The Fabrication of Value Added Cement Products from Circulating Fluidized Bed Combustion Ash

Robert B. Jewell [1], **Robert F. Rathbone** [1], **Thomas L. Robl** [1]

[1]University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511

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INTRODUCTION

The 300 MW Gilbert circulating fluidized bed combustion electric generation unit operating at East Kentucky Power Cooperative's Spurlock Power Plant in Maysville, Kentucky, is currently the cleanest in the state. It is also one of the most economical. The circulating fluidized bed combustor (CFBC) burns coal in the presence of a bed of slaked limestone, which effectively absorbs sulfur dioxide (SO_2) to form anhydrite ($CaSO_4$). Its low temperature operation produces much less thermal NO_x than pulverized coal combustion (PCC). However because it uses a higher Ca/S ratio than a scrubbed PCC system, it consumes more limestone, produces more solid waste and CO_2 than conventional coal plants. On a per megawatt basis, CFBC produces four to six times the solid waste as a conventional un-scrubbed PCC plant and about two times as much as a scrubbed PCC plant.[1,2] The Gilbert plant will produce approximately 400,000 tons of spent bed material per year and, along with two additional planned CFBC units, will add about 6% to Kentucky's generating capacity but increase the quantity of coal combustion byproducts (CCBs) by almost 14%.[1,2] This large influx of spent bed material is the reason for this research because such a large influx of CCBs will need to be addressed. Past research has shown the potential of using CFBC material as a raw material for the production of a low-energy, rapid-hardening cement.[3]

The research discussed in this paper includes the development of calcium sulfoaluminate-belite cement (CSAB)* with CFBC ash as a key ingredient. This value-added product is a high-strength, low-energy and low-CO_2 emitting cement. Although belite (C_2S) hydrates slowly and has low compressive strengths compared with alite (C_3S) [4], the early strength can be increased with the formation of calcium sulfoaluminate, C_4A_3S'. The hydration of this phase forms ettringite ($C_6AS'_3H_{32}$) which contributes to the development of early strength. Commonly, 18-22% gypsum is interground with the CSAB clinker. Synthetic gypsum, produced from flue gas desulfurization (FGD), is an ideal material for this application.

***** Cement chemistry notation: C = CaO, A = Al_2O_3, S = SiO_2, H = H_2O, s' = SO_3,
F = Fe_2O_3, c = CO_2

Recent research by Bernardo et al. [2004][4] has confirmed that high quality CSAB clinker can be produced using CFBC spent bed material as its principal feedstock, at kiln temperatures of 1200 to 1350 ^{o}C. The use of CFBC spent bed for CSAB clinker production has many benefits over using native materials. It has already been reacted at high temperatures (850 – 900 ^{o}C), thus the energy to calcine the mineral matter has been expended. Also, because it has been calcined its use in cement manufacturing will not result in the additional release of CO_2. Thus, the use of the Gilbert CFBC spent bed as a feedstock in the production of cement clinker represents a potentially high value application for this waste material and is the objective of this research. The proper processing can produce cement products that can replace Portland cement in certain concrete applications. The benefit is that Portland cement is an increasingly expensive and energy intensive product. This research is an important step toward the development of a by-product industry, based on CFBC materials.

MATERIALS CHARACTERIZATION

There are two kinds of "ash" produced from fluidized bed combustion. A fly ash and a bottom ash, these byproducts are collectively referred to as spent bed material. Approximately 40% of the CFBC spend bed material, used in this research, is bottom ash and 60% is fly ash. The CFBC bottom and fly ash differ in size. Most (61%) of the fly ash is finer than 75 µm (200 mesh) while most (58%) of the bottom ash is coarser than 300 µm (50 mesh). The bottom ash is higher in CaO and SO_3 compared to fly ash (Table 1). Chemical analysis of fly ash from the companion PCC power plant is provided in Table 1 for comparison. From Table 1 it is evident that the CFBC ash is much higher in calcium and sulfur and lower in the other major elements. The mineral content and subsequent reactivity of the materials also differs dramatically. The principal minerals in PCC fly ash typical for a boiler in Kentucky are quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), a ferrite spinel $(Fe,Mg)(Fe,Al)_2O_4$ and 70 to 80% glass. Upon exposure to moisture and weathering these minerals are relatively non-reactive.

