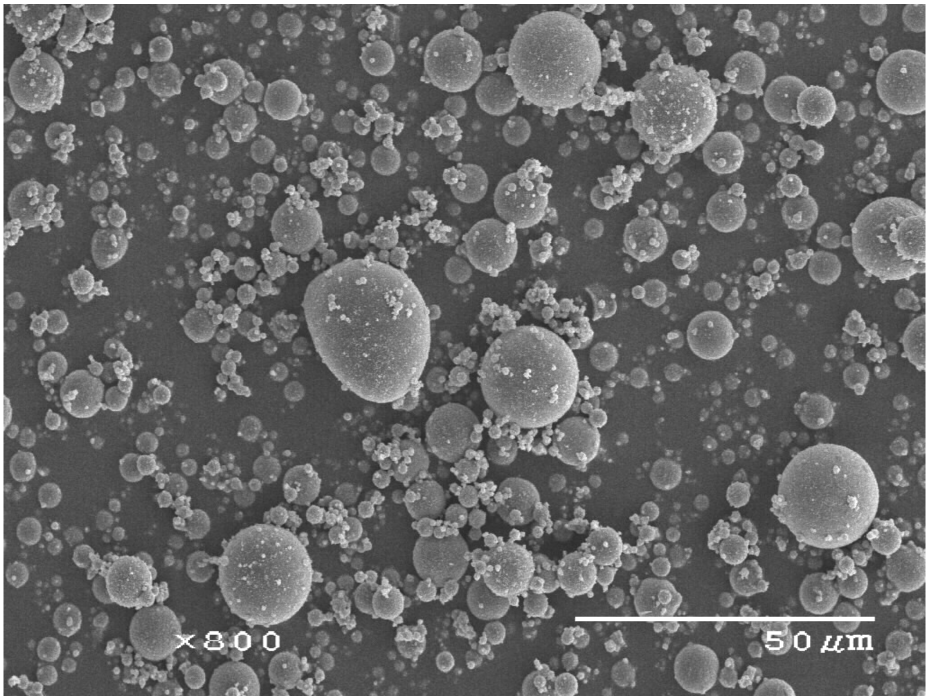
FINAL REPORT

Testing Program for the Evaluation of Co-combustion Fly Ash Produced at Ottumwa Generating Station; Phase 2 (Second Trial Burn)

(TASK 6.1.1 CHARITON VALLEY BIOMASS PROJECT)



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June 2005
Iowa State University

Project Sponsor
Chariton Valley RC&D

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Executive Summary

The purpose of this testing program was to evaluate the properties of fly ash produced at Ottumwa Generating Station (OGS) during the second trial burn of switchgrass and pulverized coal. This fly ash will be referred to as "co-combustion" fly ash throughout this report. The trial burn was conducted during late November and early December of 2003 and the testing program was designed to evaluate both the uniformity and performance of the co-combustion fly ash. The scope of the testing program was limited to the determination of bulk fly ash properties, ASTM C 618 mandatory and supplementary optional tests, and a series of concrete tests. No field trials were conducted during this project.

Sixteen fly ash samples were received for testing. The samples were obtained from both the bulk ash silo at OGS and from an autosampler that had been installed specifically for the project. Since switchgrass was only introduced into one side of the boiler, the autosampler had been installed on the pneumatic line servicing that particular precipitator bank. Hence, the samples from the autosampler reflected material representative of the nominal (theoretical) switchgrass burn rate. The samples of silo ash should have effectively been diluted by a factor of two because pneumatic lines from two banks of precipitators are sent to the ash silo. Switchgrass burn rate was varied from 0 to about 10 tons per hour during the trial burn. The maximum burn rate of 10 tons per hour corresponds to the co-firing of 5% switchgrass with 95% pulverized coal. However, due to the dilution noted above, the samples taken from the fly ash silo would only represent material produced from the co-firing of 2.5% switchgrass.

After the test results from the preliminary chemical and physical fly ash testing were reviewed, it was noted that some of the physical properties of the fly ash from the autosampler were not consistent with properties measured in the silo ash. Since the silo ash samples clearly represented material that would be marketed from the power station, and the samples exhibited physical properties consistent with historical data obtained from prior OGS testing, it was decided to concentrate further testing only on the silo ash samples. The objective of testing material obtained from the autosampler was to evaluate the uniformity of fly ash that was produced during the trial burn. However, this objective was not realized due to the anomaly in the samples obtained from the autosampler. It is important to note that the anomaly was simply a sampling issue; it did not pertain to the co-combustion process.

The purpose of conducting engineering properties testing was to ensure that the samples met specific requirements listed in ASTM C 618. As mentioned above, this phase of the research concentrated on the fly ash samples that were obtained from the ash silo. These particular fly ash samples all met the chemical requirements for Class C fly ash. The fly ash samples also met all of the physical requirements with the exception of the ASR mortar expansion tests (i.e., the effectiveness in reducing expansion due to alkali-silica reaction test). The results of the various performance tests were in good agreement with prior studies using OGS fly ash. Hence, it was concluded that the co-combustion of 2.5% switchgrass with coal had a minimal impact on the properties that are specified in ASTM C 618.

The purpose of the concrete testing was to evaluate how the co-combustion ash performed in laboratory concrete mixtures. Both plastic and hardened concrete properties were evaluated. The study failed to find any significant differences between the baseline OGS fly ash and the samples of co-combustion fly ash. Typically, all of the samples behaved in a manner that was consistent with prior studies that had utilized fly ash from OGS. Hence, it was concluded that the co-combustion of 2.5% switchgrass with coal had a minimal impact on the concrete properties that that were measured in this study.

INTRODUCTION

Background

Coal-fired power plants produce the majority of electricity that is used in Iowa. Fly ash, a common by-product of coal burning, has been marketed successfully in Iowa since the early 1980's. However, recent environmental pressures have changed the fuel strategies used at some power plants. The use of alternate fuels, such as biomass or switchgrass, is in the very early stages of becoming a reality. Prior studies of co-combustion fly ash from OGS have indicated that there were only small differences between the co-combustion ash and normal (baseline or coal only) fly ash [1, 2]. However, prior studies were limited because of the very small size of fly ash samples that had been collected during the first trial burn. In addition, the fly ash samples from the initial trial burn had been collected from individual precipitator hoppers at the power plant and this tended to complicate interpretation of the test results. Hence, a second trial burn was planned and conducted to overcome these complications and to provide researchers with large quantities of fly ash that would allow a robust evaluation of a "marketable" stream of co-combustion fly ash from OGS.

Scope

The purpose of this testing program was to evaluate the properties of fly ash produced at Ottumwa Generating Station (OGS) during the second co-combustion trial that was conducted from late November to early December 2003. The testing program was designed to evaluate both the uniformity and performance of the co-combustion fly ash. The scope of the testing program was limited to the determination of bulk fly ash properties, specific mandatory and optional tests described in ASTM C 618 [3], and a round of concrete tests that are summarized below. No field trials were conducted during this phase of the project.

Objectives

The objectives of the research project can be summarized as follows.

1. Compare the chemical and mineralogical characteristics of co-combustion ash with those from fly ash derived from burning only coal.
2. Compare the engineering properties of pastes and mortars containing co-combustion ash with the specification limits given in ASTM C 618.
3. Compare the engineering properties of concrete mixtures containing co-combustion ash with control mixtures containing only portland cement.

SAMPLES AVAILABLE FOR TESTING

The fly ash samples studied in this project were collected during the second co-fire testing at Ottumwa Generating Station (OGS). Sampling techniques and power station operating parameters have described in detail by Comer [4]. Briefly, samples were collected from November 21 through December 12, 2003. All of the samples (16) that were received for study were tightly sealed in metal paint cans (1 gallon or 5 gallon sizes, see Table 1). The samples represented fly ash sampled from the ash silo and material obtained from an autosampler. The autosampler was installed after the first trial burn. The nominal switchgrass burn rate is also given in Table 1. Keep in mind that the autosampler was located on the pneumatic line from the east precipitators to the ash silo so the nominal burn rate reflects the actual switchgrass burn rate. In the other samples (those obtained from the ash silo) the nominal burn rate needs to be divided by two to obtain the actual burn rate. A burn rate of 10 tons per hour is equivalent to burning 5% switchgrass and 95% coal.

Silo Samples

The samples for concrete testing actually consisted of three containers of fly ash (designated A, B or C); however, chemical and physical testing indicated that the samples in the three different containers bearing the same sampling date were nearly identical and could be considered as a

Table 1. Summary of fly ash samples from the fall 2003 OGS test burn.

