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Fluidized Bed Combustion Ash Utilization: CFBC Fly Ash as a Pozzolanic Additive to Portland Cement Concrete.

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ABSTRACT

Atmospheric fluidized bed combustion (CFBC) produces spent bed fly ash and bottom ash consisting primarily of lime (CaO), anhydrite ($CaSO_4$), calcined clay materials and quartz. These materials have a much larger surface areas than conventional pulverized coal combustion (PCCA) fly ash. But, problems with swelling and strength loss have limited their usefulness. The potential of the CFBC fly ash as a pozzolanic additive to portland cement was investigated. The pre-hydrated CFBC fly ash was tested "as received" and as beneficiated by hydraulic classification or screening to remove the >200 mesh materials. The CFBC was also blended with PCCA fly ash. The mortar bar tests indicated that the CFBC fly ash was dimensionally stable and beneficiating the ash further reduced expansion. The CFBC materials did not lower water demand. The CFBC fly ash initially retarded strength development but by 7 days this was not a major factor. The CFBC materials performed well in concrete.

INTRODUCTION

Fluidized bed combustion

Fluidized bed combustor technology can be divided into two general types based on the level of fluidization. In dense phase or bubbling bed units, the coal and sorbent is subjected to air flow that is sufficient to fluidize the particles but not fully entrain them. In dilute phase or circulating units (CFBC) the air flow is sufficient to fully fluidize or entrain the bed. The coal is continually recirculated as it burns (Figure 1). Both systems produce a fine particulate or fly ash and a coarse particulate or a bed ash, differing in the relative proportion of each. Many examples of both types exist. In general however, the bubbling bed units are smaller and the largest fluidized bed units (i.e. >100MW) used by the electric utility industry are based on CFBC technology.

FBC technology has several major advantages compared to conventional pulverized coal combustion. It has much higher fuel inventory and bed mass which acts as a thermal fly wheel and gives this technology great fuel flexibility. FBC can operate with relatively low heating value fuels with high ash and sulfur content. Secondly, the fuel has a longer residence time than in pulverized coal combustion furnaces which allows the sufficient time for the reaction of an in bed sorbent such as limestone or lime to react with sulfur dioxide in the combustion gas. This simplifies the gas scrubbing train. Finally, they operate at much lower temperatures (i.e. 760-1000 °C vs. 1,500 to 2,000 °C), which greatly limits the formation of thermal NO_x. [USDoE 2009].

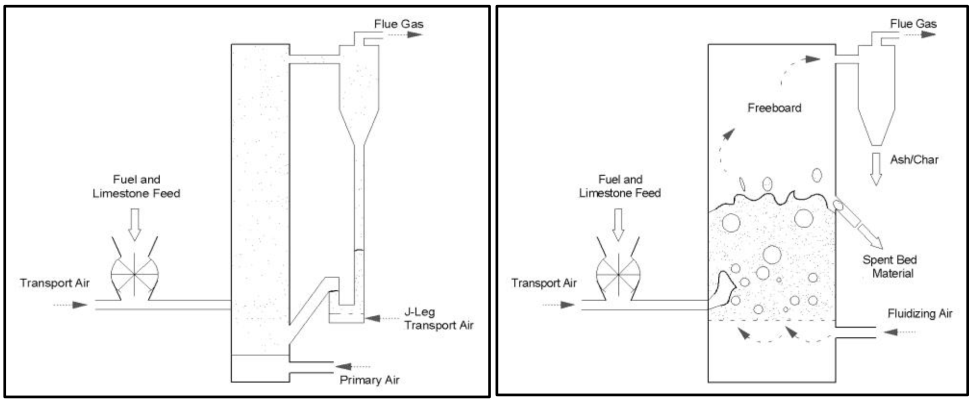

Fig. 1. Schematic Diagram Comparing Dense Phase (right) with Dilute Phase Fluidized Bed Combustors.

