The Cementitious and Pozzolanic Properties of Fluidized Bed Combustion Fly Ash

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ABSTRACT

The focus of our work is to develop an understanding of the potential for Fluidized Bed Combustion (FBC) fly ash to serve as an additive in Portland cement concrete. FBC fly ash from the E.A. Gilbert Generating Unit of the Spurlock Power Station in Maysville, KY was used in this study. In fluidized bed combustion, coal is burned in the presence of limestone at much lower temperatures than conventional pulverized coal combustion (PCC). It also produces both a fine fly ash and a coarse bottom ash product. The FBC fly ash differs from PCC fly ash as it is not fused or spherical and it is high in sulfate. Although this material is outside of the ASTM C-618 specification, it contains glassy silicates, has a relatively high surface area and has the potential to be both pozzolanic and cementitious. Samples were tested for particle size distribution, mineralogy, chemistry and BET surface area. The FBC fly ash was pre-hydrated to slake raw lime then fractions were screened and hydraulically classified. These materials were tested in mortar cubes using ASTM procedures to examine water demand and the compressive strength. The FBC fly ash material was found to initially retard strength development but rapidly gained strength, achieving strength index values as high as 94% in 7 days. Mortar bars were created to test the potential for shrinkage and expansion. Further insight into the potential use of FBC fly ash in construction was made through the examination of concrete cylinders. Compressive strength testing of these cylinders confirmed previous results from mortar cube strength analysis.

INTRODUCTION

The use of fly ash as a pozzolan in concrete has greatly increased over the past several decades, primarily due to improved performance and cost reduction.[1] This material is derived from pulverized coal combustion systems (PCC). Other systems including Fluidized Bed Combustion (FBC), which has the advantage of lower thermal NO_X emissions and greater fuel flexibility, also produce coal fly ash. However, the fly ash collected from FBC systems have characteristics, including high sulfate content, that place it outside of the ASTM C-618 standard for ash in concrete, and it is not currently used as a pozzolan.

For this study, spent bed materials from a circulating fluidized bed combustor (CFBC) were investigated. The ash was collected from the East Kentucky Power Cooperative (EKPC) Spurlock Power Station's new 268-megawatt (net) CFBC "Gilbert" unit[3], named in honor of a former board member. Spurlock Station is located in Maysville, Kentucky.

In CFBC systems, the coal and limestone are fully entrained in the bed and are continually circulated. Spent materials are removed via a cyclone (fly ash) or a drain in the lower part of the unit (bed ash). A second type fluidized bed unit is bubbling bed or dense phase where the bed is fluidized but not entrained. CFBC systems are more typical for large utility applications. Fluidized bed combustion units operate at lower temperatures than conventional PCC units do (1400-1700 °F (760-371 °C) vs. >2500 °F (1371 °C)). The lower temperature reduces the formation of the thermal NO_x[2] and is low enough to allow the formation of anhydrite ($CaSO_4$), from the reaction of calcined limestone with sulfur dioxide and oxygen.

While FBC units offer excellent benefits for the environment, they produce coal combustion products that are drastically different in composition from CCPs produced in traditional combustion (Table 1), being much higher in calcium and sulfate. FBC fly ash also differs from PCC fly ash, as it is not fused or spherical (Figure 1).

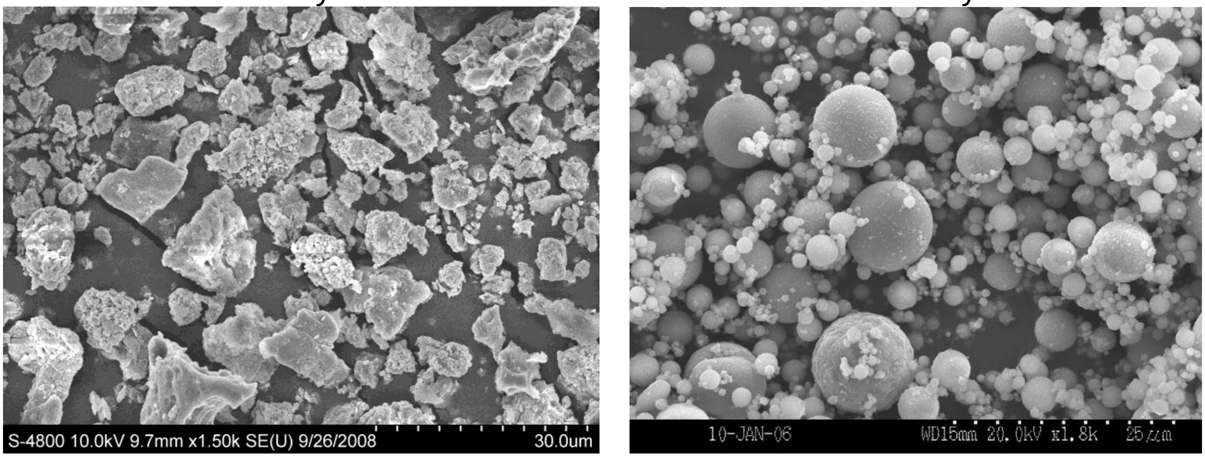
Table 1: Chemical analysis of Gilbert fly ash as received and sieved, compared to Class C and Class F fly ash.[4]