Fraction	**CFBC Fly Ash**	**CFBC Bottom Ash**	**PCC Fly Ash**	**Commercial CSAB**
%SiO_2	23.72	12.77	53.53	11.12
%Al_2O_3	10.4	5.25	26.80	26.94
%Fe_2O_3	9.63	3.15	10.42	1.76
%CaO	33.15	48.23	1.07	44.99
%MgO	3.40	2.47	0.81	3.18
%Na_2O	0.12	0.05	0.17	0.04
%K_2O	1.18	0.36	2.39	0.19
%P_2O_5	0.13	0.13	0.11	0.11
%TiO_2	0.41	0.26	1.50	0.79
%SO_3	18.08	27.83	0.01	12.23

Table 1. Comparison of the chemistry of the CFBC fly ash and bottom ash with conventional PCC fly ash and a commercial CSAB cement.

CFBC bottom ash in contrast consists mainly of anhydrite ($CaSO_4$), lime (CaO), calcite ($CaCO_3$) and quartz (SiO_2).

FORMULATION OF CSAB CEMENT FROM CFBC ASH

The formulation of the CSAB cement requires the content of belite and Klein's compound to be optimized, and that the belite is present as a relatively reactive polymorph (β-belite).[5] A sample of commercially produced CSAB cement was acquired from China to understand the major phase components present in a commercial product. China is currently the only major producer of CSAB cement, where over 1 million tons per year are currently fabricated.[7] The "commercial CSAB", as it was referred to in this study, was analyzed using X-ray diffraction (XRD) and X-ray fluorescence to determine the major cementitious phases and oxide compositions present in the sample. As is evident from the data, the FBC material is a source of CaO and SO_3 and thus can be a partial substitute for gypsum and limestone in CSAB raw material.

The compositions of the cements were initially formulated using Bogue equations that were modified for the phase composition of CSAB cement (CSAB#1). The phases assumed to be present were Klein's compound, belite, Brownmillerite (C_4AF), calcium sulfate, and a minor amount of lime (<0.5%). However, it was found that the normative equations could not be used to optimize the CSAB compositions, probably because of the formation of minor amounts of other phases such as gehlenite. Therefore, adjustments were made to the formulations to meet several objectives: 1) minimize the proportion of limestone used and thus the free lime formed (CaO), 2) maximize the proportions of byproduct (i.e. CFBC and PCC ash), and 3) produce a cement that will approach the performance of the commercial CSAB cement. The adjustments were made by analyzing each clinker using XRD until the desired composition was achieved (CSAB#2).

EFFECTS OF FIRING TEMPERATURE

The effects of the firing temperature were examined by XRD using the CSAB#1 clinker formulation. The firing program consisted of heating the raw mix at 1268°C/hour and holding for one hour at 1175°C for the first test, then 1200, 1225, and lastly 1250°C. The resulting clinker was slowly cooled within the furnace. Further studies on the effect of the cooling rate are in progress because changes in the cooling rate can modify the true constituent composition.[6] Visually there was a progressively darker and notable volume loss with increasing firing temperature as seen in Figure 2. The darkening color reflects the increased level of sintering.