Sample date	Size	Fuel Type	Type	Burn Rate (Tons/hour)	Testing Program
11/21/2003	3@5 gal. each	coal	silo	0	concrete
12/10/2003	3@5 gal. each	co-fired	silo	10	concrete
12/11/2003 am	3@5 gal. each	co-fired	silo	10	concrete
12/11/2003 pm	3@5 gal. each	co-fired	silo	10	concrete
11/25/2003	11 pounds	coal	autosampler	0	C 618
12/01/2003	11 pounds	co-fired	autosampler	11	C 618
12/02/2003	9 pounds	co-fired	autosampler	9	C 618
12/03/2003	9 pounds	co-fired	autosampler	8	C 618
12/04/2003	5 pounds	co-fired	autosampler	6	C 618
12/05/2003	11 pounds	co-fired	autosampler	10	C 618
12/06/2003	4 pounds	coal	autosampler	0	C 618
12/08/2003	11 pounds	co-fired	autosampler	8	C 618
12/09/2003	10 pounds	coal	autosampler	0	C 618
12/10/2003	10 pounds	co-fired	autosampler	10	C 618
12/11/2003	12 pounds	co-fired	autosampler	10	C 618
12/12/2003	12 pounds	coal	autosampler	0	C 618

single sample. In addition, the samples taken on 12/11/2003, denoted as “am” and “pm”, were also found to be nearly identical so they were treated as a single sample for the concrete testing phase of the project. Split samples were sent to Headwaters for verification testing.

Samples from the Autosampler

A typical sample from the autosampler consisted of about ten pounds of fly ash. All of the samples met the minimum amount of sample specified in ASTM C 311 [5]. Each individual sample was split in half. One half was shipped to Headwaters MTRF for analysis. The other half of the sample was retained for testing at Iowa State University.

RESEARCH APPROACH

The research project utilized a testing program that evaluated basic material properties, engineering properties from paste and mortar testing conducted in accordance with C 618, and the performance properties of concrete specimens. Specific uniformity and C 618 tests were conducted at two independent laboratories (ISU and Headwaters). This was done to check the validity of the test results. All these tests were conducted in accordance with ASTM C 311 [5] unless specifically noted. Details of the testing programs are summarized below. The uniformity and C 618 testing were conducted to satisfy objectives 1 and 2 of this project. The concrete tests were conducted to satisfy objective 3.

Basic Materials Properties

These tests consisted of the normal tests that are commonly used to evaluate the uniformity of fly ash. These tests include moisture content (MC), loss on ignition (LOI), fineness, density and bulk chemical composition. Iowa State University conducted these tests on all of the samples that were available for the project (samples listed in Table 1). Headwaters conducted verification testing on nearly all of the fly ash samples.

Additional studies on the fly ash samples were conducted at ISU. These fundamental studies consisted of evaluating the mineralogy of selected samples. Mineralogy was determined via X-ray diffraction. Chemical testing was conducted on specific samples to assess the rate at which alkali went into solution.

Paste and Mortar Testing

Engineering properties tests consisted of the mandatory chemical and physical requirements listed in ASTM C 618 [3]. Briefly, these tests include the bulk materials properties tests listed above, plus strength activity index at 7-days (7d SAI) and 28-days (28d SAI), water requirement, soundness, effectiveness in contributing to sulfate resistance, effectiveness in reducing expansion due to alkali-silica reaction, and the uniformity requirements for fineness and density. In addition, set time tests were conducted on samples of fly ash that were obtained from the ash silo. These mortar tests were conducted in accordance to ASTM C 403 [6]. Fly ash replacement level was varied during the study to see how replacement rate influenced setting time.

Concrete Mixtures

Concrete mixtures were tested for both plastic properties and hardened properties. All mixtures were proportioned using a nominal Iowa DOT C-3-20C mix design (see Table 2). Aggregates consisted of a natural sand from south of Ames, IA (Hallet's south pit) and a crushed limestone from Ames Mine (Martin Marietta Mine, north of Ames). Fly ash was substituted for cement on an equivalent mass basis (replacement levels of 20%, 28% and 36%). Fine aggregate was removed from the mix to compensate for the increase in volume caused by increasing fly ash replacements. All mixtures were proportioned to a constant slump (2.5 ± 1 inch) and had a target air content of 6 ± 1%. The plastic concrete mixtures were tested for slump, slump loss, air content and unit weight. The hardened concrete mixtures were tested for compressive strength (at 3, 7, 28 and 90 days of curing), rapid chloride permeability, and air-void parameters. The air void parameters were determined to estimate the frost resistance of the concrete specimens. This was done in place of the rapid freeze-thaw test because of the presence of a significant fraction of dolomite particles (Ames mine, bed 27) in the coarse aggregate. Historically, this bed of dolomite aggregate has exhibited poor resistance to cyclical freezing and thawing and it could have biased specific mixtures because the particles were not homogenously distributed in the coarse aggregate that was used in the project.

Table 2 - Summary of nominal concrete mixture proportions and coarse aggregate gradation.

Constituent	**Absolute volume**	**Mass per cubic yard lbs**
Cement (Type I/II)	0.091	484
Fly Ash	0.023	121
Water	0.154	260
Fine Aggregate (SSD)	0.302	1329
Coarse Aggregate (SSD)	0.370	1669
Air	0.060	
Total	1.000	

Coarse Aggregate Grading

Sieve Opening	**% Retained**
¾” (19.0 mm)	10
½” (12.7 mm)	40
3/8” (9.5 mm)	25
# 4 (4.76 mm)	25

EQUIPMENT AND PROCEDURES

Iowa State University, Materials Analysis & Research Laboratory (MARL)

The MARL laboratory used X-ray techniques to measure the bulk chemistry and mineralogy of the fly ash samples. The engineering properties tests were conducted in accordance with ASTM C 311 [5] (with the exceptions noted below). The MARL participates in the Cement and Concrete Reference Laboratory (CCRL) pozzolan proficiency sample testing program and the CCRL laboratory inspection program. The most recent CCRL laboratory inspection was conducted on September 28, 2004.

A Philips PW 2404 X-ray spectrometer (XRF) was used for the bulk chemical determinations that were made during this study. Specimens were presented to the spectrometer as fused disks (flux to sample ratio = 5.00). The spectrometer was equipped with a rhodium X-ray tube. All measurements were corrected for tube drift via a monitor sample (Ausmon-silicate minerals reference monitor). The spectrometer was calibrated using NIST grade certified reference materials. The bias (accuracy), precision (repeatability) and instrument stability information were consistent with the values given in the final report for the previous study [2].

A Siemens D 500 X-ray diffractometer (XRD) was used to determine the mineralogy of the fly ash samples. The diffractometer was equipped with a copper X-ray tube and a diffracted beam monochromater. Test specimens were prepared by back-loading the fly ash samples into one-inch diameter (25 mm) sample holders.

A Beckman DU-2 UV-Visible light spectrometer was used to measure the soluble (available) alkali in the fly ash samples. The spectrometer was equipped with a flame attachment and used hydrogen and oxygen as the fuel. Reagent grade calcium carbonate, sodium chloride and potassium chloride were used to make the calibration standards. The spectrometer was calibrated in accordance with the procedure described in ASTM C 114 [7].

The alkali dissolution study was conducted by extracting available alkali test specimens at curing times other than the 28-days specified in C 311. For this study, extractions were made after 3, 10 and 28 days of curing at 38ºC. Then samples were extracted and analyzed in accordance with the normal procedure for available alkali determinations.

The sulfate resistance tests were conducted in general accordance to Procedure A given in C 311. However, one exception to the standard procedure was used throughout this study. This study employed a room temperature curing method rather than the accelerated curing procedure that is described in the standard method. This was done to allow for direct comparison of the test results of this study with those from prior studies at ISU [8]. The strength criterion for immersion in the sulfate solution was still observed (3000 ± 150 psi); however, the time was determined by conducting compressive strength tests at 1, 2, 3, 4 and 7 days of curing (lime-water bath at room temperature) and then fitting a regression curve to the experimental data. Two compressive strength specimens (standard cubes) were molded with each set of test specimens and the cubes were broken immediately prior to immersion to ensure that the strength criterion had been reached.

Image analysis was used to determine the air void parameters of the hardened concrete. The tests were conducted using the MARL standard operating practice that had been developed in an earlier research project [9]. A Hitachi variable pressure scanning electron microscope was used to collect digital images of the various test specimens. The digital images were then subjected to image analysis to determine entrained air content, the void-size distribution and the apparent spacing factor of the concrete.

Iowa State University, Portland Cement Concrete Research Laboratory (PCC Lab)

All of the concrete mixtures were made in the PCC Lab at Iowa State University. The lab contains all of the equipment needed to mix, cure and test concrete test specimens. The concrete was mixed and test specimens were molded in accordance with ASTM C 192 [10]. Slump was tested in accordance with ASTM C 143 [11]. Air content was tested in accordance with ASTM C 231 [12]. The density of the concrete was determined by weighing the base of the air pot prior to conducting the air content test. Strength was determined in accordance with ASTM C 39 [13]; unbonded capping pads were used to constrain the test specimens during the compressive strength determinations.