Sample ID	Gilbert FA Raw	Gilbert FA >100	Gilbert FA 100x200	Gilbert FA <200	Class C Ash	Class F Ash
%SiO_2	24.4	17.73	19.66	26.05	42.78	45.07
%Al_2O_3	9.56	7.07	7.71	10.59	22.27	19.1
%Fe_2O_3	8.64	3.63	6.87	10.06	6.51	18.76
%CaO	32.52	43.34	35.77	29.76	18.34	3.33
%MgO	3.82	2.08	3.62	3.64	4.44	0.86
%Na_2O	0.12	0.09	0.08	0.17	1.44	0.37
%K_2O	1.18	0.38	0.98	1.36	1.22	2.4
%P_2O_5	0.1	0.09	0.09	0.1	0.95	0.2
%TiO_2	0.41	0.35	0.36	0.45	1.38	1.24
%SO_3	18.21	25.7	21.26	15.42	1.06	0.94
%LOI	8.3	7.46	6.85	9.13	0.43	1.32

STUDY OBJECTIVES

The overarching objectives of the study are to determine the potential of the CFBC materials as an additive in Portland cement concrete. More specific objectives include: the determination of the physical and chemical characteristics of the material; it's potential for processing and beneficiation; the characterization of the principal reactions that take place with the portland cement and other pozzolans including conventional fly ash; and finally, the procedures and protocols necessary for its successful use. This paper focuses primarily on the physical and chemical characteristics of the material and its potential for beneficiation.

Figure 1: SEM imagery of as received Gilbert fly ash compared to Class C fly ash.
Gilbert Fly Ash Class C Fly Ash[5]



EXPERIMENTAL PROCEDURES

Samples of the Gilbert fly ash (GFA) were analyzed for particle size distribution, mineralogy, chemistry and BET surface area. The GFA was tested on an “as received” basis and “as classified.” The GFA was classified both by screening and hydraulically using a simple elutriation technique. All samples were pre-hydrated to slake the quicklime (CaO) present. These GFA materials, along with 50/50 blends with raw fly ash, were tested using ASTM procedures for relative water demand and their compressive strength measured in mortar cubes. Shrinkage and expansion of the fly ash was determined by ASTM testing methods with mortar bars. Concrete cylinders were produced and tested for compressive strength.

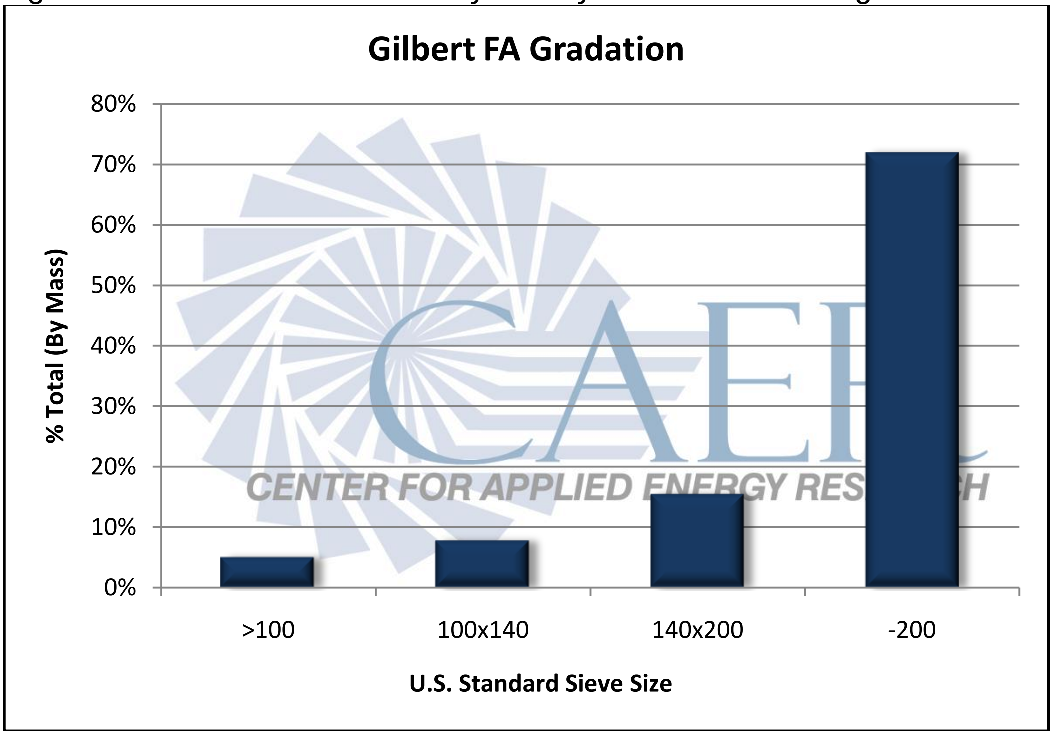
Physical Characteristics

It was necessary to gather basic data on the physical and chemical properties of the fly ash. Using ASTM procedures when applicable, gradation, chemistry, mineralogy, and BET surface area were determined.