Research Objectives

The difference in temperature and the presence of the products of sulfur absorption in FBC results in combustion products that are unlike those of conventional pulverized coal combustion. The presence of the sorbent and the resultant high sulfate content produces a composition that falls outside of the ASTM C-618 specification for both Class C and Class F fly ash.

The materials for this research were generated at Unit 3 of East Kentucky Power Cooperatives' (EKPC) Spurlock Power Station in Maysville, Kentucky, which is an Alstom designed 268-net MW (~300 MW gross) circulating fluidized bed combustor [EKPC, 2007]. Unit 3, also known as the "Gilbert" unit in honor of a retired EKPC board member, went on line in 2005. Unit 4, another Alstom 300MW combustor of a slightly newer design is scheduled to go on line in 2009. Together they will produce about 750,000 to 850,000 tons of solid byproducts per year.

The objectives of the research discussed in this and the accompanying paper was to explore the potential of fluidized bed combustion material as an additive to Portland cement and in the case of the bottom ash, as the basis for a standalone cement product. The beneficiation potential of the CFBC fly ash was also examined determine if their characteristics as a concrete additive could be improved using simple methodology.

EXPERIMENTAL PROCEDURES

Sampling

The bottom ash and the fly ash have been sampled several times since the Gilbert unit was brought on line. Our largest efforts, with over 1 ton of material collected, were made in July of 2005 and 32 months later, in February of 2008. These samples are the basis of this discussion. The split between fly ash and bottom ash from the Gilbert CFBC is ~60%:40%, somewhat higher than other CFBC we have sampled which typically produced ~20% bottom ash. Over this period of time the Gilbert CFBC has used coal from several sources, the most important however has been very high sulfur (~7%) and high ash (~15%) bituminous coal mined in southeastern Ohio. The limestone for this combustor is supplied from a nearby mine operated by the Carmeuse Lime Co. and has remain consistent over the study.

The samples were collected in steel drums in an unconditioned state directly from the collection hoppers at the plant. The materials were returned to the lab and after cooling, were transferred to Mylar bags and sealed. The raw FBC material is extremely hydroscopic and storage in sealed moisture-proof packaging is essential.

Physical Characterization

The gradation of the raw FBC fly ash was assessed using a series of ASTM E-11 standard sieves. The sieve series was shaken mechanically for eight minutes and replicated to ensure validity. Size analysis was also conducted via laser diffractometry using a CILAS 1064 and a Malvern 2000 Mastersizer. The two units gave similar results.

Chemical analysis of the various sample fractions were determined by X-ray Fluorescence (XRF) spectroscopy. Available lime index was determined in accordance with the ASTM C-25 rapid sugar test method. Loss on ignition (LOI) was measured via ASTM C-25. Mineralogy analysis was conducted using a Phillips X'Pert x-ray diffractometer (Cu K_α radiation, λ=1.54 Å). Surface area was obtained using the BET method with a Micromeritics ASAP 2020 Surface and Porosity Analyzer.

Testing Methodology

The CFBC samples were slaked with 5% water (by weight). This was found sufficient to fully convert the lime (CaO) to Portlandite ($Ca(OH)_2$). Only as small fraction of the anhydrite present was converted to gypsum.

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). Concrete cylinders were created and cured according to ASTM C-192 and their compressive strengths were determined using ASTM C-39. The cylinders were capped in accordance with ASTM C-617. Long-term length change was examined using the ASTM C-157 standard test method. Short-term shrinkage was determined by following ASTM C-596, "Drying Shrinkage of Mortar Containing Hydraulic Cement".

Beneficiation Potential

The CFBC fly ash was subjected to both mechanical screening at 200 mesh (75 µm) and hydraulic classifications to remove the coarser size fractions. This was done to increase the overall surface area of the sample and improve its reactivity.

