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Fluidized Bed Combustion Ash Utilization: CFBC Bottom Ash as a Cementitious Material

Robert Rathbone[1], David Rust[2], Adam Peterson[3], Kamyar Mahboub[3], and Thomas Robl[1]

[1]*University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, E-mail: <rathbone@caer.uky.edu>;<robl@caer.uky.edu>.*

[2]*Palmer Engineering, 400 Shoppers Drive, Winchester, KY, 40392, E-mail: <rustde@gmail.com>.*

[3]*University of Kentucky, Department of Civil Engineering, 161 Raymond Building, Lexington, Ky. 40506, E-mail: <adam7peterson@yahoo.com>;<kmahboub@engr.uky.edu>.*

ABSTRACT

Two methods employed to reduce sulfur dioxide emissions from the electricity generation are flue gas desulfurization (FGD) and circulating fluidized bed combustion (CFBC). The quantity of sulfated byproducts from these technologies will likely increase substantially over the next several years. This study focused on utilizing FGD gypsum, CFBC ash and Class F fly ash for the production of low-energy, 100% byproduct cement. There were two main components of the cement: calcium sulfate hemihydrate and a blend of CFBC spent bed material and Class F fly ash. At the outset of the study there were two potential problems identified: slow strength gain and destructive expansion during hydration. Blending calcium sulfate hemihydrate with CFBC ash and fly ash produced a 100% byproduct cement that achieved satisfactory early strength and was dimensionally stable. However, the calcium sulfate component remains an impediment towards long-term durability because of its high solubility.

INTRODUCTION

Two common methods employed to reduce sulfur dioxide emissions from the generation of electricity are flue gas desulfurization (FGD) and circulating fluidized bed combustion. The majority of FGD scrubbing systems installed and in use in the United States are wet scrubber systems because of their ability to remove large quantities (more than 90%) of sulfur dioxide from flue gas. In a wet scrubber, sulfur dioxide is removed from the flue gas using limestone or lime slurries to form calcium sulfite hydrate ($CaSO_3 \cdot \frac{1}{2}H_2O$), which can be oxidized to calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), also known as FGD or synthetic gypsum.

Another technology for sulfur dioxide emission control is circulating fluidized bed combustion (CFBC). CFBC is gaining acceptance for the utilization of “problem” or “opportunity” fuels, such as high-ash or high-sulfur coals [Berry et al, 1991]. Sulfur dioxide removal is achieved by burning the coal in the presence of limestone resulting in the formation of anhydrous calcium sulfate ($CaSO_4$). Although CFBC technology has some environmental advantages, there are notable problems. CFBC produces more ash and CO_2, for an equivalent amount of energy produced, than pulverized coal combustion (PCC) units. The ash generated in the CFBC process occurs in two forms: a coarse "spent bed" material and a finer fly ash. These byproducts can be problematic because of the large quantity that need to be landfilled, as well as the exothermic and expansive phenomena associated with the hydration of the materials. Additionally, the spent bed material has the potential to cause expansion in concrete [Montagnaro et al, 2008].

According to the American Coal Ash Association, in 2007 over 33 million tons of FGD scrubber by-products were produced in the U.S. of which just over 10.3 million tons were utilized for a 31% utilization rate. FGD gypsum was the most heavily utilized FGD material with 75% of the material utilized, the majority of which was used in the production of gypsum wallboard. Also in 2007, approximately 6 million tons of FBC ash was produced with 5.1 million tons utilized for a 84% utilization rate, mainly as fill material, waste and soil stabilization, and road base.

Because of the implementation of sulfur control technologies, according to the Energy Information Administration (EIA), electric power SO_x emissions are expected to decrease over the next 25 years or so. Over the same time period, the EIA expects the amount of electric power generated from coal to grow 42%, which means that the quantity of sulfur-containing by-products will likely increase dramatically over the next several years. New applications for their use will be needed to address the increase in production.