Gradation Analysis: The gradation of the raw FBC fly ash was initially assessed using a series of standard sieves. The series consisted of No. 100 (0.149 mm), No. 140 (0.105 mm), and No. 200 (0.074 mm) mesh sieves arranged in succession above a pan to capture all material passing through the No. 200 (0.074 mm) mesh. The sieve tests were replicated seven times (Figure 2), to ensure the validity of the results.

Additional quantities of GFA were sieved to obtain a large sample of product passing the No. 200 (0.074mm) sieve. This material, referred to as “Gilbert -200 Product” for this research, was analyzed for its comparative suitability as a construction material in further experimentation.

Figure 2: Gradation for Gilbert Fly Ash by mechanical sieving.



Particle size was also analyzed using a laser particle size analyzer. The results of this analysis confirmed data obtained from the mechanical sieving as well as providing more data on the smaller sizes. The results indicated that 10% of the raw Gilbert fly ash (D_{10}) had a diameter less than or equal to 2.6 µm, with a mean, or D_{50} particle size of 22 µm and a D_{90} of 86 µm.

Chemical analysis: The chemical composition of Gilbert Fly Ash was obtained through X-ray Fluorescence (XRF) spectroscopy (Table 1).[4] Raw Gilbert fly ash, as well as mechanically sieved samples of Gilbert fly ash, were examined. As expected, the chemistry of Gilbert fly ash was different from typical Class C or Class F ash. Gilbert fly ash has far lower silica (SiO_2) content than Class C or F ash, while also having much higher levels of lime (CaO) and sulfate (SO_3).

The GFA was also tested for its available lime index using the ASTM C-25 "rapid sugar test method". Quicklime (CaO) can cause erratic expansion in concrete as well as contribute to heat. The material's available lime index was used to determine the amount of water needed to slake it. Testing showed moderate amounts of available lime for both the raw Gilbert fly ash and the Gilbert -200 product, while the Gilbert hydraulic classification product had a very low available lime index (Table 2).

Table 2: ASTM C-25 Available Lime Index.

Material	Available Lime Index
Raw Gilbert Fly Ash	10.1
Gilbert -200 Product	10.0
Gilbert Hydraulic Classification Product	1.5

Loss on Ignition: The Gilbert fly ash was also analyzed for its percentage of material lost on ignition (LOI). The LOI was determined using test methods outlined in ASTM C-25. Results of the testing showed that Gilbert fly ash has a much higher %LOI than typical Class C or F fly ash (Table 1). This indicates a higher presence of carbon based compounds in Gilbert fly ash, which could inhibit its usability as a pozzolan.

Mineralogy: Mineralogy analysis was conducted by X-Ray Diffraction (XRD). The Gilbert fly ash as received had a high proportion of anhydrite, quartz and lime with lesser hematite and calcite.

Surface Area Analysis: Surface area was obtained using the BET method for the Gilbert fly ash as received, the sugar extraction product (from the rapid sugar test), and the Gilbert hydraulic classification product. A Micromentics ASAP 2020 Surface and Porosity Analyzer was used to obtain the results (Table 3). The high surface area of Gilbert fly ash (especially after beneficiation) contributed to its pozzolanic potential.

Table 3: BET surface area analysis.

Material	BET Surface Area (m^2/g)
Gilbert Fly Ash As Received	5.3
Sugar Extraction Product	22.0
Hydraulic Classification Product	12.1

Beneficiation

The GFA material was beneficiated by both mechanical screening and hydraulic methods. These beneficiated materials were used in mortar and concrete mixes to examine their comparative water demand, compressive strength, and expansion.

