INFLUENCE OF LATEX POLYMER ADDITION ON THE BEHAVIOR OF MATERIALS CONTAINING CSA CEMENT CURED AT LOW HUMIDITY

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ABSTRACT

The present study assesses the hydration behavior of polymer modified and non-polymer containing calcium sulfoaluminate (CSA) cement pastes containing minor phase tri-calcium aluminate (C_3A) when cured at ambient laboratory temperature with 50% relative humidity. The particular CSA cement is unique as it offers two potential paths for ettringite formation. In the presence of sufficient calcium sulfate, these two potential paths stem from either hydration of yeelimite or hydration of tri-calcium aluminate. The study assesses the microstructural behavior of cement pastes utilizing powdered x-ray diffraction (XRD) and thermogravimetric analysis (TGA/SDT). Additionally, the study utilizes direct tensile strength testing according to ASTM C307, Standard Test Method for Tensile Strength of Chemical Resistant Mortar, Grouts and Monolithic Surfacings to quantify relationships between microstructural characteristics and mechanical property performance for representative mortars. The present study is significant as it illustrates differences in microstructural behavior for CSA cement materials with and without polymer cured at constant 50% relative humidity. The present study suggests ettringite decomposition occurs within non-polymer containing CSA cement paste samples cured at constant low humidity. The present study presents polymer modification as an effective means for mitigating ettringite decomposition and subsequent strength loss in materials containing CSA cement cured at constant 50% relative humidity and 23°C.

KEYWORDS

calcium sulfoaluminate cement; latex polymer; CSA cement strength loss; ettringite decomposition

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1.0 INTRODUCTION

The challenge of sustainable development is meeting human demands while staying within the ecological limits of the planet (WBCSD 2010). In this regard, a challenge for the cement industry is finding alternative hydraulic binders to substitute for use of ordinary portland cement (CEM1) in widespread construction practices, as CEM1 production yields 0.9kg CO_2 / kg clinker (Malhotra et al, 2012). Estimates suggest the cement industry, through production of CEM1, produces approximately 5% of global manmade CO_2 emissions (Damtoft et al, 2008). Demand for cement in developing countries rose by 55% in the 1990s, and it is expected that, by 2020, global demand will have increased by 115–180% from 1990 levels, with a four-fold increase likely by 2050 (Damtoft et al, 2008). The research community is well aware of the environmental stakes associated with such future demand, and significant efforts are continually being made to reduce the environmental burden associated with perhaps the most common construction practice on the planet.

Calcium sulfoaluminate (CSA) cement is a potential environmentally friendly substitute for CEM1 is specific applications (Gartner et al, 2011). CSA cement differs from ordinary portland cement (CEM1) as its main clinker materials are not silica based but are sulfate phases produced by heating gypsum, bauxite and limestone in a conventional rotary kiln at 1300°C (2372°F) (Gastaldi et. al, 2009). CEM1 is produced by heating a mixture of limestone and shale in a kiln at 1500°C (2732°F) (Illston et. al, 2007). When compared with production of CEM1, the CSA cement production process allows lower kiln temperatures while emitting less carbon dioxide as less limestone is required to produce CSA cement (Marroccoli et. al, 2010). Although production of CSA cements are attractive from an environmental point of view, it is important to note that 1:1 complete substitution of CSA for CEM1 is not currently practical on a global scale given limited quantities of aluminate containing virgin raw materials necessary for CSA cement production. Therefore, with status quo technology, it is important to designate niche markets where demand is such that substitution of CSA for CEM1 is indeed practical.

From a long-term perspective, little is known about the use of CSA cement as a stand-alone hydraulic binder. As new types of cement are becoming increasingly popular for substituting the use of CEM1 in various applications, it is becoming increasingly important to develop a complete understanding of the hydration characteristics associated with these newer cements (Schneider et al, 2011, Scrivener et al, 2011). Different cement types hydrate to form phases of different chemistry during the process of "setting and hardening"; therefore, one cannot simply assume reported compatibility of commonly used admixtures with CEM1 will hold true for combinations of the same admixtures and hydraulic binders of different chemistry.

The present study assesses the influence of latex polymer addition on the microstructural behavior of materials based upon CSA cement containing minor phase tri-calcium aluminate (C_3A) cured at constant 50% relative humidity. Vinyl acetate / ethylene based dispersible polymer powders (VAE DPP) are widely used for modification of mortars containing CEM1 or blends of calcium aluminate cement (CAC) and CEM1. Numerous publications exist describing the interactions of these well known cementitious systems when cured under differing conditions (ACI 548.1R-09, ACI 503.5-R92, ACI 548.4-93, Ohama 1995, Chandra and Ohama 1994). Although an abundance of literature exists for polymer modified CEM1 systems, little is known about strength development for polymer modified calcium sulfoaluminate cement systems.

Additionally, the analyzed CSA cement is somewhat unique as it offers two potential hydration mechanisms for ettringite formation. Cement nomenclature is utilized in specific instances throughout this document. In cement nomenclature, C = CaO, S = SiO_2, A = Al_2O_3, $\bar{S}$ = SO_3 and H = H_2O.