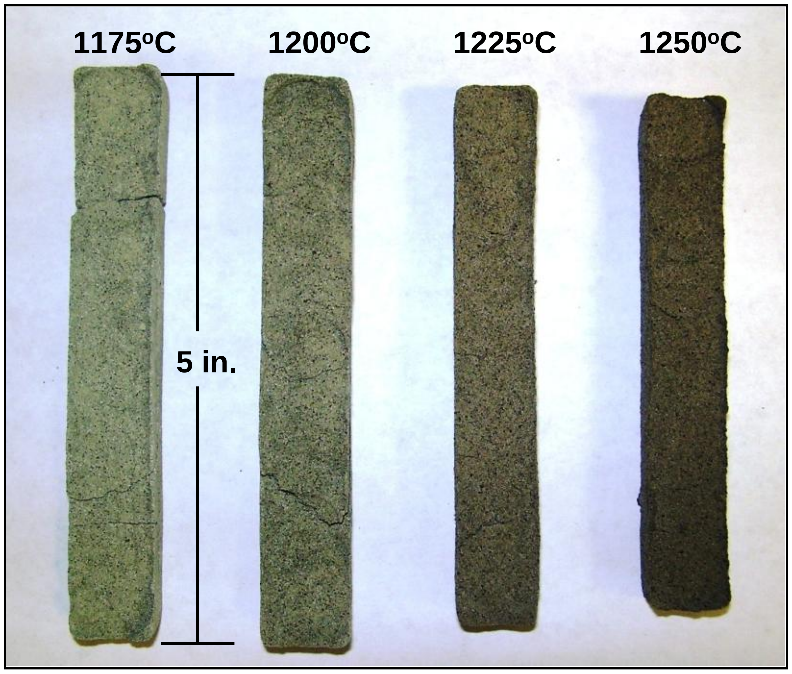

Figure 1**.** CSAB clinker demonstrating color variation and mass loss based on oven-firing temperature.

The optimum firing temperature for the FBC material based CSAB cement was chosen to be 1250°C. At this temperature the maximum amount of Klein's compound and belite is formed with minimal quantities of silicosulfate, an undesired phase which has been reported by other researchers (Roy et al., 1999)[12]. Table 2 provides a list of phases present in the cement formulations.

Phase	Composition	Ordinary Portland Cement	Commercial CSAB	CSAB#1	CSAB#2
C_4A_3S'	$Ca_4Al_6O_{12}SO_4$	—	√	√	√
C_2S	Ca_2SiO_4	√	√	√	√
C_4AF	$Ca_2(Al,Fe_{+3})_2O_5$	√	—	√	√
CS'	$CaSO_4$	√	√	√	—
C	CaO	—	—	√	—
C_2AS	$Ca_2Al_{2.22}Si_{.78}O_{6.79}(OH)_{.22}$	—	—	●	—

√ = Major phase present
● = Minor phase
— = Not detected or Trace

Table 2. Comparison of clinker phases.

PRODUCTION OF CSAB CEMENT

Based on the calculated mix proportions determined from the modified Bogue equations, the raw materials for CSAB#1 were blended with a rod mill. The mix was composed of 32% FBC bottom ash, 8% PCC Class-C fly ash, 15% bauxite, and 45% limestone. The calculated clinker composition was nearly identical to the actual clinker composition determined by XRF (Table 3). The major compounds in the clinker, determined by XRD, were C_4A_3S', C_5S_2S', C_4AF, $CaSO_4$, C_2S, and CaO. The blended mix was then packed into several zirconia combustion boats and fired in an electric furnace at 1250^{o}C for one hour and then air cooled. The resulting clinker, shown in Figure 2, was fairly soft and required little effort to grind to cement fineness. The CSAB#1 clinker was then submitted for XRD and XRF analyses.

Calcium sulfate ($CaSO_4$) is necessary in CSAB cement to promote strength development through the formation of ettringite[7]. The calcium sulfate can be added by proportioning the CSAB clinker to contain excess calcium sulfate as anhydrite[7], or by intergrinding gypsum or anhydrite with the CSAB clinker.[6] Probably the most common way is to add gypsum to the clinker through intergrinding. According to Taylor (2001)[6] intergrinding brings the gypsum particles into more intimate contact with those of the clinker. In this study, the excess calcium sulfate was added using several different methods: 1) proportioning the raw materials to form calcium sulfate in the clinker, 2) intergrinding the clinker with gypsum, and 3) adding gypsum directly to mortar along with the ground clinker cement.

Figure 2. Synthesized CSAB#2 cement clinker produced with Gilbert CFBC spent bed materials. The clinker was fired at 1250^{o}C in zirconia combustion for one hour.