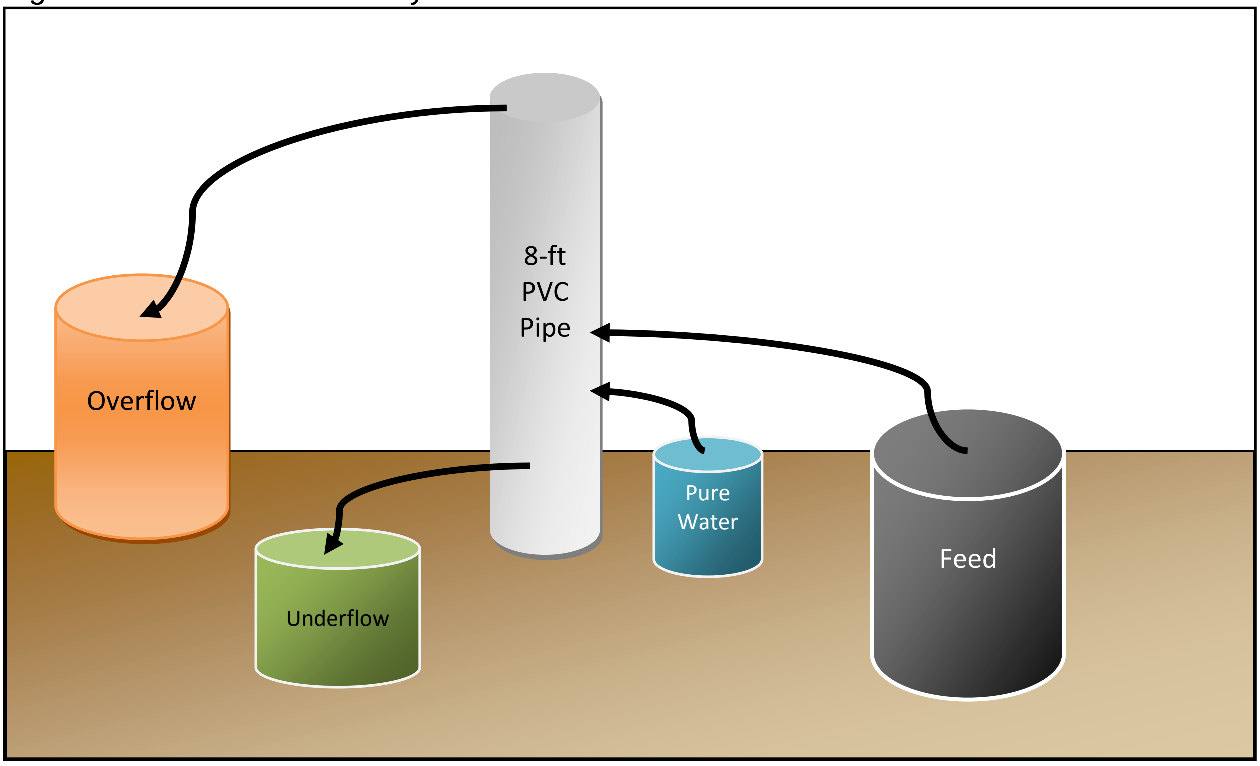
Prehydration: The GFA as received and -200 mesh materials were prehydrated to convert the CaO to portlandite ($Ca(OH)_2$). It was determined that an amount of water equal to 5% of the mass of any fly ash sample could be added to fully slake the lime. The Gilbert hydraulic classification product is naturally hydrated during the beneficiation process.

Mechanical Screening: Using the same series of sieves from the gradation analysis, large quantities of Gilbert fly ash passing the -200 sieve were collected for use in further testing.

Hydraulic Classification: As another means to obtain a large beneficiated sample of Gilbert fly ash, a system of hydraulic classification was used (Figure 3). In this system, 50 gallons (189 L) of a 0.2% solution of a polycarboxylate based dispersant was added to a drum containing 45 lbs (20.4 kg) of raw Gilbert fly ash. This feed material was constantly mixed in the drum throughout the classification. The feed and a separate bucket of pure water were pumped into a vertical 8 ft (2.44 m) length of 6 in (15.2 cm) diameter elutriation column. The feed and separate water were pumped at rates of 1 L/min and 0.5 L/min respectively.

To achieve separation of the finer particles of Gilbert fly ash, underflow was pumped out of the bottom of the pipe at a rate of 0.5 L/min, allowing the overflow to pour out of the top of the pipe and into a collection drum at 1 L/min. As the feed drum emptied of material, batches of 5 gal (18.9 L) with dispersant and 4.5 lbs (2.0 kg) of GFA were added to the drum until the desired amount of overflow was obtained.

Figure 3: Wet classification system illustration.



The hydraulic classification was used due to its potential to reduce the naturally high free lime content of GFA while simultaneously obtaining a large sample of finer particle size.

Compressive Strength

The Gilbert fly ash was tested for its compressive strength. Mortar cubes were prepared and tested for their compressive strength in accordance with all applicable ASTM specifications and procedures (ASTM C-109, ASTM C-311, and ASTM C-305). Mortar cubes were made using samples of the Gilbert hydraulically classified product, -200 product, a 50%/50% blend of hydraulically classified product and class F fly ash, and Gilbert fly ash as received. Each of these samples replaced 20% of the cementitious content in the mortar batches. Portland cement control cubes were also prepared and tested.

Concrete cylinders were also created and cured according to ASTM C-192 and compressive strengths determined by ASTM C-39. The cylinders were capped just before compressive strength testing in accordance with ASTM C-617. Concrete cylinders were created using samples of the Gilbert hydraulically classified product, -200 product, a 50%/50% blend of hydraulically classified product and class F fly ash, and Gilbert fly ash as received. These samples each comprised 20% of the total cementitious materials in their mixes.

Expansion and Shrinkage

Another important aspect of any potential construction material is its tendency to expand or contract over time. Excessive expansion or shrinkage can lead to cracking or weakening of hardened concrete mixtures. Long-term length change was examined using the ASTM C-157 standard test method. Using the procedures outlined in ASTM C-157, mortar bars were formed to test the same series of products previously examined for compressive strength. According to ASTM C-157, the bars were stored in lime-saturated water and measured initially after being removed from their molds, after 28 days of curing, 8 weeks of curing, 16 weeks, 32 weeks, and 64 weeks. To date, no products have cured for more than 16 weeks.