FBC ash and fly ash have been used to make concrete without the need of traditional portland cement, thus producing an inexpensive concrete or pavement base course [Berry et al, 1991; Hemmings, 2007; Burwell et al, 1993; Hunsucker et al, 1987]. The "no-cement" concrete produced by Bland et al [1987] consisted of a blend of spent bed and PCC fly ash along with water and coarse aggregate. The no-cement concrete and control mix (OPC concrete) had similar compressive strengths at 90 days, but the no-cement concrete had much slower early-age strength gains. Lime availability has been identified as a critical component of CFBC spent bed to achieve high strength [Burwell et al, 1993], and saturated curing was observed to cause greater expansion [Bland, 1999]. Some of these studies have indicated that expansion can result from ettringite formation in FBC/PCC fly ash mixtures [Solem-Tishmack et al, 1995; Wolfe et al, 2001], which can preclude the use of these materials in construction applications. In 1973, P.K. Mehta proposed that the presence of excess calcium hydroxide and saturated curing conditions causes the formation of colloidal ettringite in calcium-aluminum-sulfate systems, which results in substantial expansion. The research presented in this paper applied Mehta's theory and thus focused on minimizing expansion and increasing strength via the management of calcium hydroxide concentration and water ingress into the cementitious system to develop a practical product containing a large amount of CCBs. Specifically, FGD byproducts and Class F fly ash were used to produce low-energy, 100% byproduct "clinkerless" cement. This type of cementitious material has been researched for many years and often suffers from two major drawbacks: slow strength gain and deleterious expansion. This paper describes an approach devised to overcome these problems.

MATERIALS AND METHODS

Coal Combustion Byproducts (CCBs)

Four types of CCBs were used to make 100% by-product cement: FGD gypsum, CFBC spent bed material, Class F fly ash (FA) and Class F ultra fine ash (UFA). The FA, UFA and FGD gypsum were obtained from PCC power plants in Kentucky. The median particle size of the Class F fly ash was 19.1 microns. The ultra fine ash was obtained using a hydraulic classifier that produced a very fine ash product with a median particle size of approximately 5 microns. The spent bed material was obtained from the EKPC Gilbert Unit at Spurlock Power Station in Maysville, Kentucky. Their chemical compositions are provided in Table 1.

Table 1. Chemical Composition of CCPs Used in the Study

Oxide (%)	FGD Gypsum	CFBC Spent Bed	FA	UFA
SiO_2	4.54	12.77	52.75	54.34
TiO_2	0.13	0.26	1.20	1.56
Al_2O_3	1.09	5.25	22.94	31.47
Fe_2O_3	0.60	3.15	14.92	5.21
CaO	40.15	48.23	2.67	1.35
MgO	0.37	2.47	0.90	1.1
K_2O	0.06	0.36	2.72	2.66
Na_2O	< 0.01	0.05	0.42	0.41
P_2O_5	0.04	0.13	0.19	0.28
SO_3	53.67	27.83	0.64	0.07
Free Lime	nd	23.0	nd	nd

Water-Repelling Chemical Admixture

Chryso® Pave 100 is a pore blocking and water repelling admixture produced by Chryso, Inc. It was used to increase strength of the mortar produced in the study (through water reduction) in addition to inhibiting water ingress.

Preparation of Plaster

The production of calcium sulfate hemihydrate (aka “plaster”) from the FGD gypsum utilized a procedure described by Koslowski [1991]. The FGD gypsum was pressed at 24.5 kN (5500 lb) into disks that were approximately 10 cm in diameter by 1.5 cm thick. The disks were heated in saturated steam at 130°C for 4 hrs in an autoclave, followed by air drying at 100°C.

Clinkerless Cement Preparation

The CFBC spent bed material was prehydrated with 10% water by weight and dried prior to use. The prehydrated spent bed material was then milled with the fly ash and plaster in various proportions until a median particle size of approximately 15 microns was achieved. Table 2 summarizes the clinkerless cement blends reported in this paper. The cement formulation notation lists the ratio of FBC spent bed to PCC fly ash, followed by the type of Class F fly ash (i.e. FA versus UFA) and whether plaster (PL) was included. For example, 70:30 UFA PL designates cement with a FBC spent bed to ultrafine fly ash (UFA) ratio of 70:30 and with plaster included. Although many formulations were tested, only eight will be considered herein.

Table 2. Composition of Clinkerless Cements

	Cement Component (% of total cementitious material)			
Cement	**FBC Spent Bed**	**Class F FA**	**Class F UFA**	**Plaster**
70:30 UFA	70	0	30	0
40:60 UFA	40	0	60	0
70:30 UFA PL	35	0	15	50
40:60 UFA PL	20	0	30	50
50:50 FA	50	50	0	0
40:60 FA	40	60	0	0
50:50 FA PL	26.5	26.5	0	47
40:60 FA PL	21	32	0	47

Mortar Preparation and Testing

The preparation and compressive strength testing of mortar cubes was accomplished following ASTM C305 and C109 methods. Flow was kept constant at 110 ± 5%. Expansion was monitored using ASTM C157. The set time of the cement blends that contained plaster was controlled using sodium citrate at a dosage of 2g sodium citrate per 1kg of cement; this provided an initial set time of approximately 2 hours.

