Effects of combination of retarders on CSA cement systems

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Abstract

One method of increasing the sustainability of concrete construction through reductions in emissions and energy requirements is through the use of alternative binders. Calcium Sulfoaluminate (CSA) cement has been developed as a low energy cement, as it has up to 40% less embodied carbon dioxide emissions due to its lower calcium content and reduced clinkering temperature relative to Portland cement. However, despite the advantages of CSA cement, its rapid setting time limits the use of this material to applications when short working time is required. To facilitate better control of the timing of CSA hardening and strength gain, several approaches to retarder usage and dosing have been studied. In this paper, use of chemical retardants, including citric acid, tartaric acid, and borax with CSA cement used alone and in combination with each other, and their effects on phase development and hardened binder properties were evaluated and discussed in relation to their retardation mechanisms. Because of differing working mechanisms of the retarders, combinations of citric acid and borax showed relationships that averaged the properties of each retarder, while combinations of citric acid and tartaric acid showed relationships that added the effects of the two retarders together. Setting time of CSA cement was delayed successfully, using retarders both alone and in combination, however combination mixes generally decreased compressive strength compared to the strengths of equivalent total singular retarder dosage. Relationships between heat release and setting time were developed and may prove useful for prediction of largescale application field performance.

Keywords: *calcium sulfoaluminate cement, hydration, retarders, compressive strength, setting time.*

1 Introduction

Although OPC (Ordinary Portland Cement) is the most commonly used concrete binder, it consumes 10-11 EJ of energy annually, and during its manufacturing process emits high amounts of carbon dioxide (Juenger et al., 2011; Shi et al., 2011). Calcium sulfoaluminate (CSA) cement was developed in China in 1970s as an alternative, environmentally friendly and sustainable cement and has begun attracting large interest worldwide (Glasser and Zhang, 2001; Péra and Ambroise, 2004). It has lower clinkering temperature and lower calcium content relative to OPC, and therefore has up to 40% less carbon dioxide emissions (Burris et al., 2015).

CSA cement consists primarily of ye'elimite ($C_4A_3\bar{S}$), belite (C_2S), ferrite (C_4AF) and a $CaSO_4$ source, gypsum or anhydrite. When CSA cement hydrates, its main hydration products are ettringite and amorphous aluminum hydroxide. With ettringite as its primary hydration product, CSA cements experience faster hydration compared to the reaction kinetics of OPC, with setting times occurring as fast as ten minutes after mixing with water. This heat release corresponds with rapid ettringite formation, rapid setting, and early strength gain (Glasser and Zhang, 2001; Pelletier et al., 2010). Because of the rapid setting time, use of this material is limited to applications where short working times are permissible, since rapid setting of CSA prevents transportation of the CSA cement concrete in mixer trucks due to risk of hardening occurring without reaching the construction site. To prevent this issue and increase the utilization of CSA cement, chemical retardants can be used to delay reactions of CSA cement.

Previous studies have shown that citric acid, tartaric acid, and borax are effective and successful retarders in CSA cement systems (Hu et al., 2017; Pelletier et al., 2010; Winnefeld and Lothenbach, 2010; Zajac et al.,

2016). Citric and tartaric acids are both organic carboxylic acids, theorized to have similar working retardation mechanisms, preventing nucleation of ettringite, with borax operating through a different mechanism, presumed to be at least in part slowing of dissolution and nucleation due to depression of the solution's pH (Möschner et al., 2009; Zajac et al., 2016). However, there are not any explicit studies to understand the effect of combination of retarders. Therefore, the aim of this study is to evaluate the effects of combination of retarders on hydration properties and strength and phase developments.

2 Experimental Investigation

2.1 Materials

This study uses a calcium sulfoaluminate (CSA) cement sourced from Buzzi Unicem for all paste and mortar mixtures. Phase contents of CSA cement are shown in Table 1 and were determined through Rietveld analysis of quantitative X-ray diffraction (QXRD) utilizing a rutile internal standard (Alfa Aesar, 99.9%). The sand used was obtained commercially from Quickcrete and was used as fine aggregate in all batches of mortar cubes.

