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Observations of Peak Strength Behavior in CSA Cement Mortars

OBSERVATIONS OF PEAK STRENGTH BEHAVIOR IN CSA CEMENT MORTARS

Joshua V. Brien,[1] Kevin R. Henke, and Kamyar C. Mahboub

ABSTRACT

The purpose of this study was to assess the mechanical property performance behavior of calcium sulfoaluminate (CSA) cement mortar when cured at ambient laboratory temperature of ~23°C (73°F) and constant 50% relative humidity for an extended period of time. Four CSA cement mortars were tested. Three CSA cement mortars contained equivalent mass amounts of calcium sulfate; whereas, the fourth mortar contained double the amount of calcium sulfate. The three CSA cement mortars containing constant mass amounts of calcium sulfate differed as the specific type of calcium sulfate varied across the three formulations—one mortar containing solely anhydrite, one mortar contained half anhydrite and half gypsum while the other mortar solely contained gypsum. The fourth mortar contained double the amount of calcium sulfate when compared with the others while having a 1/1 blend of anhydrite and gypsum. Specific mortars were either tested for direct tensile strength according to ASTM C307 or for compressive strength according to ASTM C109. All tested mortars displayed statistically significant strength loss trends versus time when cured at constant 50% relative humidity. Cement paste samples were analyzed with TGA/SDT and XRD in an effort to identify microstructure changes corresponding to observed strength loss. Cement paste analysis suggests strength loss within the tested CSA cement mortars occurred as a result of ettringite decomposition.

KEYWORDS

CSA cement, CSA cement hydration, CSA cement strength loss, ettringite decomposition

1.0 INTRODUCTION

Klein's compound, also known as yeelimite or calcium sulfoaluminate, has been used as an expansive additive for cementitious materials since the 1940's (Kalousek, 1973). Using cement nomenclature, calcium sulfoaluminate has the chemical symbol $C_4A_3\bar{S}$, where $C = CaO$, $A = Al_2O_3$, $\bar{S} = SO_3$, $S = SiO_2$ and $H = H_2O$.

In the early years, one primary use for calcium sulfoaluminate was for production of Type K expansive cements. Type K expansive cements are typically composed of ordinary

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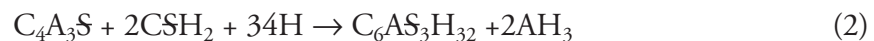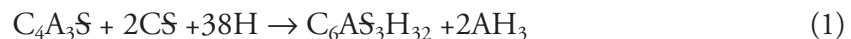
portland cement (CEM1), calcium sulfoaluminate and calcium sulfate (Kalousek, 1973). Nowadays, calcium sulfoaluminate based cements are quite popular in China where a wide range of $C_4A_3\bar{S}$ based cements have been developed and normalized under the name of the "Third Cement Series" (TCS) (Gartner 2004). In addition, a number of mature construction economies are exploring the use of calcium sulfoaluminate (CSA) cements as substitutes, either partially or wholly, for CEM1 as part of the sustainable building initiative (Scrivener 2011, Marroccoli et al, 2010, Jewell et al, 2009, Gartner 2004, Glasser 2001).

According to the World Business Council on Sustainable Development, sustainability is defined as "forms of progress that meet the needs of the present without compromising the ability of future generations to meet their needs". Reducing the total carbon dioxide (CO_2) footprint associated with status quo concrete construction practices is of paramount importance for the sustainable building initiative (Malhorta et al, 2012). Production of CEM1 clinker releases 0.9kg CO_2/kg clinker, with 0.53kg CO_2/kg clinker arising from the decomposition of calcium carbonate while 0.37kg CO2/kg clinker is attributed to the combustion of fossil fuels necessary for firing the kiln (Malhotra et al, 2012).

CSA cement is truly encouraging from an environmental point of view as a clinker containing yeelimite can be produced at temperatures 100 to 150°C lower than the temperatures required for producing CEM1 clinker (Schneider et al, 2011). Given the lower clinkering temperature and lower calcium content of the feedstock, the specific carbon-dioxide (CO_2) emissions of CSA cements are lower than those of CEM1 (Schneider et al, 2011).

Although production of CSA cement is attractive from an environmental point of view, little is know about the long-term performance behavior of materials incorporating CSA cement as a stand alone hydraulic binder. Historically, use of aluminate cements as stand alone hydraulic binders generated negative publicity due to hydrated cement phase conversion processes which resulted in significant strength loss at later ages (Taylor 1997). The present work assesses the long-term strength behavior of mortars incorporating a unique CSA cement containing minor phase tri-calcium aluminate (C_3A) as a stand alone hydraulic binding agent.

CSA cements typically hydrate to form ettringite when in the presence of sufficient calcium sulfate. The mineral name ettringite is used to refer to the calcium trisulphoaluminate hydrate found in several hydrated construction cements (Grounds et al, 1988). Two potential reaction schemes for CSA cement hydrating to form ettringite are listed below:

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \tag{1}$$

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \tag{2}$$

Reaction 1 displays yeelimite, anhydrite and water hydrating to form ettringite and aluminum hydroxide. Reaction 2 displays yeelimite, gypsum and water hydrating to form ettringite and aluminum hydroxide. The difference in the two reactions is due to the chemical water content of gypsum.

These ettringite systems are known for rapid strength development, durability and frost resistance (Gastaldi et al, 2009). However, ettringite based systems are also known to possess challenges with one example being controlling expansion associated with the hydration reaction (Gartner 2004). In addition to quirky dimensional stability characteristics, it is also known that ettringite has relatively low resistance to CO_2 attack (Sherman et al, 1995, Sato et al, 1992, Skoblinskaya, N, 1975). When cured in a controlled environment designed to accelerate carbonation behavior of cementitious materials, CSA cement materials experienced

greater degrees of carbonation and strength loss when compared with OPC materials (Jewell et al, 2009, Sherman et al, 1995).

Another perspective regarding carbonation type findings in general is that contamination by atmospheric CO_2 (carbonation) can probably be more serious in laboratory studies than in practical concrete mixes of lower surface to volume ratio (Taylor 1997). Zhang and Glasser report on two CSA cement concretes being removed from service after several years of service in very good condition showing little signs of carbonation. One sample was taken from a normal strength crane column while the other sample was taken from a high strength concrete pile (Zhang et al, 2005). The crane column sample was cored in 1997, wrapped in plastic except for one end, and stored at normal ambient temperature until examination in 2001 (Zhang et al, 2005). The high strength concrete pile sample was cut off in 1993 and transported to Beijing where it was stored outside in the elements until examined in 2001 (Zhang et al, 2005). It would be helpful to know the relative humidity for the indoor storage environment for the crane column sample. According to a climate web site, the average annual relative humidity for Beijing is 56.5% on a monthly basis with a range of 46% in April to 74% in August (http://www.beijing.climatetemp.info).

> Because it is so central to the formation and property development of cementitious systems it is critical to understand the underlying mechanisms in order to progress; particularly on the most burning challenge facing the world today—the need to continually lower environmental impact, to do more with less (Scrivener et al, 2011).

At early ages, properly formulated systems based upon CSA cement often demonstrate impressive mechanical property behavior when compared with CEM1 systems. The concept of "achieving more with less" via substituting a percentage of CSA cement for CEM1 cements in specific applications is viable. However, more research is necessary regarding the long-term performance of CSA cement systems in extreme environments.