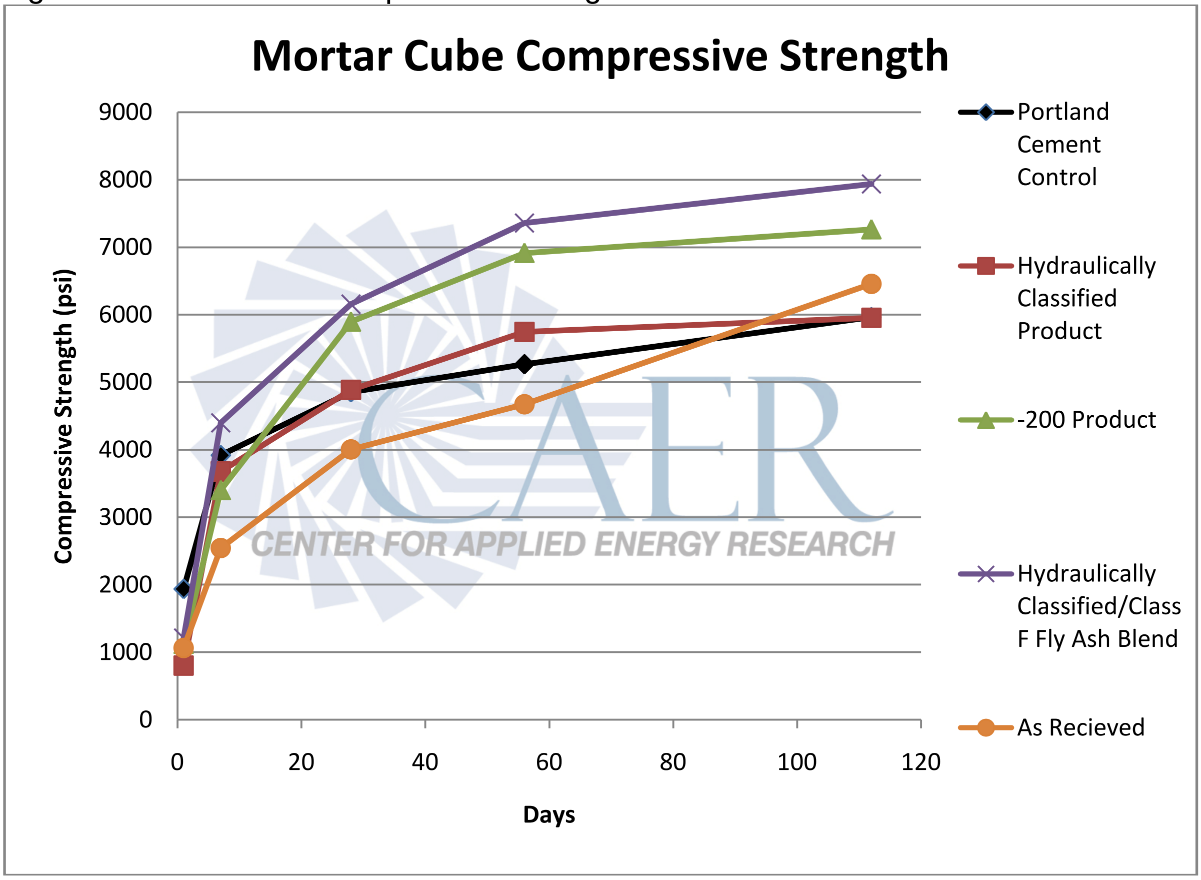
Short-term shrinkage was determined by following ASTM C-596 (Drying Shrinkage of Mortar Containing Hydraulic Cement). The same series of products was used for the measurements. In ASTM C-596, the bars are placed in air storage rather than in a lime solution (except for the first 48 hours after being removed from molds). This test method is a good indication of the initial shrinkage that can be expected as a concrete mixture containing the same cementitious materials cures.

RESULTS AND DISCUSSION

Mortar Cube Compressive Strength

In general, mortar cubes made with the various GFA products showed lower strength development rates than the Portland cement control cubes, as is typical for a Class F ash (Figure 4). However, after 28 days of curing, all of the Gilbert fly ash products except for the “as received” ash exceeded the compressive strength of the Portland cement control. Notably, the cubes containing the blend of the hydraulically classified product and a class F ash achieved 127% (6,200 psi) of the strength of the control cubes after 28 days. It was also the only product to exceed the strength of the control cubes after 7 days of curing. The high compressive strength of this blend could make it a useful option for use in heavy load bearing slabs and columns.

Figure 4: Mortar cube compressive strength results.



The -200 mesh product also performed very well compared to the control, reaching 7267 psi after 112 days of curing. The hydraulically classified product achieved slightly higher compressive strength than the control after 28 days. The commercially adaptable method of hydraulic classification and roughly equivalent strength to Portland cement cubes could make the hydraulically classified product a money saving alternative to Portland cement, especially in less critical applications like sidewalks.

