

Clinkerless Cement Produced from Flue Gas Desulphurization Residues and Fly Ash

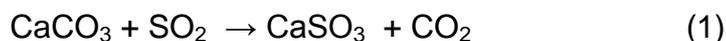
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INTRODUCTION

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:



Early on in the FGD scrubbing technology, the by-product was a calcium sulfite hydrate ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$) sludge that was not of much use. However, as the technology advanced it was discovered that the sludge could be oxidized and converted into a marketable gypsum product:



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^[1]. Sulfur dioxide removal is achieved by burning the coal in the presence of limestone resulting in two desired chemical reactions: limestone calcination and sulfur dioxide absorption:



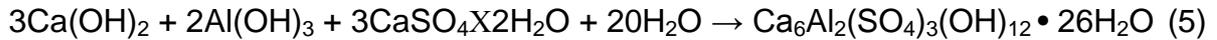
Even though CFBC technology has some environmental advantages, there are notable problems. CFBC produces more ash and CO₂, for an equivalent amount of energy produced, than Pulverized Coal Combustion (PCC) units. The ash generated in the CFBC process, known as “spent bed” material, is problematic because of the large quantity that needs to be landfilled, as well as the exothermic and expansive phenomena associated with the hydration of the material. Additionally, the spent bed material is characterized by poor pozzolanic activity and high potential to cause expansion and is therefore unsuitable for traditional recycling such as in concrete manufacturing ^[2].

According to the American Coal Ash Association, ^[3] in 2006 over 30.2 million tons of FGD scrubber by-products were produced in the United States of which just over 10.6 million tons were utilized for a 35% utilization rate. FGD gypsum was the most heavily utilized FGD material with 79% of the material utilized, the majority of which was used in the production of gypsum wallboard (7.6 million tons). Also in 2006, 1.6 million tons of FBC ash was produced with 1.1 million tons utilized for a 68% utilization rate, mainly as structural fill, waste and soil stabilization, and road base.

Because of the implementation of sulfur control technologies, according to the Energy Information Administration (EIA) ^[4], electric power sulfur dioxide emissions are expected to decrease from 9.39 million tons in 2006 to 4.67 million tons and 3.71 million tons in 2015 and 2030 respectively. The effort of the utility companies is even more significant than the overall 61% reduction in sulfur dioxide emissions suggests. Over the same time period, the EIA expects the amount of electric power generated from coal to grow 42%. Thus, the quantity of sulfur-containing by-products will likely increase dramatically over the next several years. New alternative applications for their use will be needed to address the increase in production.

The research presented in this report was devoted to utilizing sulfur dioxide removal waste products as well as Class F fly ash in the production of 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, with the goal of producing “green cement” based entirely on byproduct materials.

Fluidized bed combustion (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 ^[1,5,6,7]. These components dissolve and react with aluminum in fly ash to form ettringite:



where $\text{Al}(\text{OH})_3$ is a proxy for dissolved fly ash alumina. Calcium hydroxide in solution can also react with fly ash silica to form calcium silicate hydrate.

The optimal “no-cement” concrete produced by Bland and others^[8] consisted of a blend of spent bed and fly ash along with water and coarse aggregate. The cementitious component typically comprised about 70% spent bed and 30% fly ash. 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 was identified as a critical component of CFBC spent bed necessary to achieve high strength^[6], and saturated curing was observed to cause greater expansion^[9]. Some of these studies have indicated that expansion can result from ettringite formation in FBC/PCC fly ash mixtures^[10,11,5], which can preclude the use of these materials in construction applications. Mehta^[12] proposed that the presence of excess calcium hydroxide and saturated curing conditions causes the formation of colloidal ettringite, which results in substantial expansion. The research presented in this paper applied Mehta’s theory and thus focused on minimizing expansion and increasing early strength through the management of calcium hydroxide concentration and water ingress into the cementitious system to develop a practical product employing the use of CCBs.