Rapid chloride permeability (RCP) tests were conducted in accordance with ASTM C 1202 [14]. A Germann Instruments Proove-It apparatus was used for all RCP tests. The apparatus was controlled via computer to main the appropriate voltage on the test specimens and to collect data pertaining to the temperature of the cell and amount of charge passing the test specimens.

Headwaters Materials Testing and Research Facility (MTRF)

The MTRF participates in the Cement and Concrete Reference Laboratory (CCRL) pozzolan proficiency sample testing program and the CCRL laboratory inspection program. The most recent CCRL laboratory inspection was conducted on March 29, 2004.

An Oxford ED-2000 Energy Dispersive X-ray Fluorescence Spectrometer (XRF) was used for the bulk chemical determinations. The material was prepared for analysis as a fused bead (flux to sample ratio = 3.0) according to ASTM D 4326, Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence [15]. The instrument was calibrated with standard reference materials obtained from NIST and Brammer, which have a similar concentration and matrix to Class C and Class F Fly Ash. The calibration is verified with CCRL pozzolan proficiency samples.

The available alkali, moisture, fineness, strength activity index and autoclave expansion were all performed according to ASTM C 311. A Varian Spectra-20 Plus Atomic Absorption Spectrometer was used to measure the soluble (available) alkali in the fly ash samples. The spectrometer was calibrated using sodium chloride and potassium chloride standards. The loss on ignition (LOI) was performed using a Leco SC-444DR Carbon Sulfur Analyzer and was calibrated using a synthetic carbon calibration sample. A Quantachrome Helium Pycnometer was used to determine the specific gravity or true particle density of the fly ash.

RESULTS AND DISCUSSION

Materials Properties

The results of materials properties testing are given in Tables 3 and 4. Table 3 is a summary of the test results obtained from Headwaters MTRF. Table 4 is a summary of the test results from the MARL at Iowa State University. The chemical composition of the cements that were used at the MTRF and the MARL are summarized in APPENDIX A.

In general, there was good agreement between the two labs. The biases noted in the prior study [2] were still evident; however, test results were commonly within the precision limits of the various tests. Hence, for practical purposes the results can be considered to provide consistent information for the acceptance or rejection of fly ash. One common thing was noted at each

Table 3. Summary of results of materials properties testing conducted by Headwaters MTRF.

Sample #	Type	Date	Burn rate	Fineness	MC	LOI	Density
1	Silo	11/21/03	0	14.8	0.07	0.35	2.72
2	Silo	12/10/03	10	17.1	0.10	0.42	2.65
3	Silo	12/11/03 am	10	16.8	0.08	0.37	2.66
4	Silo	12/11/03 pm	10	17.3	0.09	0.37	2.64
5	Auto	11/25/03	0	31.0	0.08	0.37	2.65
6	Auto	12/01/03	11	34.5	0.08	0.25	2.57
7	Auto	12/02/03	9	33.1	0.09	0.36	2.57
8	Auto	12/03/03	8	27.7	0.06	0.41	2.60
10	Auto	12/05/03	11	35.4	0.08	0.34	2.63
11	Auto	12/06/03	0	37.5	0.08	0.43	2.58
14	Auto	12/10/03	10	30.0	0.08	0.43	2.56
16	Auto	12/12/03	0	32.8	0.08	0.34	2.60

Sample #	SiO_2	Al_2O_3	Fe_2O_3	SUM	SO_3	CaO	Available Alkali
1	35.45	19.20	5.35	60.00	2.08	26.41	1.45
2	34.91	19.50	5.04	59.45	2.59	25.39	2.52
3	35.48	19.82	4.96	60.25	2.41	24.82	2.56
4	35.61	20.00	4.99	60.59	2.39	24.52	2.62
5	37.47	20.17	5.21	62.85	1.72	23.95	1.94
6	39.22	19.54	5.23	63.99	1.87	22.96	1.70
7	38.31	19.59	4.75	62.65	2.22	23.33	2.04
8	37.43	19.68	4.75	61.86	2.47	23.93	2.14
10	37.09	19.06	5.08	61.23	2.24	24.31	2.18
11	40.52	20.49	4.99	66.00	1.28	21.73	1.50
14	37.91	18.53	5.14	61.58	2.26	24.04	2.18
16	40.33	18.83	4.99	64.15	1.84	22.13	1.97

Table 4. Summary of results of materials properties testing conducted by MARL.

Sample #	Type	Date	Burn rate	Fineness	MC	LOI	Density
1	Silo	11/21/03	0	15.8	0.02	0.23	2.66
2	Silo	12/10/03	10	16.7	0.03	0.30	2.62
3	Silo	12/11/03 am	10	15.9	0.03	0.29	2.59
4	Silo	12/11/03 pm	10	16.5	0.04	0.31	2.61
5	Silo	11/25/03	0	30.6	0.04	0.30	2.63
6	Auto	12/01/03	11	32.1	0.02	0.21	2.57
7	Auto	12/02/03	9	29.2	0.03	0.32	2.56
8	Auto	12/03/03	8	26.8	0.03	0.34	2.59
9	Auto	12/04/03	6	31.0	0.03	0.25	2.57
10	Auto	12/05/03	11	29.6	0.03	0.26	2.58
11	Auto	12/06/03	0	38.5	0.03	0.38	2.53
12	Auto	12/08/03	6	31.1	0.02	0.25	2.61
13	Auto	12/09/03	0	29.7	0.04	0.21	2.61
14	Auto	12/10/03	10	28.5	0.03	0.36	2.59
15	Auto	12/11/03	10	32.4	0.05	0.25	2.57
16	Auto	12/12/03	0	30.6	0.03	0.23	2.57

Sample #	SiO_2	Al_2O_3	Fe_2O_3	SUM	SO_3	CaO	Available Alkali
1	35.54	18.55	5.64	59.73	2.21	26.34	1.72
2	34.87	19.09	5.27	59.23	2.88	25.39	2.47
3	35.51	19.30	5.24	60.05	2.66	24.77	2.53
4	35.89	19.59	5.31	60.79	2.61	24.48	2.56
5	36.80	19.48	5.45	61.73	1.81	23.91	Not meas'd
6	39.69	19.29	5.52	64.50	2.01	22.80	Not meas'd
7	38.63	19.26	5.03	62.92	2.34	23.08	Not meas'd
8	37.87	19.56	5.08	62.51	2.77	24.02	Not meas'd
9	38.76	19.44	5.21	63.41	1.93	23.14	Not meas'd
10	36.60	18.69	5.26	60.55	2.32	23.65	Not meas'd
11	40.94	20.29	5.22	66.45	1.35	21.48	Not meas'd
12	37.45	17.79	5.42	60.67	2.87	24.42	Not meas'd
13	37.23	18.16	5.61	61.00	2.74	24.75	Not meas'd
14	38.41	18.39	5.41	62.21	2.42	23.91	Not meas'd
15	38.79	19.46	5.23	63.48	2.30	22.37	Not meas'd
16	40.38	18.61	5.26	64.25	1.97	22.04	Not meas'd

laboratory – samples from the autosampler were in poor agreement with those obtained from the ash silo. This is best illustrated with results from the fineness test (see Figure 1).

Fineness test results for the silo ash samples were about half of those measured for the samples obtained from the autosampler. These fineness test results were significantly different from test results that were historically obtained from samples of OGS fly ash (see Table 5). Since fineness typically has a significant impact on the engineering properties of fly ash further testing was conducted to evaluate the magnitude of the impact.