A simple elutriation system based on vertical 152 mm diameter (6 inch) PVC tubing was used to classify the fly ash. A slurry of fly ash and water with a pulp density of ~10% was mixed in a drum. The FBC fly ash was found to readily flocculate so the feed slurry was treated with a low level of a common carboxyl based dispersant. The slurry was fed to the center of the pipe and material was pumped from the bottom of the pipe at a rate less that of the feed rate by a factor of about one half. This resulted in underflow slurry mostly composed of coarse particles and a overflow slurry of fine particles. The underflow rate was adjusted until the level of solid flow reached 50% of the feed solid flow. Thus the beneficiated product yield was also 50% by weight. The recovered surface area is, of course, much higher. The hydraulic classification had the additional advantage of fully slaking the lime present in the fly ash, but the added disadvantage of requiring drying. The hydraulic classification product showed substantial improvement over the raw fly ash having a mean diameter (D_{50}) of 22 µm compared to 86 µm in the unprocessed product. The sieved ash improved to a D_{50} of 19 µm and had a product yield of 58%.

DISCUSSION OF TEST RESULTS

Physical and chemical characterization

The chemical analysis of the two sample collections are presented in Table 1 along with the average Class F composition of 25 samples of fly ash sourced from 1% to 2% sulfur bituminous coal (Group 2)[Hower, et al., 2005]. Also presented is the average of 25 samples of a Class C ash sourced from a subbituminous coal [Brownfield, 2005]. Compared to Class C and Class F fly ash, the CFBC material is found to be much higher in sulfate and calcium and lower in silica and alumina. Sulfate is generally less than 1% for most PCCA and is limited to 5% by weight by ASTM C-618.

Table 1. Chemical Analysis of CFBC Fly Ash. Major Element Oxides are in Weight Percent, Trace Element Data are in Parts per Million (ppm).

Sample Date	2005	2005	2008	2008	Class F	Class C
	FA +200	FA -200	FA+200	FA-200	PCC	PCC
Fraction.	39.1%	60.9%	42.3%	57.7%		
Major elements						
SiO_2	20.32	24.98	19.66	26.05	49.75	32.3
Al_2O_3	8.56	10.78	7.71	10.59	24.76	18.1
Fe_2O_3	7.88	10.83	6.87	10.06	12.22	6.5
CaO	32.80	28.22	35.77	29.76	4.31	26.4
MgO	3.65	3.39	3.62	3.64	1.36	5.8
Na_2O	0.17	0.23	0.08	0.17	0.48	2.4
K_2O	0.92	1.10	0.98	1.36	2.24	0.33
P_2O_5	0.13	0.14	0.09	0.1	0.32	1.0
TiO_2	0.33	0.39	0.36	0.45	1.18	1.4
SO_3	23.68	17.37	21.26	15.42	0.48	
%C	2.36	3.61	3.27	4.93	4.07	
LOI	5.73	8.27	6.85	9.13		
Trace elements						
V	18	29	<1	<1	250	
Cr	47	47	16	29	70	62
Mn	128	119	81	117	165	200
Co	20	27	10	21	41	28
Ni	<1	<1	3	19	66	32
Cu	12	12	<1	<1	225	
Zn	28	42	<1	<1	135	
As	<1	<1	88	83	153	18
Rb	67	114	102	123	24	
Sr	297	256	219	206	1072	
Zr	94	89	20	20	310	
Mo	<1	<1	<1	<1	24	
Cd	1	1	1	1	4	1
Sb	6	7	7	7	2	3
Pb	35	33	35	33	72	38

In addition, in Class F fly ash the Loss on Ignition measurement is typically close to that of carbon and essentially serves as a surrogate for this measurement. However this is not the case for the CFBC fly ash, where the LOI is much higher than the carbon.

The trace element content of the CFBC material is generally lower than PCCA, as it is substantially diluted by the limestone sorbent. There are exceptions to this however for elements, such as rubidium, that is found in higher concentrations in the limestone than the coal ash. In general the fly ash samples were similar in composition between the two collections, which we believe to be a function of the consistent source of limestone used in the combustor.