From each of the clinkerless cement blends, 5.08 cm mortar cubes were prepared to measure compressive strength, with two cubes per test. For cements containing no plaster, the cubes were de-molded after seven days curing. Those with plaster were de-molded after 1 day and were cured at 100% relative humidity in a mist room. In a separate set of experiments, cubes were “dry cured” in sealed plastic bags in a manner similar to that of Bland [1999]. This was done for two reasons: to study the effect of curing conditions on expansion, and to determine if wet curing caused significant dissolution of the gypsum component. In practice, this would be similar to placing a curing membrane or sealant on the concrete after it was placed.

Hydration Studies

Cement pastes of selected cement blends were prepared using 40 g of cement and 14 ml of water (W:CM = 0.35) and cured in tightly sealed plastic bottles. A saturated paper towel was placed in the bottle to maintain 100% RH. At selected intervals, samples of paste were ground in acetone to halt hydration, and the acetone decanted. The pastes were then dried for 1 hour at 55^{o}C and stored in a sealed dessicator over silica gel and soda lime until analysis. The samples were examined using X-Ray Diffraction (XRD) and thermo gravimetric analysis (TGA) to identify hydrated phases in the paste samples.

RESULTS AND DISCUSSION

Mortar Compressive Strength

Figure 1 displays the average compressive strength gains with curing time of the mortar cubes prepared using the clinkerless cements containing UFA. Each data point represents the average of two tests. As expected, the cements without plaster did not have sufficient strength to test prior to 7 days curing, whereas approximately 7-8 MPa was achieved within several hours when plaster was added. However the addition of plaster clearly lowered the later strengths, which was probably caused by dissolution of gypsum.

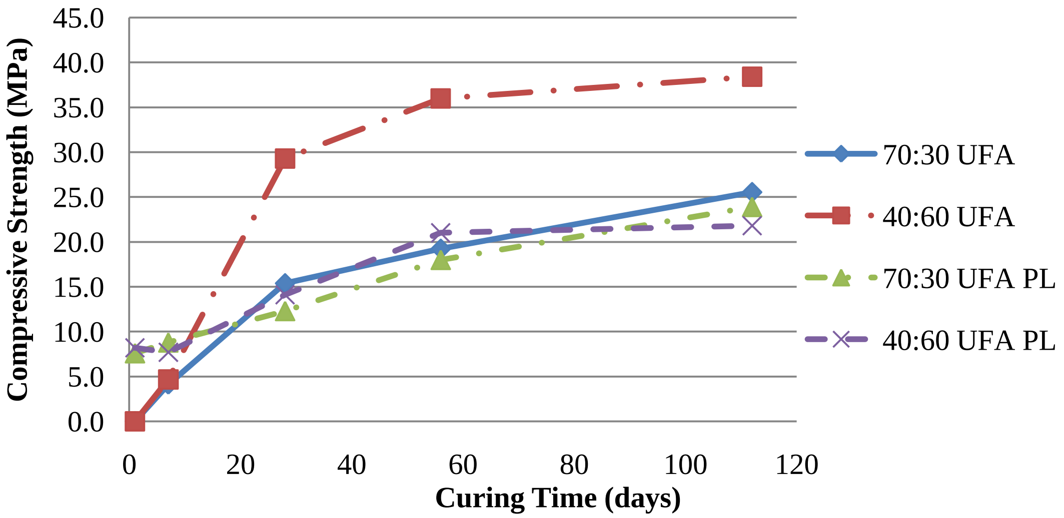

Fig. 1. Unconfined Compressive Strength of FBC/UFA Clinkerless Cement Mortars Cured Wet in Mist Room