In order to test the strength characteristics of the CSAB cements, cement mortars were prepared following ASTM C 305 and C 109 protocols. The mortar proportions are provided in Table 4. The first CSAB#1 mortar (Mix 1) was prepared without the addition of calcium sulfate: only the anhydrite present in the cement clinker was used as the excess calcium sulfate source. It comprised approximately 16% of the mass of the clinker. The Mix 1 mortar initially appeared to be structurally sound. However, within 1 week it expanded and cracked due to ettringite forming at a slow rate. This prolonged ettringite formation caused extensive cracking within the mortar cubes (Figure 3). This was probably caused by the slow dissolution of “hard burn” anhydrite that was present in the CSAB cement. Glasser and Zhang (2001)[7] noted that by adding reactive calcium sulfate to the clinker rather than to the raw meal will prevent the generation of unreactive hard burn anhydrite.

The second CSAB#1 mortar (Mix 2) was prepared by replacing 15% of the CSAB#1 cement with gypsum, which was added directly to the mortar mix. This method did not produce satisfactory results, as the gypsum formed weak agglomerates that did not disperse in the mortar. This produced low compressive strength (Figures 5 & 6), although the mortar cubes did not exhibit deleterious expansion and cracking (Figure 3). It was concluded that CSAB cement produced from the Gilbert FBC ash would require a more reactive calcium sulfate phase, such as gypsum, to be interground with the clinker.

Based on the above results, a second clinker designated CSAB#2 was formulated using 14% Gilbert FBC bottom ash, 14% PCC Class-F fly ash, 16% bauxite, and 56% limestone. The calculated clinker composition is shown in Table 3. The major compounds in the clinker were C_4A_3S' and C_2S, with only a minor amount of CaO (Figure 4). The CSAB#2 clinker was interground with 20% by mass gypsum. Mortar prepared with this cement did not experience expansive cracking and developed a substantially higher strength than CSAB#1 mortar (Figures 5 & 6).

Fraction	CFBC Bottom Ash	Class-C Fly Ash	Limestone	Bauxite	CSAB#1 Clinker		CSAB#2 Clinker	
					Calculated	Actual	Calculated	Actual
%SiO_2	12.77	42.78	4.33	8.12	12.71	18.42	16.54	17.89
%Al_2O_3	5.25	22.27	1.61	57.62	16.47	21.02	16.02	19.29
%Fe_2O_3	3.15	6.51	0.45	8.26	3.88	3.31	3.28	2.56
%CaO	48.23	18.34	47.67	0.17	48.85	46.61	48.06	49.17
%MgO	2.47	4.44	1.93	0.17	3.44	2.18	3.29	2.37
%SO_3	27.83	1.1	0.48	0.36	13.14	6.44	16.17	7.26
Other*	0.74	5.	0.49	2.77	1.52	2.02	1.59	1.61
LOI	2.	0.43	41.59	24.39				

*****Na_2O, K_2O, P_2O_5, TiO_2

Table 3. Chemical analysis of CSAB#1 and CSAB#2 clinker and raw materials for its production.

wt(g)	Control (OPC)	Commercial CSAB	CSAB#1 (Mix 1)	CSAB#1 (Mix 2)	CSAB#2
Cement	500	500	500	500	500
Gypsum	-	-	-	53	-
Sand	1375	1375	1375	1375	1375.00
Water	242	240	242	239	242
Flow	112%	105%	88%	81%	113%

Table 4. Mortar mix proportions following ASTM C 305 and C 109 protocols.