Replicate X-ray diffraction was run on several samples of the CFBC fly ash. The major minerals present from most abundant included β-anhydrite (CaSO4), quicklime or calcia (CaO), quartz (SiO_2) and minor periclase (MgO) and hematite (Fe_2O_3). This is contrasted with Class F ash which is a dominantly glassy material (generally >80%), with quartz, mullite ($3Al_2O_3\ 2SiO_2$) and magnetite (Fe_3O_4) typically found in most diffraction scans along with other minor phases. Class C ash is also mostly glassy material, (generally >50%) but has a more varied mineralogical makeup, with merwinite ($Ca,Mg(SiO_4)$), quartz, tricalcium aluminate ($Ca_3Al_2O_6$), gehlinite ($Ca_2Al(Al,Si)O_7$) lime and anhydrite typically found [Brownfield, 2005].

Another major difference is that the "hump" in the X-ray diffraction pattern from glassy scattering that is typical in PCCA was absent in the CFBC pattern. An SEM micrograph illustrates the reason for this (Figure 2). The lower temperature of the CFBC is not sufficient to melt the clay minerals in the ash. However, the lack of any clay mineral reflections in the X-ray patterns indicates that these minerals have been decrystallized. This is similar to the formation of "meta"kaoline which is an amorphous reactive form of kaolinite formed by the high temperature dehydroxylation.

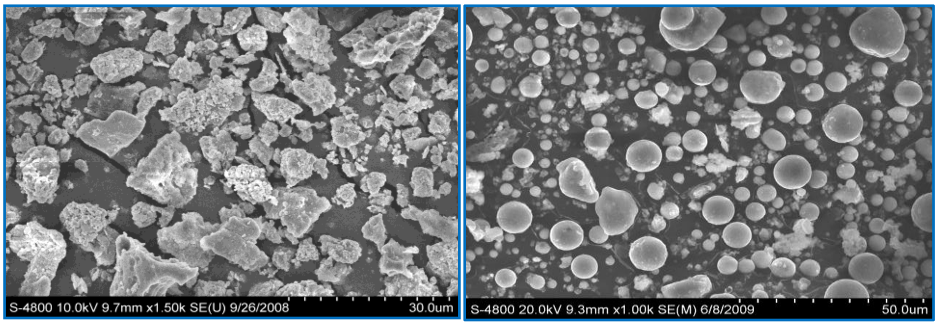

Fig. 1. SEM Micrographs of CFBC Fly Ash (Left) and a Class F Fly Ash.

Surface area was measured by nitrogen adsorption using the BET method. Measurements were made for the fly ash on an as received basis, on the hydraulically classified ash, and on a sample of sugar extracted ash (Table 2). This sample was washed repeatedly with a sugar extract which removed the lime and the anhydrite leaving primarily the unfused demineralized clay residue. As suggested by the irregular shaped particles, the CFBC materials were found to have a higher surface area than PCC ash. For example, the silicate portion of Class F PCCA typically has surface area in the range of 600 to 1,000 cm^2/g. The CFBC fly ash surface area is more than five times this range of values. Also, the beneficiation of the CFBC material greatly increased its surface area. The high surface area of Gilbert fly ash, especially after beneficiation, contributes to its pozzolanic potential.

Table 2: BET Surface Area.

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

The presence of hydrated lime or Portlandite also contributes to the reactivity of this ash. The sugar extraction test was used to measure the available lime which was 10% for both the as received and screened CFBC ash.

Strength and Dimensional Stability Testing

Mortar cubes and concrete cylinders were made using samples of the Gilbert hydraulically classified product, the slaked screened -200 mesh (75 µm) product, and slaked Gilbert fly ash as received. A 50%/50% blend of hydraulically classified product and a high quality beneficiated Class F fly ash was also tested to investigate the affect of a spell out on the CFBC ash. Each of these samples replaced 20% of the cementitious content in both the mortar and concrete batches. Portland cement control cubes and cylinders were also prepared and tested. The "as received" fly ash had the highest water demand of 105% of control followed by the hydraulic classified ash and the -200 mesh ash at 100% of control, and the blended PCCA-CFBC ash had reduced water demand (97% of control).