In the presence of sufficient calcium sulfate and water, CSA cements hydrate to form ettringite. The mineral name ettringite refers to the calcium trisulphoaluminate hydrate ($C_6A\bar{S}_3H_{32}$) found in several hydrated construction cements (Grounds et al, 1988). One potential reaction scheme for yeelimite hydrating to form ettringite is listed below (Gastaldi et al, 2009):

$$C_4A_3\bar{S} + 2CS + 38H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \qquad (1)$$

Reaction 1 displays yeelimite, anhydrite and water hydrating to form ettringite and aluminum hydroxide.

Tri-calcium aluminate (C_3A) also hydrates to form ettringite in the presence of sufficient calcium sulfate and water. Reaction 2 below lists one possible reaction mechanism (Pourchet et al, 2009):

$$C_3A + 3C\bar{S} + 32H \rightarrow C_6A\bar{S}_3H_{32} \qquad (2)$$

Reaction 2 lists tri-calcium aluminate plus anhydrite and water to form ettringite.

When compared with other hydrated cement phases, the chemical structure of ettringite possesses an abundance of water. Therefore, CSA cements tend to have high chemical water demands (CWD) and are known for somewhat rapid desiccating behavior during hydration due to ettringite formation (Glasser et al, 2001). Additionally, it is well known that ettringite has relatively low resistance to CO_2 attack (Sherman et al, 1995, Sato et al, 1992). 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 CEM1 materials (Jewell et al, 2009, Sherman et al, 1995). It is also well known that ettringite is subject to decomposition through dehydration mechanisms (Zhou et al, 2004, Zhou et al, 2001, Skoblinskaya, 1975).

Taylor (1997) reports that carbonation behavior in laboratory experiments might be extreme given large available surface area to volume ratios when compared with field type applications, which are much larger in scale. Supporting this concept, Zhang et al, (2005), report concrete specimens based upon CSA cement removed from field service after many years of service display nearly no signs of decomposition resulting from carbonation mechanisms.

In a previous work, the authors discuss observations on long-term strength loss in laboratory type samples containing CSA cement cured at constant 50% relative humidity and 23°C as a result of ettringite decomposition. The present work presents a novel means for mitigating ettringite decomposition and subsequent strength loss in laboratory type samples based upon identical CSA cement. The present work should contribute to the body of knowledge necessary for furthering the sustainable building initiative.

2.0 MATERIALS

Cement

CSA cement containing tri-calcium alumiante (C_3A) was utilized in this study. XRD analysis provides the following listing of constituent materials:

Yeelimite >> Tri-Calcium Aluminate > Belite > Anhydrite (trace quantity)

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.

Polymer

A vinyl acetate / ethylene based dispersible polymer powder (VAE DPP) with glass transition temperature (T_g) of 20°C was utilized in the polymer modified materials.

3.0 EXPERIMENTAL PROGRAM

This study provides a detailed phase analysis for CSA cement pastes cured at constant 50% relative humidity and 23°C. The study includes information derived from both thermogravimetric analysis (TGA/SDT) and powder X-Ray diffraction (XRD). The study incorporates direct tensile strength testing as a means for quantifying changes in microstructural characteristics.

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 23°C. For each respective set of analyses, 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. It is important to note that quantitative Rietveld analysis was not utilized for characterizing concentrations of constituent materials for each sample.

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.

Cement Pastes

Two CSA cement paste mix designs were analyzed after curing at 50% relative humidity. These mix designs are displayed in Table 1. Each mix design had constant mass amounts of

CSA cement, calcium sulfate and water. One mix design contained vinyl acetate / ethylene dispersible polymer powder with polymer / cement ratio (p/c) of 0.15. The water / cementitious materials ratio for each mix design was 0.31.

For preparing the cement pastes, individual components were weighed and placed into a plastic calorimeter container. After all components were added, the container was sealed and shaken vigorously by hand for approximately 10 seconds. After mixing the dry components, water was added, and the paste was then mixed to homogenous consistency by hand with a spatula. After mixing, each container was placed in a curing cabinet at 50% relative humidity and 23°C. The lids were not placed on the little plastic calorimeter containers containing the cement paste samples during the entire curing regimen.

Mortars

Two CSA cement based mortar mix designs were analyzed for direct tensile strength. The mix designs are displayed in Table 2. Each mix design had constant mass amounts of CSA cement, calcium sulfate and sand. One mix design contained vinyl acetate / ethylene dispersible polymer powder with polymer / cement (p/c) ratio of 0.15. Each mix design possessed identical water / cementitious materials ratios of 0.33. 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.

TABLE 1. CSA cement paste formulations for analytical analyses.

Paste Sample	1	1	2	2
Relative Humidity	100%	50%	100%	50%
Temperature	23°C	23°C	23°C	23°C
Materials	mass (g)	mass (g)	mass (g)	mass (g)
CSA Cement	20	20	20	20
Anhydrite	6	6	6	6
VAE DPP			4	4
Total Mass	26	26	30	30
Deionized Water	8	8	8	8

TABLE 2. CSA cement mortar formulations by mass for ASTM C307 direct tensile strength testing.

CSA Cement Mortars	Solely Anhydrite	Anhydrite plus VAE DPP
Materials	Mass (g)	Mass (g)
CSA Cement	500	500
Anhydrite	160	160
VAE DPP T_g = 20°C	0	100
Coarse Sand	125	125
Graded Sand	1375	1375
DI Water	220	220

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 ASTM C307, Standard Test Method for Tensile Strength of Chemical Resistant Mortar, Grouts and Monolithic Surfacings. During the first 24 hours of curing, each test specimen remained in the mold on the bench top covered with plastic. After this initial curing period, test specimens were removed from their molds and either tested or placed in their respective curing chambers.