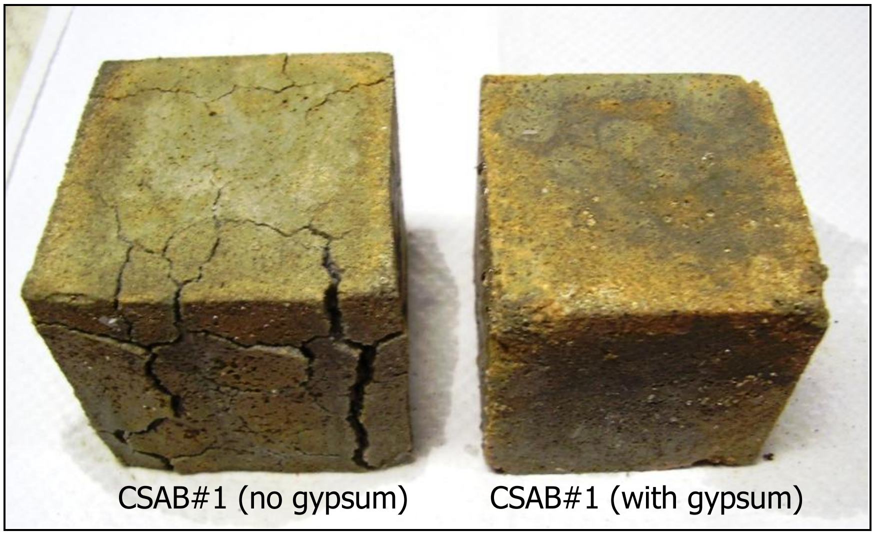

Figure 3. Expansive cracking from slow ettringite formation in mortar cubes made with CSAB#1 cement