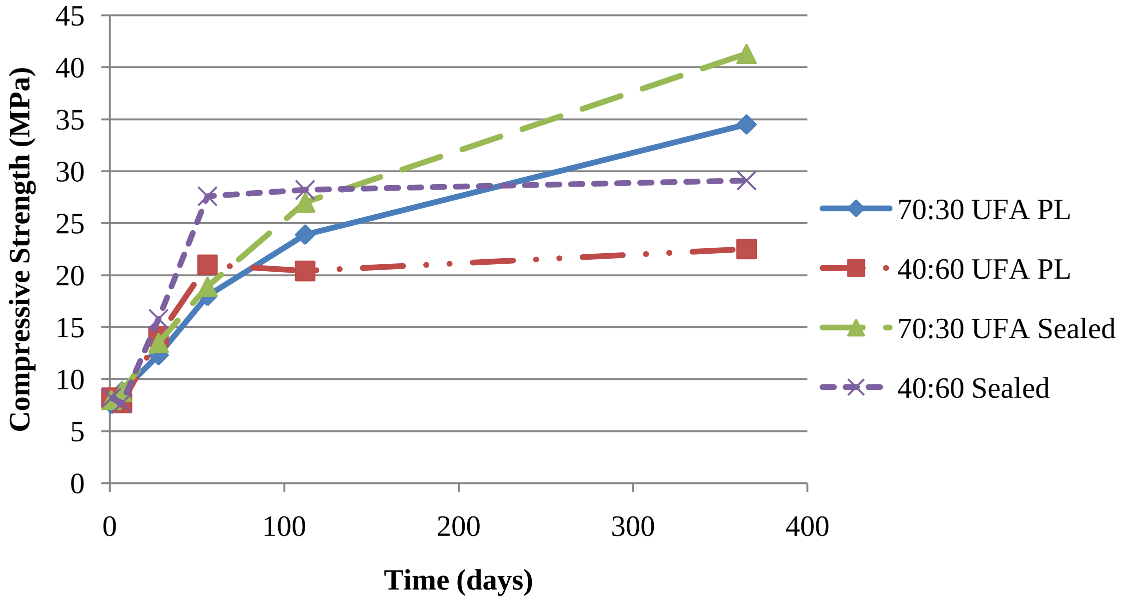

Fig. 2. Unconfined Compressive Strength of FBC/UFA Clinkerless Cement Mortars Cured in the Mist Room Versus Those Cured in Plastic Bags

Curing the mortars in sealed plastic bags increased the strengths in both sets of mortars (Figure 2), which is expected because of the relatively high solubility of gypsum, and the combination of lime and excess water causing greater expansion in the wet cured mortars (discussed below). The addition of a water-repelling admixture, Chryso Pave 100, had a similar effect on compressive strength development as sealed curing (Figure 3). This is consistent with the hypothesis that access to large quantities of water during the curing process can weaken the clinkerless cement mortars because of expansion and dissolution of the gypsum plaster. Some of the higher strengths can also be attributed to a 2% water reduction that was achieved by using the water-repelling admixture (WRA).

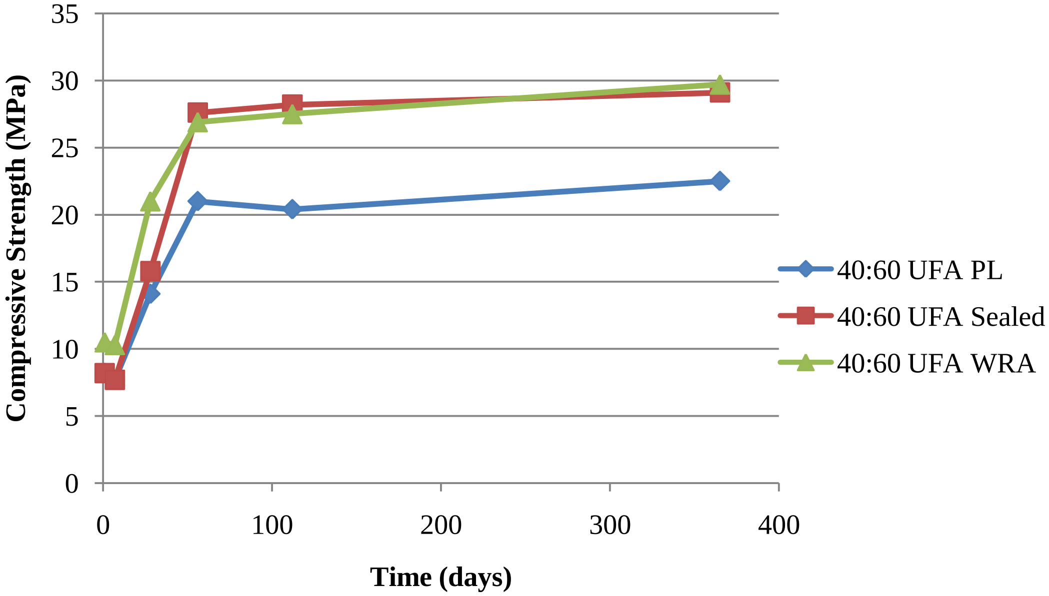

Fig. 3. Unconfined Compressive Strength of Clinkerless Cement Mortars Cured Wet, Sealed, and Wet with a Water Repelling Admixture (WRA)