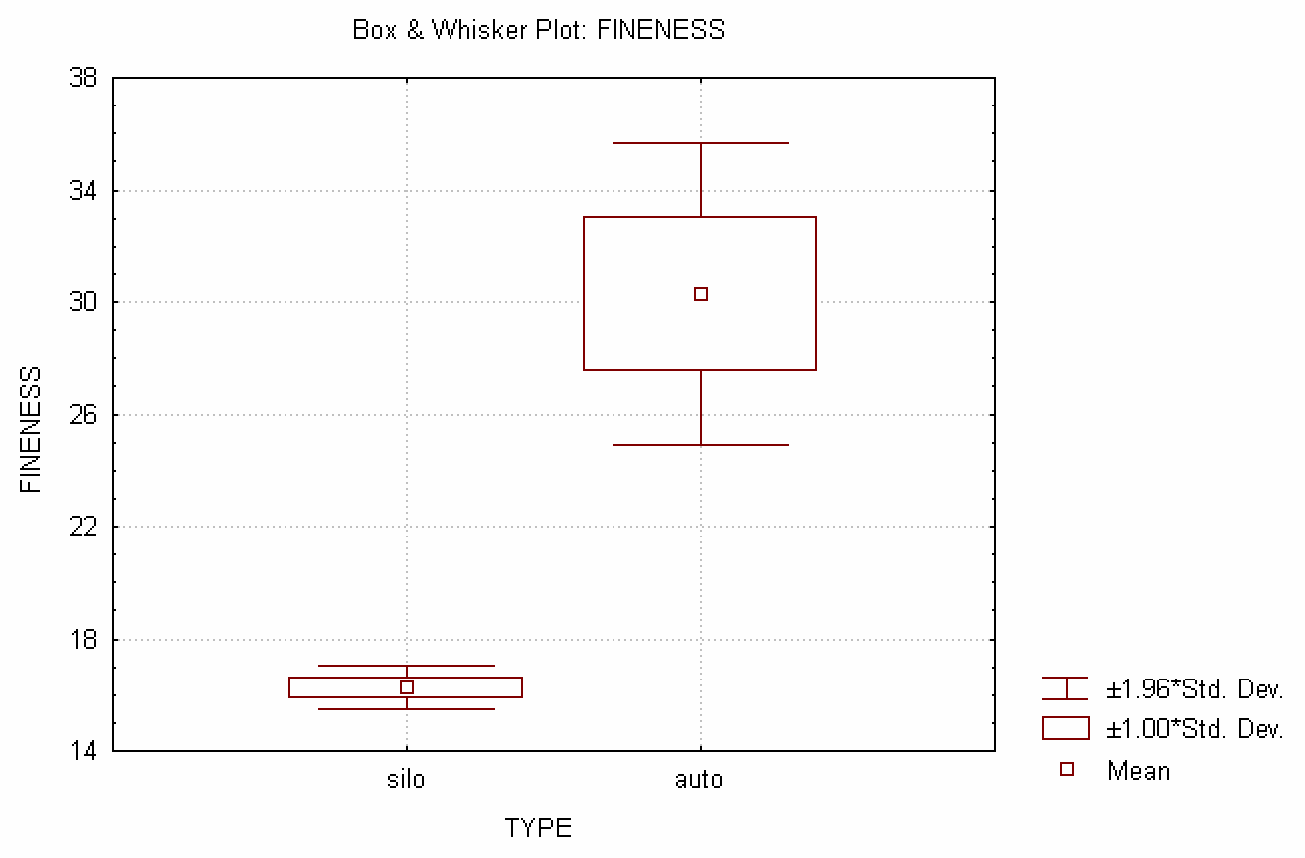

Figure 1. Illustration of fineness differences between sample types (silo versus autosampler).

Table 5. Descriptive statistics of 1998 OGS fly ash (marketed ash).

Constituent or test result	Valid N	Mean	Minimum	Maximum	Std.Dev.
SiO_2, %	23	36.15	32.98	38.33	1.46
Al_2O_3, %	23	20.48	15.81	21.67	1.33
Fe_2O_3, %	23	5.73	5.48	6.44	0.21
SO_3, %	23	1.79	0.98	3.39	0.66
CaO, %	23	22.94	20.88	28.60	1.72
MC, %	23	0.03	0.00	0.12	0.02
LOI, %	23	0.27	0.19	0.51	0.08
Available Alkali, % Na_2O_e	23	1.76	0.88	2.47	0.41
Fineness, % retained on #325 mesh sieve	23	14.71	13.1	16.78	0.85
28-d Strength Activity Index, % of control	23	102	89	119	7.30
Water Requirement, % of control	23	94	92	95	0.94
7-d Strength Activity Index, % of control	23	94	82	105	6.32

Autoclave Expansion, %	23	0.02	0.01	0.10	0.02
Density, grams per cc.	23	2.61	2.55	2.76	0.05

Additional studies were conducted on the fly ash samples taken from the silo. These fundamental studies consisted of evaluating the mineralogy and dissolution characteristics of the samples. Mineralogy was determined via X-ray diffraction. Chemical testing was conducted to assess the rate at which alkali went into solution.

X-ray diffraction (XRD) was used to identify the crystalline components present in the four samples obtained from the ash silo. In general, the minerals identified in the various samples were consistent with previous studies that have been conducted on OGS fly ash [2, 8]. Diffractograms illustrating the results of the XRD experiments are given in APPENDIX B. The minerals that were identified in the samples included a-quartz, anhydrite, a melilite group mineral (close to the gehlenite endmember), and a mineral similar to tricalcium aluminate. Occasionally, the strongest diffraction peaks for ferrite spinel (close to magnetite), lime and periclase were also observed in the diffractograms. Typically, the mineral assemblage present in the various samples was relatively fixed and the concentrations appeared to vary only by small amounts. The glass content of the various samples was about 87±7%, this is in good agreement with earlier research on samples of OGS fly ash and the composite samples from the first trial burn [2, 8].

Alkali solubility experiments were conducted to evaluate the rate at which the common fly ash alkalies (sodium and potassium) were released when the bulk ash samples were reacted with calcium hydroxide. This is very similar to the available alkali test but the samples were extracted at several ages rather than the standard curing time of 28 days. Only the four samples of fly ash that were taken from the silo were subjected to these tests. Results of the experiments are illustrated in Figure 2. All four of the samples exhibited similar test results. This suggests that the alkali are bound in a similar fashion in both the baseline and the co-combustion samples.

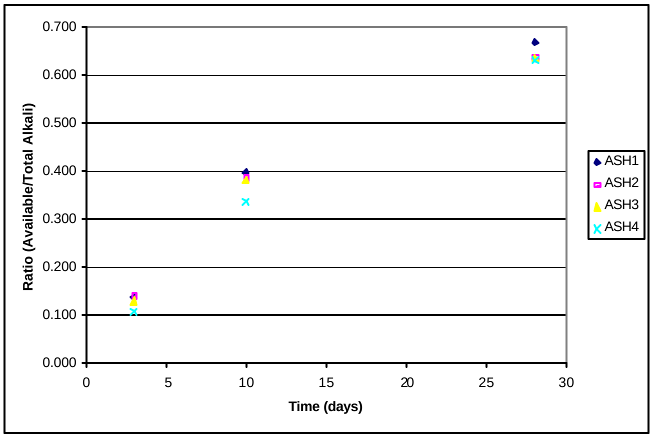

Figure 2. Soluble alkali content (as a fraction of total alkali content) versus time.

Paste and Mortar Test Results

The results of engineering properties testing (paste and mortar tests) are given in Tables 6 and 7. Table 6 is a summary of the test results for soundness, strength activity index (SAI) and water requirement from the Headwaters MTRF. Table 7 is a summary of the test results for strength activity index (SAI) and water requirement from the MARL. These tests were conducted on samples obtained from both the autosampler and the silo. Table 8 is a summary of the test results from the sulfate resistance, ASR mortar bar tests and the setting time tests.

Table 6. Summary of soundness, strength activity index and water requirement test results.

Sample #	Type	Date	Burn rate	7-d SAI	28-d SAI	Water Req'd	Autoclave expansion, %
1	Silo	11/21/03	0	96	97	95	0.06
2	Silo	12/10/03	10	89	101	95	0.06
3	Silo	12/11/03 am	10	88	99	95	0.07
4	Silo	12/11/03 pm	10	91	104	95	0.06
5	Silo	11/25/03	0	90	85	95	0.06
6	Auto	12/01/03	11	84	82	95	0.07
7	Auto	12/02/03	9	87	83	96	0.07
8	Auto	12/03/03	8	101	92	96	0.06
10	Auto	12/05/03	11	76	82	96	-0.01
11	Auto	12/06/03	0	73	76	96	-0.02
14	Auto	12/10/03	10	84	84	96	0.07
16	Auto	12/12/03	0	83	86	96	-0.01

Table 7. Summary of strength activity index and water requirement test results for the MARL.

Sample #	Type	Date	Burn rate	7-d SAI	28-d SAI	Water Req'd
1	Silo	11/21/03	0	100	106	96

2	Silo	12/10/03	10	94	96	96
3	Silo	12/11/03 am	10	95	96	96
4	Silo	12/11/03 pm	10	95	105	96
5	Silo	11/25/03	0	83	91	96
6	Auto	12/01/03	11	85	77	96
7	Auto	12/02/03	9	89	92	96
8	Auto	12/03/03	8	89	95	96
9	Auto	12/04/03	6	79	84	96
10	Auto	12/05/03	11	84	86	96
11	Auto	12/06/03	0	78	78	96
12	Auto	12/08/03	6	68	86	96
13	Auto	12/09/03	0	71	84	96
14	Auto	12/10/03	10	88	83	96
15	Auto	12/11/03	10	83	80	96
16	Auto	12/12/03	0	67	87	96

The strength activity index determinations were strongly correlated to fineness when the samples from the autosampler were included in the analysis (see Figure 3). Hence, it was concluded that the samples from the autosampler were significantly different from the silo samples and they were excluded from the remainder of the testing program. This was done for two reasons. First, the samples from the ash silo were in excellent agreement with past (marketable) fly ash produced at OGS (compare results in tables 3 and 4 to those given in table 5). And secondly, it was noted that some of the test results for the samples obtained from the autosampler were marginally failing the test criteria given in C 618. The failures were not related to co-combustion process since some of the samples were obtained when no switchgrass was being burned. The samples from the autosampler simply did not give a good representation of fly ash that is typically produced at OGS. The removal of the autosampler samples from the study was unfortunate but this was not a major setback because the silo fly ash samples were excellent examples of “marketable” OGS fly ash.