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-α)th percentile of the distribution of the Studentized range of k means with υ 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 100α% level if their absolute difference exceeds

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

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

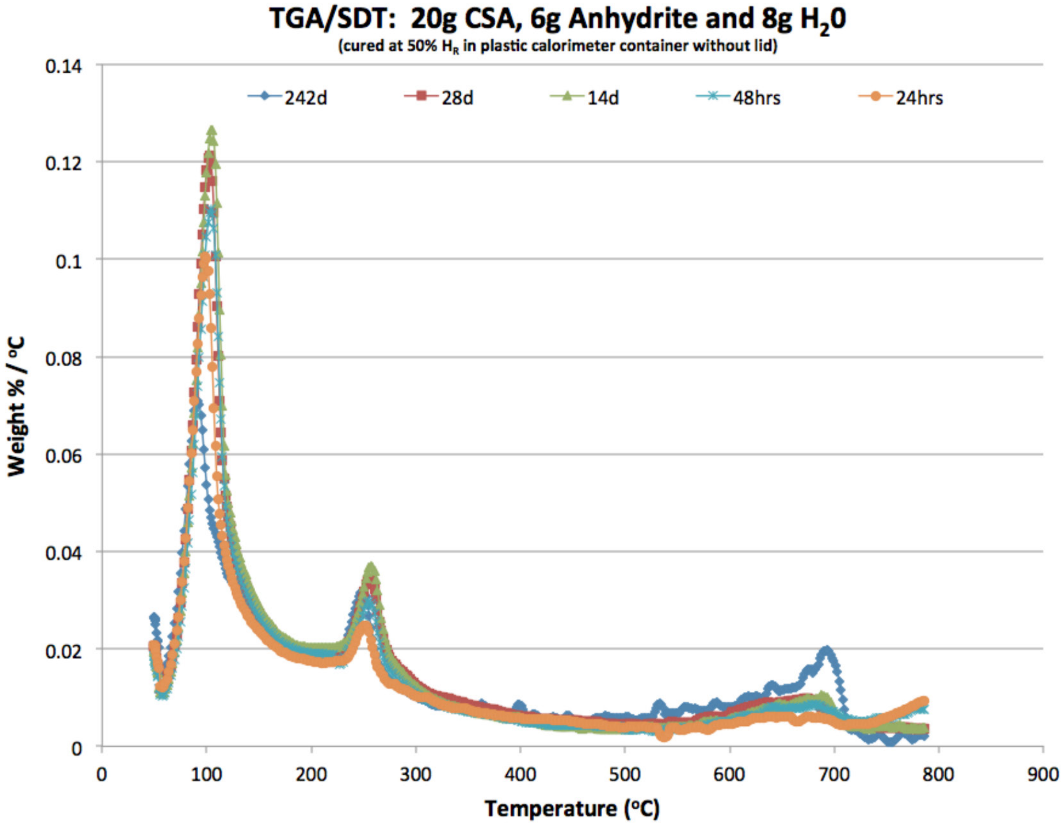
ANOVA reporting for this study presents an observed F-value written with convention F(degrees of freedom between / degrees of freedom within) = value, a significance level p-value, the pooled standard deviation and a value for R^2.

5.0 RESULTS

5.1 Hydration with anhydrite as a source of calcium sulfate at 50% H_R

Figure 1 displays TGA/SDT analysis for CSA cement paste 1 containing solely anhydrite in Table 1 after curing for periods of 24 hours, 48 hours, 7 days, 14 days, 28 days and 242 days

FIGURE 1. TGA/SDT analysis of CSA cement paste 1 containing solely anhydrite in Table 1 after curing for periods of 24 hours, 48 hours, seven days, 14 days, 28 days and 242 days at 50% relative humidity and 23°C.



at 50% relative humidity and 23°C. The peak designations for Figure 1 are in agreement with literature describing the water associated with ettringite decomposition near 120°C and aluminum hydroxide decomposition in the vicinity of 250°C (Sherman et al, 1995, Sato et al, 1992, Sato, 1985). It is interesting to note the concentration of ettringite seems to increase for hydration periods of 24 hours through 14 days, then the concentration of ettringite seems to decrease from 14 days through 242 days of hydration at constant 50% relative humidity and 23°C.

Figure 2, Figure 1 without additional curves, displays TGA/SDT analysis of CSA cement paste 1 containing solely anhydrite in Table 1 after curing for periods of 28 days and 242 days at 50% H_R. As with other TGA/SDT related figures, the peak near 120°C represents the concentration of ettringite which seems to decrease between 28 days and 242 days of hydration. The aluminum hydroxide peak near 250°C in Figure 2 seems to remain somewhat constant while the calcium carbonate peak near 700°C seems to increase slightly after 242 days of hydration. The decrease in ettringite concentration coupled with the increase in calcium carbonate concentration suggests ettringite decomposition is taking place between 28 days and 242 days of hydration at constant 50% relative humidity and ambient laboratory temperature of 23°C (Sato et al, 1992, Skoblinskaya et al, 1975).