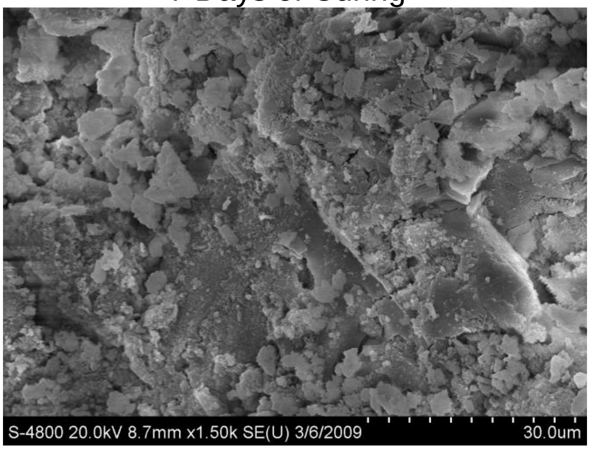
The Gilbert fly ash as received from the plant had the lowest strength of all of the tested products up to 56 days of curing. After 56 days, its strength was 89% (4,700 psi) of the Portland cement control. However, there was a large increase in strength between 56 and 112 days. The as received GFA ash is now stronger than both the control and the hydraulically classified product at 6,500 psi. Figure 5 is a series of SEM imagery for the GFA as received mortar cubes after 7, 28, and 56 days of curing. Barely any ettringite crystal growth is evident after 7 and 28 days, but large amounts of crystallization are evident after 56 days. This late crystal growth is evidence that the high 112 day compressive strength is not anomalous.

Concrete Cylinder Compressive Strength

Concrete cylinders made from Gilbert fly ash products were also tested for compressive strength. While mortar cubes are a good indicator of the compressive strength of the materials themselves, fly ash is most often used as a pozzolan in concrete mixes. Therefore, it was necessary to also test the compressive strength of concrete mixes made using the Gilbert fly ash products.

Figure 5: Series of SEM imagery for Gilbert fly ash as received mortar cubes.

7 Days of Curing

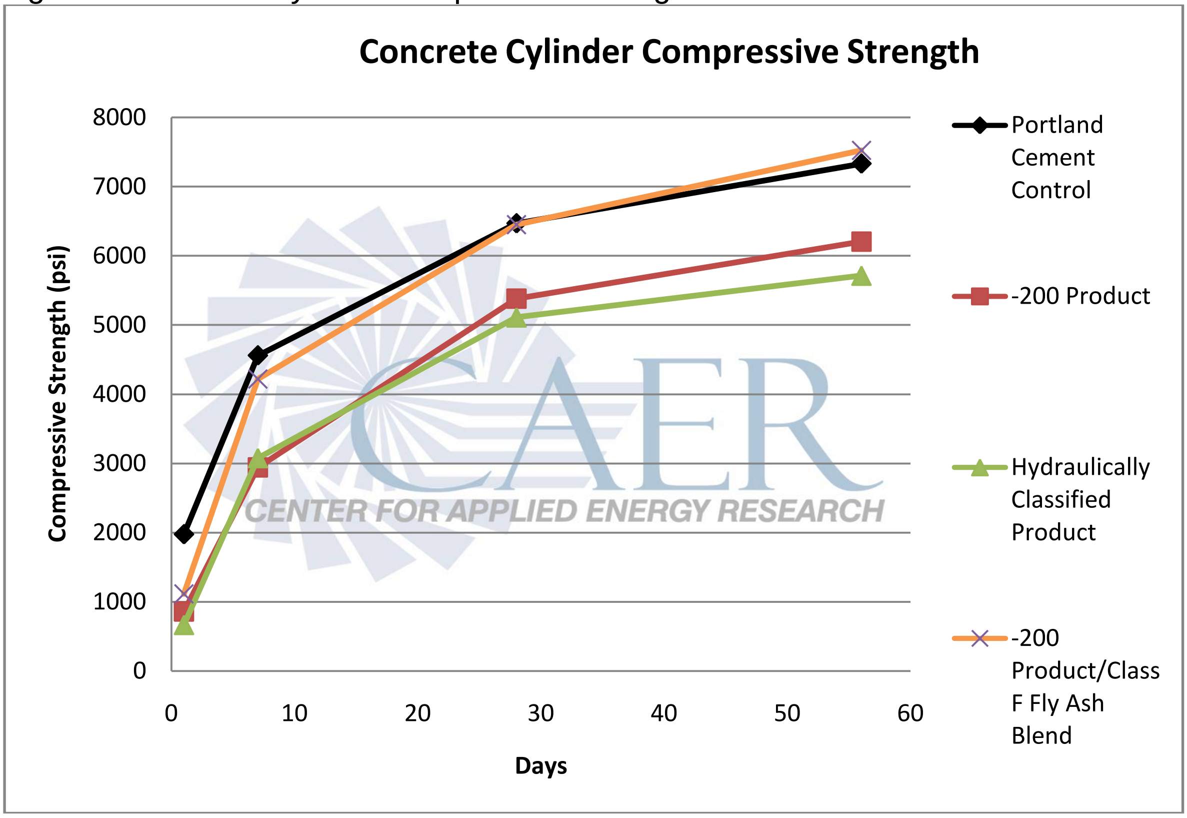


28 Days of Curing

56 Days of Curing

The compressive strength testing of the cylinders shows a similar relationship among the GFA products as was found in the mortar data. For example, the hydraulically classified product blended with the Class F ash outperformed the -200 mesh and hydraulically classified product alone. The GFA materials were lower in strength relative to the control however (Figure 6). It should be noted that the Portland cement control also had a particularly high strength compared to most controls prepared in our lab. Additionally, even though only the blend with class F ash exceeded the strength of the control after 56 days of curing, the -200 mesh product had a respectable strength of 6200 psi after 56 days. The hydraulically classified product also exhibited a compressive strength suitable for many construction applications, at 5700 psi after 56 days. The compressive strength of the concrete cylinders confirm the results obtained from the mortar cube testing, but do not exhibit the substantial increase in strength that was expected.