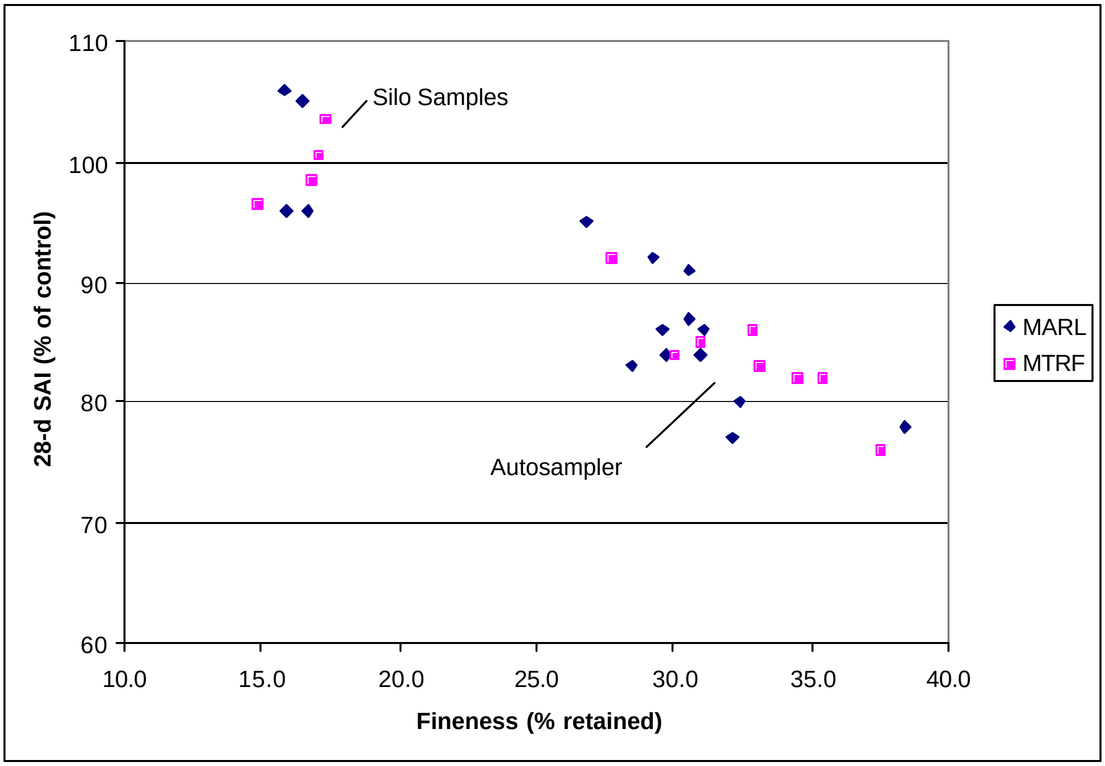

Figure 3. Correlation between strength activity index (28-day) and fineness of the fly ash samples.

The silo ash samples were subjected to tests aimed at evaluating how they influenced the sulfate resistance, ASR mortar bar tests and the setting time tests. In each instance fly ash was substituted for portland cement on an equivalent mass basis. Typically fly ash replacements were 20% and 36%. The results of these tests are summarized in a much abbreviated form in Table 8. The table simply lists the test results and how the values compare to the specification limit for each test. This is an oversimplification of the test results which are strongly time dependent (for example, see Figures 4 and 5). Hence, the interested reader should consult APPENDIX C where all the test data reside.

All four of the fly ash samples taken from the silo exhibited good sulfate resistance when tested with the Type I/II portland cement that was used in this study. All of the ash specimens exhibited expansions less than 0.05% at six months of exposure; this would be classified as “high-resistance” by the current criteria given in ASTM C 618. The observed expansion did not appear to be strongly related to ash replacement level because both the 20% and 36% replacements had expanded about the same amount after approximately 8 months of exposure to the sodium sulfate solution. These specimens will continue to be monitored until they expand to failure. It is important to note that all of the specimens containing OGS fly ash performed better than the 100% cement control mortar (see Figure 4).

Table 8. Summary of test results for sulfate resistance, ASR expansion and set-time.

		ASH 1	**ASH 2**	**ASH 3**	**ASH 4**	
Test	Ash, %	OGS112103	OGS121003	OGS121103am	OGS121103pm	**C 618 limit**
Sulfate Resistance (@ 6 months, %)	20	0.034	0.035	0.033	0.034	<0.05% for High Resistance
	36	0.039	0.036	0.036	0.032	<0.10% for Moderate Resist.
ASR Expansion	20	136	146	150	114	100% max.
(@ 14 days, % control)	36	87	106	102	118	100% max.
Mortar Set Time	0	219	219	219	219	Control Mix
Initial Set	20	263	242	244	243	No limit given
(all values in minutes)	36	329	281	270	272	No limit given
Final Set	0	326	326	326	326	Control Mix
(all values in minutes)	20	376	358	348	346	No limit given
	36	489	418	402	398	No limit given

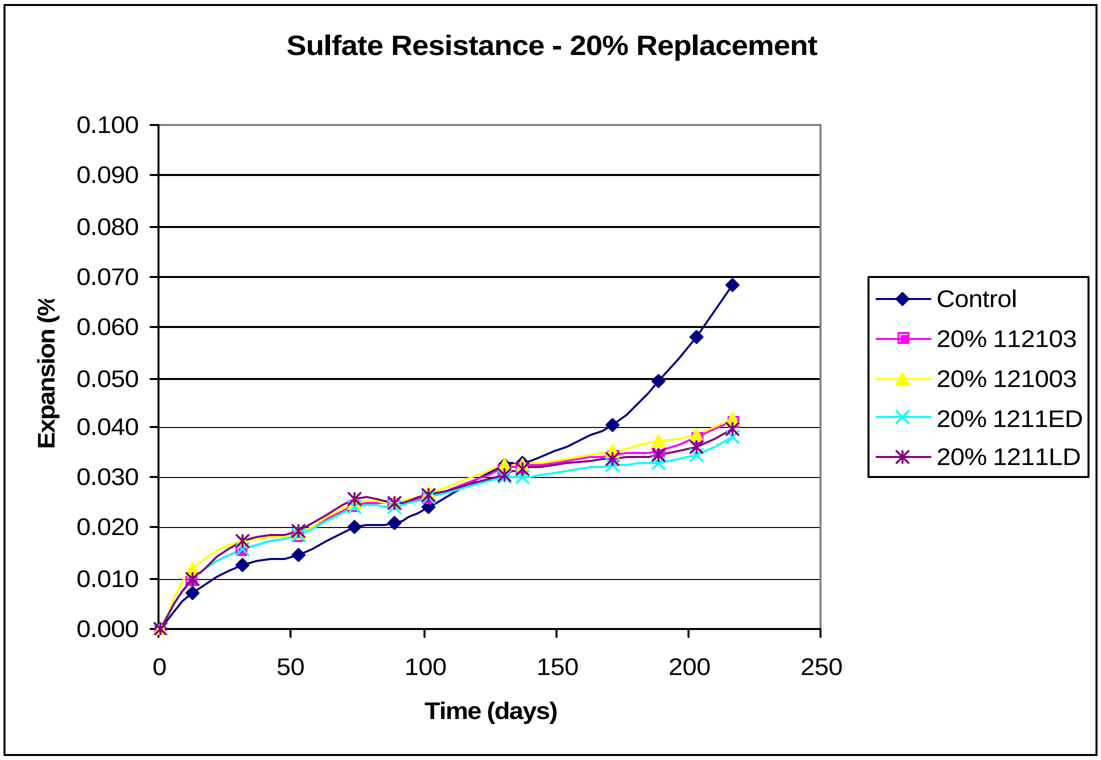

Figure 4. Illustration of the time dependent nature of the sulfate resistance tests (20% OGS silo ash).

