

Table 8.1.1 Calibration tests for TGA reproducibility.

Sample	Critical temperature [°C]	Late temperature [°C]		
Test Fly Ash - run 1	591	798		
Test Fly Ash – run 2	591	790		
Test Fly Ash – run 3	602	782		
Test Fly Ash – run 4	596	789		
	Temperature H₂O max peak [°C]	Temperature CO max peak [°C]	Temperature CO₂ max peak [°C]	
CaC₂O₄x(H₂O)	155	471	695	
CaC₂O₄x(H₂O)	157	475	704	
CaC₂O₄x(H₂O)	158	472	699	

Figure 8.1.1 shows a typical temperature profile and the weight loss curve for a class F fly ash with an LOI value 14.6 wt percent. The data set shown in Figure 8.1.1 is from class F fly ash 3 from our sample bank (see for more details in Table 4.1). The expected loss of carbon mass is seen to start at a temperature just below 600 °C, and concludes at near 800 °C. The mass gain at the end of the experiment is presumably not associated with processes involving the carbon, which should all be burned off by that point. It probably reflects, instead, a small amount of oxidation of the inorganic species present in fly ash. This sort of oxidation naturally defines some uncertainty in LOI determination. In this particular case, the uncertainty is around 0.5 wt %, for a sample with a nominal LOI of 14.6 wt %.

Figure 8.1.2 shows a typical temperature profile and the weight loss curve for class C fly ash with an LOI value 0.92 wt percent. The signal is considerably noisier than that observed for the class F ash. Note that this is a result of use of a much finer mass scale in the case of the class C ash, due to this sample's much lower LOI. The absolute increase in mass following carbon loss is actually quite similar for both class F and class C samples. The results on the Figure 8.1.2 are shown for fly ash sample 66 (from Powder River Basin coal, see details in Table 4.1). The uncertainty in LOI for this class C fly ash sample was around 0.29 wt percent.

The critical temperature (T_{cr}) has been defined as a measure of the intrinsic reactivity of carbons^{71,72}. As explained earlier, the measurement of T_{cr} involves a particular weight loss criterion, under conditions presumed to be under intrinsic chemical rate control. In this characterization the sample is heated at constant rate of 30°K/min. A

constant airflow (approximately 300 cc/min of air in our case) is fed into the TGA reactor during heating. The reaction is that between carbon and oxygen from air, leading burn-off of carbon, as CO_2 and CO evolve. The reaction rate of course begins at zero and increases with temperature. The temperature at which the reaction rate reaches 0.065 mg/mg•min (based on original carbon content in the fly ash) is taken as the “critical temperature”, T_{cr} .

Figure 8.1.3 shows a derivative of the mass loss rate data of Figure 8.1.1, and shows the identification of the critical value of rate together with T_{cr} . In order to get a smooth reaction rate curve, the differentiated curve was smoothed. In addition to T_{cr} , the second, related reactivity parameter, T_{late} has been defined in Figure 8.1.3. The presumption is that the higher the value of T_{late} the lower the reactivity of the residual carbon.

Figure 8.1.4 shows the mass loss rate as a function of temperature for the class C fly ash carbon with an LOI of 0.92 wt percent. As Figure 8.1.4 shows, the reaction rate curve is more “noisy” as compared to the class F fly ash reaction rate curve (Figure 8.1.3). The class C fly ash carbon burn-off rate curve is affected more strongly by the noise inherent in the mass signal, due to the need to perform the measurements at higher sensitivity. Nevertheless, T_{cr} and T_{late} can be clearly identified.

8.1.2 Oxidation Reaction Results for Selected Fly Ashes

Depending on the amount, the nature and the origin of the carbon in the fly ashes the critical and late temperatures varied over quite a wide range. The results of the oxidation reactivity experiments are shown in Table 8.1.2. In many cases, the values are calculated means from several reactivity experiments.