Table 3 displays XRD characterizations for the cement paste sample containing solely anhydrite in Table 1 cured at 23°C and 50% relative humidity. It is important to note that

FIGURE 2. TGA/SDT analysis of CSA cement paste 1 containing solely anhydrite in Table 1 after curing for periods of 28 days and 242 days at 50% relative humidity and 23°C.

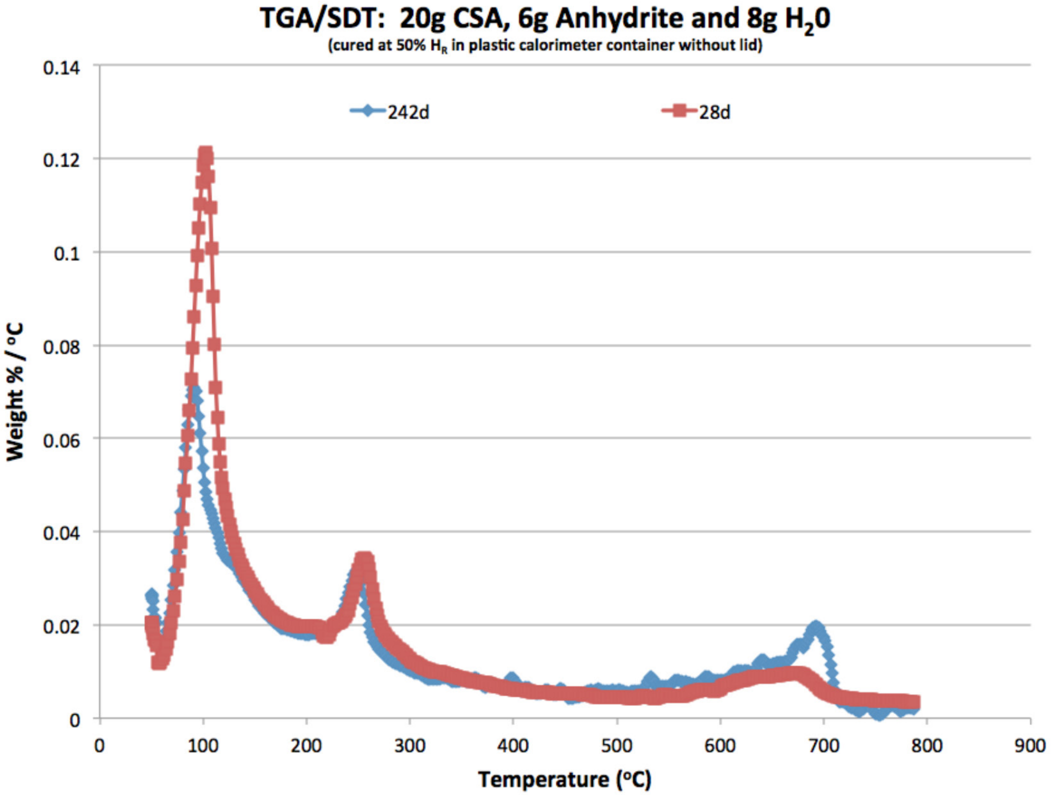


TABLE 3. Interpretations of XRD diffractograms for the cement paste containing solely anhydrite in Table 1 cured at 23°C and 50% relative humidity.

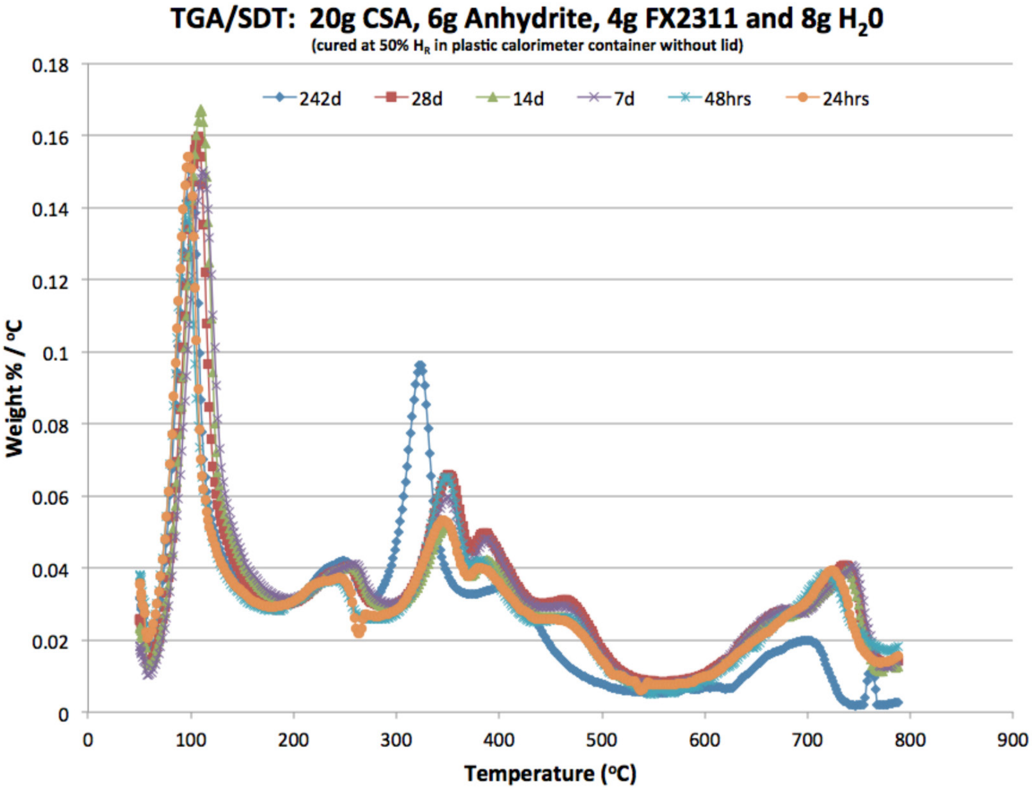
24 hours	Yeelimite > Anhydrite > Brownmillerite, $Ca_3Al_2O_6$ > alpha Ca_2SiO_4, Ettringite, Belite
21 days	Yeelimite > Anhydrite >> Brownmillerite, $Ca_3Al_2O_6$ > Ettringite, Belite, alpha-Ca_2SiO_4
28 days	Yeelimite > Anhydrite >> Brownmillerite, $Ca_3Al_2O_6$ > Ettringite, Belite, alpha-Ca_2SiO_4
242 days	Yeelimite > Anhydrite >> Ettringite, $Ca_3Al_2O_6$ > Gamma Ca_2SiO_4, Belite