Citric acid (Alfa Aesar, 99% purity), tartaric acid (LD Carlson), and borax (20 Mule Team) were used as retardants. All dosage rates are shown as a percentage of mixture cement mass. Deionized water (18 kOhm) was used for all paste mixtures and Columbus tap water was used for all mortar mixtures.

Table 1. Phase composition of CSA unhydrated cement.

Phase	Anhydrite	Belite (C_2S)	Brownmillerite (C_4AF)	C_3A	Calcite	MgCalcite	Quartz	Rutile	Ye'elimite
CSA (wt%)	13.2	18.6	6.2	5.9	2.2	1.8	0.2	11.8	40.1

2.2 Methods

Compressive strength test, Vicat needle test, quantitative X-ray diffraction (QXRD) test and isothermal calorimetry were used to investigate effects of different dosages of each retardant and combinations. CSA cement with no retarder was used as a control sample. All cement pastes and mortars were prepared at a w/c by mass of 0.40. Retardants were dissolved in the deionized or tap water prior to mixing water with cement. Table 2 shows the investigated retarder dosages for each test. In combination mixtures, retarders were used in equal amounts. Throughout this manuscript mixtures are abbreviated using the form: xR, where x is the dosage used and R is the retarder. For example, the 1 wt% borax paste is designated as 1b, while the 1% borax + 1% citric acid combination is designated as 1/1bc. Control sample, CSA paste or mortar without any retarder, is designated as 0.

Table 2. Investigated retarder dosage for each test.

Tests	**Retarders and Dosages Investigated - % of cement weight**				
	Citric Acid	Tartaric Acid	Borax	Citric Acid and Borax	Citric Acid and Tartaric Acid
Isothermal Calorimetry	0.5, 1, 2	0.5, 1, 2	0.5, 1, 2	1, 2	1, 2
Setting Time Test	0.5, 1, 2	0.5, 1, 2	0.5, 1, 2	1, 2	1, 2
Compressive Strength Test	0.5, 1, 2	0.5, 1, 2	0.5, 1, 2	1, 2	1, 2
QXRD	1, 2	1, 2	1, 2	2	2

CSA cement pastes for isothermal calorimetry were prepared with the procedures outlined in ASTM C1679 (2014). Pastes were mixed with a 6-speed hand mixer from Hamilton Beach at the lowest speed for 30 s and at the highest speed for 90 s. After mixing, 5g of each paste was placed into a glass ampoule, sealed, and put in the calorimeter, with heat evolution tracked for 48 hours for citric acid and tartaric acid combination samples and 96 hours for citric acid and borax combination samples. All samples were placed into the calorimeter within 2-3 minutes of water-cement contact.

For setting time, pastes were prepared according to ASTM C305 (2014). Initial and final setting times were measured using a Vicat needle test apparatus according to ASTM C191 (2019). Initial and final setting times of each sample were tested in duplicate, with results averaged. 50 mm mortar cubes were prepared to evaluate compressive strength following ASTM C109 (2010). All of the mixtures have same cement, sand and water amounts. Absorption capacity of sand was calculated as 2.5% based on ASTM C128 (2015) and extra amount of water added to the mix design to account for the absorption. After placing mortars in the molds, molds were cured at room temperature, 100% RH, demolded after 24 hours, and kept in 100% RH until test day.

Quantitative x-ray diffraction (QXRD) was used to determine phase content of hydrated cement pastes at 1, 7 and 28th days. Cement pastes were prepared using the same procedure as outlined for isothermal calorimetry pastes. At each test age hydration was stopped by grinding pastes to <1mm, and immersing in isopropanol for 24 hours, followed by drying under vacuum for 24 hours. Samples were then stored in a plastic bag, in a sealed container in the 100% RH room until the test day to prevent carbonation. Pastes were ground to pass a #200 sieve, then mixed with a rutile internal standard, interground using isopropanol and an agate mortar and pestle, into the pastes at 10 wt%. XRD scans were performed with a BRUKER D8 XRD in Johannsson mode, using a copper x-ray source producing CuKα radiation. The diffractometer was operated at 40 kV and 40 mA and scans were run from 5 to 60 degrees 2θ with a step size of 0.02°. The samples were rotated by 30 rpm to minimize the surface texture variation and preferred orientation. Crystalline phases in each sample were determined through Rietveld refinement on duplicates using the Profex software (Döbelin and Kleeberg, 2015).