This study presents destructive mechanical property test results for CSA cement mortars cured at ambient laboratory temperature and constant 50% relative humidity. This environment is somewhat extreme due to such a constant low humidity; however, such an environment is plausible for either arid or perhaps some leeward mountainous environments. The study assesses both compressive strength behavior and direct tensile strength behavior. Direct tensile strength testing was included to highlight any changes in strength characteristics resulting from changes in microstructural characteristics. Tensile type testing seeks out the weakest link, as it appears to give a more accurate indication of the concrete deterioration than measurements of compressive strength (Chandra et al, 2003). Cement pastes samples were analyzed by TGA/SDT and XRD in an effort to correlate mechanical property behavior with microstructural behavior.

2.0 MATERIALS

2.1 Cement
CSA cement containing C_3A was utilized in this study. XRD analysis provides the following listing of constituent materials:

Yeelimite >> C_3A > Belite > Anhydrite (trace quantity)

2.2 Anhydrite
Calcium sulfate anhydrite for this study was sourced from Allied Custom Gypsum. This anhydrite has a variable particle size, typically with approximately 50% passing three microns while having a top size of approximately 10% retained on a 45 micron sieve with the remainder being a continuous distribution down to dust.

2.3 Gypsum
Terra Alba gypsum was sourced from US Gypsum (USG) with particle size within the range of 12 to 15 microns. (USG TDS)

2.4 Aggregate
ASTM finely graded sand from Ottawa Illinois was used in all formulations. A coarser, 20/30 sand, was also used in all formulations.

3.0 EXPERIMENTAL PROGRAM
This study involved both hydration analysis for CSA cement pastes and mechanical strength analysis for CSA cement mortar. The hydration analysis included thermogravimetric analysis (TGA/SDT) and powder X-Ray diffraction (XRD). Direct tensile strength testing was performed according to ASTM C307, Standard Test Method for Tensile Strength of Chemical Resistant Mortars, Grouts and Monolithic Surfaces. Compressive strength testing was performed according to ASTM C109, Standard Test Method for Compressive Strength of Hydraulic Cement Mortar using standard cubes. All samples were cured at ambient laboratory temperature and 50% relative humidity. Three samples were tested to arrive at each reported average value.

3.1 Powder X-ray Diffraction (XRD)
Cement pastes were cured in small, plastic calorimeter containers without lids in a humidity chamber controlled at 50% relative humidity and ambient laboratory temperature of 23°C. For each mix design, all test specimens were taken from the same hydrating CSA cement paste sample. Cement paste test specimens were ground to a fine powder using a mortar and pestle. The samples were washed with acetone to remove water in an effort to mitigate the hydration reaction. After washing with acetone, the samples were thoroughly dried in an oven at 45°C for an hour. Powder X-ray diffraction (XRD) analyses were performed with a Philips X'Pert diffractometer (model PW3040-PRO) operating at 45 kV and 40 mA. The samples were dry mounted in aluminum holders and scanned at 8-60° 2θ with Cu K-α radiation.

3.2 TGA/SDT
All TGA/SDT sample specimens were prepared with the same procedures as the XRD specimens; that is, after curing they were ground, washed with acetone and dried at 45°C. TGA analyses utilized one cycle with a temperature ramp rate of 20°C per minute through a final cycle temperature 800°C. TGA analysis was performed with a SDT 600 from TA Instruments.

3.3 Mortars
Three CSA cement based mortar mix designs were analyzed for direct tensile strength. These mix designs are displayed in Table 1. Each mix design had constant mass amounts of CSA

cement, calcium sulfate and sand. Two mix designs possessed identical water / cementitious materials ratios while one mix design possessed a slightly higher water / cementitious materials ratio. The water / cementitious materials ratio for the two mix designs containing anhydrite was 0.33. The water / cementitious materials ratio for the mix design containing gypsum was 0.35. These low water / cementitious materials ratios resulted in very interesting results which illustrate the relationship between direct tensile strength and developments within the microstructure for these specific CSA cement mortars. Each mix design differed in type of specific calcium sulfate comprising the constant mass amount of calcium sulfate. One mix design contained solely anhydrite. The second mix design contained 50 weight % anhydrite and 50 weight % gypsum. The third mix design solely contained gypsum.

The mortar containing solely gypsum was also analyzed for compressive strength testing along with another mortar containing 50 weight % gypsum and 50 weight % anhydrite. The sample containing 50 weight % gypsum and 50 weight % anhydrite for compressive strength testing contained double the amount of calcium sulfate when compared with the mortar tested for direct tensile strength displayed in Table 1. Mortar formulations for compressive strength testing are displayed in Table 2.

TABLE 1. CSA cement mortar constituent components by mass for ASTM C307 direct tensile strength testing.

Mortar Information for Tensile Strength Testing			
	Solely Anhydrite	**50% Anhydrite / 50% Gypsum**	**Solely Gypsum**
Materials	**Mass (g)**	**Mass (g)**	**Mass (g)**
CSA Cement	500	500	500
Anhydrite	160	80	0
Gypsum	0	80	160
Coarse Sand	125	125	125
Graded Sand	1375	1375	1375
DI Water	220	220	230

TABLE 2. CSA cement mortar constituent components by mass for ASTM C109 compressive strength testing.

Mortar Information for Compressive Strength Testing		
Cement Mortar Data (ASTM C109)	**50% Anhydrite / 50% Gypsum**	**Solely Gypsum**
Materials	**Mass (g)**	**Mass (g)**
CSA Cement	500	500
Anhydrite	160	0
Gypsum	160	160
Coarse Sand	125	125
Graded Sand	1375	1375
DI Water	240	230

TABLE 3. CSA cement paste constituent components by mass for both TGA/SDT and XRD analysis.

Cement Paste Formulations			
Cement Paste Data	Sample 1	Sample 2	Sample 3
Materials	Mass (g)	Mass (g)	Mass (g)
CSA Cement	20	20	20
Anhydrite	6	3	0
Gypsum	0	3	6
Total Mass	26	26	26
DI Water	8	8	8

For preparing the dry mix mortars, individual mortar components were weighed and placed into a plastic mixing bag. After all components were added, the bag was sealed and shaken vigorously by hand for approximately ninety seconds. This type of mixing is an industry proven simulation for blending operations manufacturing dry mix mortar products containing minute quantities of additives such as accelerators and retarders.

Experimental specimens were cast according to both ASTM C307 and ASTM C109. Three test specimens were cast for each test series. During the first 24 hours of curing, each test specimen remained in the mold covered with plastic. After this initial curing period, test specimens were removed from their molds and either tested or placed in a chamber at ambient laboratory temperature and 50% relative humidity until time for testing.

4.0 STATISTICAL ANALYSIS

Minitab statistical software was utilized for both analysis of variance testing and post hoc comparisons. Analysis of variance is particularly useful when the basic differences between the groups cannot be stated quantitatively (Bethea et al, 1975). One-way analysis of variance is used to test the equality of J population means. The procedure is based on assumptions that each of J groups of observations is a random sample from a normal distribution and that the population variance $s^2_x = s^2$ is constant among the groups (Bethea et al, 1975). Pooled variances were used for the analyses.

The Tukey comparison method is an example of a post hoc method, that is, it can be used after the analyst looks at the data (Mickey et al, 2004). Hypothesis tests performed using Tukey's Honestly Significant Difference comparison method tend to have greater power than those performed using either Bonferroni's or Scheffe's method (Mickey et al, 2004). Tukey's Honestly Significant Difference (HSD) method tests all pairs against:

$$W_k = q_{k,u,1-a} * (s^2/n)^{1/2}$$

Where $q_{k,u,1}$ is the 100(1-a)th percentile of the distribution of the Studentized range of k means with u d.f. (Fisher's LSD = W_2) (ESS Vol. 8).