Figure 8.1.5 gives a plot of the reactivity T_{cr} of the fly ash carbons as a function of LOI. As may be seen from Figure 8.1.5, the critical temperatures of the class F fly ash carbons did not vary very much in the range of LOI from 10 to 70 wt percent. The T_{cr} values varied between 580° and 620°C for these higher LOI fly ash carbons. Fly ashes with LOI under 10% had a tendency to exhibit somewhat greater variation in T_{cr} , and many had considerably lower values of T_{cr} . The differences between class C and class F ashes are most likely explanation for the large variation in T_{cr} at low LOI. This is especially apparent in Figure 8.1.6.

Class C fly ashes of low LOI were generally more reactive than the class F ash carbons of comparable LOI. Critical temperatures for class C ash carbons were in the range from 410° to 490°C. The higher reactivity of class C ash carbons could be understood in terms of the origin of the fly ash carbon. Class C Fly ash carbons mostly come from low rank coals, which give chars that are more reactive than chars from high rank coals which give class F ashes. This is a likely reason why the LOI of class C fly ashes did not exceed 1.6 % in our sample bank.

The higher reactivity of class C vs. class F carbons could have its origin in the different nature of the starting organic matter of the two classes. In addition the catalytic effects of the fly ash minerals could influence reactivity of the fly ash carbons. Class C fly ashes having high CaO content have a natural source of oxidation catalyst, which is not present in the same quantities in Class F fly ash. The catalytic effects of alkalis could also play a role.

It is perhaps logical to expect a correlation of reactivity with char surface area. Figure 8.1.7 shows the reactivity of the fly ash carbons as a function of surface area.

The correlation between surface area and reactivity appears at first glance to be quite good. The higher reactivity carbons had higher available surface. There are enough exceptions to raise concerns about a correlation. There are a few class F fly ash carbons, which were “unusual”, which were prepared under unusual conditions. These samples demonstrate that it is naive to accept a simple correlation at face value. It should be noted that class C fly ash carbons in Figure 8.1.7 were generally located at the bottom-right corner of the figure, indicating their high surface area and high reactivity, while class F ashes clustered at the upper left. Within either group, a good correlation with surface area is not as apparent, though a weak trend is seen. These facts suggest that the apparent correlation of surface area with reactivity may not be indicative of cause and effect, but rather, indicate a secondary correlation of both parameters through coal rank.

Figure 8.1.8 shows late temperature, T_{late} , as a function of critical temperature for the same set of samples discussed above. This plot provides information about the width of the reaction rate distribution curve. The bigger the difference between T_{cr} and T_{late} , the wider the reaction rate distribution characterizing the carbon. Most of the class F fly ashes showed both high late temperature and high critical temperature indicating that reaction rate curve was of constant width. Class C fly ash carbons did not show a consistent correlation between critical temperature and late temperature. In this case, the reactivity distribution in the carbon was quite broad. It could be argued that the key parameter for the correlation between T_{cr} and T_{late} was the fly ash carbon content, as it was low LOI class C and class F ashes that showed the poorest correlation. On the other hand, at very low values of LOI (roughly less than 0.7 wt %), the reaction rate did not reach the 0.065 mg/mg·min criterion and critical temperature was impossible to

determine (these points therefore are not seen on the plots). As the LOI increased, the reaction rate curve spread out both vertically and horizontally. Further increase in LOI led to a narrowing of the reactivity profile.

Figure 8.1.9 shows the correlation between fly ash carbon reactivity and the measure of its air entraining agent (AEA) adsorption activity (Specific Foam Index, SFI). As can be seen from this plot, there was no apparent relationship between reactivity and specific foam index. Quite a number of class F fly ash carbon samples clustered at the upper left corner of the plot. Class C fly ash carbons showed somewhat different behavior. Some of the class C fly ash carbons were quite reactive and active at the same time, while others were reactive but not active. Class C ashes are known to exhibit a wide range of behavior in practical situations, and the specific foam index parallels this. This clearly indicates that no correlation exists between reactivity and AEA activity, and reactivity tests will be of little value for characterizing suitability for concrete.