Based on initial testing with the ultrafine fly ash, clinkerless cement mortars were prepared for strength testing using the ordinary Class F fly ash described above. Pave 100 was used as a water repelling admixture at a dosage of 5.2 ml/kg cement. As expected, the strength gain for the FBC/Class F FA cement mortars (Figure 4) was substantially slower than when the UFA was used, probably because of the lower particle surface area of the former. When UFA is used, there are numerous small particles that are highly dispersed throughout the system, thus providing a large number of nucleation sites for cement hydrate (i.e. ettringite) formation. In order to test this hypothesis, a second mortar formulation was devised in which 10.8% of the Ottawa sand was replaced with the Class F FA. This would produce approximately the same ash surface area that would be present if the UFA were used, but without replacing any sand in the mortar. Figure 5 shows that the sand replacement caused a substantial increase in the rate of strength development, which is consistent with the hypothesis that the fly ash component should be highly dispersed in order to maximize strength development.

Mortar Expansion

All of the clinkerless mortars exhibited some degree of expansion when immersed in water, regardless of whether UFA or FA was used in the cement. However, the cements containing UFA generally expanded to a greater extent than the equivalent FA cement mortar (Figure 6). The expansion was likely caused by ettringite formation in the presence of excess calcium hydroxide and water, via the mechanism proposed by Mehta [1973]. The effect of calcium hydroxide on ettringite formation, expansion, and strength development is discussed below.

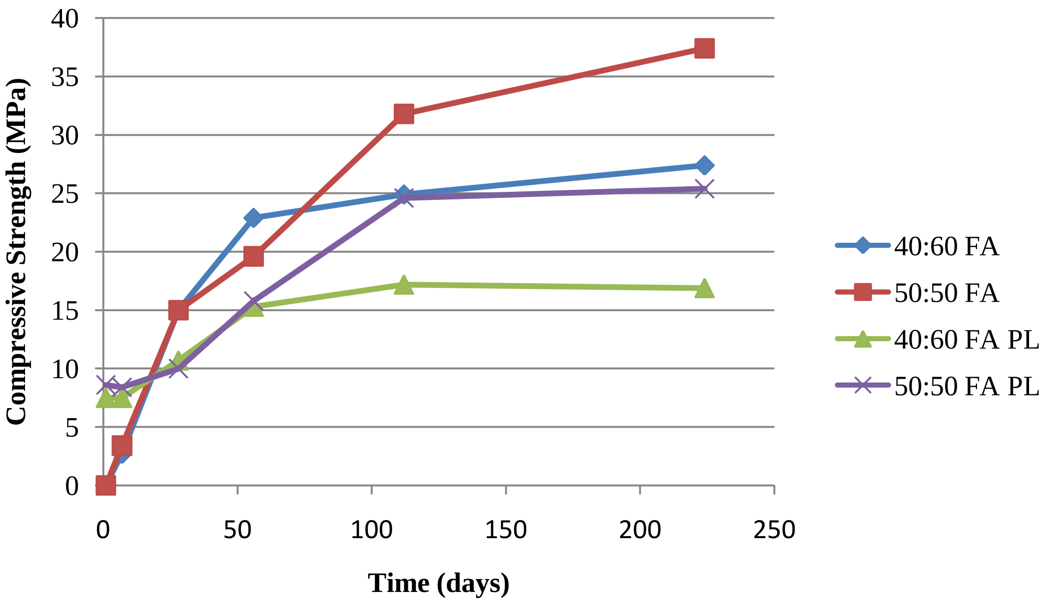

Fig. 4. Unconfined Compressive Strength of Clinkerless Cement Mortars Containing Class F Fly Ash