Fisher's protected least significant difference method is identical with the Student's t-test, except that it requires a significant F-test for the equality of all k means before individual paired differences may be tested (ESS Vol. 8). None of the other STPs and SMCPs have this

prerequisite (ESS Vol. 8). Two sample means y_i and y_j will be declared to be significantly different at the 100a% level if their absolute difference exceeds

$$LSD = t_{u,1-(a/2)}*((s^2*(n_i^{-1} + n_j^{-1}))^{1/2}$$

Where tu,g is the (100g)th percentile of Student's t-distribution with u degrees of freedom (d.f.) and s^2 (with u d.f.) is the pooled estimate of s^2 (ESS Vol.8).

ANOVA reporting for this study presents an observed F-value written with convention F(degrees of freedom between / degrees of freedom within) = value, a significance level p-value, the pooled standard deviation and a value for R^2.

5.0 RESULTS

Figure 1 displays average direct tensile strength values versus time for the mortars displayed in Table 1. Three samples, cured at 50% relative humidity and 23°C, were tested for each formulation. These results were largely unexpected as CSA cements are not well known for displaying strength loss during use in plausible environments. This series of tests was originally designed to conclude at 28 days. Interesting observations during 28 day testing resulted in continued research in an effort to determine the dependence of strength loss on microstructural characteristics. The ad hoc nature of presented data stems largely from a shortage of cast materials utilizing identical raw materials.

The mortar containing 50 weight % anhydrite and 50 weight % gypsum in Table 1 demonstrated the following strength behavior: the period from initial hydration through 28 days is clearly a period of increasing direct tensile strength; whereas, the period from 28 days through 56 days is clearly a period of decreasing direct tensile strength. The direct tensile strength results for 24 hours, 48 hours, 7 days and 28 days are 387psi (2.668MPa), 492psi (3.392MPa), 491psi (3.385MPa) and 597psi (4.096MPa), respectively. Whereas, the direct tensile strength results for 28 days and 56 days are 597psi (4.096MPa) and 313psi (2.158MPa), respectively.

The mortar containing solely gypsum in Table 1 demonstrated the following strength behavior: the period from initial hydration through 7 days is clearly a period of increasing direct tensile strength; whereas, the period from 7 days through 28 days is clearly a period of decreasing direct tensile strength. The direct tensile strength results for 24 hours, 48 hours and 7 days are 346psi (2.386MPa), 371psi (2.558MPa) and 463psi (3.192MPa), respectively. Whereas, the direct tensile strength results for 7 days and 28 days are 463psi (3.192MPa) and 343psi (2.365MPa), respectively.

The mortar containing solely anhydrite in Table 1 demonstrated the following strength behavior: the period from initial hydration through 28 days is clearly a period of increasing direct tensile strength; whereas, the period from 28 days through 109 days is clearly a period of decreasing direct tensile strength. The direct tensile strength results for 24 hours, 48 hours, 7 days and 28 days are 275psi (1.896MPa), 488psi (3.365MPa), 493psi (3.399MPa) and 633psi (4.364MPa), respectively. Whereas, the direct tensile strength results for 28 days, 56 days and 109 days are 633psi (4.364MPa), 567psi (3.909MPa) and 539psi (3.716MPa), respectively.

One-way ANOVA was used to test the equality of the population means for direct tensile strength testing of the CSA cement mortar containing solely anhydrite when cured for

FIGURE 1. Display of peak strength behavior during direct tensile strength testing of CSA cement mortars in Table 1 cured at constant 50% humidity (3 samples each).
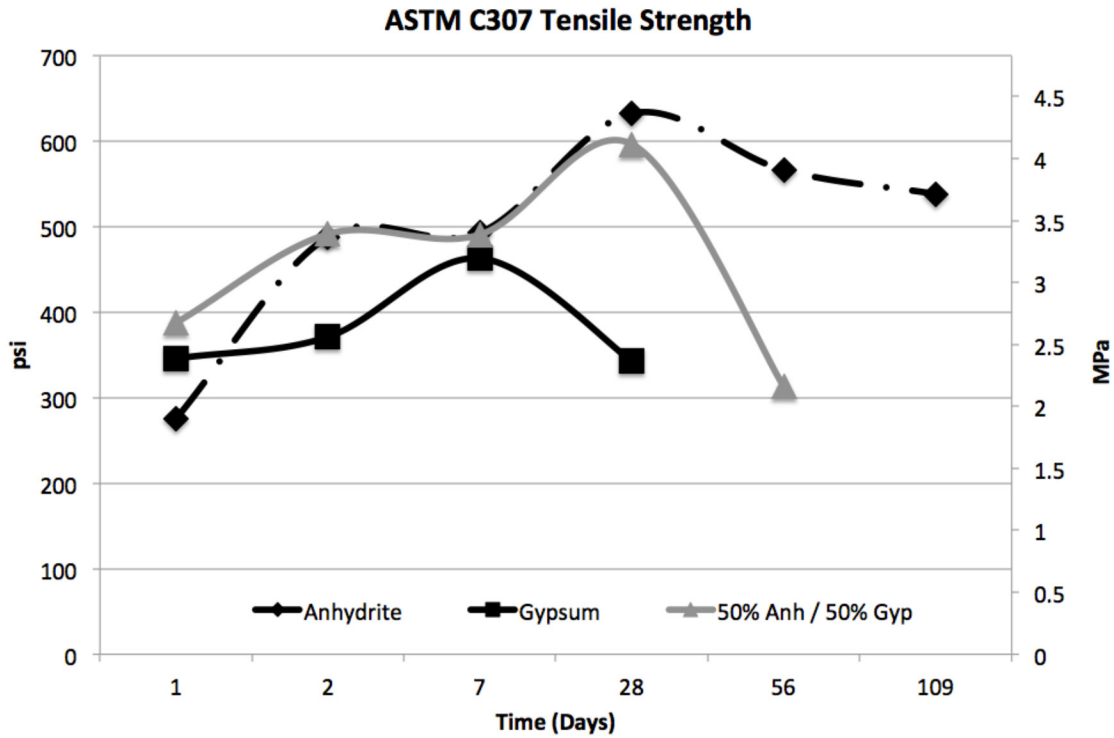

24 hours, 48 hours, 7, 28, 56 and 109 days at ambient laboratory temperature and constant 50% relative humidity. Results from ANOVA are: $F(5/12) = 43.76$, $p = 0.000$, pooled standard deviation $= 31.91$ and $R^2 = 94.8\%$. Based upon the F value of 43.76 and corresponding p-value $= 0.000$, if an alpha value of 0.05 is chosen, it is safe to reject the null hypothesis and ultimately conclude that at least two means differ from one another, and this inequality is highly unlikely due to chance. Further statistical comparison methods utilizing Tukey's Honestly Significant Difference test along with Fisher's test can be seen in Table 4. In Table 4, average direct tensile strength values for specific curing regimens not sharing the same letter strength classification are significantly different. Therefore, direct tensile strength loss versus time for the CSA cement mortar containing anhydrite in Table 1 is statistically significant for the period from 28 days to 109 days.

Figure 2 displays average values from compressive strength testing for mortars displayed in Table 2, which were also cured at 50% relative humidity and 23°C. All cubes were cast with like constituent materials.

TABLE 4. Direct tensile strength classifications as assigned by statistical comparison methods for the CSA cement mortar containing solely anhydrite in Table 1. Direct tensile strength results for specific curing regimens not sharing the same letter are significantly different.