8.2 Surface Area Development during Burnout

Surface area development in fly ash carbons was also investigated using a simple TGA-based technique. These experiments were carried out in the kinetically controlled regime up to a certain extent of burn-off at which point the process was quenched and the carbon analyzed. An Arrhenius analysis was performed in order to find the temperature range over which the burn-off occurs in the kinetic control regime. A typical fly ash mass-temperature versus time correlation for Arrhenius analysis is given in Figure 8.2.1. Figure 8.2.1 was prepared from the data recorded when a fly ash 22 fraction of $45 < d < 106 \mu\text{m}$ was burned out at different temperatures. At least 6 or 7 different mass

loss rates were recorded in the kinetically controlled regime. It was quite difficult to obtain as many reaction rate points for most of the samples, due to their low LOI values. As seen from Figures 8.2.2 to 8.2.9 reproducibility experiments with different samples were carried out and a cumulative Arrhenius correlation obtained. Reproducibility runs are marked on the plots as run 1, run 2 and etc. As can be seen from Figures 8.2.2-8.2.9, all experiments had good reproducibility. The activation energy and pre-exponential constants have been determined according to an Arrhenius analysis and presented cumulatively in Table 8.2.1 The data in Table 8.2.1 were obtained from Figures 8.2.2-8.2.9.

The apparent activation energy for the all fractions of class F fly ash 22 is about 141 kJ/mol, and the pre-exponential about $3.5 \cdot 10^7 \text{ min}^{-1}$. The activation energies for class F ash 22 fractions are quite typical of those found for many chars. However a similar study of the class F ash 74 fractions reveals that the apparent activation energy is slightly less, 115 and 122 kJ/mol respectively, for the same size fractions as used with fly ash 22. There would be no reason to expect that the values would be in any better agreement; both are quite typical of many other carbons. The results in Table 8.2.1 also show that the two class C ash fractions have the highest apparent activation energies, about 151 kJ/mol. Again, there is nothing out of the ordinary in this value. What is worth noting, however, is that these latter two samples also have much higher pre-exponential factors than do the class F ash carbons. Thus these two samples show themselves to be more reactive in this way.

Figures 8.2.2-8.2.6 show that the kinetic control regime is confirmed at around 500°C when using class F ashes. The comparable temperature value for the class C ashes

is around 400°C (see Figures 8.2.7-8.2.9). As discussed earlier, class C ashes are more reactive and have lower critical temperatures relative to class F ashes.

It is interesting to note in connection with the data on class C fly ash 65 (Figure 8.2.8), that two reaction regimes are strongly suggested. There is a lower temperature regime in which a very typical activation energy of 152 kJ/mol is obtained (see Figure 8.2.9 for an expanded view of this temperature range). On the other hand, at higher temperatures, the data become somewhat more scattered (see Figure 8.2.10) but the activation energy is clearly lower. The best fit value in this range of temperatures is around 74 kJ/mol. What this very strongly implies is a transition from the kinetic control regime to a pore diffusion control regime. The approximately factor of two decrease in activation energy is quite typical of this transition, and can be theoretically predicted for solids with monodisperse pores.

Based upon the above results, the temperature at which all subsequent class F fly ash burn-off experiments were (isothermally) conducted was 496°C. After each TGA burn-off experiment, nitrogen isotherms were obtained on the solid product, from which the specific BET area was calculated according to equation 6.2.3. Figure 8.2.11 presents the specific surface area vs. burn off curve obtained for the class F fly ashes 22 and 74, for cuts of $45 < d < 106$ and $106 < d < 180$ micrometers. In Figure 8.2.11 zero burn off corresponds to the raw fly ash carbon fraction, and 100% burn off corresponds to the state when the all carbon in the ash fraction is burned off.

The carbon surface area increases with burn-off for all samples shown in Figure 8.2.11. Slightly higher surface increases are shown by both smaller fly ash smaller fractions ($45 < d < 106$ micrometers). The surface area for these cuts reaches to about 140

m^2/g carbon at about 40% burn off. This value is about three times higher than the initial surface area of $50 \text{ m}^2/\text{g}$, at nominal zero burn-off.

The above results are typical of the activation process that carbons undergo during oxidation. Oxidation under purely kinetic-control conditions may not mirror the conditions in an actual boiler, in which at least porous, if not external, mass transfer limitations clearly play a role. Still, the potential for development of porosity, even at the already high extent carbon burnout that these samples represent, is evident.