3 Results and Discussion

In order to understand the effects of combination of retarders (citric acid, tartaric acid, and borax) on CSA cement, isothermal calorimetry, setting time, compressive strength and quantitative x-ray diffraction tests were performed and results were compared with CSA cement without retarder and with singular retarders.

3.1 Hydration kinetics

Shown in Figures 1 and 2, CSA hydration, without retarders, began with rapid heat release evidencing the rapid hydration reaction of CSA cement. Increasing retarder dosages delayed the hydration reactions and reduced the rate of heat release for both singular retarders and retarders used in combinations.

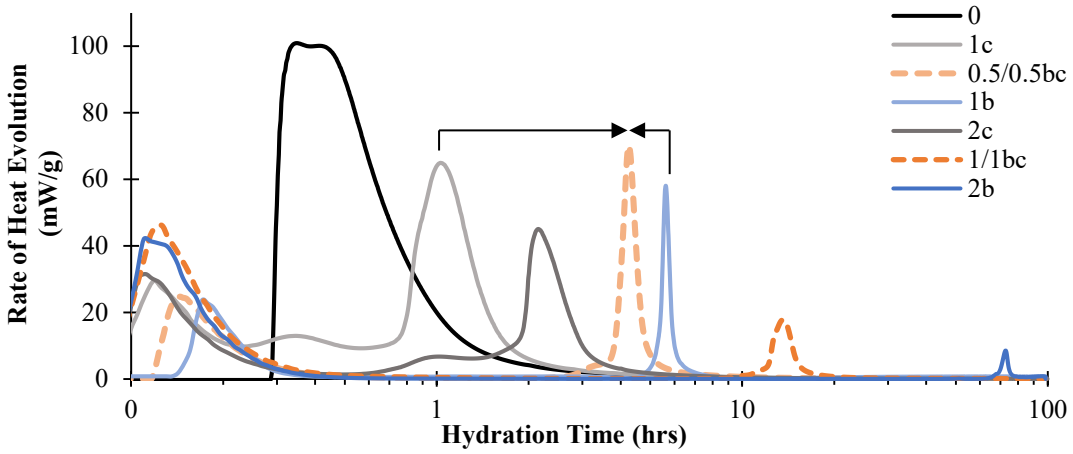


Figure 1. Heat evolution of CSA cement with citric acid and borax and their combinations dosages varying 0, 1 and 2% by cement mass. Note that time is shown on a logarithmic axis in order to show the highly retarded reactions of the borax-retarded mixtures.

The effects of borax and citric acid and their combination mixtures on CSA hydration are shown in Figure 1. Due to the large difference in the timing of hydration reactions of the other samples and 2b sample, a logarithmic axis was used to better visualize their relationship. Borax was found to be a much more effective retarder than citric acid for same dosages, in terms of retarding hydration reactions. The main peak of heat evolution for 2c occurred at 2-3 hours, while it was 72-73 hours for 2b. The relationship between rate of heat release and hydration time of citric acid and tartaric acid samples are shown in Figure 2. Although tartaric acid and citric

acid had similar general effect on heat release relative to the retarder dosage in CSA samples, tartaric acid resulted in peak broadening of the heat release curve, indicating longer time required to complete hydration reactions.

