Title: Economical Treatment of High Carbon Fly Ash to Produce a Low Foam Index Product with Carbon Content Retained

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Principal Authors: Robert B. LaCount, Douglas G. Kern - Waynesburg College 51 W. College St. Waynesburg PA 15370

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Technical Report

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Abstract

The overall objective of this research effort was to provide a potentially commercial thermal treatment of fly ash to decrease the interaction between fly ash and the surfactants used to entrain air in concrete when fly ash replaces a portion of the Portland cement in concrete. The thermal treatment resulting from this research effort, and described in this report, fulfill the above objective. This report describes the thermal treatment developed and applies the treatment to six different fly ashes subsequently used to prepare concrete test cylinders that show little or no difference in compressibility when compared to concrete test cylinders prepared using untreated fly ash.

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Introduction

The overall objective of this research effort was to develop a method that will decrease the interaction between fly ash and the surfactants used to entrain air in concrete. The amount of surfactant required to entrain a given amount of air should decrease after treatment and thus increase the quantity of fly ash suitable for use in concrete products.

Fly ash is used commercially as a replacement for some of the Portland cement in concrete products. Air-Entraining Admixtures (AEA's) are surfactants used to entrain air in concrete mixtures, improve the workability of the mixtures and the durability of the concrete products to freeze-thaw cycles (Dodson, 1990). This report describes continuing work directed toward treatment of high-carbon fly ashes to decrease the amount of AEA required in concrete applications utilizing fly ash. The background studies were described in a paper presented at the 18th Annual International Pittsburgh Coal Conferences (Appendix A).

The thermal treatments utilized to significantly lower the Foam Index are described in a paper presented at the 21st Annual International Pittsburgh Coal Conference (Appendix B).

Executive Summary

The overall objective of this research effort was to develop a method that will decrease the interaction between fly ash and the surfactants used to entrain air in concrete. The amount of surfactant required to entrain a given amount of air should decrease after treatment and thus increase the quantity of fly ash suitable for use in concrete products. This report describes a successful thermal treatment of fly ash that decreases the amount of surfactant required to entrain a given amount of air when this fly ash is used to replace a portion of the Portland cement in concrete. All tasks in this project have been successfully completed. A summary of the research effort is briefly described in the paragraphs below.

A total of 6 fly ash samples of differing carbon content were thermally treated using both anoxic and oxidative conditions, through two temperatures (500°C and 800°C).

To optimize conditions a fly ash was:

1. Thermally treated with various temperature-programming rates up to 500°C.
2. Thermally treated to 500°C using a 30°C min^{-1} temperature-programming rate followed by maintaining the temperature at 500°C for different time periods.
3. Treated at various temperature-programming rates followed by maintaining the sample at temperature so that the total heat time was equal to that of thermal treatment to 500°C using a 3°C min^{-1} temperature program rate.

Little difference was observed among the foam index values of the thermally treated products produced by variation in the temperature-programming rate but, the foam index values for all of the thermally treated fly ash samples were significantly less than that of the untreated fly ash. Thus the parameters chosen for this study consisted of a flow rate of 100cm^3 min^{-1} and a temperature-programming rate of 3^oC min^{-1} up to the treatment temperature.

A batch scale thermal reactor for treatment of larger quantities of fly ash, was also constructed. The reactor was designed to permit thermal treatment of 400 - 500 g of fly ash. It was used to treat 6 different fly ash samples to produce representative samples of beneficiated fly ash in quantities suitable for the preparation of concrete test samples.

The batch scale fly ash samples were used to produce concrete test samples. These concrete test samples were tested for compressibility and for air entrainment. The results were compared with those from the corresponding concrete samples prepared using the same fly ash prior to thermal treatment. There was little or no difference in strength performance as a function of the thermal beneficiation process. These tests show that the thermally treated fly ashes may be utilized to produce concrete with compressibility test results comparable to untreated fly ash.

Experimental

CAPTO: All Fly ash samples were characterized using CAPTO. The carbon forms and total carbon content were determined from the overall CO_2 evolution profiles. A 250 mg sample of each fly ash was thoroughly mixed with 12 g of tungsten trioxide and positioned in a quartz combustion tube to ensure gas plug flow through the sample. A 100 cm^3 min^{-1} flow of gas (10% oxygen/90% argon or 100% argon) through the sample was maintained as the combustion tube was heated from room temperature to 1050°C at a temperature ramp of 3°C min^{-1}. The resultant H_2O, CO_2 and SO_2 evolution gases, are swept from the combustion tubes through a secondary furnace, maintained at 1050°C to ensure complete oxidation and consistent temperature/equilibrium conditions, into FTIR gas cells. An FTIR was used to measure the distinctive H_2O, CO_2, SO_2 patterns evolving from the sample. Integration of the gas evolution patterns provided the forms and total hydrogen, carbon, and sulfur content of the sample.

Six fly ash samples of commercial importance were selected for oxidization and pyrolysis to 500 and 800°C in quantities suitable for the preparation of concrete test samples. The carbon content of two of the samples was between 7-9%; two contained between 4-6% carbon; and two contained between 0-2% carbon.

Thermal treatment of fly ash samples for Foam Index measurements was accomplished using CAPTO with 5 g samples of fly ash positioned in quartz combustion tubes. Oxidation treatments were completed using 10% oxygen/90% argon, and the pyrolysis treatments were completed using a 100% argon gas stream. The residues were then recovered from the combustion tubes and FI measurements were completed.

Foam Index: FI measurements were carried out in duplicate using representative samples of the residue recovered from each oxidation or pyrolysis experiment as well as the untreated fly ash samples. A modification of the FI test described by (Dodson, 1990; Gao et al. 1997), and others was used. Two grams of each untreated or thermally treated fly ash sample was mixed with 5 mL of distilled water in a 15 mL i.d. 24 mm x 45 mm vial, and shaken for 1 min. A mixture of the AEA in distilled water (1:40) was added to the mixture in 0.05 mL increments using a 2 mL microburet. The vial was shaken for 15 s, placed upright, opened, and the center portion of the foam layer observed using a microscope light source positioned at the side of the vial above the fly ash and below the foam layer. A stable foam that persisted for 15 s. and obscured all but a small fraction of light transmitted at the center of the foam layer was designated as the endpoint.

Preparation of Concrete Samples: The concrete test samples were obtained using a Concrete Minimix and the results computed for comparison to a full size mix. The "minimix" trial mix procedure is conducted with the exclusion of the coarse aggregate, thus reducing the amount of materials needed, as well as reducing the number of variables. The basic mix proportions for all mixes included the following:

- 452 lbs/cu.yd. cement
- 113 lbs/cu.yd. fly ash (20% of total cementitious)
- 1650 lbs/cu.yd. rock (theoretical only, to determine the appropriate sand and water contents.)
- 4.5-inch slump as target
- 5.5% air as target, as determined by theoretical air-free unit weight and actual unit weight of fresh mortar. AEA - Vinsol Resin

Sand and water were adjusted as necessary to maintain the intended yield and the desired slump. The water/cement ratio was 0.50. Water requirement to achieve a target slump (4 inches +/-) was not affected by the fly ash beneficiation treatments.

Compressibility tests were completed at 3, 7, and 28 days. Air-entrainment values were obtained for all concrete test samples.

Results and Discussion

Task 1: A survey of additional high carbon fly ash samples was completed just prior to funding of this Subcontract. A total of 13 fly ash samples of differing carbon content were thermally treated using both anoxic and oxidative conditions, through two temperatures (500°C and 800°C). Table 1 (Appendix C) shows the % Carbon for 13 fly ashes. A paper presented at The Fourteenth International Symposium on Management and Use of Coal

Combustion Products (CCPs) describes this work. In all cases the products derived from thermal treatment to 500ºC or 800ºC using either anoxic or oxidative conditions show a significant decrease in foam index values compared to those of the untreated fly ashes. This confirms behavior observed with several previous thermally treated fly ash samples and suggests that the treatment may be applicable to a wide variety of fly ashes.

Six of the 13 fly ash samples noted above were obtained in quantities suitable for production of thermally treated fly ash in amounts required for preparation of concrete test samples. These new samples were analyzed and thermally treated to 500^{o}C in 20% oxygen and to 800^{o}C in argon using the optimum conditions developed in Task 2 and the batch furnace described in Task 3.