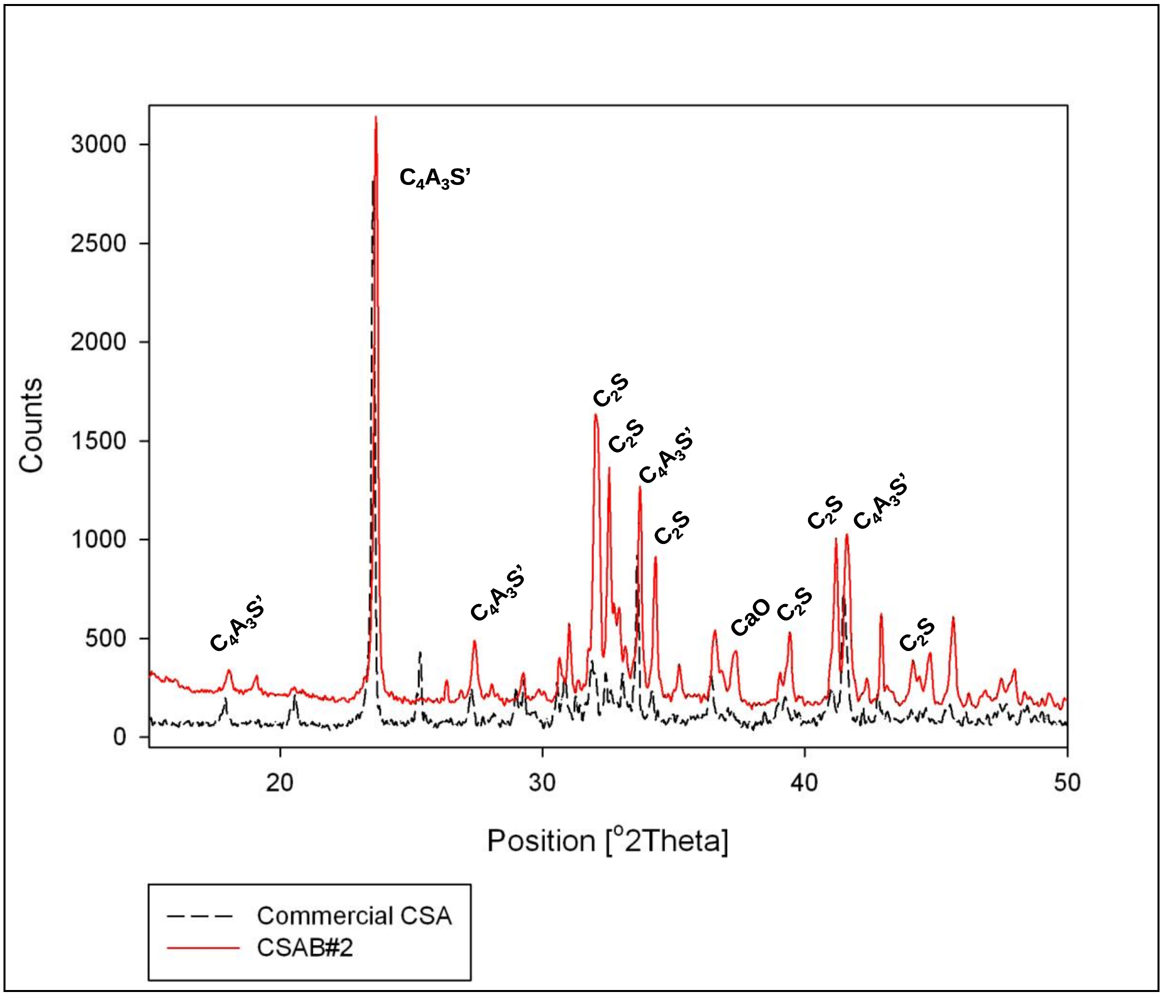

Figure 4. XRD pattern of the Commercial CSAB and CSAB#2 cement clinker.

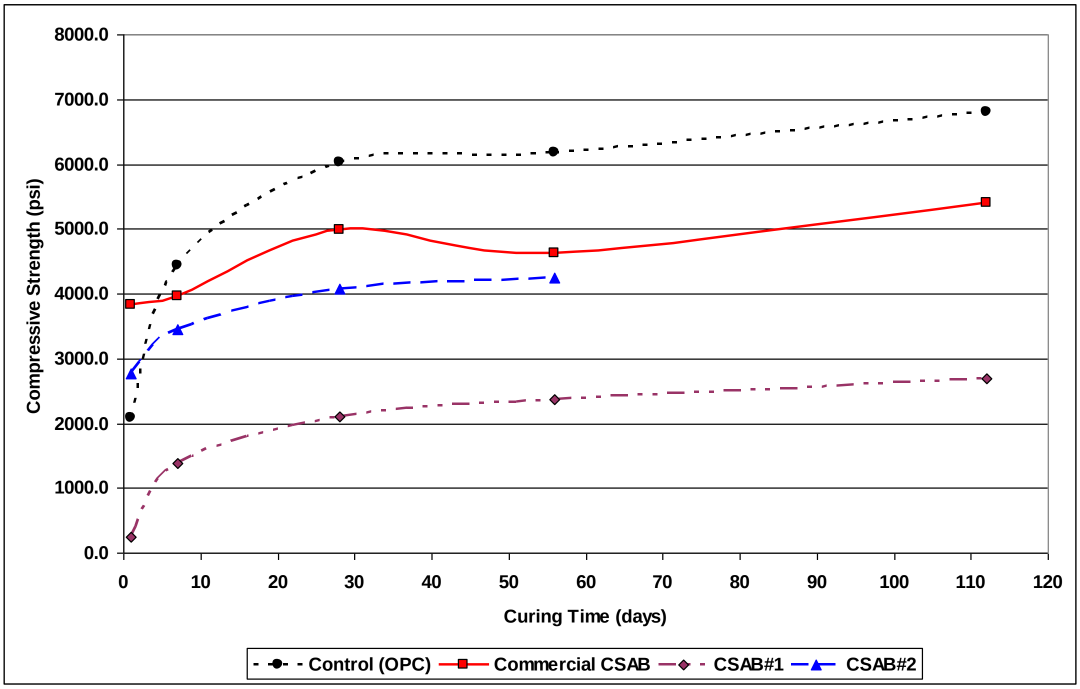

Figure 5. Comparison of the strength performance of mortar containing Ordinary, Type-I Portland cement and CSAB synthesized cement.