Each of the retarder combinations showed different relationships when compared to their equal weight % dosage counterpart. For the bc mixtures, samples showed an 'averaging' behavior, with the hydration time of the combination mixture between that of the hydration peak times obtained for singular borax and citric acid samples. A different effect was seen for tc samples, with the combination mixture's peaks delayed for quantity of time equal to the singular times of each retarded added together. These results are illustrated for the 1c, 1b, and 1/1bc mixtures in Figure 1 and the 1c, 1t, 1/1tc mixtures in Figure 2. Differences in these effects are likely a result of differing retardation mechanisms between the carboxylic acid (citric and tartaric) retarders and the borax retarder. It is hypothesized that citric and tartaric acids retard hydration through precipitation of a salt on the surface of the cement grain, while borax slows dissolution and precipitation reactions through depression of system pH (Zajac et al., 2016). These results indicated that using small amount of both retardants can give greater set time delays by combining retarder effects with lower dosages of the retarding admixtures and can avoid the extreme delays when only borax is used.

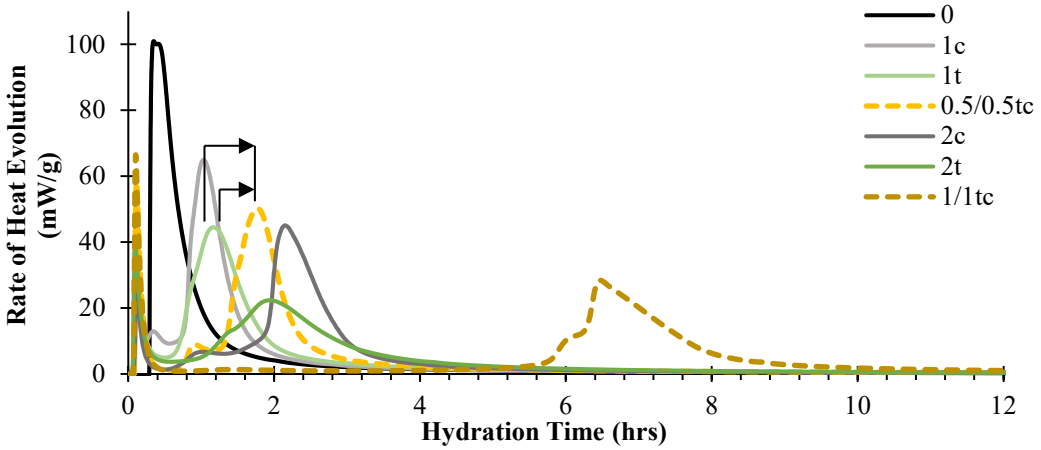


Figure 2. Heat evolution of CSA cement with citric acid and tartaric and their combinations dosages varying 0, 1 and 2% by cement mass

3.2 Setting time

Setting time of CSA cement with the three retarders and their combinations in varying dosages are shown in Figure 3. Without retarder, CSA cement completely hardened in 10-15 minutes. For mixtures with singular retarders, when retarder dosage increased, setting time increased proportionally. In addition to increases in setting time, increasing retarder dosage increased the time between initial and final set for all retarders. In general, tartaric acid retarded setting time more than citric acid, however borax had the strongest effect. Similar to the isothermal calorimetry results, the mixtures were extremely sensitive to borax dosage and it took more than 3 days to 2b sample reach its initial and final setting time.

Since setting times in excess of 1 day is typically not acceptable for construction field applications, using combinations of borax and citric acid may be a good option due to averaging relationship between them. Citric acid had a predominant effect on these combination mixtures with setting times of the 1/1bc combination in between 2b and 2c singular mixtures but closer to that of the 2c mixture. The same effect was not repeated for tartaric acid and citric acid combination samples where setting time increased for combinations of retarders by an amount greater than the equivalent additive replacement percentage, e.g. the setting time for the 0.5/0.5tc sample was greater than for either the 1t or 1c samples, suggesting synergistic interactions of the retarders.