Task 2: Identify optimum parameters for fly ash treatment. The method of treatment involved plug flow of a gas/gas mixture through a fly ash sample along with a controlled temperature ramp. Before scale up of the treatment from laboratory to larger batch treatments, some parameters were optimized, including:

- Establish optimum controlled atmosphere parameters (static or flow)
- Establish thermal treatment regime and treatment time

Fly ash sample #3 was selected from the available samples to evaluate the effect of temperature-programming rate and total time at temperature on the amount of surfactant required in the foam index test completed on the thermally treated products. The effect of the temperature-programming rate versus foam index on fly ash #3 thermally treated up to 500°C was investigated. Little difference was observed among the foam index values of the thermally treated products produced by variation in the temperature-programming rate (Figure 1) but, the foam index values for all of the thermal treatment test regimes were significantly less than those of the untreated fly ash.

The #3 fly ash was also thermally treated to 500°C using a 30°C min^{-1} temperature-programming rate followed by maintaining the temperature at 500°C for different time periods. The foam index test was performed on each thermally treated product and no significant decrease in the foam index value with time at temperature was observed. The experiment was repeated using various temperature programming rates followed by maintaining the sample at temperature so that the total heat time was equal to that of thermal treatment to 500°C using a 3°C min^{-1} temperature program rate. Foam index results of the treated samples show no significant differences among the samples produced using different temperature programming rates (Figure 2) or differing times at temperature (Figure 3). Thus the parameters chosen for this study consisted of a flow rate of 100cm^{3} min^{-1} and a temperature-programming rate of 3^{o}C min^{-1} up to the treatment temperature.

The decrease in foam index with thermal treatment appears to be independent of the rate of temperature programming (up to 30°C min^{-1}) and length of time (up to 140 minutes) that the sample is held at temperature. Significance: The data suggest that a thermal treatment of the fly ash samples at a temperature increase of 30ºC min^{-1} up to a temperature of 500ºC produces a product with a foam index value not significantly different from that obtained from samples temperature-programmed at a slower rate and/or held at temperature for an extended period of time.

Figure 1: Temperature Ramp vs. Foam Index for Fly Ash #3
(treatment temperature: 500 Deg. C)

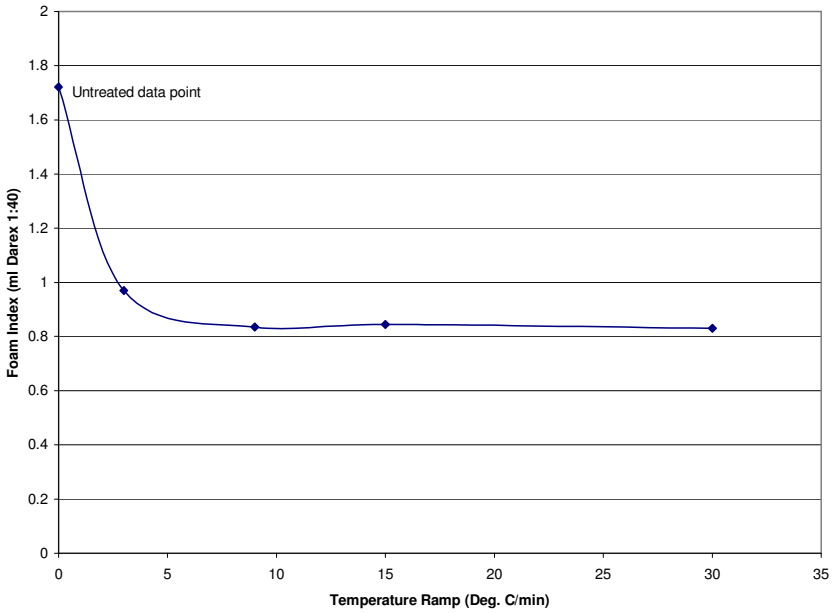


Figure 2: Hold Time vs Foam Index for Fly Ash #3
(treatment temperature: 500 Deg. C)

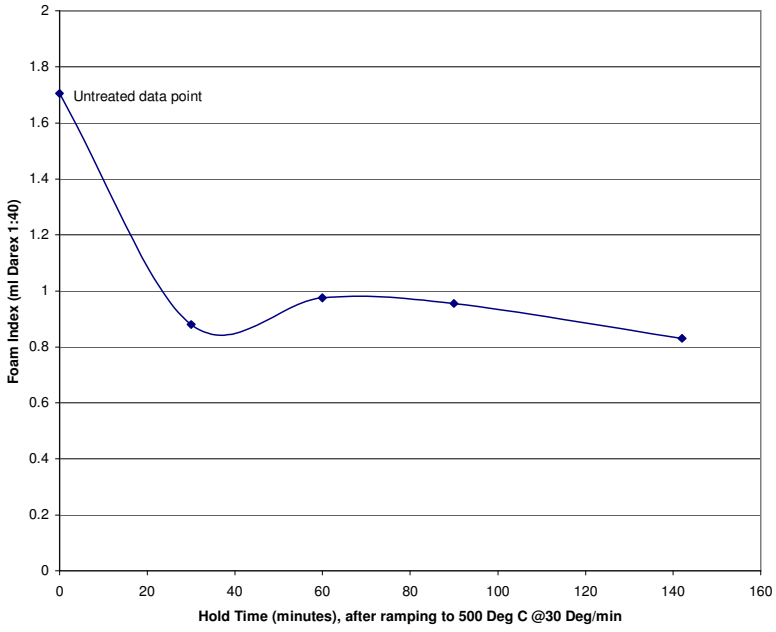
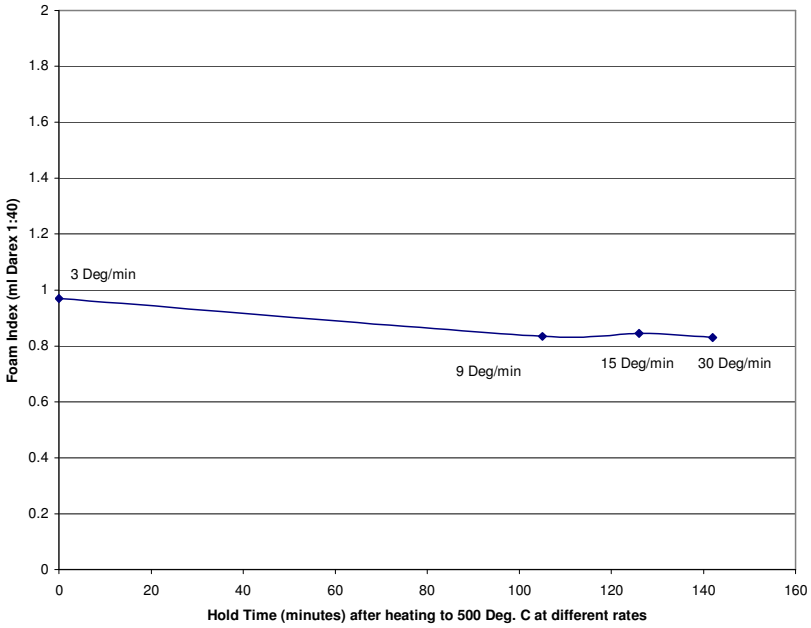


Figure 3: Hold Time (at different rates) vs Foam Index for Fly Ash #3
(treatment temperature: 500 Deg. C)



Task 3 - Construction of a laboratory batch scale system to treat high carbon fly ash using optimized parameters from task 2.

For thermal treatment of quantities of fly ash in the 5 - 6 gram range a steel reaction vessel was constructed. A batch scale thermal reactor for treatment of larger quantities of fly ash, was also constructed. The reactor portion has been enlarged to permit thermal treatment of 400 - 500 g of fly ash instead of the 200 g as indicated in the original task. The gas flow and uniformity of temperature throughout the reaction chamber of this batch system designed for thermal treatment of larger amounts of fly ash (Task 4) was found to be directly comparable to the 5-6 gram reactor system. Oxygen and argon flows are introduced with mass flow controllers capable of flowing 0 - 100-cm^3 min^{-1}.

The reactor vessels are mounted in a Fisher Isotherm Programmable Ashing Furnace Model 495. The furnace is capable of temperatures up through 1100°C, and is programmable from 1°C min^{-1} through 35°C min^{-1}. Initial work consisted of testing the heating capabilities of the batch scale furnace system using 300 – 400 gram quantities of several fly ash samples.

Task 4 - Prepare batch quantities of several fly ash samples in quantities suitable for concrete testing, using parameters identified in Task 2.

Six fly ash samples selected from the 13 fly ash samples previously evaluated were obtained in quantities sufficient for the preparation of concrete test samples. These samples were dried, passed through a 60 mesh sieve, riffled and thermally treated to 500°C and 800°C in the 400-500 gram reactor using the optimum parameters identified in Task 2 to produce representative samples of beneficiated fly ash suitable for the preparation of concrete test samples.