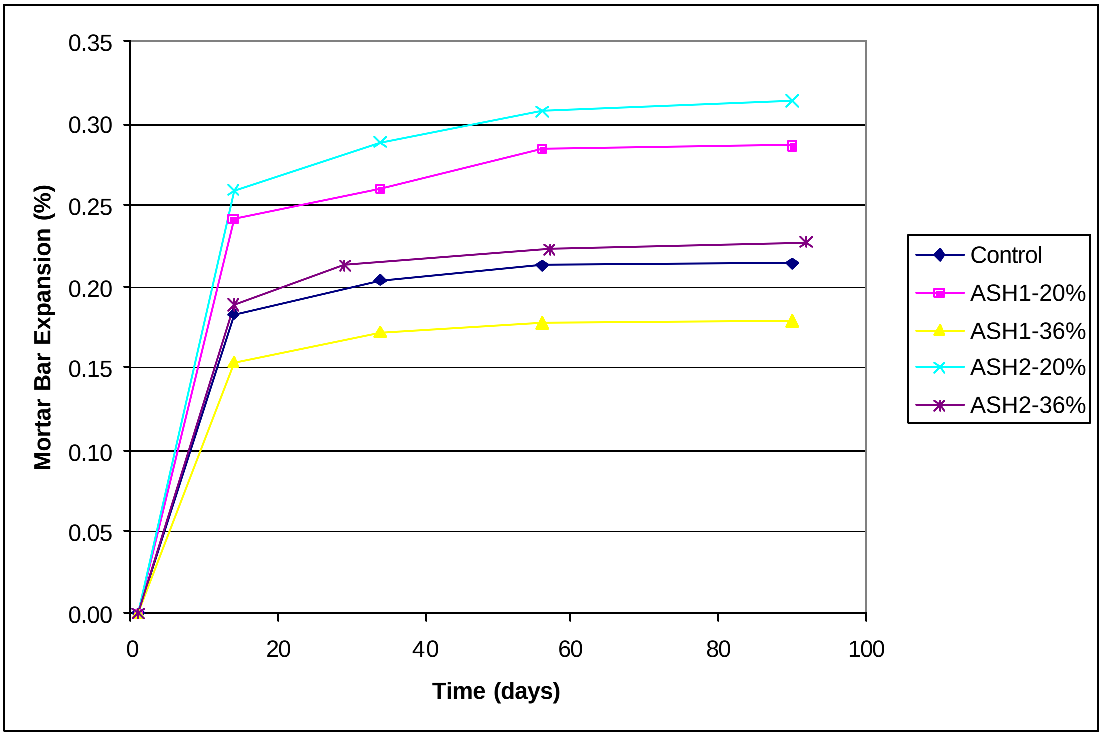

Figure 5. Illustration of typical results from the ASR mortar bar expansion tests.

All four of the fly ash samples taken from the silo exhibited poor ability to mitigate expansion caused by alkali-silica reaction (ASR). Only the baseline sample, denoted as ASH1 or OGS112103, when substituted at the 36% replacement level, was able to reduce the mortar bar expansion below that of the control cement (see Table 8 and Figure 5). This is in good agreement with prior studies [8], which have indicated that the sodium carbonate doping rate used by the power station and the reactive silica content of the fly ash dominate the ASR performance of the fly ash. Hence, the reduction in available alkali from about 2.5% Na_2O_e (in the sample denoted as OGS121003) to about 1.6% Na_2O_e (in the sample denoted as OGS112103, the baseline sample) was enough to show a positive impact on mortar bar expansion when the fly ash replacement was increased to 36%. Note, that the change in alkali content was not caused by the co-combustion process. Rather the sodium doping rate at the power plant changed between the time that the baseline and the other three fly ash samples (co-combustion) were taken.

The various fly ash samples all had an impact on the test results of the set time experiments. Typically, the fly ash tended to increase both the initial and final set times of the mortar mixtures. The observed set times were correlated with the replacement rate of the fly ash (see Figure 6). This is in good agreement with common knowledge about the influence of fly ash on setting time. It did appear that the high alkali fly ashes tended to set a little faster than the low alkali fly ash (the baseline sample); however, the test results are only good to about ±40 minutes so more testing would be need to ensure that the differences are not simply statistical fluctuations.

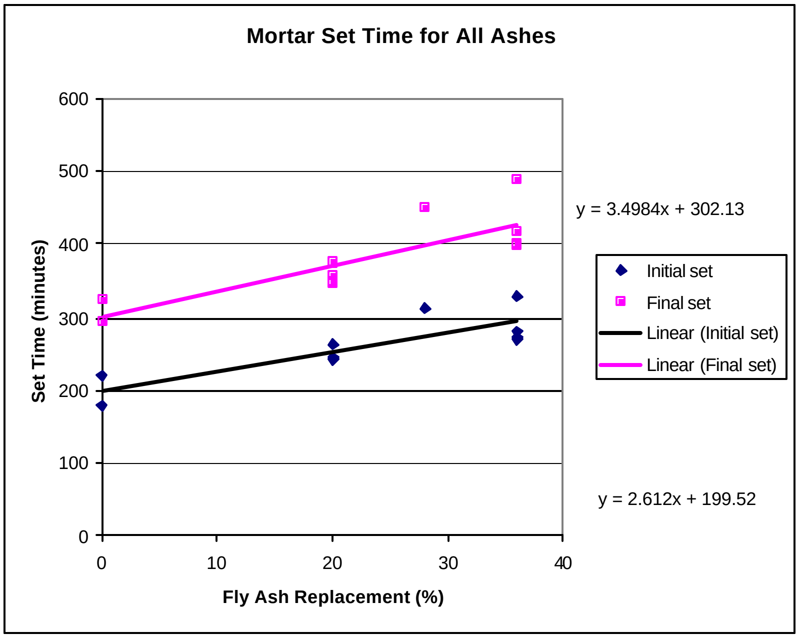

Figure 6. Illustration of mortar set time versus fly ash replacement rate for the four silo ash samples.

Test Results from the Concrete Mixtures

The results of the concrete testing program are given in Tables 9, 10 and 11. Table 9 is a summary of the test results obtained from the plastic concrete mixtures. Table 10 is a summary of the test results from the compressive strength tests. Table 11 summarizes the results from the rapid chloride permeability (RCP) tests and the hardened air-void parameters that were determined via image analysis.

The results of tests conducted on the plastic concrete indicated that all of the fly ashes behaved similarly, they all behaved like low-range water reducers. Slump and air content were controlled via target values of 2.5±1 inch and 6±1%, respectively. In all instances but one (mix 3), the mixtures met the target values. It was planned to repeat the batching of mix 3; however, cement ran out before the mix could be repeated. The low air content obtained on mix 3 was simply a batching error. Too little air entraining solution was used during the mixing stage. A linear relationship was observed between unit weight and air content (see Figure 7), this was expected due to the similar nature of the mixtures investigated in this study.

Table 9. Summary of concrete testing (plastic properties of the various mixtures).

Mix #	Fly Ash	% Ash	Slump, inches	Slump, at 30 min,	Unit weight, pcf	Pressure Meter Air, %	w/cm ratio
0	Control	0	2.25	1.50	143.0	5.1	0.43
1	OGS112103	20	3.25	2.00	142.8	5.2	0.41
2	OGS112103	28	2.50	1.50	143.2	5.2	0.39
3	OGS112103	36	2.50	1.25	145.0	4.0	0.38
4	OGS121003	20	2.50	1.25	141.8	5.7	0.40
5	OGS121003	28	2.50	1.25	141.4	6.3	0.39
6	OGS121003	36	2.75	1.25	140.8	6.5	0.38
7	OGS121103 am	20	2.50	1.50	141.6	6.0	0.40
8	OGS121103 am	28	3.50	1.75	140.0	6.8	0.39
9	OGS121103 am	36	2.50	1.25	140.6	6.6	0.38

Table 10. Summary of concrete testing (compressive strength test results).

Mix #	Fly Ash	% Ash	**Compressive Strength at 3 days, psi**	**Compressive Strength at 7 days, psi**	**Compressive Strength at 28 days, psi**	**Compressive Strength at 90 days, psi**
0	Control	0	4000	4950	6320	6990
1	OGS112103	20	3470	4780	6170	7210
2	OGS112103	28	3400	4690	6290	7070
3	OGS112103	36	3540	5250	7370	8360
4	OGS121003	20	3620	4820	6370	7140
5	OGS121003	28	3400	4550	6140	6800
6	OGS121003	36	3110	4240	6100	6810
7	OGS121103 am	20	3500	4760	6350	7130
8	OGS121103 am	28	3250	4290	6010	6620
9	OGS121103 am	36	3310	4470	6110	6940

Table 11. Summary of concrete testing (RCP test results and hardened air parameters).