quantitative Rietveld analysis was not utilized to arrive at the results displayed in Table 3. Overall, the information displayed in Table 3 supports the information presented in Figures 1 and 2. Ettringite is present after 24 hours of hydration and reactants yeelimite and anhydrite display the greatest concentration of materials, which confirms onset of hydration reactions as previously described. After hydrating for 21 days, ettringite continues to display a minor concentration relative to other materials while reactants yeelimite and anhydrite show the greatest material concentrations with concentration of yeelimite being greater than concentration of anhydrite. Again, this is to be expected with water conceivably being the limiting reagent for such materials with low water / cement ratio given the rapid desiccating nature of ettringite formation. Between 21 days and 28 days of hydration, essentially no significant differences exist for microstructural constituent materials. After hydrating for 242 days, the material composition of the cement paste sample seems to have changed considerably as brownmillerite and alpha-Ca_2SiO_4 are no longer detected while ettringite continues to display a minor concentration relative to other materials.

5.2 Hydration with materials incorporating VAE DPP utilizing anhydrite as the source of calcium sulfate cured at 50% H_R

Figure 3 displays TGA/SDT analysis of CSA cement paste 2 containing anhydrite and VAE dispersible polymer powder with T_g = 20°C in Table 1 after hydrating for periods of 24 hours, 48 hours, 7 days, 14 days, 28 days and 242 days at 50% relative humidity and 23°C. The interesting aspects of Figure 3 are the somewhat constant concentrations of ettringite for all curing periods, the increase in aluminum hydroxide concentration and the apparent decrease in calcium carbonate content. The peaks near 120°C suggest the concentration of ettringite remains relatively constant for hydration periods ranging from 24 hours to 242 days. Additionally, a new peak seems to have emerged near 300°C for the polymer modified CSA cement paste after hydrating for 242 days at constant 50% relative humidity and 23°C. Before labeling this peak, it is important to note a number of items, one of which is that VAE DPP includes anti-caking agents added during production. Examples of typical anti-caking agents are calcium carbonate and kaolin clay, which are often added in the range of 10 to 15 percent by total dry mass. The indirect addition of calcium carbonate is interesting as Winnefeld and Lothenbach, (2013), report the ternary system, yeelimite, calcium sulfate, calcium

FIGURE 3. TGA/SDT analysis of CSA cement paste 2 containing anhydrite and VAE dispersible polymer powder with T_g = 20°C in Table 1 after hydrating for periods of 24 hours, 48 hours, 14 days, 28 days and 242 days at 50% relative humidity and 23°C.



carbonate has potential to form either hemicarbonate or monocarbonate in addition to the primary hydration assemblages ettringite, monosulfate and aluminum hydroxide (Winnefeld and Lothenbach, 2013). Furthermore, the authors suggest hemi-carbonate may initially form and coexist for some period of time, likely due to slow formation kinetics of moncarbonate as observed in ordinary portland cement, before reacting with yeelimite and calcite to form either ettringite or monocarbonate (Winnefeld and Lothenbach, 2013). Additionally, literature reports for CSA cements containing accessory phases, C-S-H, C_2ASH_8 or calcium aluminate hydrates, mainly CAH_{10} or C_4AH_{13}, can be formed in addition to the aforementioned primary hydration assemblages (Pelletier-Chaignat et al, 2012). Before labeling the new late age peak at 300°C, consideration should also be given to reports suggesting the constituent material belite reacts slower than yeelimite ultimately forming stratlingite at later ages (Romain et al, 2013). It is well known metastable aluminate hydrates, with examples being CAH_{10}, C_4AH_{13} or C_2ASH_8 may convert to C_3AH_6, hydrogarnet, at later ages (Taylor, 1997). Literature reports thermal decomposition characteristics of monocarbonate, gamma aluminum hydroxide and hydrogarnet possessing similar peaks near 300°C (Chowaniec, 2012, Gameiro et al, 2012, Gabrovsek et al, 2008, Scrivener and Capmas, 1998, Taylor, 1997). The size of the new peak at 300°C is significant relative to other materials. Given this information, it is theorized the new peak near 300°C is associated with monocarbonate. The theory is further supported by the peaks near 450°C for the early age samples, likely representing hemicarbonate, which are not visible with analysis of the later age sample. The presence of hemicarbonate at early ages of hydration suggests the polymer modified CSA cement paste containing minor amounts of calcium carbonate hydrated to form ettringite, aluminum hydroxide, hemicarbonate and possibly monosulfate during the early ages, where the hemicarbonate converted to monocarbonate at later ages, which agrees with literature (Winnefeld and Lothenbach, 2013). In further support, Chowaniec, (2012), displays thermogravimetric analysis (TGA) charts for decomposition of both hemicarbonate and monocarbonate where the peak near 450°C is noted as a means for differentiating hemicarbonate from monocarbonate, as the peak does not appear during TGA analysis of monocarbonate. Additionally, the relatively constant concentrations of ettringite throughout the duration of all analyses together with the either constant or decreasing concentrations of calcium carbonate suggest latex polymer addition as an effective means for mitigating ettringite decomposition in the tested CSA cement pastes. The peaks between 700 and 800°C suggest the calcium carbonate concentration decreased between 28 days and 242 days hydration, which also supports formation of monocarbonate at later ages. The relatively constant concentrations of ettringite throughout the duration of all analyses together with the either constant or decreasing concentrations of calcium carbonate suggest latex polymer addition as an effective means for mitigating ettringite decomposition in the tested CSA cement pastes.