Figure 4 shows the relationship between heat releases, obtained by isothermal calorimetry, and times to initial and final sets. All singular retarder mixtures are shown in black and gray, for initial set and final set, respectively, with the exception of the 1b mixtures, shown in blue. To highlight the combination mixtures, they are shown with different colors. A linear relationship existed between time to the main hydration peak and time to both initial and final set for most retarders and dosages. However, this relationship did not hold for the high

dosage borax samples (1b and 2b), although the 0.5b and combinations of borax and citric acid (0.5/0.5bc and 1/1bc) did fit the trend. This may suggest that heat release and microstructural formation are not as closely linked in systems retarded by borax as in other CSA systems (Burris and Kurtis, 2018). This relationship between setting time and heat release may be useful for increasing utilization of CSA cement by allowing for determination of required retarder dosages based on isothermal calorimetry results.

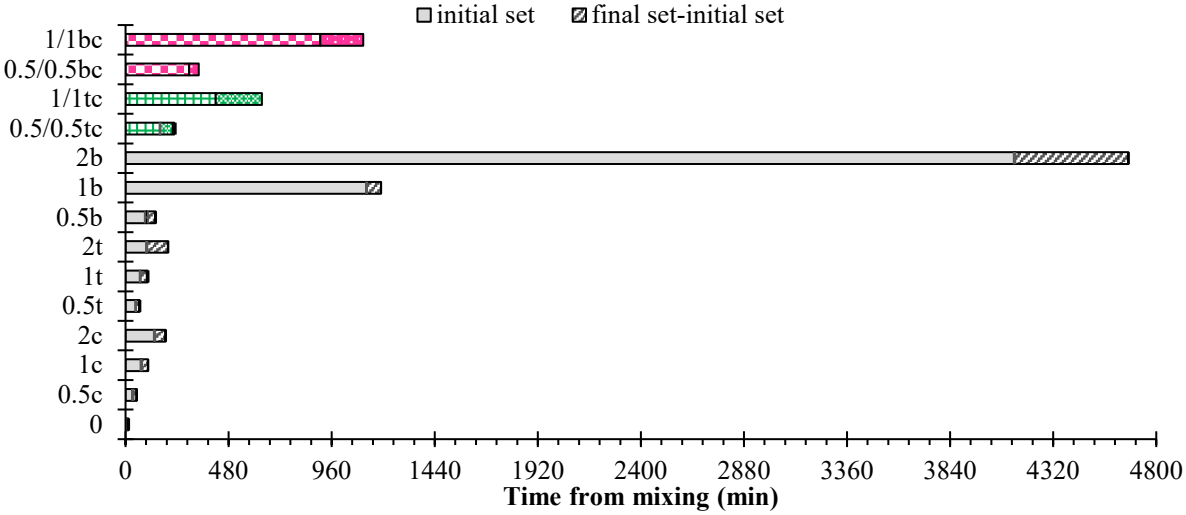


Figure 3. Setting time results of CSA cement paste with different retarders and combinations in varying dosages (% of cement mass)

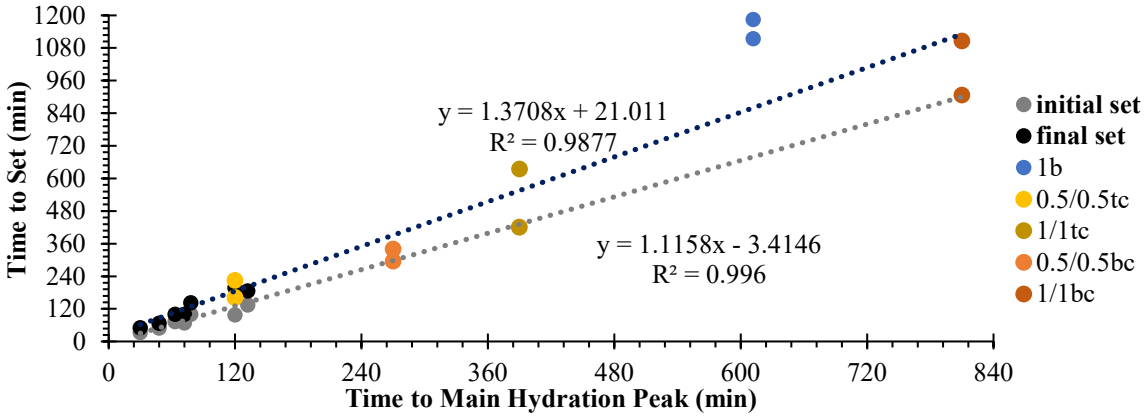


Figure 4. Relationship between the time to set and time to main hydration peak of CSA cement pastes with all singular retarders and combinations