MATERIALS AND METHODS

Coal Combustion Byproducts (CCBs)

Three types of CCBs were used to make “low-energy, 100% by-product cement”: FGD gypsum, CFBC spent bed material, and Class F ultra fine ash (UFA). The UFA and FGD gypsum were obtained from the Kentucky Utilities Ghent Power Plant located in Carroll County, Kentucky. The ultra fine ash was obtained using a hydraulic classifier that produced a very fine ash product with a median particle size of 5 microns. The UFA had a high surface area that promoted rapid reaction with dissolved calcium hydroxide from the spent bed to form ettringite and calcium silicate hydrates as cementitious phases. The spent bed material was obtained from the East Kentucky Power Cooperative Gilbert Unit at Spurlock Power Station in Maysville, Kentucky. All three samples represented typical by-products from their respective applications. Their chemical compositions are provided in Table 1.

Table 1. Chemical composition of CCPs used in the study

Oxide (%)	FGD Gypsum	FBC Spent Bed	UFA
SiO ₂	4.54	12.77	54.34
TiO ₂	0.13	0.26	1.56
Al ₂ O ₃	1.09	5.25	31.47
Fe ₂ O ₃	0.60	3.15	5.21
CaO	40.15	48.23	1.35
MgO	0.37	2.47	1.1
K ₂ O	0.06	0.36	2.66
Na ₂ O	< 0.01	0.05	0.41
P ₂ O ₅	0.04	0.13	0.28
SO ₃	53.67	27.83	0.07
Free Lime	nd	23.0	nd

Commercial Calcium Sulfate Hemihydrate/OPC Blend

Duracal® is a 50% plaster and 50% ordinary portland cement (OPC) product distributed by the United States Gypsum Company. The product is marketed as a rapid setting roadway patching material and was used in this study to provide information on the behavior of cements containing significant amounts of plaster.

Water-Repelling Chemical Admixture

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

“Clinkerless Cement” Preparation

Bland^[8] found that a substantial amount of heat was generated as the result of hydration of unslaked lime (CaO) in spent bed, thus requiring a prehydration step.

In this study, the FBC spent bed was therefore prehydrated with 10% water by weight, then dried prior to use. The prehydrated spent bed material was then milled with PCC fly ash to approximately 15 microns median particle size.

The preliminary cement blends were produced to determine which ratio of spent bed / ultra fine ash would produce the best strength results. Similar research using materials with similar chemical composition determined that a spent bed / fly ash ratio of 70/30 provided optimum strength in mortar and concrete^[8]. Therefore, the initial experimentation focused on the 70/30 ratio of spent bed/ultra fine ash, although other different ratios were examined. From each of these “clinkerless cement” blends, 12 mortar cubes were prepared to measure the 7, 28, 56, 112, and 224-day compressive

strengths, with two tests per age. Due to the slow strength gains of the clinkerless cement blends, the cubes were de-molded after seven days curing. Table 2 summarizes the clinkerless cement blends that were produced and tested in the research project.

Table 2. Composition of the “Clinkerless” cement blends prepared using prehydrated spent bed

Cement	Spent Bed	Ultra Fine Ash	d₅₀ (µm)	w/c Ratio
CL #1	0.80	0.20	15	0.47
CL #2	0.70	0.30	14	0.45
CL #3	0.60	0.40	14	0.44
CL #4	0.90	0.10	14	0.50
CL #5	0.10	0.90	15	0.39
CL #6	0.40	0.60	14	0.42

Hemihydrate/Clinkerless Cement Preparation

It was previously stated that two significant problems with FBC/PCC fly ash cements are potential for excessive expansion and slow strength gain. Gypsum-based cements were probably the first to be used on a wide scale by man and are currently utilized primarily in plaster applications. Gypsum-based cements can be made to be very strong, dimensionally stable, and relatively inexpensive. They are also very energy efficient as the slaking of the gypsum to form hemihydrate is conducted at low temperatures. The principal disadvantage is that gypsum is relatively soft, which limits its application in construction materials. However, the strength and durability of gypsum cements can be greatly enhanced by inducing the formation of supplementary cementitious phases using silico-pozzolanic and sulfo-pozzolanic reactions^[5]. Based on this rationale, cements were produced in this study by blending FGD gypsum-based hemihydrates with the clinkerless cement blends described above. The objective was to produce a rapid hardening material that is dimensionally stable.