The present results strongly suggest that the raw samples from the boiler have not seen true kinetic control conditions. Even the smallest fraction, which showed significant fragmentation upon microscopic examination, had a carbon surface area of only $75 \text{ m}^2/\text{g}$ carbon. Much higher surface areas can be obtained under kinetic control conditions. This lower surface area in actual boiler samples is entirely expected, as it is unlikely that purely kinetic control would exist at the much higher temperatures in the boiler.

While such activation studies might be of interest with regard to understanding char morphology and burnout, they do not offer much insight into the foam index behavior. The very modest degree of activation observed in these chars does not lead to a major increase in AEA adsorptive surface. Rather, it is the particle fragmentation behavior that must be key to explaining foam index trends.

TABLES

Table 8.1.2 Oxidation reactivity results for fly ash carbons.

Fly Ash	LOI	Type of ash	T_{cr}	T_{late}	BET Surface Area	Specific Foam Index
	wt %		(°C)	(°C)	m²/g-carbon	ml Dar II/g-carbon
1	6.5	class F	616	806	42.6	1.637
2	3.1	class F	592	773	60.5	0.951
3	14.6	class F	595	794	68.4	1.666
4	14.6	class F	590	787	64.9	1.628
5	1.9	class F	640	773	53.4	0.348
6	3.4	class F	612	783	56.7	1.945
7	2.6	class F	596	796	69.8	1.009
8	3.8	class F	588	768	63.6	1.162
9	66.0	class F	578	787	65.3	1.941
10	2.6	class F	589	766	66.2	0.994
11	2.5	class F	602	760	64.5	1.505
12	2.3	class F	579	767	76.3	1.427
13	3.8	class F	587	769	66.9	1.032
16	1.5	class F	548	716	126.7	8.812
19	3.6	gas co-fired	548	721	108.5	1.815
20	2.0	class F	580	725	69.2	0.582
21	6.1	class F	614	790	51.2	2.475
22	33.6	class F	586	784	51.2	1.788
23	65.5	class F	591	795	53.6	1.847
24	2.7	class F	604	793	42.0	0.476
25	2.5	class F	650	777	39.3	0.335
26	4.0	class F	628	806	32.8	0.66
28	2.4	Petroleum coke	563	702		0
29	1.5	class F	597	746	67.8	0.86
30	35.1	class F	621	826	42.0	2.082
32	44.7	class F	589	786	47.2	1.681
33	29.1	class F	593	795	41.8	1.482
34	4.9	class F	624	808	50.2	1.203
35	17.5	Petroleum coke	557	718	4.6	0
37	4.9	class F	448	567	39.6	0.807
39	0.8	class F	440	720	311.8	6.18
40	1.1	class C	487	683	281.8	0.508
41	1.1	class C	463	570	308.9	0.495
43	0.6	class C	452	738	364.7	0

45	0.7	class C	408	728	335.2	0.814
46	11.1	class F	592	795	56.0	1.674
47	41.5	class F	580	784	63.8	1.987
49	19.9	class F	604	796	20.3	0.927
50	22.2	class F	609	801	28.0	1.251
51	20.9	class F	603	798	41.1	1.646
52	1.1	class F	492	641	282.3	8.426
53	4.0	class F	595	714	50.2	1.621
54	4.1	class F	588	718	37.1	0.968
56	1.2	class F	623	690	178.8	4.153
57	0.8	class F	535	690	101.9	0.000
58	1.9	class F	603	756	36.1	0.000
59	1.0	class F	583	721	60.5	1.024
60	6.0	class F	608	784	24.9	0.505
61	1.6	class F	560	707	37.6	4.173
62	3.9	class F	646	808	38.8	1.801
63	7.1	class F	597	766	45.3	0.428
64	7.4	class F	551	747	69.1	1.778
66	0.9	class C	444	603	392.9	4.396
68	0.8	class C	448	605	325.7	3.393

Table 8.2.1 Activation energies and pre-exponential constants for selected fractionated ashes.