Task 5 - Prepare hardened concrete samples and test for levels of air entrainment and compressibility.

The fly ash samples produced in task 4 were used to produce concrete test samples. These concrete test samples were tested for compressibility and for air entrainment. The results were compared with those from the corresponding concrete samples prepared using the same fly ash prior to thermal treatment.

The concrete test results are shown in Table 2 (Appendix C). The concrete test data was obtained using a Concrete Minimix and the results computed for comparison to a full size mix. The "minimix" trial mix procedure is conducted with the exclusion of the coarse aggregate, thus reducing the amount of materials needed, as well as reducing the number of variables. The basic mix proportions for all mixes included the following:

- 452 lbs/cu.yd. cement
- 113 lbs/cu.yd. fly ash (20% of total cementitious)
- 1650 lbs/cu.yd. rock (theoretical only, to determine the appropriate sand and water contents.)
- 4.5-inch slump as target
- 5.5% air as target, as determined by theoretical air-free unit weight and actual unit weight of fresh mortar.

Sand and water were adjusted as necessary to maintain the intended yield and the desired slump. The water/cement ratio was 0.50. Water requirement to achieve a target slump (4 inches +/-) was not affected by the fly ash beneficiation treatments.

The percent air entrainment as well as the 3, 7, and 28-day compressibility test results are shown in table 2. The average air entrainment of the concrete test samples prepared using untreated fly ash samples was 5.92%; 5.87% for test samples prepared using fly ash treated to 500^{o}C and 5.73% for samples prepared using fly ash treated to 800^{o}C. The compressibility tests results were completed at 3, 7, and 28 days using 2" test cylinders and the average values are in or above the expected range for an air entrained product with a water/cement ratio of 0.50. The results show very little or no difference in strength performance as a function of ash beneficiation (i.e. thermal treatment to decrease foam index).

Task 6 - Evaluate concrete products test results to determine suitability for commercial application.

Other than for fly ash sample #1 treated to 500^{o}C, which showed considerably lower compression strengths, which the testing laboratory indicated was probably an anomaly that is not necessarily repeatable, there was little or no difference in strength performance as a function of the thermal beneficiation process. These tests show that the thermally treated fly ashes may be utilized to produce concrete with compressibility test results comparable to untreated fly ash.

Task 7 - Preparation of periodic and final reports.

With the completion of this final report, all technical and financial reports related to the project have been completed.

Conclusion

Thermally treated fly ash produced from this study and used in concrete mixtures results in a decrease in the amount of surfactant required to entrain a given amount of air in the concrete.

Other than for fly ash sample #1 treated to 500^{o}C, which showed considerably lower compression strengths, which the testing laboratory indicated was probably an anomaly that is not necessarily repeatable, there was little or no difference in strength performance as a function of the thermal beneficiation process. These tests show that the thermally treated fly ashes may be utilized to produce concrete with compressibility test results comparable to untreated fly ash.

References

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2. Gao, Y.-M., Shim, H.-S., Hurt, R.H., Suuberg, E.M., "Effects of Carbon on Air Entrainment in fly ash concrete: the role of soot and carbon black", *Energy & Fuels*, 11,457-462, 1997.

A number of other references are found in Appendix A and B.

Appendix A

LOWERING FOAM INDEX IN HIGH-CARBON FLY ASHES FOR CONCRETE APPLICATIONS

Robert B. LaCount[1, 2], John P. Baltrus[3], Timothy L. Banfield[4], J. Rodney Diehl[3], Keith A. Giles[1], Douglas G. Kern[1, 2], Tiffany A. Leyda[1], Patrice J. Pique[1]

rlacount@waynesburg.edu

[1]Dept. of Chemistry, Waynesburg College, 51 West College Street, Waynesburg, PA 15370 USA
[2]ViRoLac Industries, 403 Arbor Court, Waynesburg, PA 15370 USA
[3]National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA 15236-0940 USA
[4]Allegheny Energy Supply, 4350 Northern Pike, Monroeville, PA 15146 USA

Keywords: Fly Ash, carbon, oxidation, pyrolysis, concrete, characterization

Disclaimer

Introduction

The overall objective of work in this area is to develop a commercial method that will decrease the interaction between fly ash and the surfactants used to entrain air in concrete. This will decrease the amount of surfactant required to entrain a given amount of air and thus increase the fly ash suitable for use in concrete products.

Fly ash is often used commercially as a replacement for some of the Portland cement in concrete products. Air-Entraining Admixtures (AEA's) are surfactants used to entrain air in concrete mixtures, improve the workability of the mixtures and the durability of the concrete products to freeze-thaw cycles (Dodson, 1990). This paper describes continuing work directed toward treatment of high-carbon fly ashes to decrease the amount of AEA required in concrete applications utilizing fly ash. The background studies were described in a paper presented at the 18th Annual International Pittsburgh Coal Conference (LaCount et al. 2001) and are summarized below.

Inefficient combustion and the use of low-NO_x burners in coal-fired boilers has resulted in variable amounts of unburned carbon in fly ash (Baltrus et al., 2001). The use of high-carbon fly ashes in concrete often increases in the amount of AEA required for proper air entrainment. Variations in carbon content and amount of AEA required directly impact the sale of fly ash for use with cement to produce concrete products. Even though fly ash meets loss on ignition (LOI) specifications, variation in the adsorption properties of the fly ash may result in variation of the amount of surfactant required (Freeman et al., 1997). The foam index (FI) test involves titration of a portion of the concrete mixture with an aqueous solution of the AEA until a stable foam results, and is used to determine the amount of AEA required in the concrete. A number of factors that affect air entrainment in concrete mixtures have been identified. For example, as the carbon content of the pozzolans increase, the level of entrained air decreases (Dodson, 1990). Freeman et al. (1997) examined the interactions of carbon-containing fly ash with surfactants and found that the interactions are time dependent and the degree of interaction correlates only roughly with carbon content.

Gao et al. (1997) examined the interaction between several fly ash carbons and carbon blacks and an air-entraining admixture (AEA) and found that surfactant interaction increased with an increase in carbon surface area. Yu et al. (2000) found that a low specific area fly ash containing 17 wt % carbon produced by co-firing coal and petroleum coke had no measurable surfactant adsorptivity. Hill et al. (1998) examined a number of fly ash samples using thermal and optical microscopy methods. They found that: differential thermal analysis was not a useful predictive tool for performance of fly ash in air-entrained mortar; optical characterization of the forms of carbon in fly ash did not relate fly ash performance to mortar air entrainment, but it did indicate that a significant portion of carbon in fly ash is sub-micron in size; potential effects of carbon chemistry on surfactant adsorption capacity cannot be identified using surface areas determined with an inert gas such as nitrogen. Gao et al. (2001) reported ozonation for chemical modification of the carbon surfaces in fly ash as a route to reducing the adsorptivity of fly ash carbon toward surfactants.

One approach to characterization of fly ash carbon is to focus on partial oxidation to selectively remove each carbon form followed by characterization of the carbon form or forms remaining in the fly ash residues. Accordingly, two different fly ash samples derived from eastern bituminous coals were thermally treated under both oxidizing and inert conditions (LaCount et al., 1997, 2001) to a range of temperatures from 100°C to 769°C. Each residue was characterized using a controlled-atmosphere programmed-temperature oxidation instrument (CAPTO), and FI (using an alkaline solution of fatty acids as AEA). The CAPTO results indicated the presence of at least four different carbon forms in the untreated fly ash samples (LaCount et al., 1998 and 2000). In all cases, a decrease in FI value was observed. A significant decrease in the FI value occurred at approximately 400°C prior to significant loss of carbon indicating that factors other than carbon content may play a role in determining a sample's FI. In order to identify those factors, the thermally treated fly ash residues were examined by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and petrographic analysis. XPS has previously been used to distinguish the presence of various graphitic carbon types in the untreated fly ash. The types of carbon were found to vary as a function of oxidation temperature (LaCount et al., 2001). All of the bulk carbon was removed by oxidation to 769°C. SEM measurements of the untreated and oxidized fly ash samples showed no change in morphology of the ash after oxidation. Petrographic analysis showed no difference in carbon anisotropy at the various temperatures prior to the complete oxidation of carbon.