Post Hoc Statistical Analysis	Tukey	Fisher
24 hour	C	D
48 hour	B	C
7 days	B	C
28 days	A	A
56 days	A B	B
109 days	B	B C

FIGURE 2. Display of peak strength behavior during compressive strength testing of CSA cement mortars in Table 2 cured at constant 50% humidity (3 samples each).
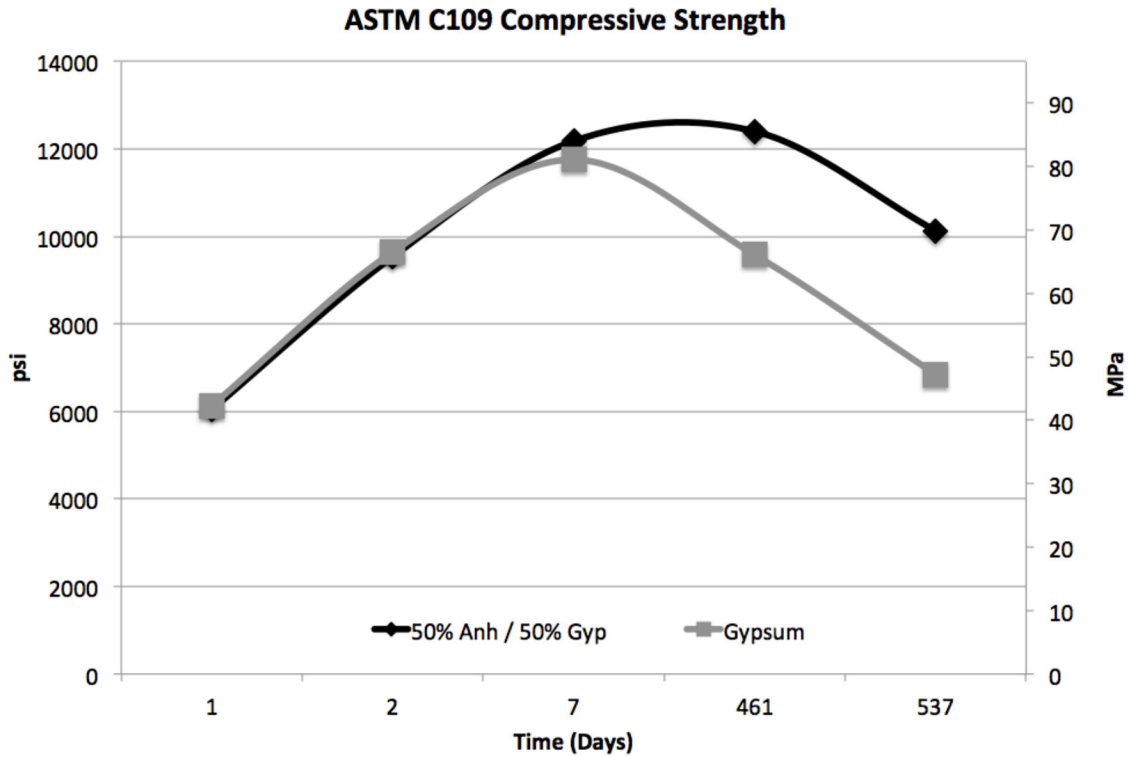
Originally planned testing for both 28 and 56 day samples for the two mix designs was postponed to later ages in an effort to determine if peak strength behavior actually occurred in both tensile and compression type testing scenarios for samples cast from like constituent materials.

For the mix design containing solely gypsum in Table 2, the period from initial hydration through 7 days is a period of increasing compressive strength; whereas, the period from 7 days through 537 days of hydration clearly displays a period of decreasing compressive strength. The compressive strength results for 24 hours, 48 hours and 7 days are 6,092psi (42MPa), 9,717psi (67MPa) and 11,748psi (81MPa); respectively, whereas, the compressive strength results for 7 days, 460 days and 537 days are 11,748psi (81MPa), 9,572psi (66MPa) and 6,818psi (47MPa), respectively.

Results for the mix design containing 50 weight % anhydrite and 50 weight % gypsum as a combined source of calcium sulfate in Table 2 display compressive strength behavior such that the period from initial hydration through 461 days is a period of increasing compressive strength; whereas, the period from 461 days through 537 days of hydration is clearly a period of decreasing compressive strength. The compressive strength results for 24 hours, 48 hours, 7 days and 461 days are 6,092psi (42MPa), 9,572psi (66MPa), 12,183psi (84MPa) and 12,473psi (86MPa), respectively. Whereas, the compressive strength results for 461 days and 537 days are 12,473psi (86MPa) and 10,153psi (70MPa), respectively.

One-way ANOVA was used to test the equality of the population means for compressive strength testing of the CSA cement mortar containing half anhydrite and half gypsum when cured for 24 hours, 48 hours, 7 days, 461 days and 537 days at ambient laboratory temperature and constant 50% relative humidity. Results from ANOVA are: $F_{(4/10)} = 158.77$,
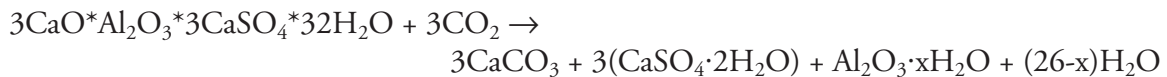
p = 0.000, pooled standard deviation = 353.2 and R^2 = 98.45%. Based upon the F value of 158.77 and corresponding p-value = 0.000, if an alpha value of 0.05 is chosen, it is safe to reject the null hypothesis and ultimately conclude that at least two means differ from one another, and this inequality is highly unlikely due to chance. Further statistical comparison methods utilizing Tukey's Honestly Significant Difference test along with Fisher's test can be seen in Table 5. In Table 5, average compressive strength values for specific curing regimens not sharing the same letter strength classification are significantly different. There-

TABLE 5. Compressive strength classifications as assigned by statistical comparison methods for the CSA cement mortar containing half anhydrite and half gypsum in Table 2.

Post Hoc Statistical Analysis	Tukey	Fisher
24 hour	C	C
48 hour	B	B
7 days	A	A
461 days	A	A
537 days	B	B

fore, compressive strength loss versus time for the CSA cement mortar containing 50 weight % anhydrite and 50 weight % gypsum in Table 2 is statistically significant for the period from 461 days to 537 days.

6.0 DISCUSSION

Ettringite has a possible disadvantage in that it may decompose under extremes of normal, ambient conditions (Zhou et al, 2001). The mechanism and reaction kinetics of ettringite decomposition and reconstitution are not well known (Zhou et al, 2001). The principle decomposition products of ettringite are calcium sulfate dihydrate (gypsum), calcium carbonate and aluminum hydroxide (Grounds et al, 1988). Others describe ettringite decomposition products as C_4A_3S, $CaSO_4$ and CaO, in agreement with reports cited in Lea (Zhou et al, 2001). Furthermore, it has been suggested that ettringite decomposes to calcite, gypsum and alumina gel by carbonation as follows (Sato et al, 1992):

$$3CaO*Al_2O_3*3CaSO_4*32H_2O + 3CO_2 \rightarrow$$
$$3CaCO_3 + 3(CaSO_4 \cdot 2H_2O) + Al_2O_3 \cdot xH_2O + (26\text{-}x)H_2O$$

Water is especially important to ettringite stability because of the high water content of the solid, which has the constitution, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 30 + xH_2O$, where x is in the range of 0 to 2 (Zhou et al, 2001)."

A four stage process for water loss from ettringite is described as follows (Skoblinskaya et al, 1975):

- Water present in the channels will withdraw first thus reducing the total number of water molecules down to 30
- Second, the water molecules from the Ca pohyhedra of the columns should withdraw, namely those which are at the additional apices of the trigonal prisms. These 12 being out, the number of water molecules is now reduced to 18
- Water molecules at the main vertices of the trigonal prisms will be displaced from their previous positions in the column and that will change somewhat the conditions of their interaction with SO_4 groups. Therefore a part of the bonds between the columns will be strained between loss of water molecules within the range from 18 to 6

TABLE 6. Average mass loss values for compressive strength testing of mortar cubes corresponding to formulations displayed in Table 2 after being cured at ambient laboratory temperature and 50% relative humidity for each specified interval (3 cubes each).