Figure 4 displays TGA/SDT analysis of CSA cement the polymer modified CSA cement paste containing anhydrite and VAE dispersible polymer powder with T_g = 20°C in Table 1 after hydrating for periods of 28 days and 242 days at 50% relative humidity and 23°C. As previously mentioned, the peaks near 120°C represent a somewhat constant concentration of ettringite for both samples, while the peaks between 700 and 800°C are theorized to represent a decrease in calcium carbonate content, further supporting the theory associated with the conversion of hemicarbonate to monocarbonate at later ages.

Table 4 displays XRD characterizations for the cement paste sample containing anhydrite and VAE DPP with T_g = 20°C cured at 23°C and 50% relative humidity. It is important

FIGURE 4. TGA/SDT analysis of CSA cement paste 2 containing anhydrite and VAE dispersible polymer powder with T_g = 20°C in Table 1 after hydrating for periods of 28 days and 242 days at 50% relative humidity and 23°C.

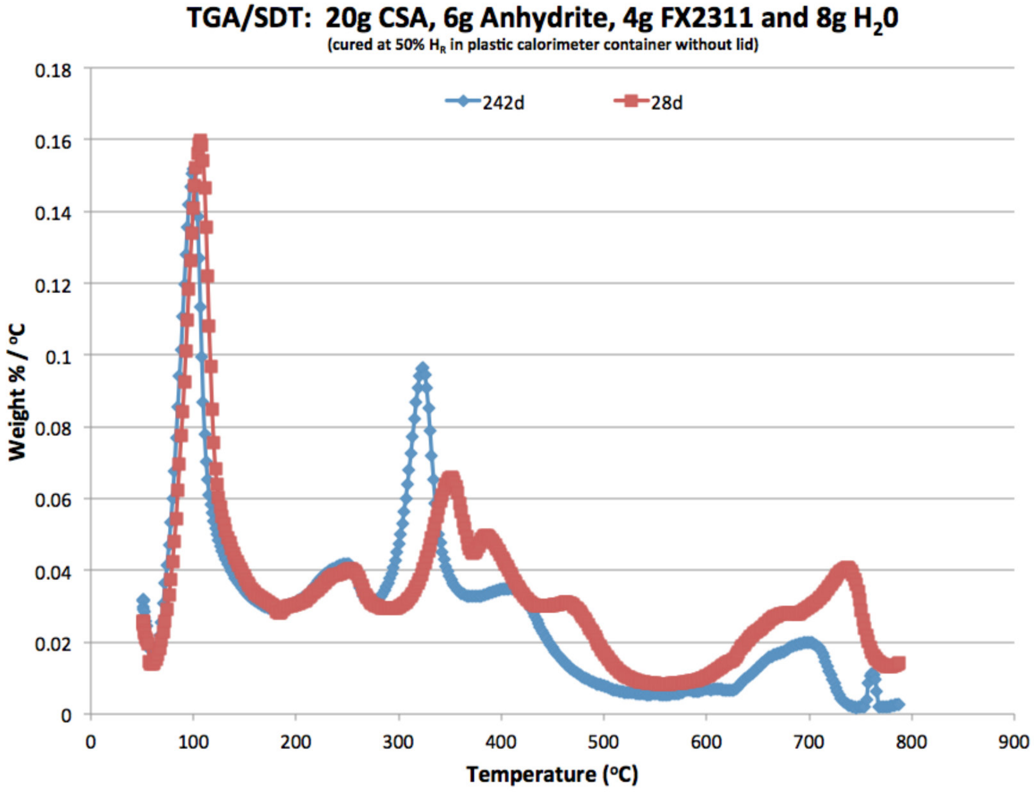


TABLE 4. Interpretations of XRD diffractograms for the cement paste containing solely anhydrite and VAE DPP with T_g = 20°C cured at 23°C and 50% relative humidity.