Mortar bars of each of the materials were also prepared for shrinkage and expansion testing.

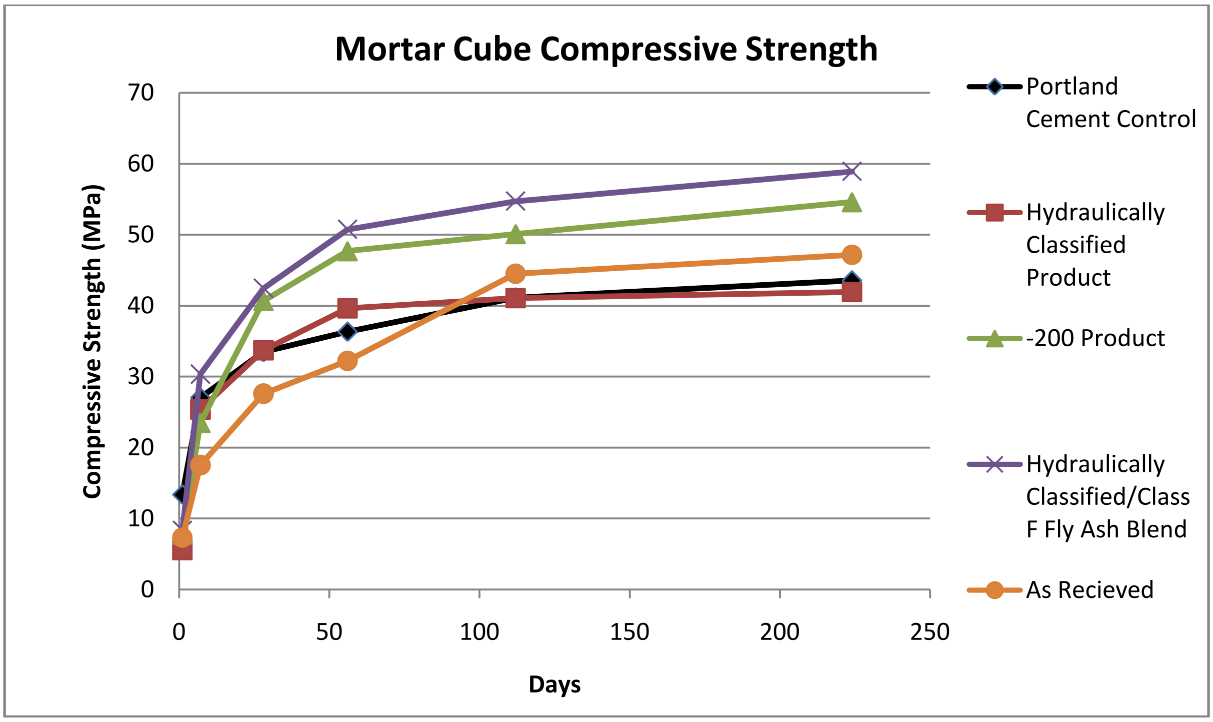

Fig. 2: Mortar cube compressive strength results.

The various Gilbert CFBC fly ash products initially retarded strength development relative to the Portland cement control cubes (Figure 2). 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. The large difference between the as received and the blended CFBC ash was most probably related to water demand differences.

Notably, the cubes containing the blend of the hydraulically classified product and a class F ash achieved 127% (42.4 MPa, 6157 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 -200 mesh product also performed very well compared to the control, reaching 50 MPa (7267 psi) after 112 days of curing. The hydraulically classified product achieved slightly higher compressive strength than the control after 28 days. 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% (32.2 MPa, 4673 psi) of the Portland cement control. However, there was a large increase in strength between 56 and 112 days. The “as received” CFBC fly ash is now stronger than both the control and the hydraulically classified product at 6456 psi.