Sample	Ash Type	Activation Energy	Pre-exponential
		[kJ/mol]	[min ⁻¹]
FA 22, 45<d<106µm	Class F	141	3.7*10 ⁷
FA 22, 106<d<180µm	Class F	142	4.2*10 ⁷
FA 22, 180<d<355µm	Class F	142	2.9*10 ⁷
FA 74, 45<d<106µm	Class F	115	7.2*10 ⁵
FA 74, 106<d<180µm	Class F	122	1.8*10 ⁶
FA 65, 180<d<355µm	Class C	152	1.1*10 ¹⁰
FA 75, 180<d<355µm	Class C	151	2.7*10 ¹⁰

FIGURES

Figure 8.1.1 Typical TGA weight loss and temperature curves for class F fly ash carbon reactivity characterization. Results for fly ash 3.

Figure 8.1.2 Typical TGA weight loss and temperature curves for class C fly ash carbon reactivity characterization. Fly ash 66, with an LOI of 0.92 wt percent.

Figure 8.1.3 Derivative of the mass loss rate as a function of temperature for the class F fly ash 3 carbon, with an LOI of 14.6 wt percent.

Figure 8.1.4 Derivative of the mass loss rate as a function of temperature for the class C fly ash carbon with an LOI of 0.92 wt percent.

Figure 8.1.6. Expanded plot of the critical temperatures as a function of LOI.

Figure 8.1.7 Fly ash carbon reactivity as a function of carbon surface area.

Figure 8.1.8 Fly ash carbon critical temperature as a function of late temperature.

Figure 8.1.9 Fly ash critical temperature as a function of its specific foam index.

Figure 8.2.1 Typical mass fraction/temperature versus time data for Arrhenius analysis. Class F ash 22, fraction $45 < d < 106 \mu\text{m}$.

Figure 8.2.2 Arrhenius plot for class F fly ash 22 fraction of $45 < d < 106$ micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.3 Arrhenius plot for class F fly ash 22 fraction of $106 < d < 180$ micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.4 Arrhenius plot for class F fly ash 22 fraction of $180 < d < 355$ micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.5 Arrhenius plot for class F fly ash 74 fraction of $45 < d < 106$ micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.6 Arrhenius plot for Class F fly ash 74 fraction of $106 < d < 180$ micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.7 Arrhenius plot for class C fly ash 75 fraction of 180<d<355 micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.8 Arrhenius plot for class C fly ash 65 fraction of $180 < d < 355$ micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.9 Arrhenius plot for class C fly ash 65 fraction of 180<d<355 micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.10 Arrhenius plot for class C fly ash 65 fraction of 180<d<355 micrometer size. Experiments carried out at atmospheric pressure, in stationary air.

Figure 8.2.11 Surface area development vs. burn off at 496 °C, in air, for class F fly ash fractions of 45<d<106 micrometer size.

9.0 CONCLUSIONS

Today only about 15% of all coal-derived fly ash is used as pozzolanic additives in the concrete industry. Still, this makes this industry one of the largest single markets for fly ashes. Fly ashes typically consist of 90-99+ wt.% minerals, with the remainder being unburned carbon derived from the fuel. The amount of carbon depends on the nature of the original fuel, and upon the temperature and oxidation conditions in the boiler units in which the fuel has been burned. It is the mineral portions that are of value in concrete mixtures. In concrete mixtures, these fly ash minerals react with Ca(OH)_2 and form a strong cementitious matrix.

In 1990 the Clean Air Act Amendment (CAAA) required utilities to make changes in pulverized coal combustion processes, in order to achieve mandated reductions of NO_x in flue gases. Undesired changes were observed in many fly ashes after so-called low NO_x retrofits. These changes have made the combustion process slightly less efficient, in terms of carbon burnout, resulting in higher "Loss-On-Ignition (LOI)" values (unburned carbon fractions) in the fly ash. Perhaps equally important have been some more subtle changes in the nature of the ashes. There have been many reports by the concrete industry concerning problems in using fly ash produced in low NO_x retrofit boilers as concrete additives. The main concern of the concrete industry is related to the poor air entrainment properties of the concrete mixes produced using these low NO_x retrofit ashes.