Mortar Mass Loss Information		
	cube mass loss: 50% anhydrite / 50% gypsum	cube mass loss: solely gypsum
7 day average for 3 cubes (g)	1.7	1.8
standard deviation	0.3	0.1
537 day average for 3 cubes (g)	7.0	8.2
standard deviation	0.6	0.4

- Finally, one should expect the withdrawal of the OH group from the Ca and Al polyhedral that will decrease n from 6 to 0…In this case the greatest reduction in strength for each column and for bonds between the columns can be expected. It may be accompanied by appearance of longitudinal and transverse cracks in the crystals as well as by their disintegration

Table 6 displays mass loss data for all ASTM C109 compressive strength cubes. The mass value corresponding to each cube was recorded both upon initial removal from the mold and immediately before testing. The CSA cement mortar cubes containing half gypsum and half anhydrite experienced mass loss of 1.7g and 7g after curing for 7 days and 537 days, respectively. The CSA cement mortar cubes containing solely gypsum experienced mass loss of 1.8g and 8.2g after curing for 7 days and 537 days, respectively.

The compressive strength behavior displayed in Figure 2 together with the mass loss information displayed in Table 6 seem to correspond to the ettringite decomposition through dehydration mechanisms described by Skoblinskaya et al, (1975). The rationale presented by Zhou et al, (2004), for ettringite decomposition to metaettringite might also be utilized for describing the observed behaviors. Other important items to note are:

- Contamination by atmospheric CO_2 (carbonation) can probably be more serious in laboratory studies than in practical concrete mixes of lower surface to volume ratio (Taylor 1997)
- Carbonation was verified by XRD, indicating that after 1 year at room temperature the specimens carbonated only slightly, and some small quantities of carbonation products, namely calcite, vaterite (μ-$CaCO_3$) and traces of hemihydrate were present (Sherman et al, 1995)

The remaining paragraphs utilize both TGA/SDT analysis and XRD analysis to discuss the observed direct tensile strength trends.

Figure 3 displays TGA/SDT analysis for cement paste 1, containing solely anhydrite, in Table 3 after hydrating for 28 days and 242 days at 50% relative humidity and 23°C. The peak near 110°C represents the weight % of ettringite per degree Celsius in each sample. Such a designation for ettringite is in agreement with literature (Clark et al, 2008, Sherman et al, 1995). For cement paste 1 in Table 3, the concentration of ettringite after hydrating for periods of 28 days and 242 days are 12% and 7%, respectively. Figure 1 shows the CSA

FIGURE 3. TGA/SDT analysis for CSA cement paste containing solely anhydrite as a source of calcium sulfate in Table 3.
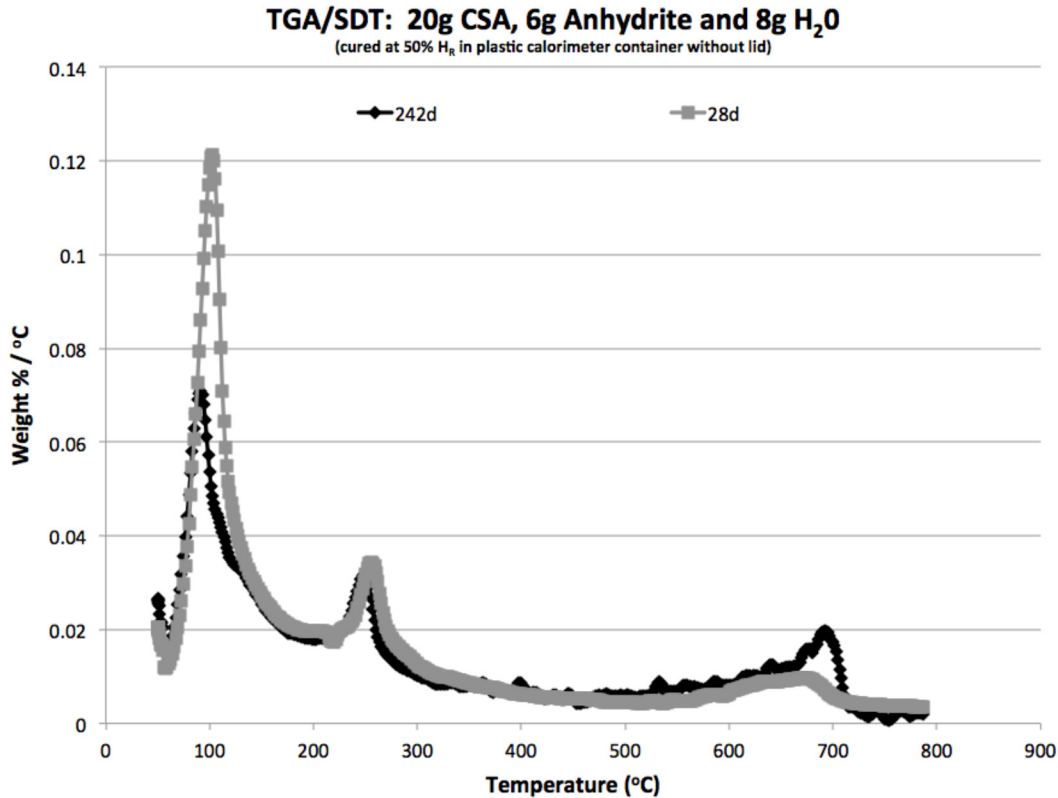
cement mortar corresponding to cement paste 1 in Table 3 beginning to show a decreasing direct tensile strength trend between 28 days and 56 days of hydration. The results listed in both Figure 1 and Figure 3 suggest a relationship exists between direct tensile strength and ettringite concentration. However, with such limited information, it is not wise to adopt a linear relationship between ettringite concentration and observed average direct tensile strength values.

The author believes the peaks located near 690°C in Figure 3 represent calcium carbonate. It is interesting to note the increase in calcium carbonate concentration for cement paste 1 in Table 3 after hydrating for both 28 days and 242 days at 50% relative humidity and 23°C. Such an increase in calcium carbonate concentration at such a late stage in the hydration cycle suggests ettringite decomposition (Sherman et al, 1995, Sato et al, 1992). Whether the ettringite decomposition is via carbonation as explained by Sato et al, (1992), or some other mechanism due to low humidity environment is an excellent project for future research.