24 hours	Yeelimite > Anhydrite > $Ca_3Al_2O_6$, Ettringite, Brownmillerite > alpha Ca_2SiO_4 > Belite
21 days	Yeelimite > Anhydrite > Brownmillerite , Ettringite, $Ca_3Al_2O_6$ > Belite, alpha Ca_2SiO_4
28 days	Yeelimite > Anhydrite >> Brownmillerite , Ettringite, $Ca_3Al_2O_6$ > Belite, alpha Ca_2SiO_4
242 days	Yeelimite > Anhydrite > Ettringite > $Ca_3Al_2O_6$ > Belite

to note that quantitative Rietveld analysis was not utilized to arrive at the results displayed in Table 4. Overall, the information displayed in Table 4 supports the information presented in Figures 3 and 4. Ettringite is present after 24 hours of hydration and reactants yeelimite and anhydrite display the greatest concentration of materials. After hydrating for 21 days, ettringite continues to display a minor concentration relative to other materials while reactants yeelimite and anhydrite show the greatest material concentrations with concentration of yeelimite being greater than concentration of anhydrite. Essentially no significant differences exist for microstructural constituent materials between 21 days and 28 days of hydration. After hydrating for 242 days, the material composition of the cement paste sample changed somewhat as both Brownmillerite and alpha Ca_2SiO_4 disappeared from the characterization.

6.0 DISCUSSION

The results of this study were largely unexpected as materials based upon CSA cement are not well known for demonstrating ettringite decomposition and subsequent strength loss when applied in plausible environments. Presented mechanical property results appear "ad hoc" in nature as previously cast mortar samples were re-assigned to this study in an effort to validate the analytical analyses. Unfortunately, only a limited number of data points exist for mechanical property testing, as these were the only samples remaining which were cast from the same buckets of materials.

Tensile strength testing is ideal for quantifying changes in microstructural characteristics as tensile testing seeks out the weakest link (Chandra et al, 2003). Figure 5 is a long-term comparison of average direct tensile strength values for the non-polymer modified mortar containing solely anhydrite in Table 2 when cured at 50% relative humidity and 23°C. As displayed, the strength development trend increased from the point of initial hydration up through some period between 28 days and 56 days, with a recorded peak at 28 days of 633psi (4.364MPa). Afterward, the trend turned negative clearly illustrating a period of decreasing direct tensile strength with a 109 days average value of 539psi (3.716MPa).

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 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

FIGURE 5. Direct tensile strength for CSA cement mortar containing anhydrite as a source of calcium sulfate cured at ambient temperature and constant 50% relative humidity.

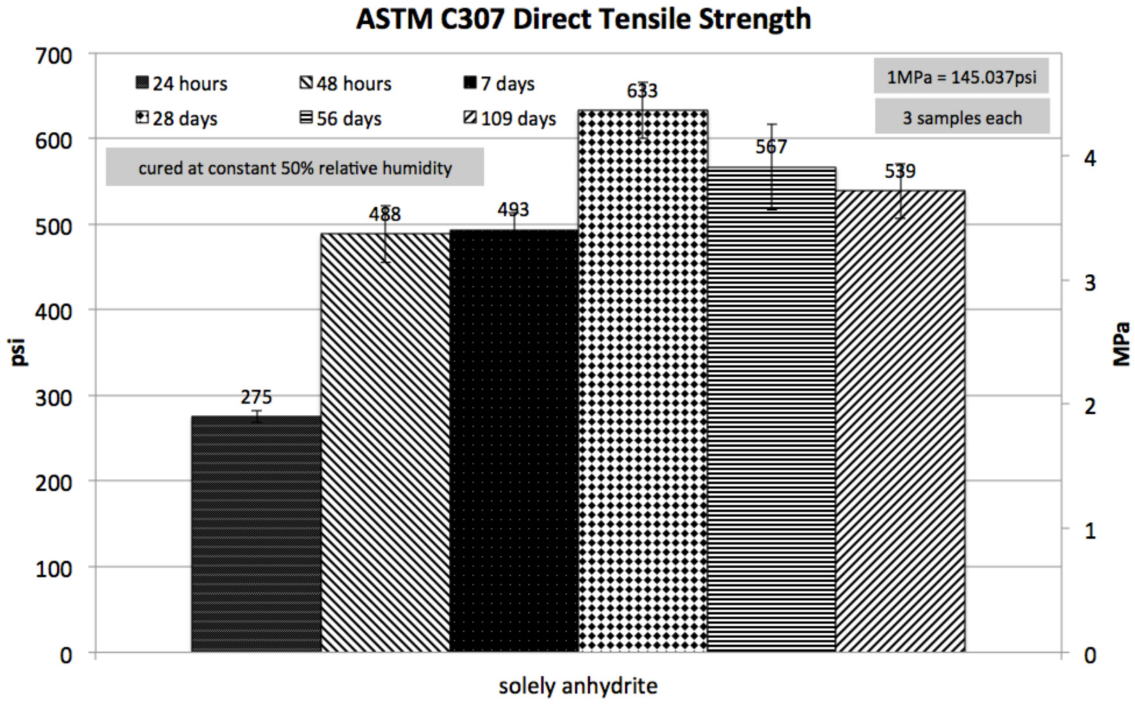


TABLE 5. Direct tensile strength classifications as assigned by statistical comparison methods for the CSA cement mortar containing solely anhydrite in Table 1. Direct tensile strength results for specific curing regimens not sharing the same letter are significantly different.