Table 3. Concrete Cylinder Control Composition.

Material	**Kg/m^3 actual**	**M^3 actual**
OPC	330.7	0.105
Coarse Aggregate #57	530.5	0.196
Coarse Aggregate #9	353.7	0.131
Fine Aggregate	861.4	0.326
Water	347.8	0.348

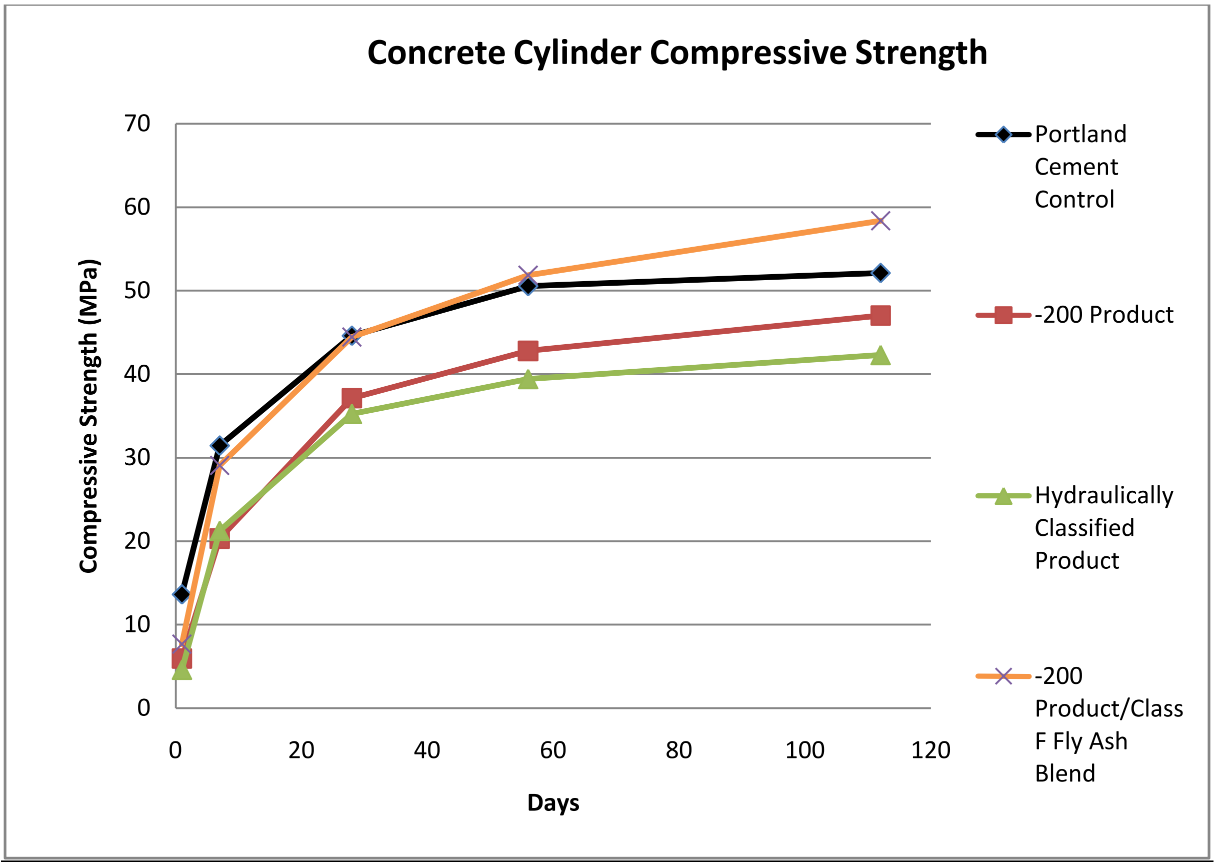

Fig. 3: Concrete Cylinder Compressive Strength.