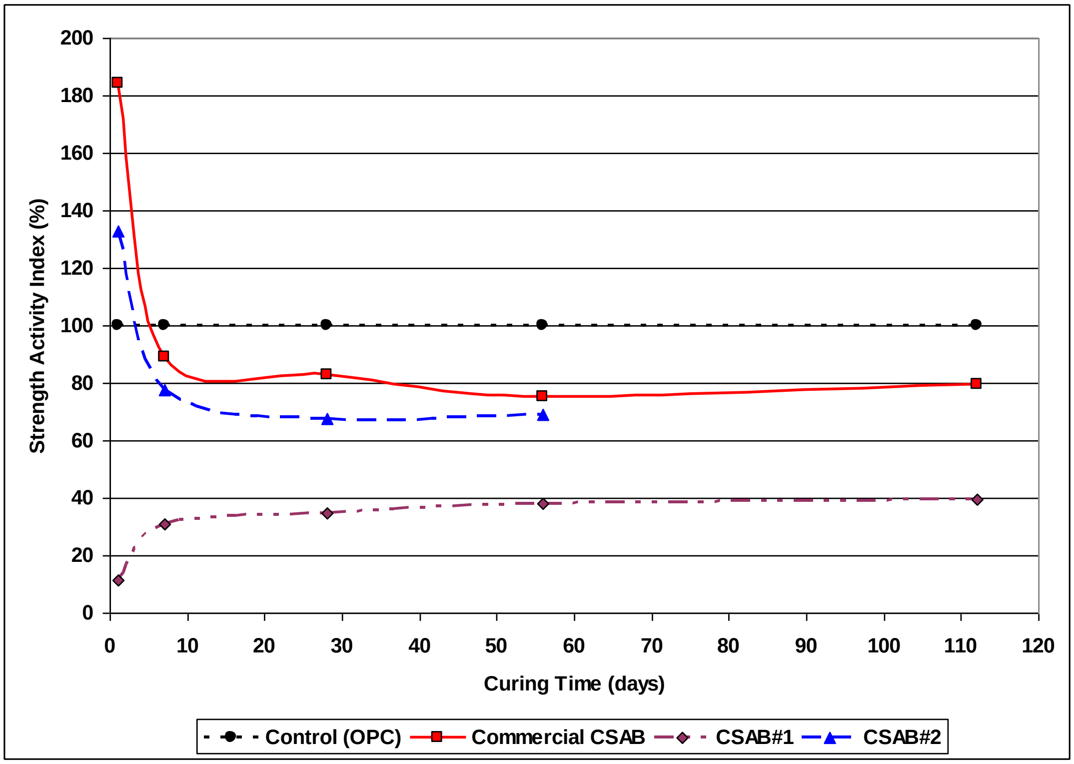

Figure 6. Strength activity index of the synthesized CSAB cements. Characteristic of CSA cements is the early high strength followed by a drop in strength as the formation of ettringite ceases.

Compared with ordinary Portland cement (OPC) mortar, the commercial CSAB and CSAB#2 exhibited high early strength (i.e. after 1 day curing) (Figure 6). The rapid strength gain exhibited by the CSAB mortar cubes is characteristic for these cements, and is caused by the rapid formation of ettringite.[7] The commercial CSAB exhibited higher strengths than CSAB#2 mainly because of the former's higher content of Klein's compound (Figure 4). The faster clinker cooling rate of the commercial CSAB process may also have produced a more reactive cement. As was discussed earlier, a major objective of this study was to maximize the use of byproducts, which resulted in a smaller content of Klein's compound and a higher content of belite in CSAB#2. It is expected that, similar to the OPC mortar, the CSAB#2 mortar will slowly gain strength as the belite continues to hydrate.

A key issue with the CSAB cements is their resistance to damage caused by freezing and thawing, deicer salts, and carbonation. The durability of calcium sulfoaluminate cement (SAC) and ferroaluminate cement (FAC) concrete has been studied by Quillin[4], who found that concrete prepared with these cements exhibited excellent sulfate resistance but carbonate more rapidly than OPC concrete. Durability testing of the commercial CSAB and CSAB#2 is ongoing.

CONCLUSIONS

Fluidized bed combustion material has potential for use in the production of calcium sulfoaluminate belite cements. Heating FBC bottom ash, PCC fly ash, limestone, and bauxite at 1250°C, produced a large quantity of Klein's compound and belite. The synthesized cement clinker was soft and could be easily ground to cement fineness. The compressive strength of the CSAB cement produced high early strengths that exceed those of ordinary Portland cement. Additional long-term strength is supported by the additional formation of C_2S within the clinker. The early trial mixes show utilization of the CFBC material in the order of 28 – 40% of the raw mix, by weight. The utilization of the Gilbert CFBC spent bed material in CSAB cement shows great potential as a large-volume use for the material. This may be one definite solution for decreasing the amount of CFBC material that will be produced in Kentucky during the coming years.

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