In order to predict the setting time changes for combination mixtures, theoretical relationships between setting time for singular and combinations of retarders were found. Equations for theoretical calculations of setting time of combination samples, which are shown in Eqs. (4) - (7), were found from the singular mixtures with equivalent total retarder dosage. Since bc samples show averaging behavior and citric acid samples dominates the setting time results of bc mixtures, theoretical equations were calculated by balancing singular citric acid and borax samples, and scalar factors in Eqs, (4) and (5) gave the best fitted result. Due to the additive relationship of tc samples, setting time of combinations were predicted from singular mixtures by adding the results of singular mixtures and multiplying the sum by a scalar factor, calculated based on total retarder dosage (e.g. 2 for a 1/1bc mixture). Since dosage increases did not lead to linear increase in setting time, different scalar factors were used for 0.5/0.5tc and 1/1tc samples. Differences between experimental and theoretical results of initial and final set of samples with combination of retarders can be seen in Figure 5. The error of the theoretical calculations for bc samples of initial and final sets were calculated as 3.72% and 3.86%, respectively and for tc samples of initial and final sets were calculated as 4.46% and 1.98%, respectively.

$$0.5/0.5bc = (1b * 0.2) + (1c * 0.8) \quad (4)$$

$$1/1bc = (2b * 0.2) + (2c * 0.8) \quad (5)$$

$$0.5/0.5tc = (1t + 1c) * ([0.6 * total\ dosage] + 0.5) \quad (6)$$

$$1/1tc = (2t + 2c) * ([0.6 * total\ dosage] + 0.5) \quad (7)$$

This predictability also helps to evaluate the relative of each of the retarders used in the combination. The relationships between dosage and setting time suggest that in the bc combinations citric acid has a predominant effect on setting time. Borax's effect contributed less to the overall increases in setting time than the citric acid when used in combination, perhaps indicating its inhibition by the presence of another retarder.

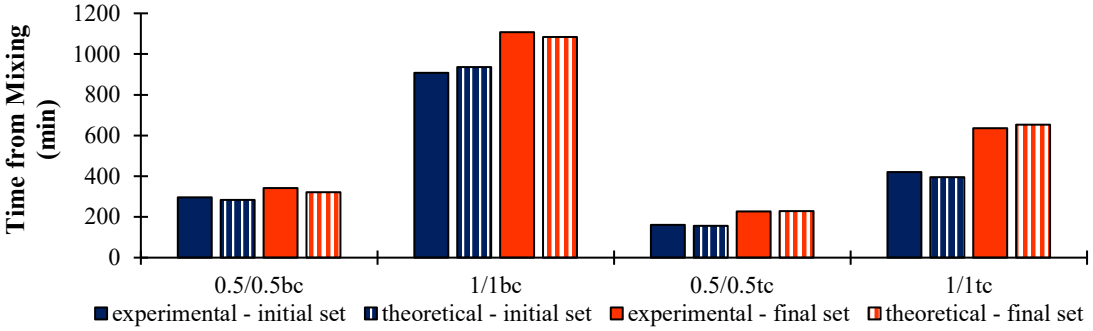


Figure 5. Differences between experimental and theoretical results of initial and final set of CSA cement pastes with combination of retarders

3.3 Compressive Strength Development

Based on these results, using low dosages of multiple retarders in conjunction may be more efficient, allowing for further extensions of setting time. However, it is important to ensure that use of these mixtures will not negatively impact strength and durability of CSA concretes. Figure 6 shows the compressive strength development of a 0.4 w/c CSA mortars with varying types and dosages. It indicates that use of tartaric and citric acid in combination resulted in slightly increased strength at 1 day, but reduced the compressive strength of the mixtures for all other times, reducing the strength by approximately 15% at 28 days relative to the singular mixtures with equivalent total retarder dosage (for example: 0.5/0.5tc has lower strength than the 1c and the 1t samples).