A mid to high strength mix (Table 3) was chosen for the concrete test work. The CFBC fly ash and Class F blend product were substituted at a 20% rate in the total cementitious component.

As in the mortars, the CFBC products initially retarded strength development in concrete but this effect was largely diminished at 28 days. The compressive strength testing of the cylinders would show a similar relationship among the Gilbert CFBC fly ash test products with the blended Class F and hydraulically beneficiated ash showing the highest performance, followed by the -200 mesh and the hydraulic product. Unlike the mortar data however, only the mixed product exceeded the control strength.

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. The highest recorded shrinkage was 0.134% for the hydraulically classified product at 18 days of curing. This means that a slab of 30.5 m (100 feet) long would shrink only 40.6 mm (1.6 inches).

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.

Gilbert CFBC 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. Overall, Gilbert fly ash exhibited excellent dimensional stability, bolstering its potential for use as a pozzolan in the construction industry.

CONCLUSIONS

- The CFBC fly ash has major compositional differences from conventional PCCA with anhydrite, quartz and hematite present as important crystalline components.

- The composition of this material, particularly the high level of sulfate and free lime, lies outside the boundary of ASTM C-618 compliant materials.

- The silicate fraction of the CFBC ash is non crystalline as indicated by X-ray diffraction but SEM work revels this material to be unfused.

- The CFBC fly ash is irregularly shaped and has a considerably higher surface area than conventional PCCA which contributes to its reactively and also an increased water demand.

- The mortar and concrete data indicate that these materials are clearly reactive having pozzolanic properties.

- The hydration and reaction of the anhydrite with the calcined clay fraction to produce etteringite (i.e. $3\ CaSO_4 + 3\ Ca(OH)_2 + 2\ Al(OH)_3 + 26\ H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \bullet 26H_2O$) clearly plays a role in contributing strength to mortar and concrete.

- The overall strength of all of mixtures was acceptable and within mix design.

- The level of free lime (10%) in the CFBC fly ash will require a slaking pretreatment to reduce excessive heat in this application. The beneficiated CFBC produced improved results over the “as received” ash, particularly early in the testing.

- The dimensional testing of the mortars indicated that the CFBC fly ash should be safe and stabile if used as a pozzolanic additive.

FUTURE RESEARCH

This work was a preliminary round of testing which verified the potential value of CFBC ash as an additive in Portland concrete. Additional work including the role of ettringite in strength development, the potential for delayed ettringite formation, and longer term dimensional stability work is needed before this material could reasonably be employed on a commercial basis.

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REFERENCES

American Coal Ash Association, (2009) "ACAA Coal Combution Products Survey"

Brownfield, M.E. Cathcart, J. D., Affolter, R. H., Brownfield, I. K., Rice, C. A., O'Connor, J. T., Zielinski, R. A., Bullock, Jr. J. H., Hower, J. C. and Meeker, G. P. (2005). "Characterization and modes of occurrence of elements in feed coal and coal combustion products from a power plant utilizing low-sulfur coal from the Powder River Basin, Wyoming." *USGS Scientific Investigations Report*, 2004-5271, 42 p.

East Kentucky Power Cooperative (2007) "Spurlock Station". <http://www.ekpc.com/spurlock.html> (13 February 2009).

Hower, J. C., Robl, T. L., Anderson, Thomas, G.A., Sakulpitakphon, T., Mardon, S.M., Clark, W.L., (2005). "Characteristics of coal combustion products (CCP's) from Kentucky power plants, with emphasis on mercury content." *FUEL*, 84, p. 1338-1350.

United States Department of Energy. (2009). Fossil Energy Office of Communications. DOE - Fossil Energy. "Overview of fluidized bed technology" http://fossil.energy.gov/programs/powersystems/combustion/fluidizedbed_overview.htm (13 February 2009)