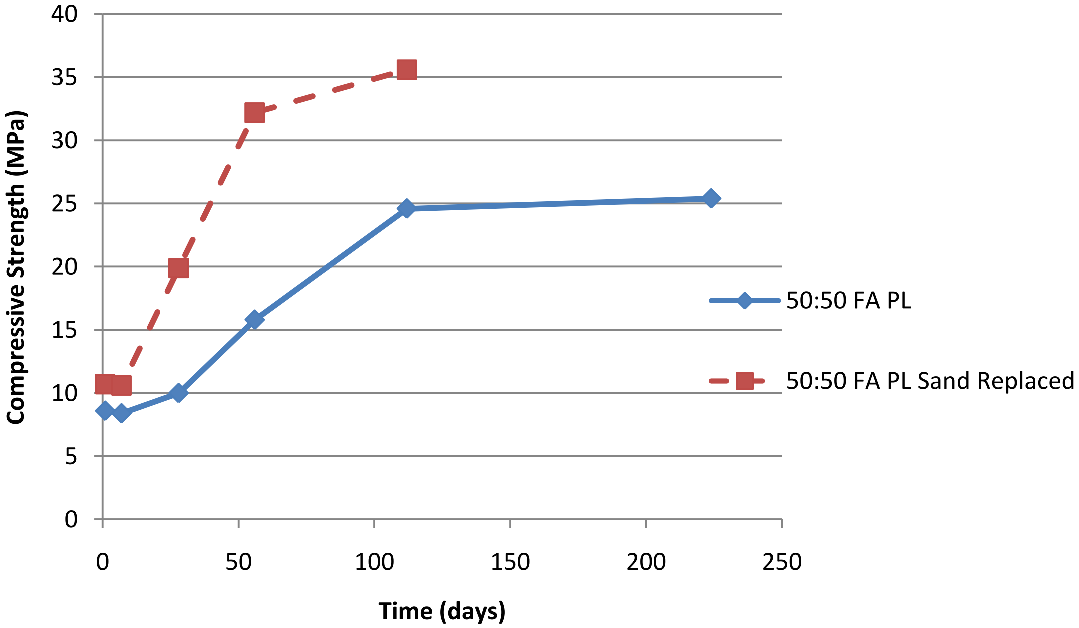

Fig. 5. Compressive Strength of Clinkerless Cement Mortars Containing Class F Fly Ash and Plaster, With and Without Replacement of Sand with Fly Ash

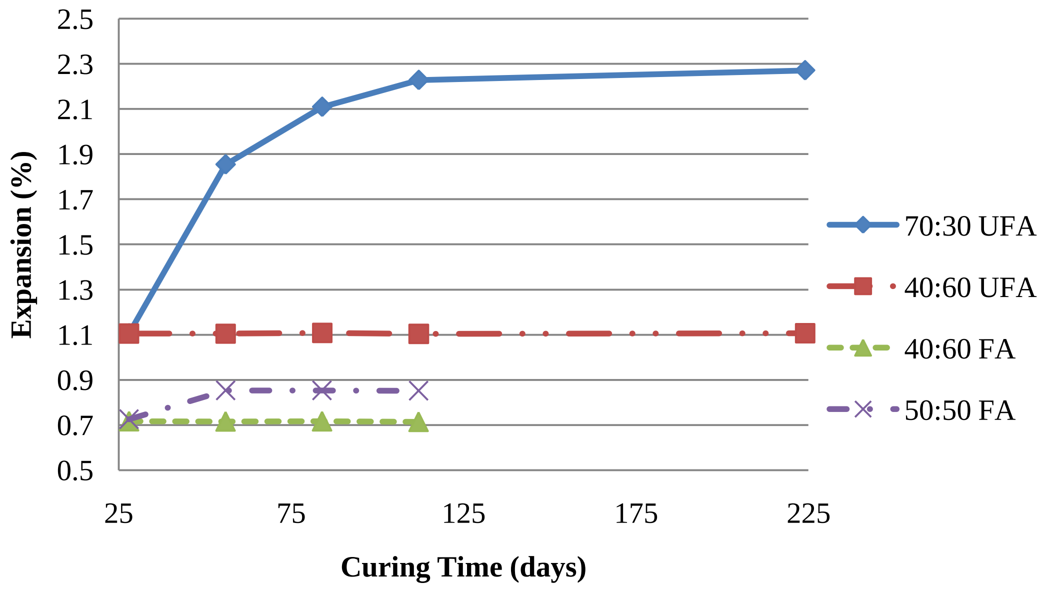

Fig. 6. Expansion of Mortar Prisms Prepared Using Clinkerless Cements

Paste Analysis

X-Ray Diffraction (XRD)

All of the clinkerless cement formulations exhibited broadly similar trends as regards hydration reactions. Calcium hydroxide and anhydrous calcium sulfate decreased with time, while ettringite increased:

$$CaSO_4 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O \qquad (1)$$

$$3Ca(OH)_2 + 3CaSO_4{\cdot}2H_2O + 2Al(OH)_3 + 20H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O \qquad (2)$$

The hydrated calcium sulfate (gypsum) first increased from the hydration of the anhydrous phase, and then decreased as it was consumed to form ettringite, which is the primary cementitious phase in these hydrated systems. The hydration trends are shown in Figures 7 and 8 for two of the clinkerless cement formulations cured for 1 to 56 days. The intensity of the diffraction peaks for quartz (SiO_2) and mullite ($Al_2Si_6O_{13}$) remained more-or-less unchanged throughout the experiments, which is expected because of their very low solubility.