ASTM mortars were prepared from the hemihydrate/clinkerless blends and were moist cured immediately after casting. In a separate set of experiments, the cubes were “dry cured” in sealed plastic bags in a manner similar to that of Bland^[9]. 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. A third curing method was to incorporate a water-repelling admixture (Chryso PAVE 100) into the mortar, followed by moist curing. Both commercial (Hydrostone) and FGD-based plaster were used in these experiments. The FGD plaster was

prepared by heating FGD gypsum in a saturated steam atmosphere using a procedure described by Koslowski¹³. The blends are shown in Table 3.

Table 3. Composition of cement blends containing hemihydrate

Cement Name	Spent Bed %	UFA %	Hemihydrate %	PAVE100 (ml/kg CM)	w/c Ratio
HHCL#2	0.35	0.15	0.50	0	0.40
HHCL#6	0.20	0.30	0.50	0	0.40
HHCL#6 PV1	0.20	0.30	0.50	5.2	0.40

Mortar Preparation and Testing

The preparation and compressive strength testing of mortar cubes was accomplished following ASTM C 305 and C 109 methods. Expansion was monitored using ASTM C 157. The set time of the hemihydrate/clinkerless cement blends was controlled using sodium citrate; 2g of sodium citrate per 1kg of cement provided an initial set time of approximately 2 hours. Without the set retarder, the cement hardened during mixing.

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°C and stored in a sealed dessicator over silica gel and soda lime until analysis. The samples were examined using X-ray Diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) to track changes in hydrated phases during the hydration process.

RESULTS AND DISCUSSION

Mortar Compressive Strength

Figure 1 displays the average compressive strength gains with curing time of the mortar cubes prepared using the preliminary “Clinkerless” cement blends. Each data point represents the average of two tests. The lowest strengths were obtained for the blends with excess lime and insufficient fly ash surface area (90/10 and 80/20), or insufficient lime (10/90). These blends were not considered for additional testing. The best strength was achieved for the 40% spent bed/60% UFA cement, whilst the 60/40 and 70/30 cements also produced good strengths. However, these cements only achieved 500-600 PSI (3.5-4.1 MPa) after 7 days curing. Thus, the 70/30 and 40/60 cements were blended with hemihydrate to improve early strength (Table 3).