Figure 4 displays a XRD diffractogram for sample 1 in Table 3 after curing for 242 days at 50% relative humidity with the following characterization:

Yeelimite > Anhydrite >> Ettringite, $Ca_3Al_2O_6$ > Gamma Ca_2SiO_4, Belite

The concentration of ettringite in the XRD characterization relative to other constituent materials supports the TGA/SDT results displayed in Figure 3. The cement paste behavior displayed in Figures 3 and 4 suggests the CSA cement mortar containing solely anhydrite
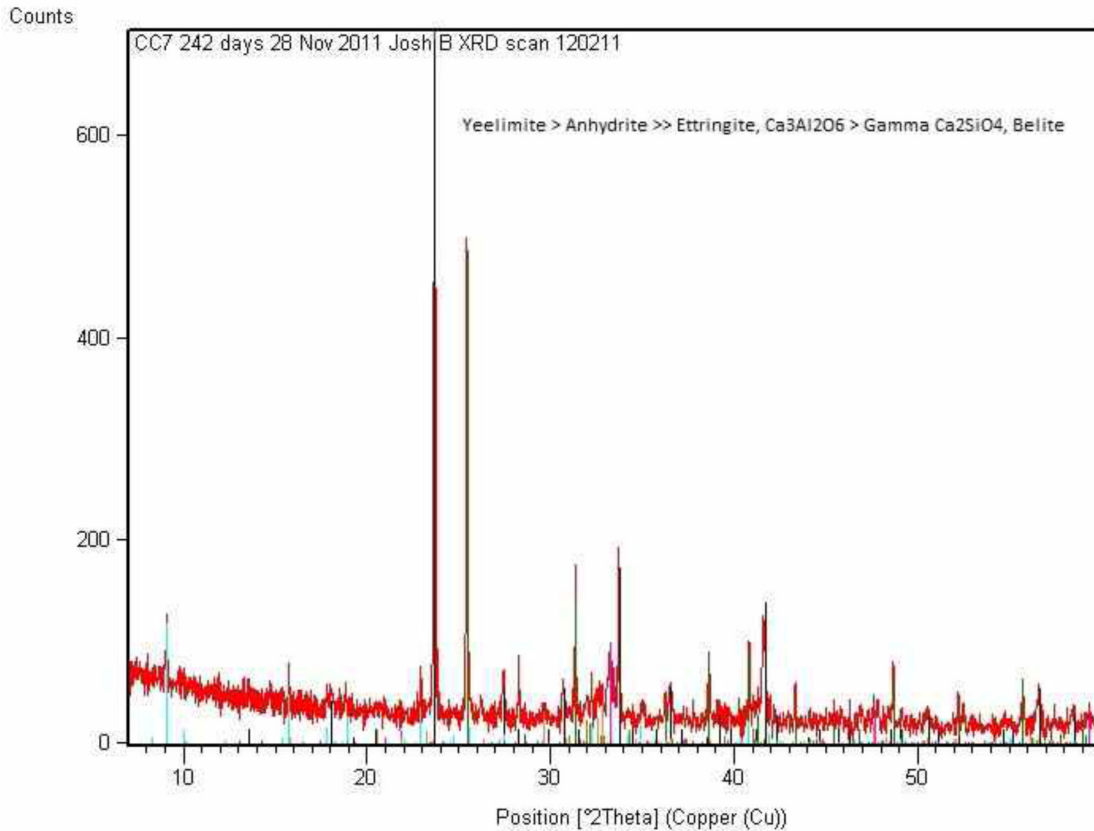
is experiencing a decrease in ettringite concentration versus time. A decrease in ettringite concentration must create changes in the microstructure for the CSA cement mortar. Such microstructural changes could very well explain the decreasing direct tensile strength trend displayed in Figure 1. Such changes suggest ettringite decomposition via dehydration or some other mechanism.

Figure 5 displays TGA/SDT analysis for cement paste 2, containing 50 weight % gypsum and 50 weight % anhydrite, in Table 3 after hydrating for 28 days and 242 days at 50% relative humidity and 23°C. As with Figure 3, the peak near 110°C represents the weight % of ettringite per degree Celsius in each sample. This peak designation for ettringite agrees with literature (Clark et al, 2006 and Sherman et al, 1995). For cement paste 2 in Table 3, the concentration of ettringite after hydrating for periods of 28 days and 242 days are 17.9% and 5%, respectively. The second peak in Figure 5 near 140°C with concentration of 8% is theorized to represent gypsum. Figure 1 shows the CSA cement mortar corresponding to cement paste 2 in Table 3 beginning to show a decreasing direct tensile strength trend between 28 days and 56 days of hydration. The results listed in both Figure 1 and Figure 5 suggest a relationship exists between direct tensile strength and ettringite concentration. Defining the specific relationship is a wonderful project for future research.

As before, the peaks located near 690°C in Figure 5 represent calcium carbonate. It is interesting to note the increase in calcium carbonate concentration for cement paste 2 in

Table 3 after hydrating for both 28 days and 242 days at 50% relative humidity and 23°C. As with all other presented trends, this data suggests ettringite decomposition as described by Skoblinskaya et al, (1975).

Figure 6 displays a XRD diffractogram for sample 2 in Table 3 after curing for 249 days at 50% relative humidity with the following characterization:

Yeelimite > Anhydrite > Gypsum > $Ca_3Al_2O_6$ > Ettringite, Wairakite, Belite, alpha Ca_2SiO_4

The concentration of ettringite in the XRD characterization relative to other constituent materials supports the TGA/SDT results displayed in Figure 5. The cement paste behavior displayed in Figures 5 and 6 suggests the CSA cement mortar containing 50 weight % anhydrite and 50 weight % gypsum is experiencing a decrease in ettringite concentration versus time. As with the other tested CSA cement materials, a decrease in ettringite concentration must create changes in the microstructure for the CSA cement mortar. Such microstructural changes could very well explain the decreasing direct tensile strength trend displayed in Figure 1.

Figure 7 displays TGA/SDT analysis for cement paste 3, containing solely gypsum as a source of calcium sulfate, in Table 3 after hydrating for 28 days and 242 days at 50% relative humidity and 23°C. As with the other TGA/SDT results, the peak near 110°C represents the weight % of ettringite per degree Celsius in each sample. For cement paste 3 in Table 3, the concentration of ettringite after hydrating for periods of 28 days and 242 days are 17%