To ensure that the decrease in foam index observed above was applicable to other fly ashes, a series of 13 different fly ashes derived from eastern bituminous coals were thermally treated to 500°C and 800°C. Both oxidative and inert conditions were used and the products characterized using FI and conductance (LaCount et al., 2001). In all cases the FI values (using an alkaline solution of fatty acids as AEA) of the thermally treated fly ash samples were lower in comparison to those of the untreated samples. Additionally, the conductance of samples thermally treated to 800°C under inert conditions was found to be lower than that of the untreated fly ash samples indicating that the thermal treatments may lessen the solubility of ions that can interfere with the AEA in the FI measurement. These results prompted the further work described in this paper. Baltrus et al. (2001) optimized an ultraviolet-visible spectrophotometric method for measuring the adsorption of air-entraining surfactants on the components of cement. It was found that FI was a poor means for measuring adsorption capacity in high carbon fly ashes due to an insufficient equilibration time used in the foam index measurements.

A better understanding of the interactions of air-entraining surfactants with unburned carbon forms and the mineral components in fly ash concrete mixtures may lead to improved methodology for maintaining the level of air as the concrete cures. A better prediction of AEA performance with different fly ash samples may help to minimize variability in concrete products.

Experimental

CAPTO: All Fly ash samples were characterized using CAPTO. The carbon forms and total carbon content were determined from the overall CO_2 evolution profiles. A 250 mg sample of each fly ash was thoroughly mixed with 12 g of tungsten trioxide and positioned in a quartz combustion tube to ensure gas plug flow through the sample. A 100 cm^3 min^{-1} flow of gas (10% oxygen/90% argon or 100% argon) through the sample was maintained as the combustion tube was heated from room temperature to 1050°C at a temperature ramp of 3°C min^{-1}. The resultant H_2O, CO_2 and SO_2 evolution gases, are swept from the combustion tubes through a secondary furnace, maintained at 1050°C to ensure complete oxidation and consistent temperature/equilibrium conditions, into FTIR gas cells. An

FTIR was used to measure the distinctive H_2O, CO_2, SO_2 patterns evolving from the sample. Integration of the gas evolution patterns provided the forms and total hydrogen, carbon, and sulfur content of the sample.

Six fly ash samples of commercial importance were selected for oxidization and pyrolysis to 500 and 800^oC in quantities suitable for the preparation of concrete test samples. The carbon content of two of the samples was between 7-9%; two contained between 4-6% carbon; and two contained between 0-2% carbon.

Thermal treatment of fly ash samples for Foam Index measurements was accomplished using CAPTO with 5 g samples of fly ash positioned in quartz combustion tubes. Oxidation treatments were completed using 10% oxygen/90% argon, and the pyrolysis treatments were completed using a 100% argon gas stream. The residues were then recovered from the combustion tubes and FI measurements were completed.

Foam Index: FI measurements were carried out in duplicate using representative samples of the residue recovered from each oxidation or pyrolysis experiment as well as the untreated fly ash samples. A modification of the FI test described by (Dodson, 1990; Gao et al. 1997), and others was used. Two grams of each untreated or thermally treated fly ash sample was mixed with 5 mL of distilled water in a 15 mL i.d. 24 mm x 45 mm vial, and shaken for 1 min. A mixture of the AEA in distilled water (1:40) was added to the mixture in 0.05 mL increments using a 2 mL microburet. The vial was shaken for 15 s, placed upright, opened, and the center portion of the foam layer observed using a microscope light source positioned at the side of the vial above the fly ash and below the foam layer. A stable foam that persisted for 15 s. and obscured all but a small fraction of light transmitted at the center of the foam layer was designated as the endpoint.

Conductance: Conductance measurements were performed to determine the relative solubility of conductive ions in a number of the fly ash samples before and after pyrolysis. The measurement was carried out by placing 0.1 g of fly ash in a 100 mL beaker to which 25 mL of deionized water was added along with a Teflon-coated stirring bar. The solution was stirred for 10 minutes and filtered. The filtrate was then tested using a conductance meter.

Preparation of Concrete Samples: The concrete test samples were obtained using a Concrete Minimix and the results computed for comparison to a full size mix. The “minimix” trial mix procedure is conducted with the exclusion of the coarse aggregate, thus reducing the amount of materials needed, as well as reducing the number of variables. The basic mix proportions for all mixes included the following:

- 452 lbs/cu.yd. cement
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- 4.5-inch slump as target
- 5.5% air as target, as determined by theoretical air-free unit weight and actual unit weight of fresh mortar. AEA - Vinsol Resin

Sand and water were adjusted as necessary to maintain the intended yield and the desired slump. The water/cement ratio was 0.50. Water requirement to achieve a target slump (4 inches +/-) was not affected by the fly ash beneficiation treatments.

Compressibility tests were completed at 3, 7, and 28 days. Air-entrainment values were obtained for all concrete test samples.

Results and Discussion

The initial goal of this work was to thermally treat commercially important fly ash samples under oxidative conditions as a route to decrease surfactant adsorption by the fly ash. Six fly ash samples of commercial interest were selected for thermal treatments and testing with air-entraining surfactants to evaluate the FI value (using both an alkaline solution of fatty acids and a Vinsol resin as AEA's). These fly ash samples were prepared in quantities suitable for the preparation of concrete test samples. Concrete test samples prepared from thermally treated fly ashes were evaluated for the amount of entrained air and compressibility and the data compared with that from concrete test samples prepared using the untreated fly ashes. These results are described below.

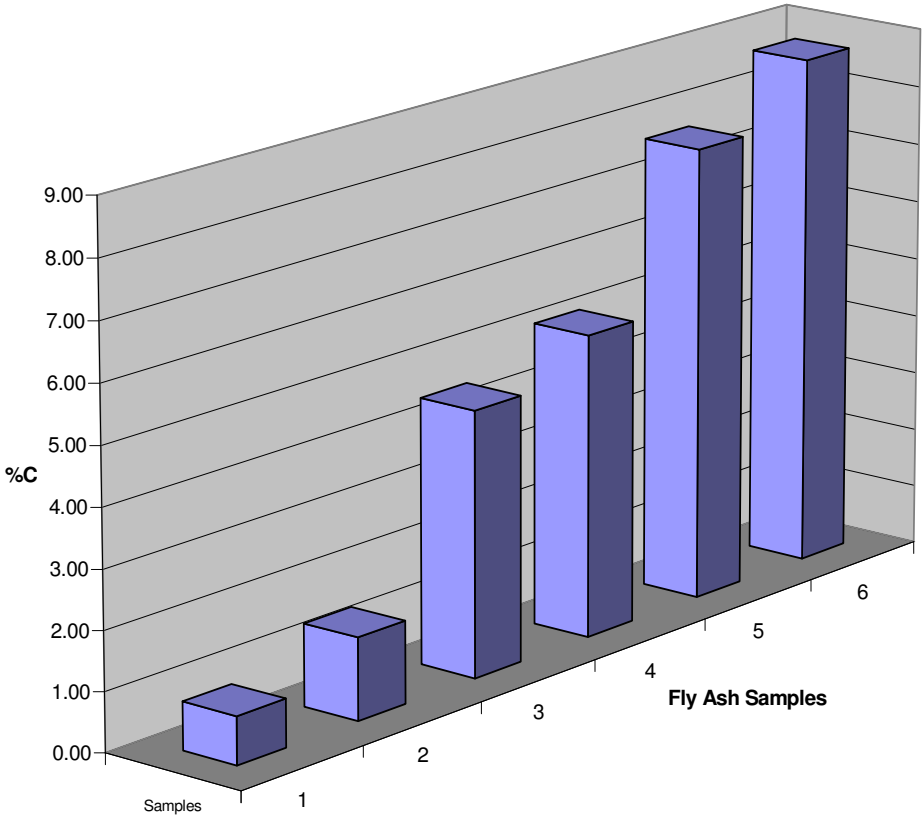

Figure 1: % Carbon for Fly Ash Samples

Figure 1 shows the carbon content of the six fly ash samples selected for this study. Note that two low carbon content (0.81, 1.39 %), two medium carbon content (4.49, 5.13 %) and two higher carbon content samples (7.70, 8.69 %) are included in the selection.

The results of oxidative thermal treatment are shown in figure 2. Note that a significant decrease in FI (using an alkaline solution of fatty acids as AEA) resulted when the samples were thermally treated to 500^{o}C. In all cases the fly ash samples thermally treated to 800^{o}C show an even lower FI value.