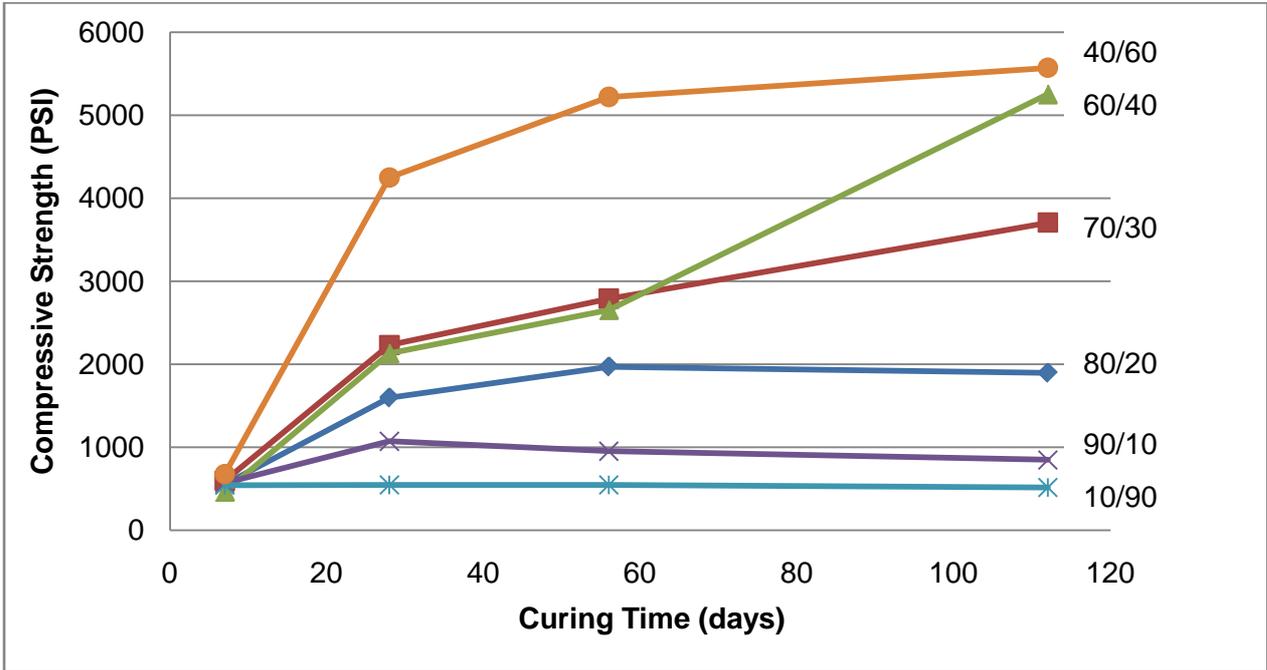


Figure 1. Compressive strength of clinkerless cement mortar cubes. Ratios on the right side provide the FBC/UFA proportions.

Compressive strength of the hemihydrates/clinkerless cement blends is shown in Figure 2. Compared to the clinkerless cement mortars, the hemihydrates/clinkerless blends gained strength rapidly to 1000-1500 PSI (6.9-10.3 MPa) within 1 day. The strength remained more-or-less constant until after 7 days curing, whereupon the pozzolanic reaction rates increased and caused longer-term strength gains. The HHCL#6 cement mortar gained strength more rapidly than the HHCL#2 cement mortar until about 2 months. Thereafter, the former's strength remained constant while the latter's strength continued to increase.

Dry curing increased the strengths in both sets of mortars, which is expected because of the relatively high solubility of gypsum, and the combination of lime and excess water causing greater expansion (discussed below). Interestingly, the compressive strength of the dry-cured HHCL#6 mortar cubes and of the moist-cured mortar containing a water repelling admixture (HHCL#6 PV1) were nearly identical. This is consistent with the hypothesis that access to large quantities of water during the curing process can weaken the mortar.

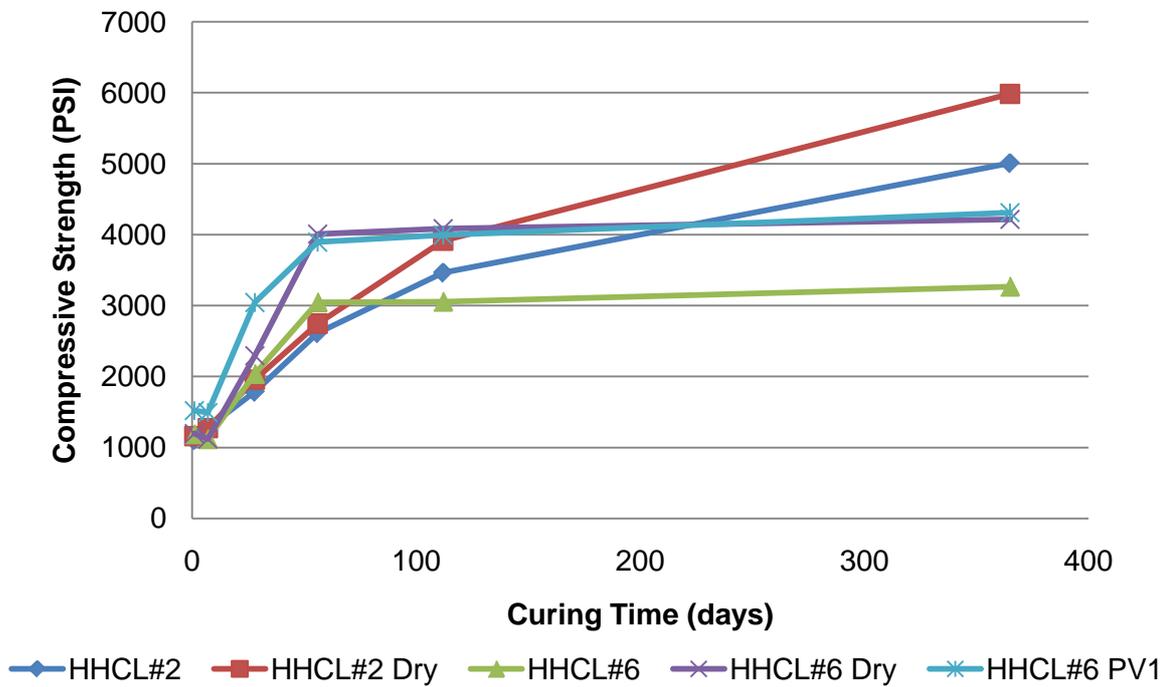


Figure 2. Compressive strength of clinkerless/hemihydrate cement mortar cubes.