FIGURE 5. TGA/SDT analysis for CSA cement paste with the source of calcium sulfate comprising 50 weight % anhydrite and 50 weight % gypsum in Table 3.
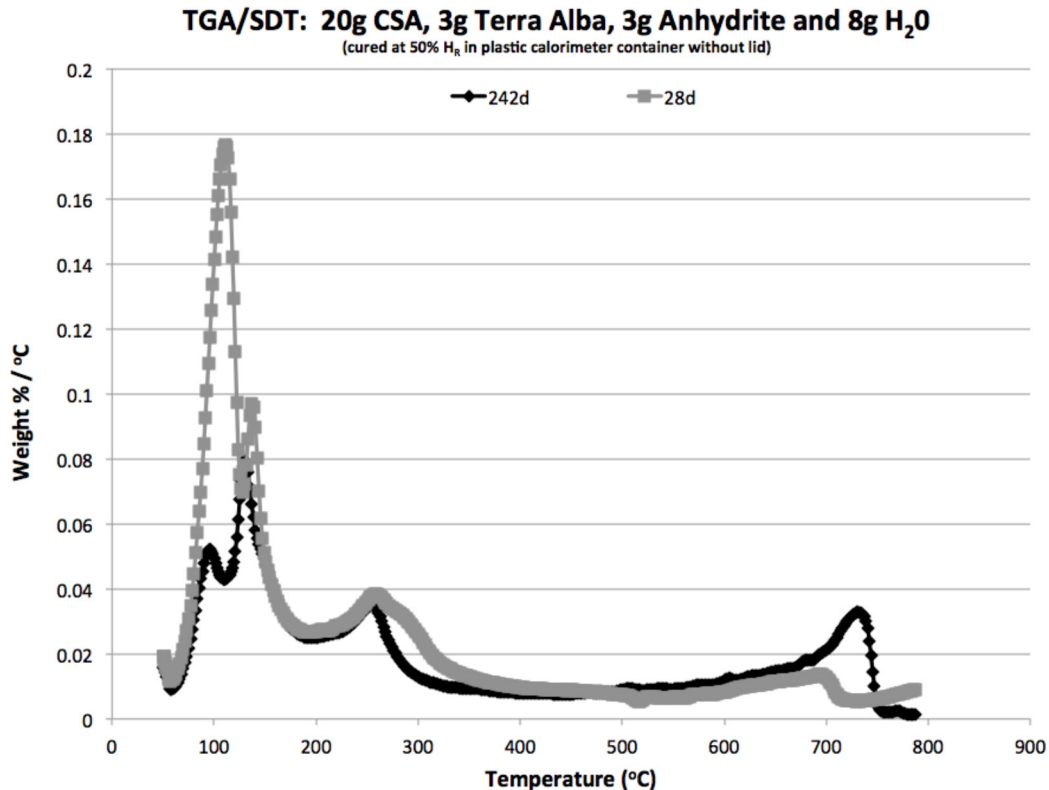
FIGURE 6. XRD diffractogram for CSA cement paste containing 50 weight % gypsum and 50 weight % anhydrite after curing for 242 days at 50% relative humidity.
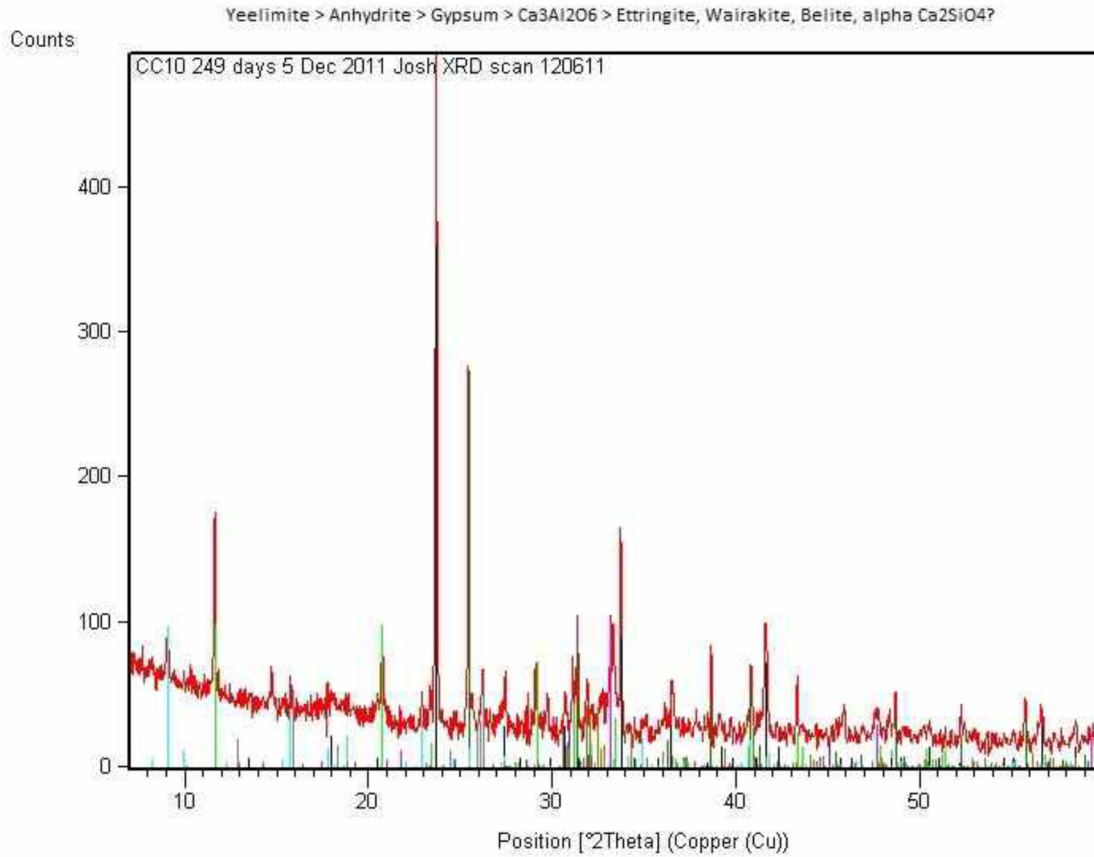

and 4%, respectively. The peak at approximately 140°C with 14% concentration is theorized to be gypsum. Figure 1 shows the CSA cement mortar corresponding to cement paste 3 in Table 3 beginning to show a decreasing direct tensile strength trend between 7 days and 28 days of hydration. The results listed in both Figure 1 and Figure 7 suggest a relationship exists between direct tensile strength and ettringite concentration; however, more data is needed to quantify the relationship.

The peaks located near 690°C in Figure 7 represent calcium carbonate. As with the other cement paste samples, it is interesting to note the increase in calcium carbonate concentration for cement paste 3 in Table 2 after hydrating for both 28 days and 242 days at 50% relative humidity and 23°C. In similar fashion to other present trends, this data suggests ettringite decomposition (Sherman et al, 1995, Sato et al, 1992). The author ponders dehydration as potentially the correct mechanism for ettringite decomposition in this low humidity curing environment.

Figure 8 displays a XRD diffractogram for sample 3 in Table 3 after curing for 249 days at 50% relative humidity with the following characterization:

Yeelimite, Gypsum >> $Ca_3Al_2O_6$ > Ettringite, Belite, Wairakite, Alpha Ca_2SiO_4?,
Gamma Ca_2SiO_4 > Anhydrite
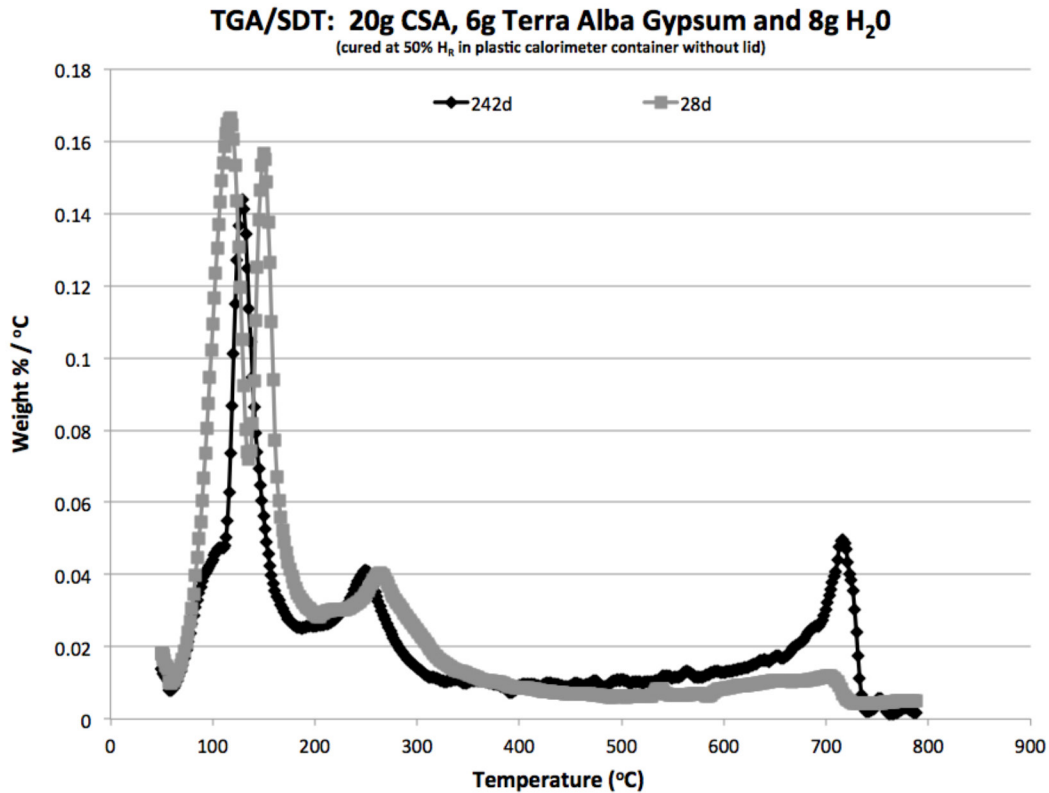
The concentration of ettringite in the XRD characterization relative to other constituent materials supports the TGA/SDT results displayed in Figure 7. As with all other presented information, the cement paste behavior displayed in Figures 7 and 8 suggests the CSA cement mortar containing solely gypsum is experiencing a decrease in ettringite concentration versus time. This and all other data suggests dehydration to be a potential mechanism for ettringite decomposition and related strength loss for the tested CSA cement mortars.