Thermogravimetric Analyis (TGA)

The decrease in calcium hydroxide is particularly of interest in the hydration reactions because of its potential influence on expansion. Therefore, the calcium hydroxide content was quantified on the pastes using a TGA method described by Marsh and Day [1988]. The data for the UFA and FA pastes are provided in Tables 3 and 4 .

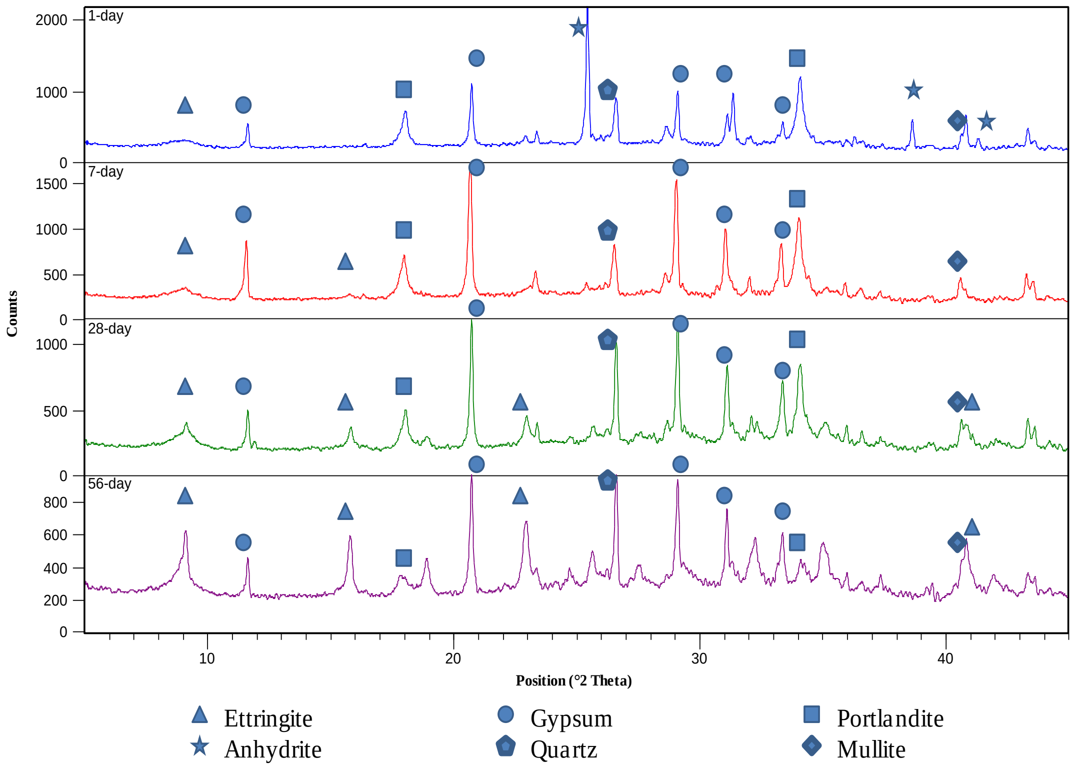

Fig. 7. XRD Spectra for 70:30 UFA Paste

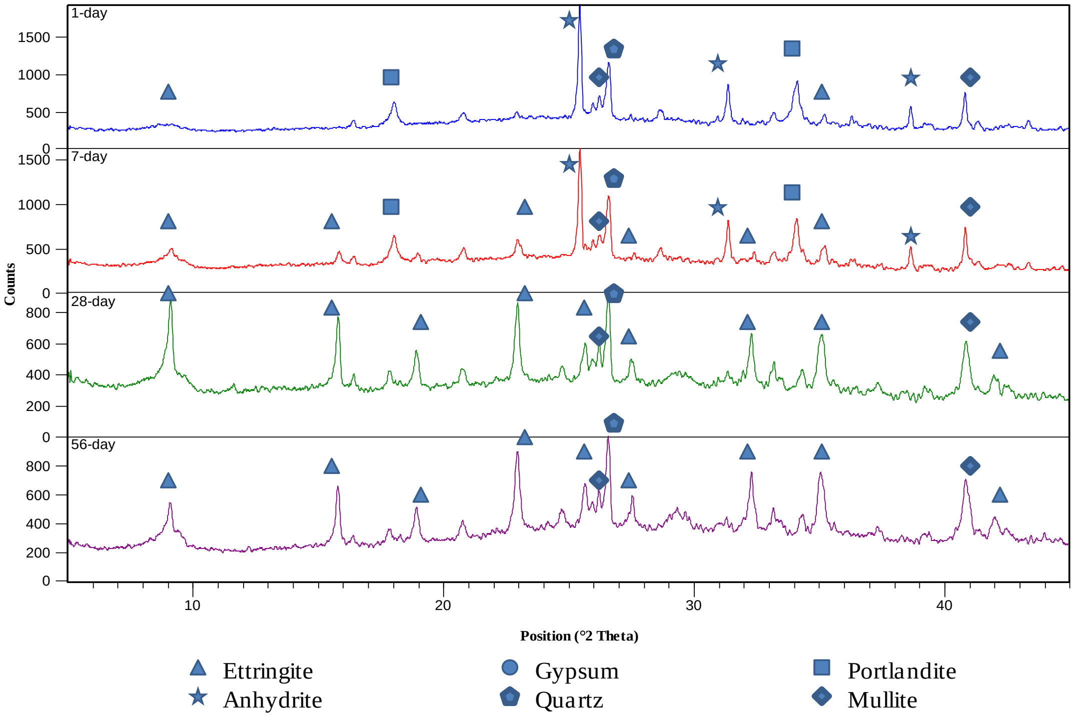

Fig. 8. XRD Spectra for 40:60 UFA Paste

Table 3. $Ca(OH)_2$ Content of Cement Pastes with UFA

Curing Time	$Ca(OH)_2$ Content (%)	
	70:30 UFA	**40:60 UFA**
1 day	17.7	10.1
7 day	15.4	6.3
28 day	8.2	0
56 day	2.2	0
112 day	0	0

Table 4. $Ca(OH)_2$ Content of Cement Pastes with FA

Curing Time	$Ca(OH)_2$ Content (%)	
	50:50 FA	**40:60 FA**
7 day	7.0	4.3
14 day	4.8	2.4
28 day	1.3	0
56 day	0	0

The TGA data confirmed that the quantity of calcium hydroxide in the pastes decreased with curing time as it reacted with aluminum, in the UFA and FA, and sulfate to form ettringite. After 56 days of curing, calcium hydroxide was still detected in the 70:30 UFA paste and was below detection by 112 days. However the quantity of calcium hydroxide present in the 40:60 UFA cement, which contains less spent bed and thus lime, was below detection within 28 days of curing (Table 3). Similarly, the 50:50 FA cement paste contained measurable calcium hydroxide after 28 days curing, whereas none was detected for the 40:60 FA cement paste at the same curing time (Table 4). These data are consistent with expansion data on the cement mortars and indicate that expansion was being caused by ettringite formation in the presence of excess calcium hydroxide. The length-change prisms prepared using the 40:60 UFA and FA cements (Figure 6) stopped expanding by 28 days, whereupon calcium hydroxide was no longer detected in