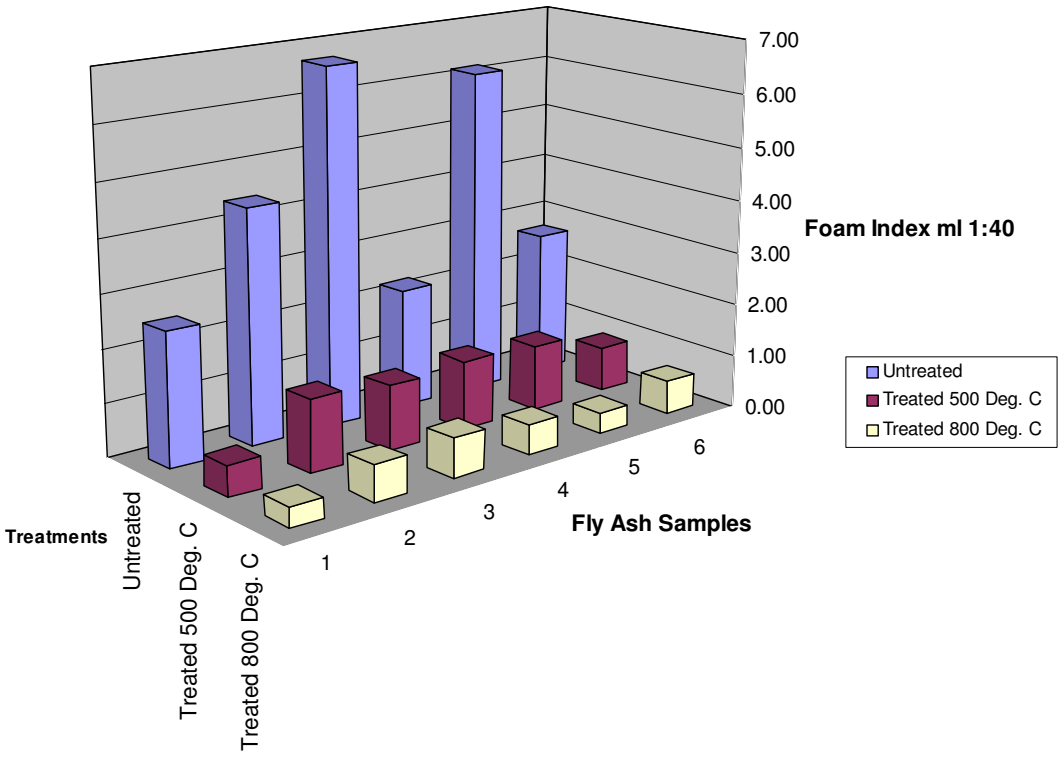

Figure 2:Foam Index Results Using Alkaline Solution of Fatty Acids as AEA

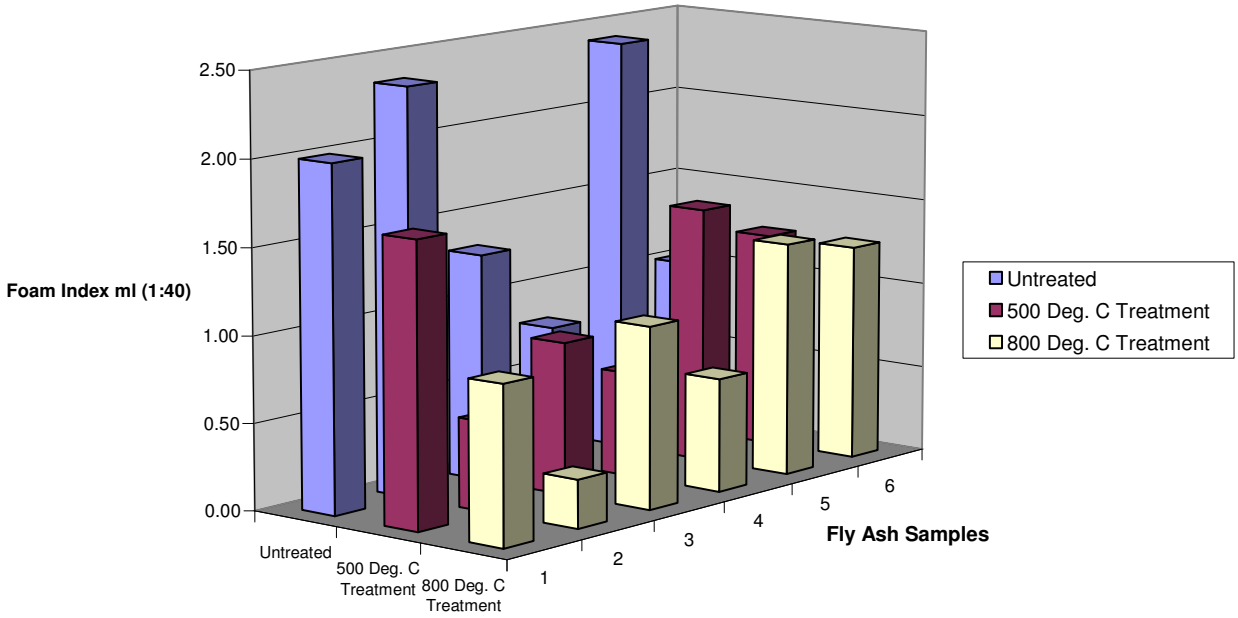

Figure 3: Foam Index Results Using Vinsol Resin as AEA

The AEA used in the preparation of the concrete test samples was a Vinsol resin. This resin is complex and contains phenolic structures, waxes and terpenes, and resin acids. The FI was measured for the fly ash samples with the same Vinsol resin used to prepare the concrete test samples. The results are shown in figure 3. The untreated fly ash samples 1 - 5 required a significantly greater amount of AEA compared to samples thermally treated at 500°C. Fly ash sample 6 required somewhat less surfactant prior to thermal treatment than after treatment. Samples 3 and 6 thermally treated to 800°C showed a slight increase in the amount of AEA required compared to thermal treatment to 500°C.

The AEA's used in the FI titrations reported here, are (1) an alkaline solution of fatty acid salts and (2) a Vinsol resin. The surfactant properties of such "soaps" are affected by alkaline earth ions such as calcium and magnesium. Any affect that thermal treatment may have on the solubility of such ions in solution was determined by measuring the conductance of solutions exposed to the untreated and treated fly ashes.

Conductance results are shown in Table 1. Note that the conductance is lower in all cases after thermal treatments under inert conditions. However, the magnitude of the decrease shows no apparent correlation with changes in FI. This may be due to the fact that conductance is also affected by ions other than calcium and magnesium that have no effect on the surfactant. The decrease in conductance is probably due to incorporation of some of the previously soluble ions into insoluble structures induced by thermal treatment. However, the thermal treatment likely does not render all of the calcium and magnesium insoluble.

Table 1. Conductance for Fly Ash Samples, Untreated and after Pyrolysis

Fly Ash Sample #	*Conductance,(μS/g ash) Untreated*	*Conductance,(μS/g ash) Pyrolysis to:*	
		500 ° C	*800 ° C*
1	160.1	127.5	113.6
2	127.5	99.5	84.7
3	125.0	118.6	70.7
4	163.8	108.6	84.2
5	73.5	58.0	21.7
6	175.9	141.9	135.8

The air-entrainment and compressibility test results for concrete test samples are shown in table 2. The percent air entrainment as well as the 3, 7, and 28-day compressibility test results are shown. The average air entrainment of the concrete test samples prepared using untreated fly ash samples was 5.92%; 5.87% for test samples prepared using fly ash treated to 500°C and 5.73% for samples prepared using fly ash treated to 800°C. The compressibility tests results were completed at 3, 7, and 28 days using 2" test cylinders and the average values are in or above the expected range for an air-entrained product with a water/cement ratio of 0.50. The results show very little or no difference in strength performance as a function of ash beneficiation (i.e. thermal treatment to decrease foam index).

Table 2: Summary of Fly Ash Concrete Test Results

	Fly Ash #1			*Fly Ash #2*			*Fly Ash #3*		
Treatment	Unt.	500°C	800°C	Unt.	500°C	800°C	Unt.	500°C	800°C
Air content %	5.9	6.4	5.6	6.1	6.4	6.5	6.9	6.2	5
Water/cy	269	276	280	279	278	277	276	288	280
Slump	4.25	4.5	4.5	4.5	4	4.5	4.25	5	4.5
3-day psi	2770	1750	2740	2580	2610	2360	2290	2450	2040

7-day psi	3720	2550	3790	3600	3250	2990	3280	3370	3310
28-day psi	4941	3565	5305	4688	4930	4379	4400	4030	4680
	Fly Ash #4			*Fly Ash #5*			*Fly Ash #6*		
Treatment	Unt.	500°C	800°C	Unt.	500°C	800°C	Unt.	500°C	800°C
Air content %	6.2	6.5	6.1	4.9	3.8	4.7	5.5	5.9	6.5
Water/cy	278	277	278	295	307	294	287	286	284
Slump	4	4.25	4	4.5	5	4.25	4.5	3.75	4
3-day psi	2360	1880	2420	2320	2610	2230	2360	2130	2260
7-day psi	3470	3340	3370	3530	3690	3150	3600	3370	3250
28-day psi	4710	4680	4540	4640	4930	4700	4340	4600	4410

Conclusions

These experiments indicate that both unburned carbon and soluble ions such as calcium and magnesium can have an impact on FI. Their relative effects are most likely dependent on the properties of the carbon and mineral components of the fly ash and not their relative proportions in the ash.