Mix #	Fly Ash	% Ash	**RCP test, corrected coulombs passed**	**Hardened air content, %**	**Apparent spacing factor, inches**
0	Control	0	2988	4.6	0.006
1	OGS112103	20	1350	5.6	0.006
2	OGS112103	28	1135	6.0	0.005
3	OGS112103	36	789	4.0	0.009
4	OGS121003	20	1441	6.3	0.006
5	OGS121003	28	1168	6.8	0.005
6	OGS121003	36	821	8.0	0.006
7	OGS121103 am	20	1472	5.4	0.006
8	OGS121103 am	28	1189	6.7	0.005
9	OGS121103 am	36	775	6.4	0.005

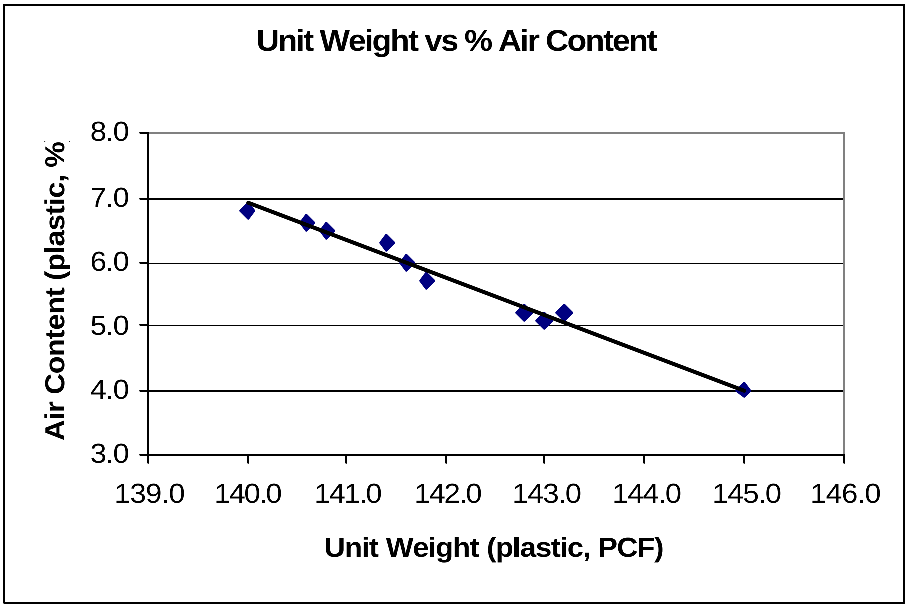

Figure 7. Relationship between air content and unit weight that was observed in this study.

The compressive strength of the concrete mixtures containing the co-combustion ash was evaluated at four different ages. Fly ash replacement ranged from 20% to 36% (by equivalent mass of cement). The results indicated that increasing fly ash replacement tended to lower early strength development but had little impact on the ultimate strength of the concrete (see Figure 8). In fact, the use of fly ash tended to enhance the ultimate strength of the concrete; however, keep in mind the fact that the air content of the concrete is also of prime importance to the compressive strength of the test specimens. The use of co-combustion fly ash in the mixtures appeared to have a negligible influence on the compressive strength of the test specimens.

The rapid chloride permeability tests exhibited dramatic improvement as the fly ash replacement was increased (see Figure 9). The highest value for the test was obtained from the portland cement control specimen. Substituting 20% fly ash for an equivalent amount of cement reduced the amount of charge passed by approximately a factor of two. Increasing the replacement to 36% caused over a three-fold reduction in the amount of charge passed. This was a very significant reduction in Cl permeability. Again, it was difficult to differentiate the test results from the baseline fly ash from those obtained with the co-combustion fly ash.

The hardened air contents were typically in good agreement with the plastic air determinations (see Figure 10); this was to be expected for laboratory concrete that is compacted by rodding. All of the mixtures, with the exception of mix 3 – the mix with the low dosage of air entraining solution, had apparent spacing factors less than 0.008 inches. All of these test results are indicative of a concrete mixture that should exhibit good resistance to cyclical freezing and thawing (assuming the mixture incorporates sound aggregates and adequate curing is provided prior to exposure). No apparent differences were detected between the test results from baseline fly ash and the co-combustion fly ashes.

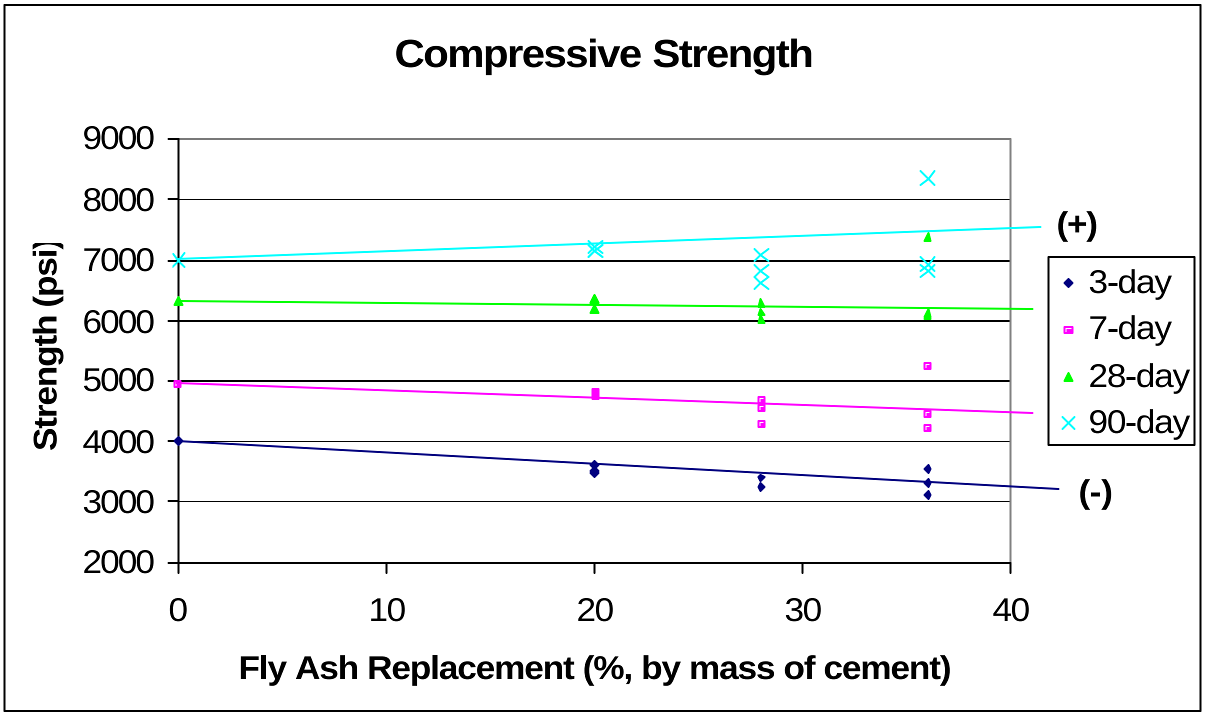

Figure 8. Illustration of how compressive strength varied with fly ash replacement.

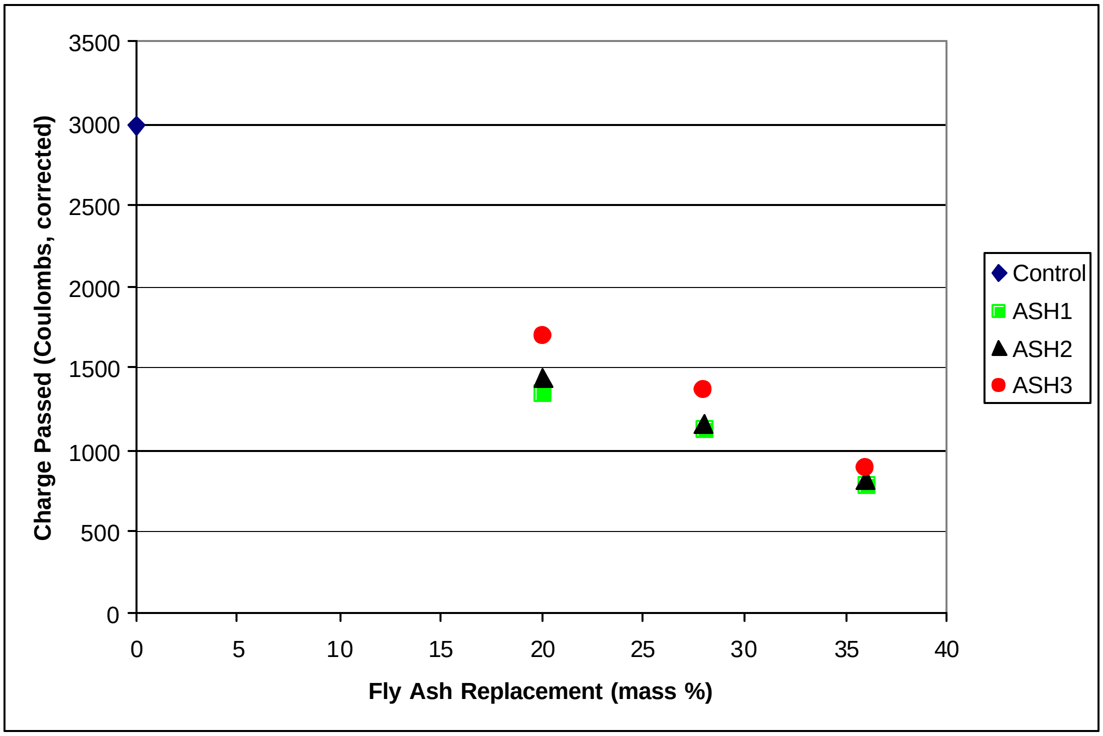

Figure 9. Illustration of how rapid chloride permeability varied with fly ash replacement.