Mortar Expansion

Figure 3 shows expansion data for the clinkerless cements and clinkerless/hemihydrate cement blends.

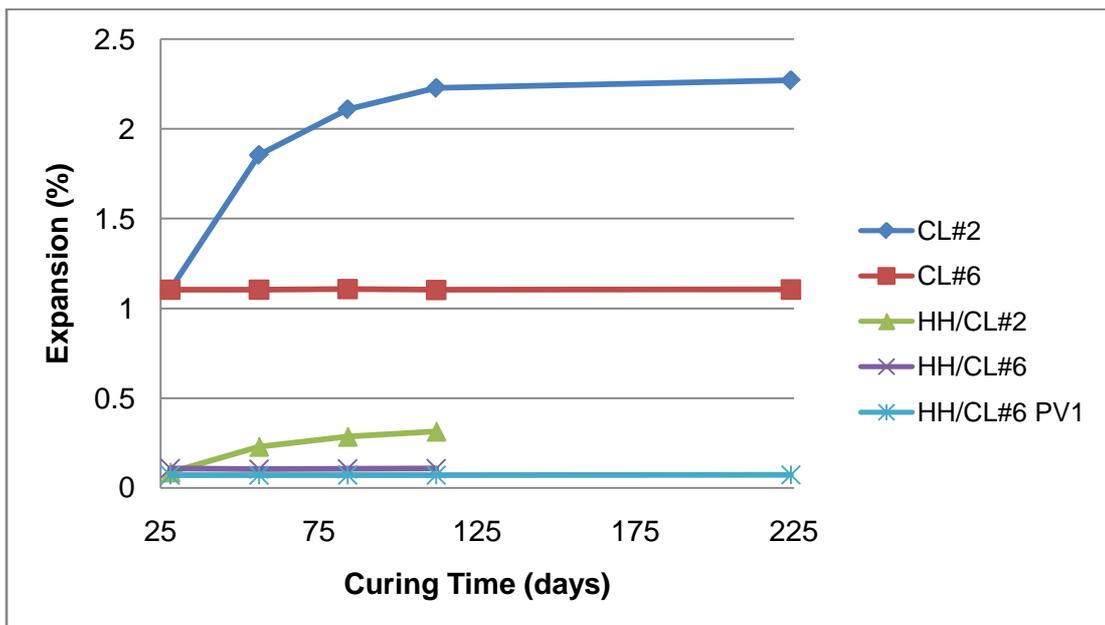


Figure 3. Expansion data of length-change mortar prisms prepared using clinkerless cement and hemihydrate/clinkerless cement blends

As expected, the clinkerless cements (i.e. FBC/PCC fly ash) expanded more than the corresponding blends containing hemihydrate (e.g. CL#6 vs. HH/CL#6). Also, the cements containing a greater proportion of FBC spent bed, and thus larger amounts of lime, exhibited greater expansion. Although the expansions for the two clinkerless cements were identical after 28 days of curing, the CL#6 cement blend stopped expanding after 28 days of curing, while the CL#2 prisms continued expanding for approximately 8 months (Figure 3). The addition of hemihydrate to the cement resulted in a substantial decrease in expansion. However, the gypsum solubility caused these prisms to deteriorate after approximately 3 months submerged curing. Addition of the water repellent (PAVE 100) to the mortar greatly improved the durability of the prisms, such that they remained competent past the 8 month test duration shown in Figure 3.

To provide evidence that ettringite was causing the observed expansion, silica fume was selected as a pozzolan in place of UFA to investigate if it would result in the same degree of expansion. Silica fume will react with lime in the spent bed to form calcium silicate hydrates, but lacks aluminum required to form ettringite.