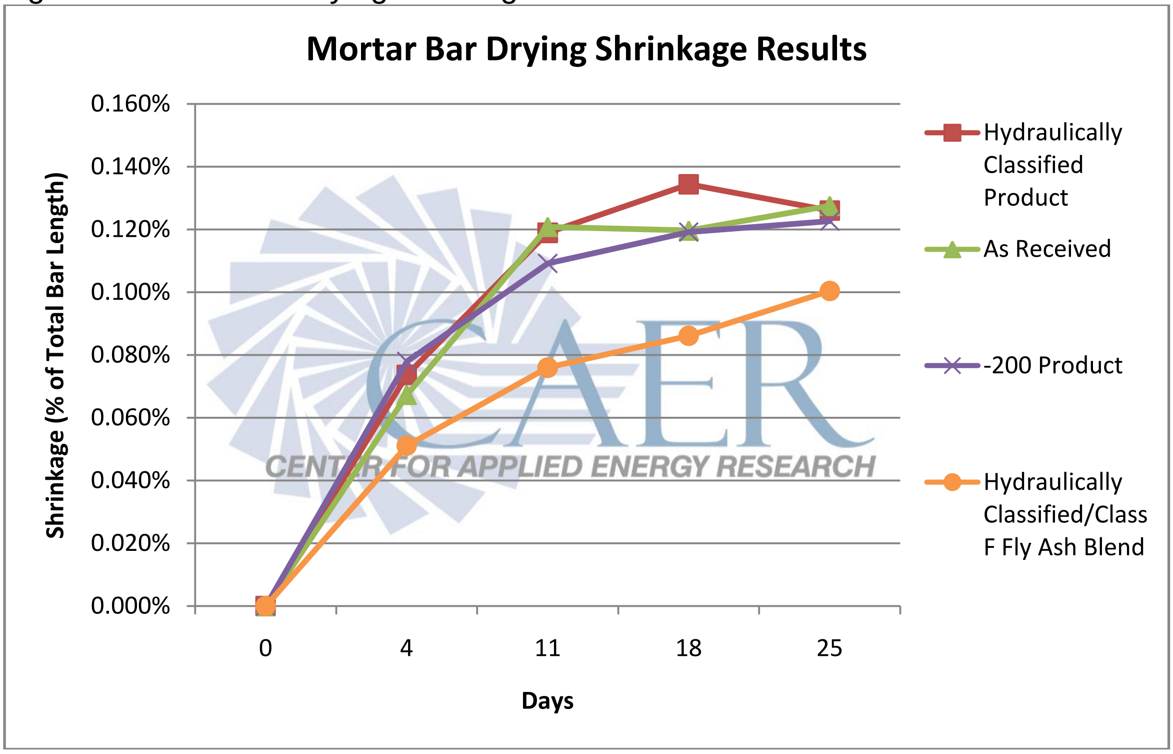
Figure 6: Concrete cylinder compressive strength.



Dimensional Stability

Drying Shrinkage: Mortar and concrete products tend to shrink slightly during early stages of curing. This is due to the loss of free water from the mix during its consumption in hydration reactions as well as from evaporation. Mortar bars made from the Gilbert fly ash products were tested for their extent of drying shrinkage. Overall, the Gilbert fly ash products exhibited extremely low amounts of shrinkage (Figure 7). The highest recorded shrinkage was 0.134% for the hydraulically classified product at 18 days of curing. This means that a slab of 100 feet (30.5 meters) would shrink only 1.6 inches (40.6 mm). This seems to be a strong indication that drying shrinkage will not be a barrier for the use of Gilbert fly ash as a pozzolan.