Thermal treatment of the fly ashes under oxidative conditions clearly has an impact on FI. Conductance measurements of fly ash thermally treated under inert conditions does suggest a decrease in the solubility of ions which are known to interfere with the fatty acids surfactant in the FI test, thus lowering the FI values.

The average air entrainment of the concrete test samples prepared using untreated fly ash samples was 5.92%; 5.87% for test samples prepared using fly ash treated to 500°C and 5.73% for samples prepared using fly ash treated to 800°C. These averages are near the target air-entrainment values.

The compressibility tests results are in or above the expected range for an air-entrained product with a water/cement ratio of 0.50. The results show very little or no difference in strength performance as a function of thermal treatment to decrease foam index.

Acknowledgements

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Appendix B

TREATMENTS FOR LOWERING FOAM INDEX IN HIGH-CARBON FLY ASHES FOR CONCRETE APPLICATIONS

Robert B. LaCount[1, 2], John P. Baltrus[3], Timothy L. Banfield[4], J. Rodney Diehl[3], Keith A. Giles[1], Douglas G. Kern[1, 2], Tiffany A. Leyda[1], Patrice J. Pique[1]

rlacount@waynesburg.edu

[1]Dept. of Chemistry, Waynesburg College, 51 West College Street, Waynesburg, PA 15370 USA
[2]ViRoLac Industries, 403 Arbor Court, Waynesburg, PA 15370 USA
[3]National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA 15236-0940 USA
[4]Allegheny Energy Supply, 4350 Northern Pike, Monroeville, PA 15146 USA

Keywords: Fly Ash, carbon, oxidation, pyrolysis, concrete, characterization

Disclaimer

Introduction

Commercially, fly ash is often used as a replacement for some of the Portland cement in concrete products. Surfactants, used to entrain air in the concrete mixtures, improve the workability of the mixtures and the durability of the concrete products to freeze-thaw cycles (Dodson, 1990).

Inefficient combustion and the use of low-NO_x burners in coal-fired boilers, has resulted in variable increases in the unburned carbon content of fly ash (Baltrus et al., 2001). When high-carbon fly ashes are used in concrete, often an increase in the amount of surfactant is required. These variations in carbon content and amount of surfactant required directly impact the sale of fly ash for use with cement to produce concrete products. Even when fly ash meets loss on ignition (LOI) specifications, variation in the adsorption properties of the fly ash may result in changes in the amount of surfactant required (Freeman et al., 1997). The foam index (FI) test, which involves titration of a portion of the concrete mixture with an aqueous solution of the surfactant until a stable foam results, is used to determine the amount of surfactant required in the concrete.

Factors affecting air entrainment in the concrete mixtures have been identified. For example, as the carbon content of the pozzolans increase, the level of entrained air decreases (Dodson, 1990). Freeman et al. (1997) examined the interactions of carbon-containing fly ash with surfactants and found that the interactions are time dependent and that the degree of interaction correlates only roughly with carbon content

Gao et al. (1997) examined the interaction between several fly ash carbons and carbon blacks and an air-entraining admixture (AEA) and found that surfactant interaction increased with an increase in carbon surface area. Yu et al. (2000) found that a low specific area fly ash containing 17 wt % carbon produced by co-firing coal and petroleum coke

had no measurable surfactant adsorptivity. Hill et. al. (1998) examined a number of fly ash samples using thermal and optical microscopy methods. They found that: differential thermal analysis was not a useful prognostic tool for performance of fly ash in air entrained mortar; optical characterization of the forms of carbon in fly ash did not relate fly ash performance to mortar air entrainment, but it did indicate that a significant portion of carbon in fly ash is sub-micron in size; potential effects of carbon chemistry on surfactant adsorption capacity cannot be identified using surface areas determined with an inert gas such as nitrogen. Gao et al. (2001) reported ozonation for chemical modification of the carbon surfaces in fly ash as a route to reducing the adsorptivity of fly ash carbon toward surfactants.

One approach for characterization of fly ash carbon is to focus on partial oxidation to selectively remove each carbon form followed by characterization of the carbon form or forms remaining in the fly ash residues. LaCount et al. (1997), using this approach, characterized the carbon in several fly ash samples using a controlled-atmosphere programmed-temperature oxidation (CAPTO) instrument and found oxidation generally occurring in four different temperature zones. Several of the oxidation temperatures are well above those of coals, activated carbons, and other chars but significantly below the oxidation temperature of graphite. The amount of carbon dioxide evolving in each temperature range was evaluated. That work prompted progressive partial oxidation and pyrolysis studies of numerous fly ash samples followed by foam index (FI) measurements to assess any change in surfactant adsorption properties of each partially oxidized or pyrolyzed residue (LaCount et al., 1998 and 2001). A major decrease in FI occurred between room temperature and approximately 400^{o}C prior to significant loss of carbon and resulted in further work described in this paper. Baltrus et al. (2001) optimized an ultraviolet-visible spectrophotometric method for measuring the adsorption of air-entraining surfactants on the components of cement. It was found that FI was a poor means for measuring adsorption capacity in high carbon fly ashes due to an insufficient equilibration time used in the foam index measurements.

A better understanding of the variation in interactions of air entraining surfactants with unburned carbon forms and the mineral components in fly ash concrete mixtures may lead to improved methodology for maintaining the level of air as the concrete cures. A better prediction of
surfactant performance with different fly ash samples may help to minimize variability in concrete products.

Experimental

CAPTO: All Fly ash samples were characterized using CAPTO. The carbon forms and total carbon content were determined from the overall CO_2 evolution profiles. A 250 mg sample of each fly ash was thoroughly mixed with 12 g of tungsten trioxide and positioned in a quartz combustion tube to ensure gas plug flow through the sample. A 100 cm^3 min^{-1} flow of gas (10% oxygen/90% argon or 100% argon) through the sample was maintained as the combustion tube was heated from room temperature to 1050^{o}C at a temperature ramp of 3^{o}C min^{-1}. The resultant H_2O, CO_2 and SO_2 evolution gases, are swept from the combustion tubes through a secondary furnace, maintained at 1050^{o}C to ensure complete oxidation and consistent temperature/equilibrium conditions, into FTIR gas cells. An FTIR was used to measure the distinctive H_2O, CO_2, SO_2 patterns evolving from the sample. Integration of the gas evolution patterns provided the forms and total hydrogen, carbon, and sulfur content of the sample.

Six fly ash samples of commercial importance were selected for oxidization and pyrolysis to 500 and 800^{o}C in quantities suitable for the preparation of concrete test samples. The carbon content of two of the samples was between 7-9%; two contained between 4-6% carbon; and two contained between 0-2% carbon.

Thermal treatment of fly ash samples for Foam Index measurements was accomplished using CAPTO with 5 g samples of fly ash positioned in quartz combustion tubes. Oxidation treatments were completed using 10% oxygen/90% argon, and the pyrolysis treatments were completed using a 100% argon gas stream. The residues were then recovered from the combustion tubes and FI measurements were completed.

Foam Index: FI measurements were completed in duplicate using representative samples of the residue recovered from each oxidation or pyrolysis experiment as well as the untreated fly ash samples. A modification of the FI test described by (Dodson, 1990; Gao et al. 1997), and others was used. Two grams of each untreated or thermally treated fly ash sample was mixed with 5 mL of distilled water in a 15 mL i.d. 24 mm x 45 mm vial, and shaken for 1 min. A mixture of Darex® II surfactant (W.R. Grace & Co.) in distilled water (1:40) was added to the mixture in 0.05 mL increments using a 2 mL microburet. The vial was shaken for 15 s, placed upright, opened, and the center portion of the

foam layer observed using a microscope light source positioned at the side of the vial above the fly ash and below the foam layer. A stable foam that persisted for 15 s. and obscured all but a small fraction of light transmitted at the center of the foam layer was designated as the endpoint.