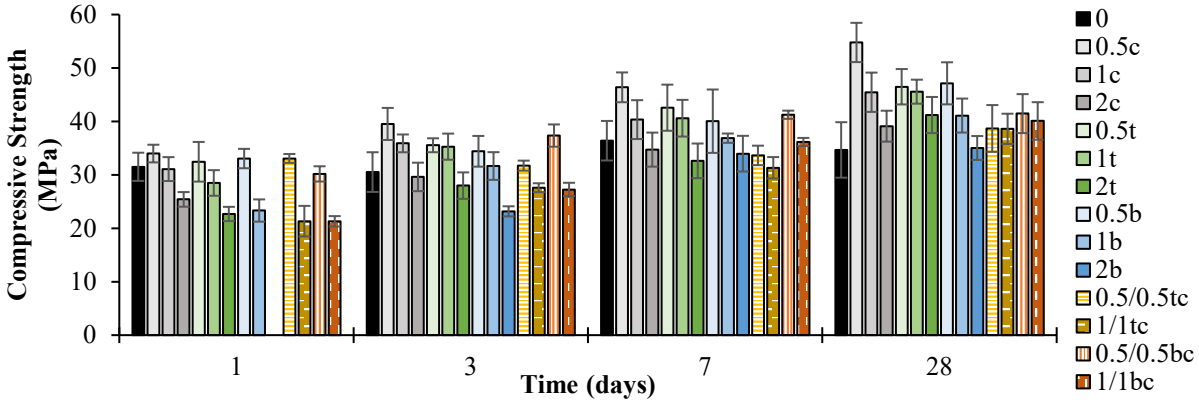


Figure 6. CSA mortars with varying types and dosages of retarders. Note that the 2b sample had gained no strength at the time of testing at 1 day.

For the bc samples, the strength of the combination samples is generally less than those of the citric acid samples. However, for the high dosage mixtures (2c and 1/1bc), strength of the combination mixture exceeds that of the citric acid mixture at 7 and 28 days. Compressive strengths for the combination mixtures exceed those of the singular borax samples at early ages, prior to 28 days. However, the strength gain for the 1b sample

continues at a greater rate than strength gain in the combination samples up to 28 days, with the borax sample likely to surpass their strength after 28 days. It appears that the effect of the combinatorial use of citric acid and borax promotes earlier strength development at the cost of long-term ultimate strength.

Figure 7 shows the relationship between final setting time and 28-day compressive strengths. In general, increased setting time correlated with decreased compressive strength for all samples, with similar trends for retarders used both singularly and in combination. For the combination mixtures, higher setting times were achievable, but with slightly decreased strengths compared to others with similar final setting time.

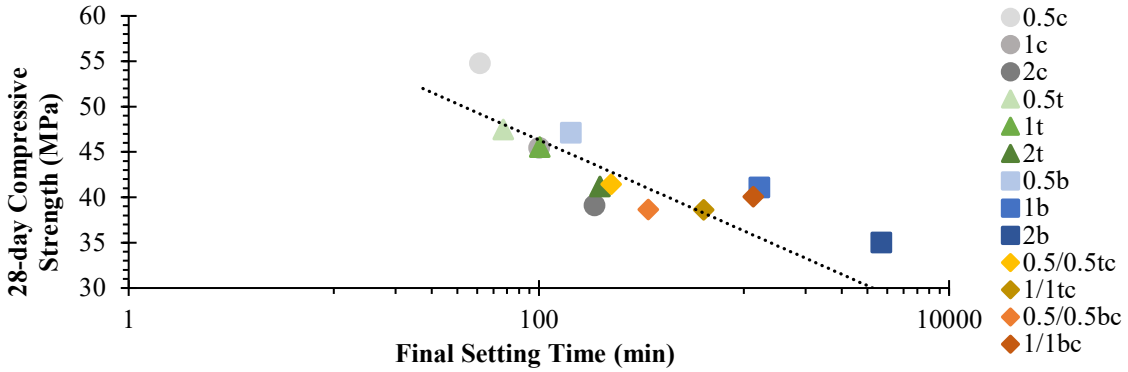


Figure 7. Relationship between the compressive strength at 28-day of CSA mortars and final setting time of CSA pastes with all singular retarders and combinations