This project focused on the causes of these problems, how to properly characterize them, and ultimately what to do about the problem. The main goal was to develop a deeper understanding of the nature of the unburned carbon in fly ash in order to

help in identifying possible solutions. Fly ash in general, and the unburned carbon material in particular, has been previously studied to a very limited extent. It is only as a result of the increasing pressure on utilities to find more markets for fly ash, combined with the abrupt change in the quality of the materials, that has focused attention on the problem.

9.1 A Fly Ash Sample Bank was Created

A sample bank of about 80 fly ashes, from all over the US (and a few from elsewhere in the world) was assembled. The majority of the ash samples in our bank were class F ashes, generally originating from bituminous coals. A second main group of fly ashes in our bank is the class C ashes, generally originating from sub-bituminous and other low rank coals. Two petroleum coke co-fired fly ashes, four international coal ashes, and four other non-coal ashes, are also included in the sample bank.

Fly ashes in our sample bank have been characterized with respect to LOI, foam index, surface area, porosity, polarity, morphology and reactivity. LOIs, foam indexes, surface area and porosity measurements have been performed for all the ashes in our sample bank. Other tests have been performed for selected ashes from the bank.

The LOIs of class F ashes varied over quite a large range from almost 0 to all the way 66 wt%. The class C ashes in our bank had very low LOIs by comparison, only up to 1.6wt %. Most of the ashes were examined in an as-received state, straight from ash hoppers at the plant site. A few of the highest LOI samples, had been subjected to a preliminary separations process, designed to segregate the minerals from the carbon. Thus the very high LOI samples in our bank were products of the separation process.

9.2 Recommendation for an Improved Foam Index Test

A key assay for judging the acceptability of the ashes for concrete use is the foam index test. This is the commonly applied field test, used for judging a candidate ash. Because this test is, in some form, the commonly accepted industry standard, the decision was made to employ it here as well. The foam index test is a titration test, which measures the adsorption capacity of the ash for air entraining admixtures (AEAs). The carbons in the fly ashes adsorb the AEAs, thus destroying the air-holding capacity of the mix. In our research, commercial Darex IITM (W.R. Grace & Co., Cambridge, MA) and Air 40 (Boral Material Technologies, Inc) AEA solutions were examined. It was seen that the chemical nature of the AEAs influence the absolute values of the foam index. The problems in working with natural product-derived AEAs became apparent during the course of this work, as they were somewhat variable from batch-to-batch, and they tended to age.

Since commercial AEAs, have unknown molecular compositions, a search was conducted for materials that would model the behavior of the actual AEAs, but which would avoid the problems of variability found with the commercial agents. In order to find a suitable replacement several common surfactants or related compounds were examined, including sodium dodecyl sulfate (SDS) $[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}]$, dodecylbenzenesulfonic acid sodium salt (DBS) $[\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}]$ and abietic acid. The conclusion was that the DBS salt could be used in a standardized laboratory test as a model for commercial AEA surfactants. The advantages of the DBS acid salt are its known molecular composition, the ease of preparing the solution, and its low expense.

In addition, the foam index testing study revealed how sensitive the commercial surfactant Darex II was to the particular solution environment of the test solution. This indicated that any changes made in the test mix could have unintended consequences, as regards the numerical values obtained. For example, the results of the test are sensitive to the amount of ash used (they do not scale linearly), to the time of AEA addition, and the pH/ composition of the mixture.

9.3 Conclusions Regarding the Variables Affecting Foam Index

Foam index values for fly ashes varied over quite a large range. The AEA uptake on the ashes was most dependent on the amount of carbon in ash (LOI). The fly ash mineral portion, as well as the cement, repeatedly showed no tendency to adsorb AEA (i.e., they gave zero foam index). This result was independent of the origin of the mineral, class F or class C.

The LOI value is not the only factor deciding foam index test behavior, and thus suitability of the ash for concrete. As shown in this research, the nature of the carbon in the ash also plays a significant role in determining the suitability of the ash. Fly ash surface area appears important in determining the AEA adsorption capacity. Despite the small quantities of carbon in ashes, the active adsorption surface area in the ash was mostly contributed by its carbon portions.