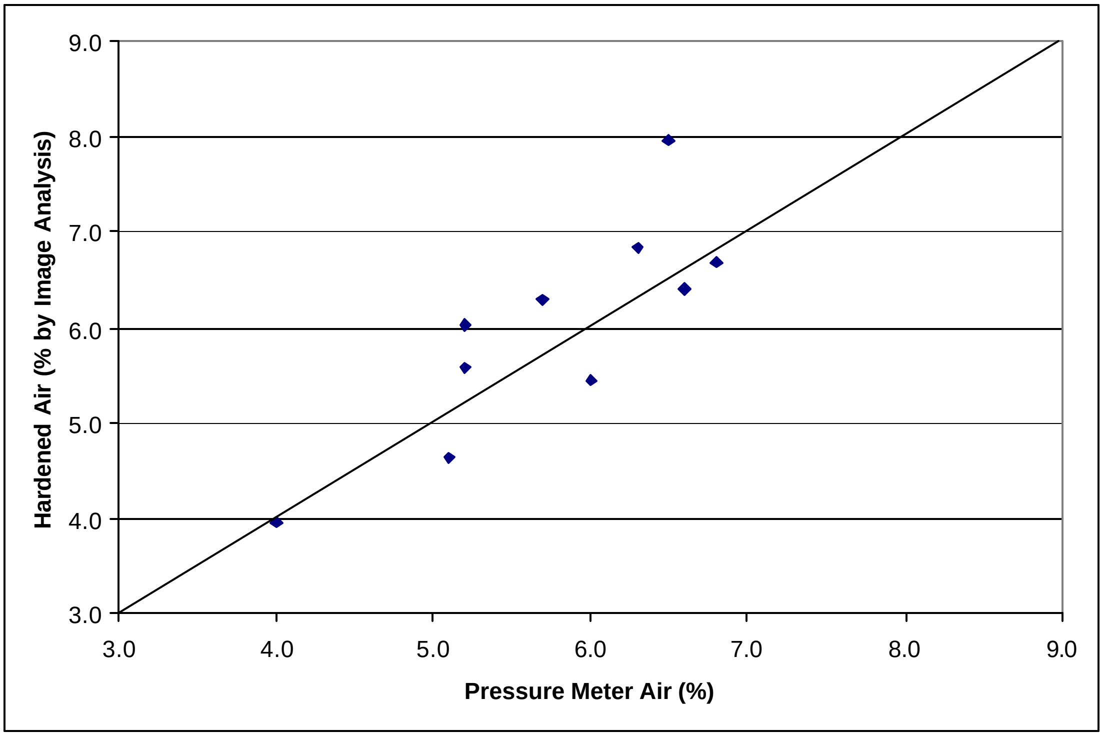

Figure 10. Relationship between hardened air content and plastic air content in the concrete mixtures.

SUMMARY AND CONCLUSIONS

In summary, this research project was directed at evaluating the properties of fly ash produced at Ottumwa Generating Station (OGS) during the second co-combustion trial burn. The second trial burn was conducted from late November to early December 2003. The testing program was designed to evaluate both the uniformity and performance of fly ash generated during the co-combustion of coal and switchgrass. The testing program evaluated bulk fly ash properties, specific mandatory and optional tests described in ASTM C 618, and a round of concrete tests that evaluated strength and durability (e.g., rapid chloride permeability and hardened air void parameters). No field trials were conducted during this project.

The purpose of conducting the bulk fly ash properties testing was to evaluate basic chemical and uniformity characteristics of the co-combustion fly ash. The test results were compared to the test results from the baseline samples (coal only fly ash) and to prior samples of fly ash collected from Ottumwa Generating Station. The specific conclusions from the bulk properties testing can be summarized as follows:

- All of the sixteen fly ash samples that were available for testing met the chemical requirements for Class C fly ash.
- All of the fly ash samples had negligible moisture contents (less than about 0.1%) and low values for loss on ignition (less than about 0.4%). These values did not appear to be correlated to the burn rate of switchgrass in the boiler.
- The fineness of the fly ash from the autosampler was nearly two times larger than fineness values for samples taken from the ash silo. This appeared to be a timing issue with the autosampler and was not related to the co-combustion process. The significant discrepancy between silo ash and autosampler ash impacted the ability of this study to generate uniformity information about fineness measurements.
- The density values from the sixteen samples met the requirements for uniformity (± 5% of the mean density of the ten prior samples).
- The mineralogy and glass content of the fly ash samples from the silo were consistent with prior studies. The baseline fly ash (coal only) and the co-combustion fly ash were nearly indistinguishable.
- The base line fly ash (coal only) and the co-combustion fly ash exhibited very similar trends in the alkali solubility experiments. This suggested that there was not a fundamental change in the way that the alkalies were bonded in the co-combustion fly ash.

The purpose of conducting ASTM C 618 testing was to evaluate the performance characteristics of the co-combustion fly ash and to compare the test results with the baseline ash (coal only fly ash) and prior fly ash collected at Ottumwa Generating Station. It is important to note that the switchgrass burn rate was held constant at a nominal rate of 10 tons per hour during the time that the silo ash samples were collected. In addition, the high fineness values obtained from fly ash samples collected using the autosampler lead researchers to question the reliability of the samples. Hence, it was not possible to make detailed investigations of how switchgrass burn rate influenced performance characteristics. Rather, after conducting strength activity index and soundness testing on the samples from the autosampler, it was decided that the test results were biased (too dependent on fineness) and further testing was only conducted with the four samples of fly ash that were obtained from the ash silo. The specific conclusions from ASTM C 618 testing are summarized below.

- The strength activity index values of fly ash samples obtained from the autosampler tended to be strongly correlated to fineness. This tended to produce test results that were in poor agreement with those obtained from normal fly ash (both silo ash from this study and historical data) obtained from OGS.
- All four of the silo ash samples met the mandatory chemical and physical requirements given in ASTM C 618.
- All four of the silo ash samples met the requirements for high resistance to sulfate attack when they were used with the Type I/II cement employed in this study.
- All four of the silo ash samples failed to meet the requirements for effectiveness in reducing expansion due to alkali-silica reaction (ASR mortar bar expansion test) when a 20% replacement rate of fly ash was used in the test specimens. Increasing the replacement rate to 36% fly ash helped to decrease the expansion of the test specimens; however, test results were still marginal when compared to the low alkali control cement. These test results were consistent with those from prior studies on OGS fly ash.
- All four of the silo ash samples tended to increase the amount of time required for a mortar to set and harden. The influence was small (about a 30 minute increase in setting time) when the fly ashes were used at the 20% replacement level, but increased with increasing fly ash replacement. These test results were in reasonable agreement with those from prior studies on OGS fly ash.

The purpose of conducting the concrete mixture phase of this study was to evaluate plastic properties, rate of strength development and durability characteristics of concrete containing co-combustion fly ash. The mixtures were proportioned using an Iowa DOT C-3-20C mix design. The slump of the concrete was held constant while the water-cementitious material ratio was allowed to vary. The specific conclusions from the concrete study are summarized below.

- Plastic concrete properties (slump, slump loss, unit weight and air content) of mixtures containing the co-combustion fly ash all behaved similar to mixtures containing the baseline (coal only) fly ash. All of the mixtures containing fly ash required more air-entraining solution to reach the target air content; however, dosage rate was relatively uniform for all samples of fly ash. These test results were in good agreement with prior studies of concrete containing fly ash from OGS.
- The rate of strength gain in the mixtures containing fly ash was dependent on the amount of fly ash in the mixture. When used at a replacement rate of 20% (by equivalent mass of cement) it generally took between 3 and 7 days of curing to reach a compressive strength equivalent to the control (no fly ash) mixture. Higher replacements (28% and 36%) took about 28 days and 90 days, respectively, to reach a compressive strength equivalent to the control mixture. No significant differences in compressive were noted between specimens containing the baseline fly ash or the co-combustion fly ash.
- Dosage rate of fly ash had a major impact on the amount of charge passed during the rapid chloride permeability (RCP) tests. Increasing fly ash dosage significantly decreased the amount of charge passed. At 20% fly ash replacement of fly ash for cement, the charge passed by a RCP specimen was decreased by about a factor of two. This is a major improvement in resistance to penetration by Cl ions. No significant differences in test results were noted between specimens containing the baseline fly ash or the co-combustion fly ash.
- All of the mixtures tested (with the exception of mix 3, a batching error was noted on this mixture) produced concrete with adequate entrained air void parameters. All of the specimens contained an adequate volume of air bubbles. The void size distribution curves were reasonably consistent with samples that exhibited excellent freeze-thaw durability and the apparent spacing factors were less than 0.01” (a value which prior studies have shown to provide reasonable resistance to frost).

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