3.4 Phase Development

Further work was done to understand the cause of reduced strengths in the combination mixtures and the relationship between phase development and compressive strengths. Ettringite content and compressive strength, shown in Figure 8, appear to correlate, with greater ettringite contents correlated with increased compressive strengths. One interesting note is that ettringite contents of the combination mixtures were consistently within the group average at each time, yet their compressive strength lagged behind that of the other mixtures. This may suggest that factors other than ettringite formation determine strength development in combination retarder mixtures, or that combinations of retarders affect structural formation and bonds within the ettringite crystal structure (Csetenyi and Glasser, 1992). Despite this effect, by 7 days, the citric and tartaric combination's ettringite-compressive strength relationship had normalized to that of the other mixtures, with the citric and borax combination catching up by 28 days.

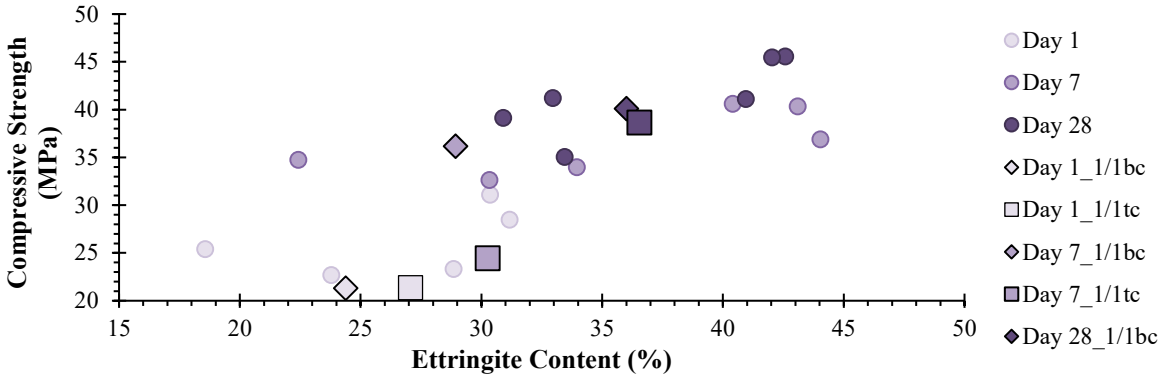


Figure 8. Relationship between the compressive strength of CSA mortars and ettringite content of CSA pastes with dosages varying 1 and 2% by cement mass

4 Conclusion

In order to upscale the use of CSA cement and investigate the effect of the combination of retarders on CSA cement systems, citric acid, tartaric acid, and borax were used both singularly and in combination. Toward the

goal of evaluating the influence of different retarders and varying dosages hydration kinetics, setting time, compressive strength and phase development were measured and key findings are:

- Extended setting times were successfully achieved using both singular and combinatorial retarder mixtures.
- Borax and citric combinations led to setting times averaging those of the singular mixtures while citric and tartaric combinations led to additive effects. These differences likely result from similarities or differences in retardation mechanism for the retarding chemicals used in combination.
- Combination mix setting times could be predicted from singular mixture setting times. Differences in the relationships required for prediction further illustrate the effects of differing retardation mechanisms between the carboxylic acids and borax.
- In general, heat release and setting time correlate for CSA mixtures, but use of borax disrupts this relationship, especially at high dosage rates.
- Ettringite content was found to correlate with compressive strengths. However, borax did not fit closely to the trends seen with the other mixtures.
- Use of retarder combinations reduced strength relative to the strengths of equivalent dosage singular retarders, for most mixtures.
- Use of retarder combinations were generally more successful in increasing setting times, but at the cost of longer-term compressive strengths.

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