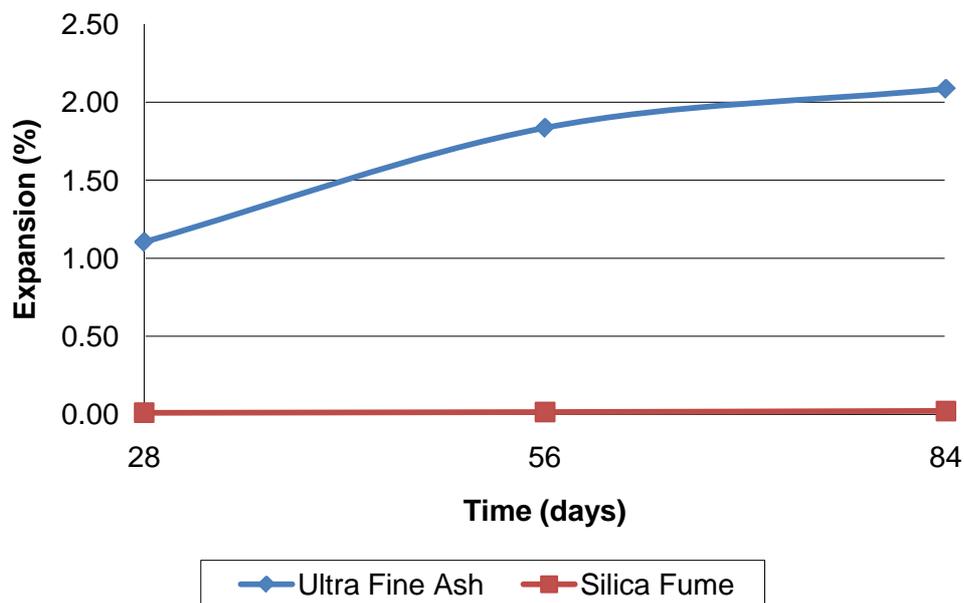


Figure 4. Expansion data of length-change prisms prepared using a 70/30 ratio of spent bed / UFA or silica fume

After 84 days of curing, the length-change prisms prepared using silica fume as the pozzolan had only expanded 0.02% (Figure 4). Conversely, the length-change prisms prepared using ultra fine ash as the pozzolan had expanded 2.09% after 84 days of curing. These data are consistent with ettringite causing the cement system to expand. The effect of alumina on mortar expansion was also observed with the commercial

hemihydrate/OPC cement Duracal®. The Duracal® neat cement mortar, which contains a small amount of alumina in the OPC component, expanded less than 0.1% after 8 months, whereas the Duracal® with UFA expanded considerably more (Figure 5). By adding the Class F ultra fine ash to the system, all of the ingredients for the formation of ettringite were present: the OPC provided the calcium hydroxide, the sulfate was provided by the hemihydrate, and the aluminum was provided by the UFA.

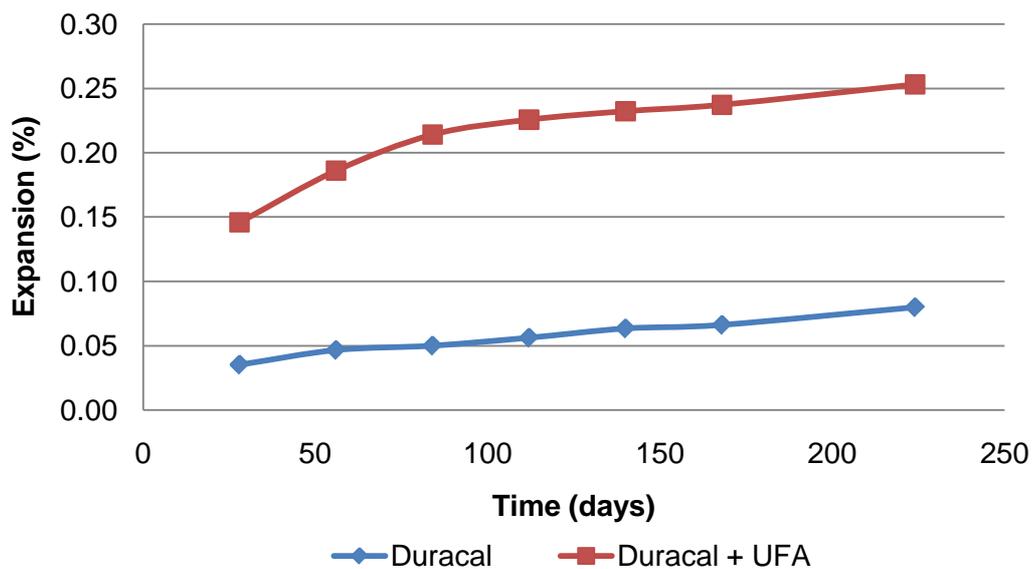


Figure 5. Expansion data of length-change prisms prepared using Duracal® cement

Paste Analysis

X-Ray Diffraction (XRD)