Conductance: Conductance measurements were performed to determine the relative solubility of conductive ions in a number of the fly ash samples before and after pyrolysis. The measurement was carried out by placing 0.1 g of fly ash in a 100 mL beaker to which 25 mL of deionized water was added along with a Teflon-coated stirring bar. The solution was stirred for 10 minutes and filtered. The filtrate was then tested using a conductance meter.

Results and Discussion

The initial goal of the present work was to thermally treat commercially important fly ash samples under both oxidative and inert conditions as a route to decrease surfactant adsorption by the fly ash. In order to evaluate the effectiveness of the thermal treatments in lowering surfactant adsorption, both the untreated and thermally treated samples were characterized using both FI, and conductance measurements.

The overall objective of this work is to develop a method that will decrease the interaction between fly ash and the surfactants used to entrain air in concrete products thus increasing the amount of fly ash suitable for use in concrete products. Thermally treated fly ash samples that have a decreased interaction with air entraining surfactants as evidenced by a significantly lower FI value will be prepared in quantities suitable for the preparation of concrete test samples. Concrete test samples prepared from these thermally treated products will be evaluated for the amount of entrained air as well as compressibility and the data compared with that from concrete test samples prepared using the untreated fly ashes.

Previously (LaCount et al., 2001) two different fly ash samples derived from eastern bituminous coals had been thermally treated under both oxidizing and inert conditions to a range of temperatures from 100^{o}C to 769^{o}C and each residue characterized using CAPTO, and FI. The CAPTO results indicated the presence of at least four different carbon forms in the untreated fly ash samples. In all cases, a decrease in FI values was observed. A significant decrease in the FI values occurred prior to significant loss of carbon indicating that factors other than carbon content may play a role in determining a sample's FI. In order to identify those factors, the thermally treated fly ash residues were examined by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and petrographic analysis. XPS has previously been used to distinguish the presence of various graphitic (LaCount et al., 2001) carbon types in the untreated fly ash. The types of carbon were found to vary as a function of oxidation temperature. All of the bulk carbon was removed by oxidation to 769^{o}C. SEM measurements of the untreated and oxidized fly ash samples showed no change in morphology of the ash after oxidation. Petrographic analysis showed no difference in carbon anisotropy at the various temperatures prior to the complete oxidation of carbon.

To ensure that the decrease in foam index observed above was applicable to other fly ashes, a series of 13 different fly ashes derived from eastern bituminous coals were thermally treated to 500^{o}C and 800^{o}C under both oxidative and inert conditions and characterized using FI and conductance (LaCount et al., 2001). In all cases the FI values of the thermally treated fly ash samples were lower in comparison to those of the untreated samples. Additionally, the conductance of samples thermally treated to 800^{o}C under inert conditions was found to be lower than that of the untreated fly ash samples indicating that the thermal treatments may lessen the solubility of ions that can interfere with the surfactant in the FI measurement.

Based on the previous observations described above that FI values of thermally treated fly ashes are significantly lower than those of untreated fly ash samples, an additional series of six commercially important fly ash samples were subjected to similar treatments and used for further study of the relation between FI, conductance, and their behavior under CAPTO. These results are described below. Each untreated fly ash is being used to generate quantities of thermally treated fly ash required for the preparation and testing of concrete samples. These results will be described in a future report.

Figure 1: % Carbon for Fly Ash Samples

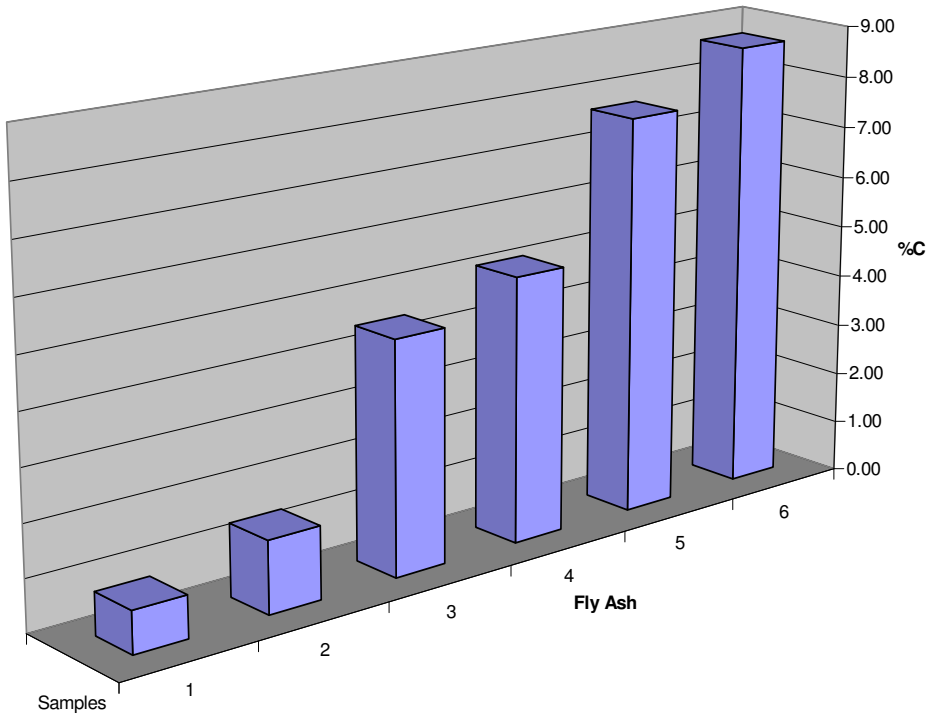


Figure 1 shows the carbon content of the six fly ash samples selected for this study. Note that two low carbon content (0.81, 1.39 %), two medium carbon content (4.49, 5.13 %) and two higher carbon content samples (7.70, 8.69 %) are included in the selection.

The FI results for the fly ash samples treated under inert conditions to the two different temperatures are summarized in figure 2. Note that a significant decrease in FI resulted when the samples were treated to 500^{o}C. In all cases the fly ash samples thermally treated to 800^{o}C under argon flow show an even lower FI value. These lower FI values are observed even though loss of carbon content during this thermal treatment is minimal.

The results of oxidative thermal treatment are shown in figure 3. Note that the same trend observed in figure 2 is retained in this plot. However, samples 2 and 5 show a further significant decrease in FI under oxidative thermal treatment to 500^{o}C compared to the thermal treatment under argon flow. Additionally, sample 5 in figure 3 treated to 800^{o}C under oxidative conditions also shows a further significant decrease in FI compared to the corresponding treatment under argon flow. It is of interest to note that only three of the oxidized samples showed significantly lower FI values compared to the FI values obtained from thermal treatment under argon flow where carbon loss is minimal.