Class C ashes had higher surface areas per unit mass of carbon than did class F ashes. The specific BET surface areas of class C ashes were measured to be in a range of 200–400 m²/g-carbon. The BET surface areas for class F ash were in range 20-80 m²/g-carbon. Most of the surface area in both of the ashes was available in their carbon

micropores. Class C ashes had higher micropore and mesopore volumes relative to class F ashes, but its surface area tended to be used less efficiently.

Even though ash carbon microporosity contributes the majority of the surface area, this does not necessarily lead to high AEA adsorption uptake in micropores. Most of the microporous carbon surface is not accessible to the relatively large AEA molecules, during the short foam index test (up to about 10 minutes in duration). Porosity analysis alone proved unable to explain the different trends observed in the sample bank.

Optical microscopy, as well as Scanning Electron microscopy, generally supported the porosity results, suggesting that class F carbons had lost much of their porosity during burn off in the boiler. Many of the carbon particles in class F ashes looked like pieces or fragments or carbon skeletons. The carbon particle size in class F ash varied from submicron up to 60 μm on average.

Class C ash analysis revealed that there are two groups of carbons present in these ashes. There are the large particles, which were in a size range from around 180 to 500 μm . The second fraction of carbon appears as tiny soot (carbon fragments) particles which had generally submicron diameter. Optical microscopy revealed that most of the carbon particles were heavily covered with minerals. Whether this was a result of adhesion or fusion of the minerals on top of the carbon particles remains unclear.

Fine carbon particles in class C ash fractions below 106 micrometers, which had BET surface areas about 150-250 m^2/g -carbon, contributed 90% of the specific foam index of the ash. Huge class C ash carbon particles, which were measured to have BET surface area about 300-500 m^2/g -carbon, were measured to be quite ineffective towards AEA adsorption, contributing only 10% to relative specific foam index. Similarly the

smallest particle fractions in class F ashes accounted for 90% of the foam index. Thus the fine particles were the most effective at adsorbing AEA molecules. This helped to explain why carbon surface area alone was not sufficient for predicting AEA sorption capacity. The adsorption surface needed to be readily available, near the geometrical surface of a particle. This is because the foam index test is a dynamic test. The time available in the foam index tests was not enough to permit the large AEA molecules to penetrate deeply into the carbon particles.

9.4 The Role of Carbon Surface Polarity and its Modification

The mineral portion of fly ash is mostly polar, whereas the fly ash carbon can be either polar or non-polar depending on the concentration of oxygen functional complexes covering the surface. The non-polar portion of the carbon is a primary site for adsorption of the non-polar portion of the AEA molecules. The higher the non-polar carbon surface area in the ash, the higher the AEA uptake. The polarity of the ashes was directly related to the extent of oxidation of the carbon surface. The greater the degree of oxidation, the more polar the surface. Fly ash polarity, together with the amount of small carbon particles in the ash, are the key parameters that determine the AEA uptake in the foam index test.

Fly ash ozonation at room temperature is a technique that allows changing fly ash surface characteristics in a relatively short time. Depending on the ozone input concentration, ash amount and contact time, the surfactant adsorptivity decreased by a factor of two or more with only 0-3 g O₃/kg-ash ozone introduced into the ozonation system. Class C ashes required about 5-8 times by mass more ozone for surface

passivation relative to class F ashes. This appeared directly related to the higher surface areas in class C ashes, which was higher by the same factor of about 5-8, relative to class F ashes.

9.5 Directions for Future Work

The present project has not attempted to define any particular practical process or solution for handling the ash problem. There has, however, resulted from this work a clear sense of what strategies might offer some hope of solving the problems. On the one hand, limiting the content of fine carbonaceous material, that provides good access to AEA, is more important than reducing LOI itself. It needs to be understood, though, that the ability to make combustion modifications to address these issues is generally very limited, because of the serious consequences these might have for the main utility operations. To define such a strategy would be somewhat like the tail wagging the dog.

On the other hand, ozonation-type post-combustion processes are moving forward. Under EPRI sponsorship, this technology is moving into pilot plant testing. It is hoped that this will lead to a commercially promising alternative or adjunct to the currently practiced carbon separation techniques.

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