the paste. The 50:50 FA mortar exhibited expansion after 28 days, but essentially stopped expanding by 56 days, whilst the cement comprising the greatest amount of spent bed (70:30 UFA) continued its expansion after 112 days curing, albeit the expansion had markedly diminished after 112 days.

CONCLUSIONS

Based on the results the following conclusions were made:

1. Reducing the amount of spent bed ash in clinkerless cements resulted in a reduction in expansion. However, a sufficient quantity of lime must be present in the cementing system to form ettringite and other hydrates to give the system sufficient strength.
2. The expansion of the clinkerless cement blends was caused by the formation of ettringite in the presence of excess calcium hydroxide and water; the cements essentially stopped expanding when the quantity of calcium hydroxide was no longer detectable by XRD and TGA.
3. When calcium sulfate hemihydrate was added to the FBC/fly ash mixtures, mortar specimens achieved compressive strengths of up to 1500 PSI (10.3 MPa) within several hours and did not crack throughout the experiment duration. Expansion of the mortar was also reduced when hemihydrate was used.
4. Sealed-curing of the 100% by-product cement blends increased compressive strength and decreased expansion compared to traditional moist-curing. The reduction in expansion was attributed to free water being kept out of the system and thus minimizing colloidal ettringite formation. Mortar specimens that contained a water-repelling admixture and that were moist-cured behaved similar to specimens that were cured in plastic bags.

5. Admixtures that induce a degree of water repellency and hydrophobicity to clinkerless cement mortar and concrete have the potential to increase durability by decreasing deleterious expansion and dissolution of gypsum.

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