Figure 2: Foam Index Values Argon Treatment

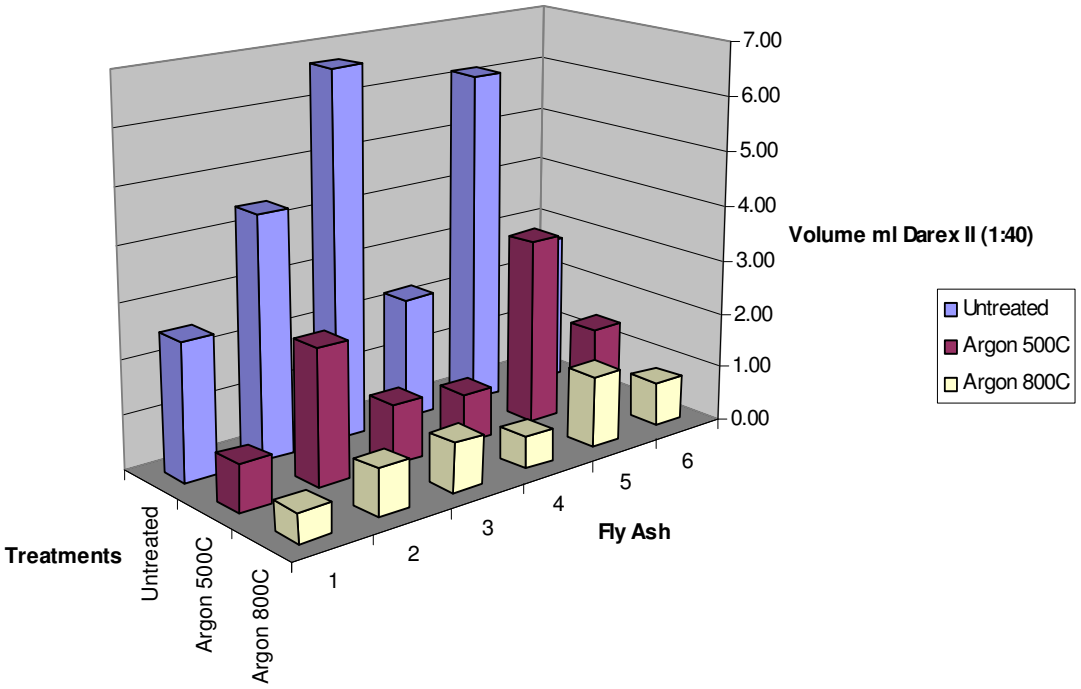
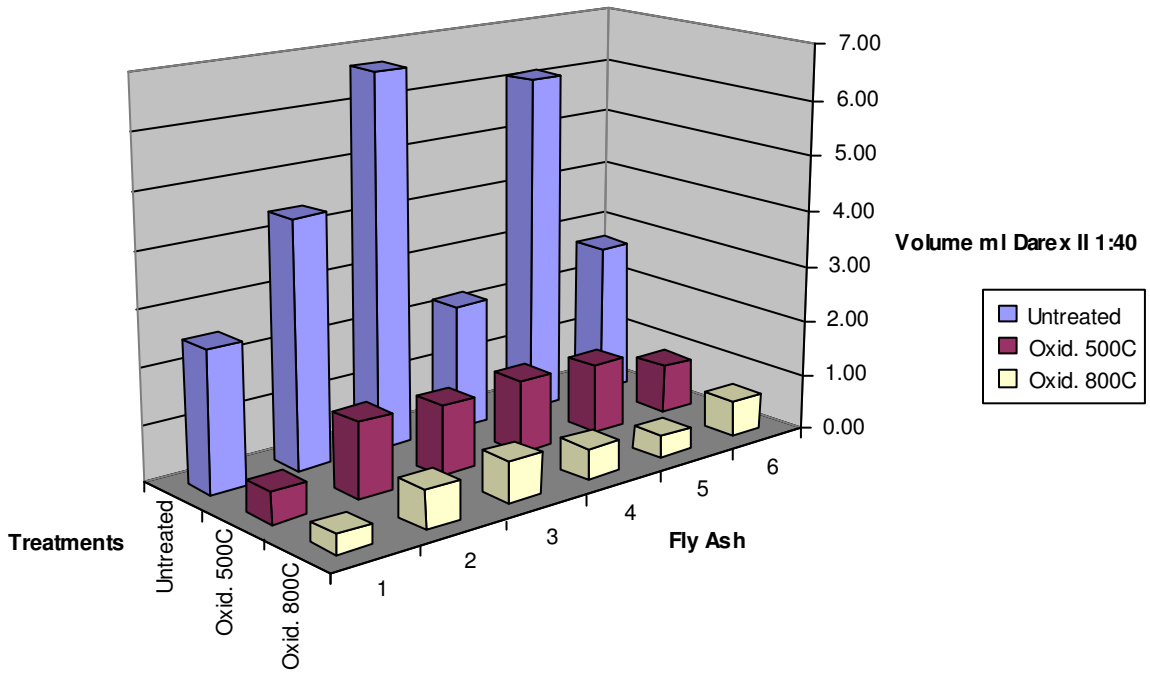


Figure 3: Foam Index Values Oxidized Treatment



Darex® II, the surfactant used in the FI titrations reported here, is an alkaline solution of fatty acid salts, and the surfactant properties of such "soaps" are affected by alkaline earth ions such as calcium and magnesium. Any affect that thermal treatment may have on the solubility of such ions in solution was determined by measuring the conductance of solutions exposed to the untreated and treated fly ashes.

Conductance results are shown in Table 1. Note that the conductance is lower in all cases after thermal treatments under inert conditions. However, the magnitude of the decrease shows no apparent correlation with changes in FI. This may be due to the fact that conductance is also affected by ions other than calcium and magnesium that have no effect on the surfactant. The decrease in conductance is probably due to incorporation of some of the previously soluble ions into insoluble structures induced by thermal treatment. However, the thermal treatment likely does not render all of the calcium and magnesium insoluble.

Table 1. Conductance for Fly Ash Samples, Untreated and after Pyrolysis

Sample	*Conductance,(μS/g ash) Untreated*	*Conductance,(μS/g ash) Pyrolysis to:*	
		500 ^{o}C	*800 ^{o}C*
1	160.1	127.5	113.6
2	127.5	99.5	84.7
3	125.0	118.6	70.7
4	163.8	108.6	84.2
5	73.5	58.0	21.7
6	175.9	141.9	135.8

Conclusions

These experiments indicate that both unburned carbon and soluble ions such as calcium and magnesium can have an impact on FI. Their relative effects are most likely, dependent on the properties of the carbon and mineral components of the fly ash and not their relative proportions in the ash.

Thermal treatment of the fly ashes under oxidative as well as inert atmosphere conditions clearly has an impact on FI. Conductance measurements of fly ash thermally treated under inert conditions does suggest a decrease in the solubility of ions that can interfere with the surfactant in the FI test, thus lowering the FI values. The ions that are rendered insoluble may be incorporated into amorphous "glass like" phases.

We are continuing to examine the effects of treatment to higher temperatures and other possible modes of surfactant adsorption by fly ash.

Acknowledgements

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Appendix C

Table 1: 13 Fly Ash Samples

Number	% Carbon
1	14.64
2	12.21
3	9.01
4	8.01
5	7.71
6	6.95
7	5.35
8	4.54
9	4.03
10	3.76
11	2.65
12	1.04
13	0.27

Table 2: Summary of Fly Ash Concrete Test Results

	Fly Ash #1			*Fly Ash #2*			*Fly Ash #3*		
Treatment	Unt.	500°C	800°C	Unt.	500°C	800°C	Unt.	500°C	800°C
Air content %	5.9	6.4	5.6	6.1	6.4	6.5	6.9	6.2	5
Water/cy	269	276	280	279	278	277	276	288	280
Slump	4.25	4.5	4.5	4.5	4	4.5	4.25	5	4.5
3-day psi	2770	1750	2740	2580	2610	2360	2290	2450	2040
7-day psi	3720	2550	3790	3600	3250	2990	3280	3370	3310
28-day psi	4941	3565	5305	4688	4930	4379	4400	4030	4680
	Fly Ash #4			*Fly Ash #5*			*Fly Ash #6*		
Treatment	Unt.	500°C	800°C	Unt.	500°C	800°C	Unt.	500°C	800°C
Air content %	6.2	6.5	6.1	4.9	3.8	4.7	5.5	5.9	6.5
Water/cy	278	277	278	295	307	294	287	286	284
Slump	4	4.25	4	4.5	5	4.25	4.5	3.75	4
3-day psi	2360	1880	2420	2320	2610	2230	2360	2130	2260
7-day psi	3470	3340	3370	3530	3690	3150	3600	3370	3250
28-day psi	4710	4680	4540	4640	4930	4700	4340	4600	4410

Appendix D

PUBLICATIONS RELATED TO DOE AWARD #DE-FC26-98FT40028 CBRC SUBCONTRACT 98-166-WC AWARDED TO WAYNESBURG COLLEGE

LaCount, R. B., Baltrus, J. P., Banfield, T. L., Diehl, J. R., Frommell, E. A., Giles, K. A., Irdi, G. A., Kern, D. G., Leyda, T. A., Martello, D. V., Tamilia, J. P., "Treatment of High Carbon Fly Ash To Produce a Low Foam Index Product With Carbon Content Retained", Proceedings:14th International Symposium on Management and Use of Coal Combustion Products(CCP's), San Antonio, Texas, January 22-25, 2001: Volume I, EPRI, Palo Alto, CA:2001.1001158 pp 15-1 to 15-13.

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LaCount, R. B., Baltrus, J. P., Banfield, T. L., Diehl, J. R., Giles, K. A., Kern, D. G., Leyda, T. A., Pique, P. J., "Treatments for Lowering Foam Index In High-Carbon Fly Ashes for Concrete Applications", Proceedings: 18th Annual International Pittsburgh Coal Conference, Newcastle, New South Wales, Australia, December 3-7, 2001.

LaCount, R.B, Baltrus, J.P., Banfield, T.L. , J. Rodney Diehl, J.R., Giles, K.A., Kern, D.G., Tiffany A. Leyda, T.A, Pique, P.J. "Treatments for Lowering Foam Index in High-Carbon Fly Ashes for Concrete Applications", Proceedings: 21th Annual International Pittsburgh Coal Conference, Osaka, Japan, September , 2004.

U.S. Utility Patent Application "Fly Ash Modification" filed, 2003.