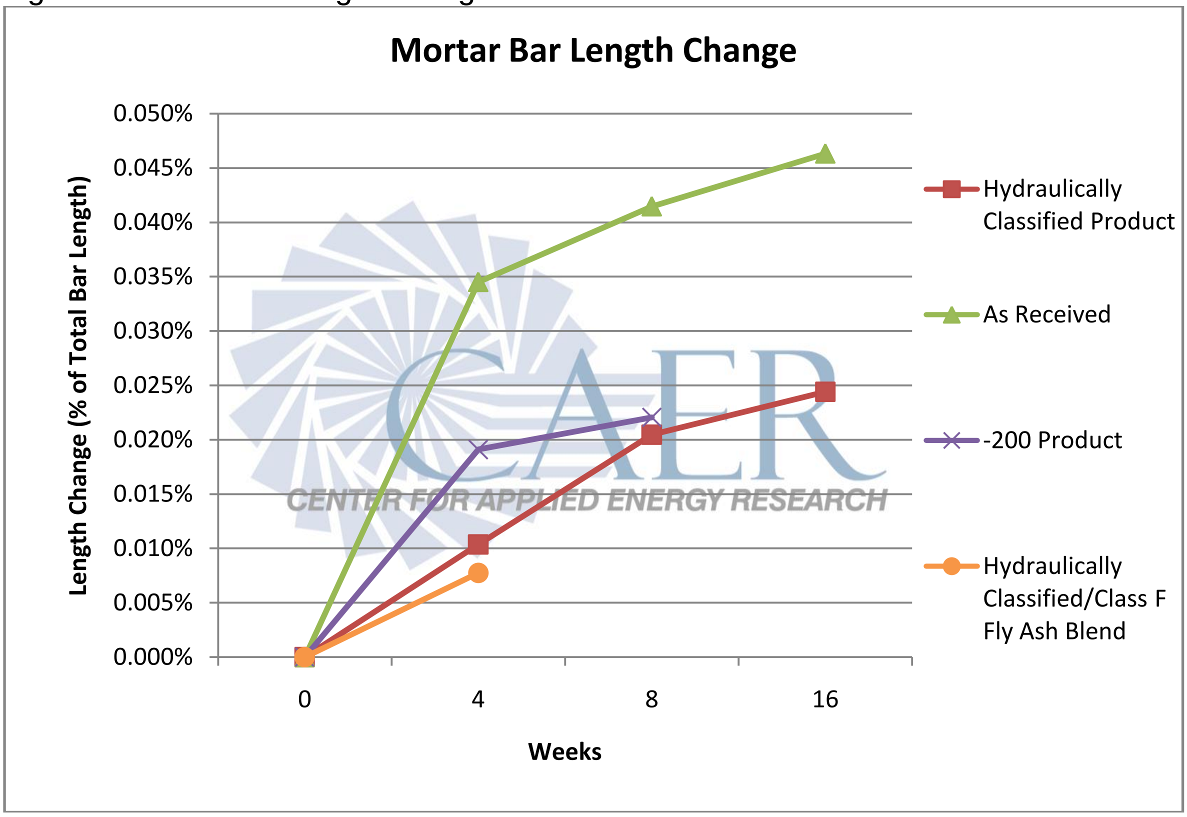
Figure 7: Mortar bar drying shrinkage results.



Length Change: The mortar bar length change test calls for the bars to be placed in a lime-saturated solution for the duration of their storage. This gives an unlimited supply of fuel for the hydration reactions to occur, leading to the maximum possible amount of expansion in the mortar bars. As this is a long-term test, not all of the data for the various Gilbert fly ash products has been obtained at this time. However, current results indicate very low amounts of expansion (Figure 8).

Gilbert fly ash as received from the plant exhibited the highest amount of expansion among the various products. After 16 weeks of curing, it had expanded by 0.046%. This is still extremely low, but the comparatively high amount of expansion could be explained by the high lime content of the as received product. As the fly ash cures, the free lime will expand as it hydrates to become calcium hydroxide.

Figure 9: Mortar bar length change results.



CONCLUSIONS AND FUTURE WORK

Gilbert fly ash shows promise as a usable pozzolan. It exhibited high compressive strength (especially in mortar cubes) and excellent dimensional stability. Both the strength and dimensional stability of the Gilbert fly ash was maximized when it was blended with a class F ash. Hydraulic classification proved to be a potential commercially viable method to slake free lime from the raw fly ash while improving its strength and dimensional stability.

Further compressive strength testing of concrete cylinders made from the fly ash should be carried out to determine if the current strength results are anomalous. In addition, work to determine the causes of the strength delays in the GFA materials and the principle reactions controlling strength development should be conducted.

REFERENCES

[1] American Coal Ash Association. "ACAA Coal Combution Products Survey." 27 January 2009. ACAA - Promoting & Advancing Coal Combustion Products. 13 February 2009 <http://www.acaa-usa.org/associations/8003/files/1966-2007_CCP_Svy_Prod_and_Use_Charts%28As%20of%2012-29-08%29.pdf>.

[2] United States Department of Energy: Fossil Energy Office of Communications. DOE - Fossil Energy: Overview of Fluidized Bed Technology. 13 February 2009. 13 February 2009 <http://fossil.energy.gov/programs/powersystems/combustion/fluidizedbed_overview.html>.

[3] East Kentucky Power Cooperative. Spurlock Station. 5 November 2007. 13 February 2009 <http://www.ekpc.com/spurlock.html>.

[4] Thomas, Gerald. "X-Ray Fluorescence Spectroscopy." Lexington, KY: University of Kentucky Center for Applied Energy Research, 23 September 2008.

[5] Jewell, Robert. "Class C Fly Ash SEM Imagery." Lexington, KY: University of Kentucky Center for Applied Energy Research, 10 January 2006.

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