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

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 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 non-polymer modified CSA cement mortar containing anhydrite in Table 2 is statistically significant for the period from 28 days to 109 days. It is theorized this statistically significant strength loss trend for smaller, laboratory type samples stems from the ettringite decomposition behavior highlighted in both Figure 2 and Table 3.

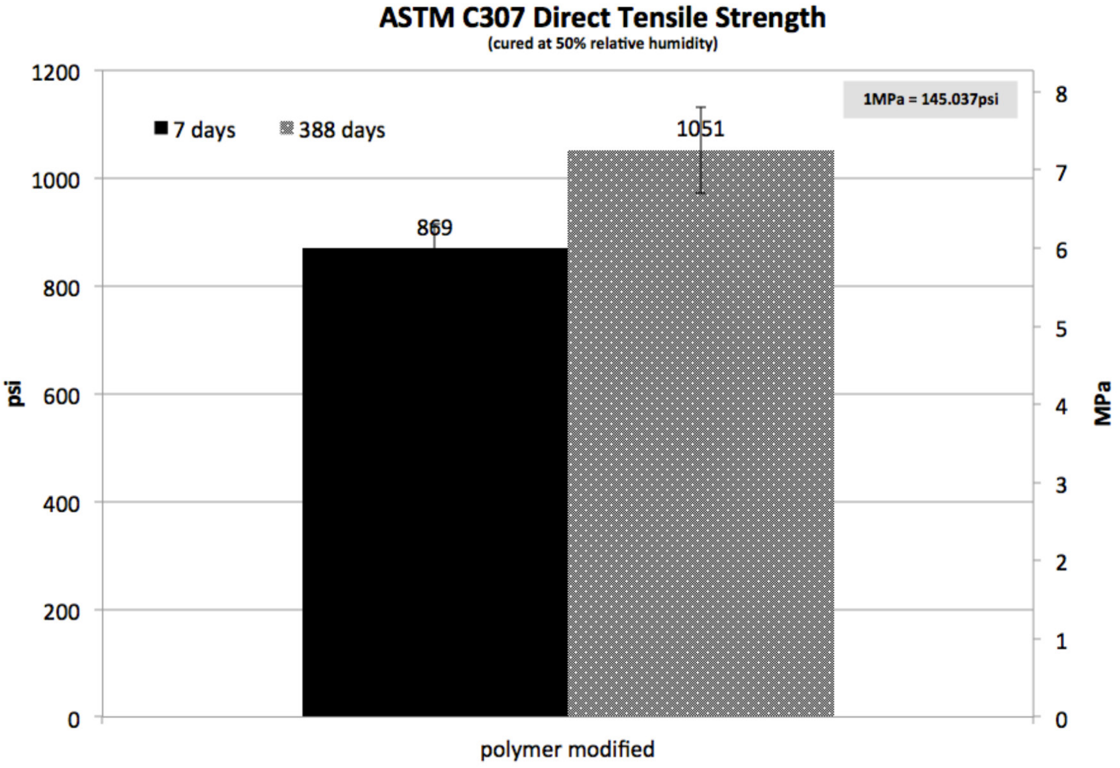
Figure 6 displays the polymer modified CSA cement mortar displayed in Table 2 having average direct tensile strength values of 869psi (5.9MPa) and 1051psi (7.2MPa) after curing for 7 days and 388 days, respectively. The results presented in Figure 6 support latex polymer addition as a viable means for mitigating strength loss in materials based upon CSA cement when applied in low humidity environments. Such a trend of increasing direct tensile strength over the long-term further supports information presented in both Figure 4 and Table 5 suggesting ettringite decomposition does not occur in polymer modified CSA cement pastes cured at constant 50% relative humidity and 23°C with p/c = 0.15.

CONCLUSIONS

In conclusion, the presented calcium sulfoaluminate (CSA) cement study indicates microstructural behavior for this cement containing minor phase tri-calcium aluminate is influenced by addition of vinyl acetate / ethylene dispersible polymer powder (VAE DPP) at a polymer / cement ratio of 0.15. The experimental results indicate VAE DPP and CSA cement are compatible materials when cast with p/c = 0.15 and dry cured at 23°C with constant 50% relative humidity.

CSA cement pastes containing solely anhydrite displayed ettringite decomposition behavior for later age samples cured at constant 50% relative humidity and 23°C, as the concentration of ettringite decreased between 28 days and 242 days of hydration. Likewise, direct tensile strength testing for the CSA cement mortar containing solely anhydrite displayed a statistically significant trend of decreasing strength between 28 and 109 days of curing at constant 50% relative humidity.

FIGURE 6. Direct tensile strength according to ASTM C307 for the polymer modified CSA cement mortar displayed in Table 2.



CSA cement pastes containing anhydrite and VAE polymer with T_g = 20°C and p/c = 0.15 did not experience a significant decrease in ettringite concentration at later ages suggesting latex polymer addition as an effective means for mitigating ettringite decomposition in materials based upon CSA cement. Additionally, the limited direct tensile strength data for the corresponding polymer modified CSA cement mortar displayed an increase in direct tensile strength for later age samples cured at 23°C and 50% relative humidity.

The presented results are of great value as they suggest latex polymer addition as an effective means for mitigating ettringite decomposition and subsequent strength loss in CSA cement materials cured at constant low humidity.

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