The results presented in this study suggest further research is necessary for truly understanding the long term strength behavior of calcium sulfoaluminate (CSA) cement systems cured at low humidity for extended periods of time. The statement from Taylor (1997), that carbonation behavior of cementitious systems may be overstated in laboratory conditions given higher exposed surface / total volume ratios for the tested samples may indeed be applicable to the presented results. Or, perhaps such a statement can also be extrapolated to the case of ettringite decomposition through dehydration, as sample size will certainly influence the heat and mass transfer processes necessary for desiccation.

Nevertheless, the presented results demonstrate statistically significant strength loss for four CSA cement mortars cured at ambient laboratory temperature and constant 50% relative humidity for both tensile and compression type testing scenarios. Furthermore, the results presented in this study suggest that onset of both strength loss and theorized ettringite decomposition are influenced by both amount and type of calcium sulfate incorporated into specific formulations. The water / cement (w/c) ratio for all mortars was low. However, the w/c for a

FIGURE 8. XRD diffractogram for CSA cement paste containing solely gypsum after curing for 242 days at 50% relative humidity.
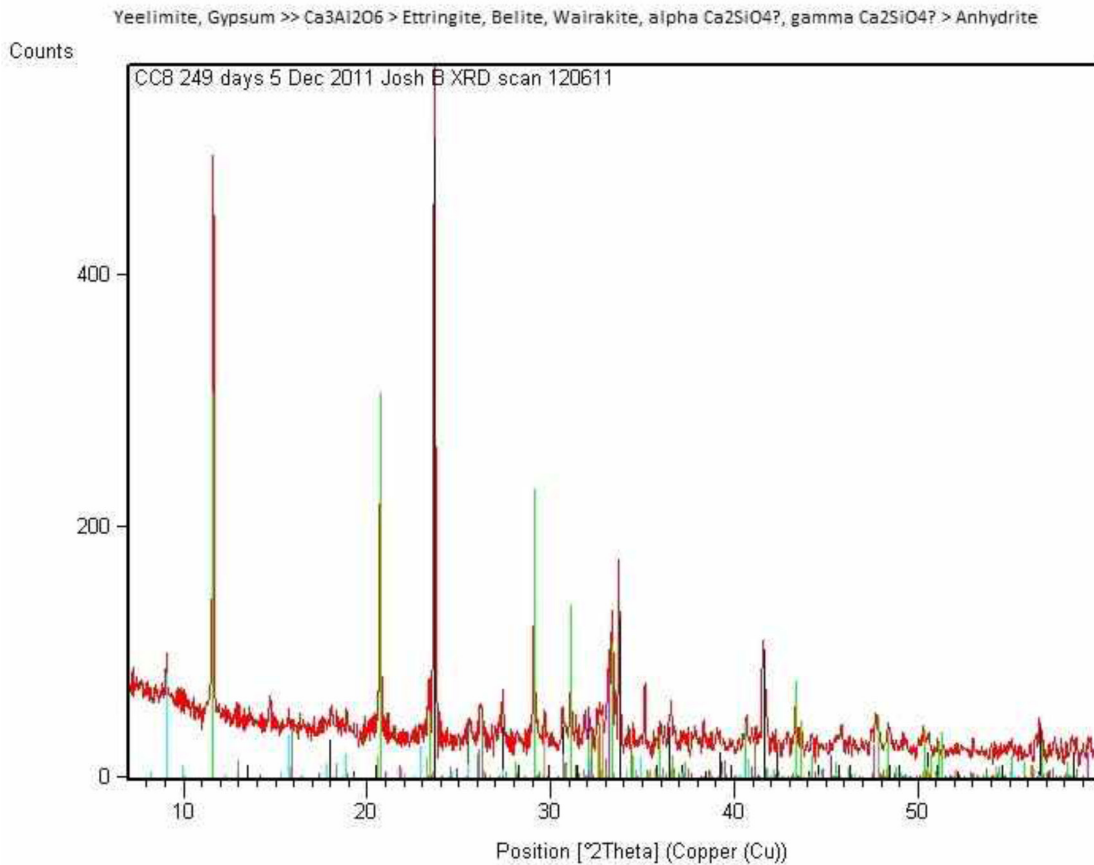
gypsum containing mortar was higher than w/c for the anhydrite containing mortars, even excluding the chemically bound water inherent to gypsum. Given this information, it is quite interesting to note that this gypsum containing mortar with the highest w/c ratio experienced the earliest onset of strength loss when compared with the other mortars.

The presented results raise questions regarding which mechanical property performance values to utilize during design of reinforced concrete structures based upon CSA cement.

CONCLUSIONS

This study assessed long-term behavior for calcium sulfoalumiante (CSA) cement materials when cured at ambient laboratory temperature and constant 50% relative humidity. The results of this study are very interesting and were largely unexpected. The results of this study suggest the rate of ettringite decomposition at ambient laboratory temperature and 50% relative humidity is dependent upon both amount and type of calcium sulfate for the tested CSA cement materials containing C_3A cast with low water / cement (w/c) ratios.

All tested CSA cement mortars, the mortar containing solely anhydrite, the mortar containing half gypsum and half anhydrite along with the mortar containing solely gypsum, displayed peak tensile strength behavior with each material experiencing a trend of decreasing direct tensile strength when cured at ambient laboratory temperature and 50% relative

humidity for extended periods of time. The results are statistically significant. The mortar containing solely gypsum was first to experience strength loss between 7 days and 28 days of hydration. The mortar containing 50 weight % gypsum and 50 weight % anhydrite as a combined source of calcium sulfate was second to experience strength loss at some point between 28 days and 56 days of curing. The mortar containing solely anhydrite was the last to experience statistically significant strength loss between 28 days and 109 days.

Additionally, CSA cement mortars displayed peak strength behavior during compressive strength testing. All results are statistically significant. The mortar containing solely gypsum as a source of calcium sulfate experienced a decreasing trend for compressive strength between 7 days and 460 days of curing at ambient laboratory temperature and constant 50% relative humidity. The mortar containing 50 weight % gypsum and 50 weight % anhydrite as a combined source of calcium sulfate experienced a decreasing compressive strength trend between 461 days and 537 days of curing at ambient laboratory temperature and constant 50% relative humidity.

The analytical results presented in this study suggest microstructural behavior in CSA cement paste systems containing C_3A cured at ambient laboratory temperature and constant 50% relative humidity is strongly dependent upon amount and type of calcium sulfate present during hydration. CSA cement pastes containing constant mass amounts of calcium sulfate but differing in specific type, solely anhydrite, half anhydrite and half gypsum, and solely gypsum, displayed different microstructural characteristics from the point of initial hydration throughout the duration of the study. The CSA cement paste containing solely gypsum displayed the most severe symptoms of ettringite decomposition followed by the CSA cement paste containing half anhydrite and half gypsum. When compared with the other pastes, the CSA cement paste containing solely anhydrite exhibited symptoms of ettringite decomposition at the latest age.

The results presented in this study support dehydration as the root cause of ettringite decomposition.

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