The XRD spectra for CL#2 and CL#6 cements are shown in Figure 6 to provide insight into the compressive strength and expansion characteristics. From the XRD plots of CL#2 and CL#6, it can be seen that an abundance of anhydrite was present at one day of curing. After 7 days of curing, the anhydrite in CL#2 had reacted with water to form gypsum, and some ettringite had also formed. After 3 months of curing, gypsum was still abundant in the paste, but the amount of ettringite had increased substantially. Portlandite was still detected after 56 days of curing, but was no longer detectable after 3 months. These data are consistent with the continued expansion of CL#2 cement beyond 56 days of curing as seen in Figure 3, further indicating that ettringite was causing the mortar to expand. Unlike CL#2, gypsum was not detected in the CL#6 paste (Figure 7), and Portlandite decreased to very low levels within 28 days. However, the diffraction peaks for ettringite increased in intensity even after 3 months curing.

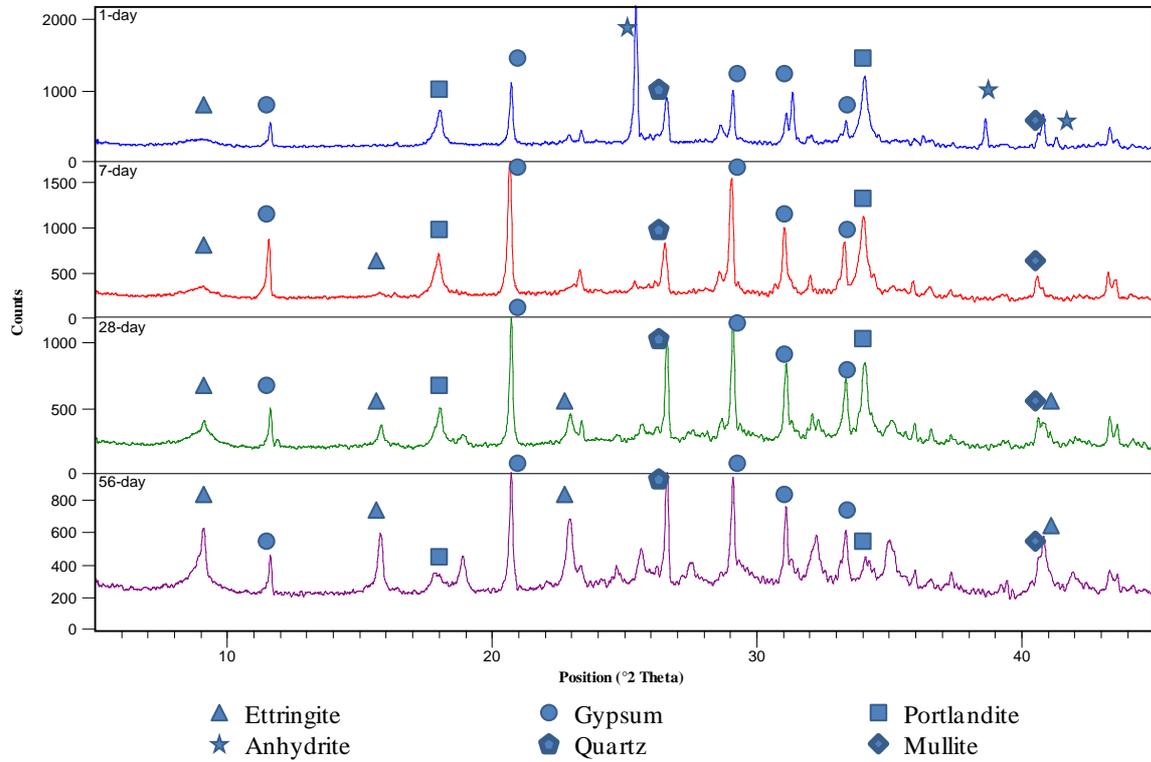


Figure 6. XRD spectra for CL#2 paste

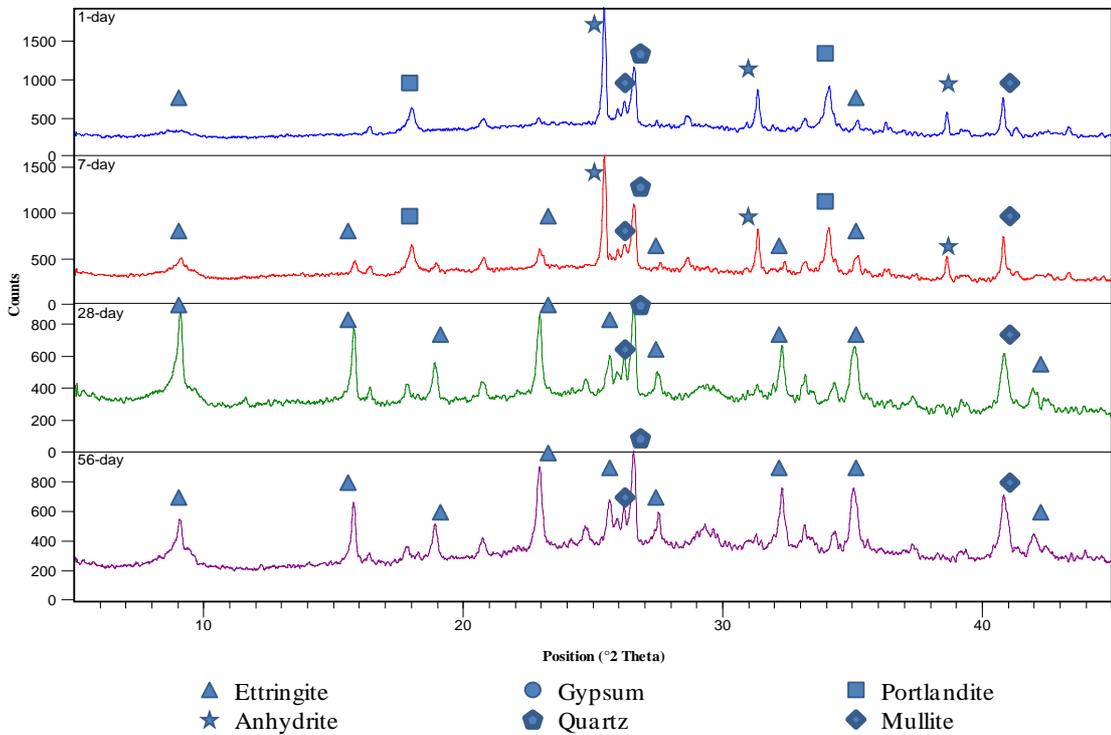


Figure 7. XRD spectra for CL#6 paste

Thermogravimetric Analysis

Thermogravimetric analysis was conducted on CL#2 and #6 pastes. The derivatives of the mass loss data were used to calculate the calcium hydroxide content^[14]. The quantity of calcium hydroxide present in the pastes decreased with curing time as it reacted with aluminum in the UFA and sulfate in the anhydrite to form ettringite (Table 4). After 56 days of curing, calcium hydroxide was still detected in the CL#2 paste and was below detection by 112 days. However, the amount of calcium hydroxide present in the CL#6 cement was below detection within 28 days of curing. These data were 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 CL#6 cement (Figure 3) stopped expanding at 28 days, when calcium hydroxide was no longer detected in the paste. However, the length-change prisms of the CL#2 cements were still expanding at 56 days curing because excess calcium hydroxide was still present as ettringite was forming.

Table 4. Calcium hydroxide content of clinkerless cements

	CL #2	CL #6
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%

CONCLUSIONS

Based on the results the following conclusions were made:

1. By reducing the amount of spent bed ash in the “Clinkerless” cements, expansion was reduced. 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 system stopped expanding when the quantity of calcium hydroxide was below detection limits.
3. By introducing hemihydrate to the FBC/UFA mixtures, expansion was reduced up to 90%. Most importantly, the mortar specimen prepared using the cement blends that contained 50% hemihydrate (with a water reducing admixture) achieved a compressive strength of approximately 1500 PSI (10.3 MPa) within several hours and did not crack throughout the experiment duration.

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.

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