

INFLUENCE OF EXTERNAL ENVIRONMENT ON EARLY-AGE EXPANSION CHARACTERISTICS OF CALCIUM SULFOALUMINATE CEMENT-BASED BINDERS

Vaishnav Kumar Shenbagam (1), Rolands Cepuritis (2) and Piyush Chaunsali (1)

(1) Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India

(2) Department of Structural Engineering, Norwegian University of Science and Technology, Trondheim, Norway

Abstract

Calcium sulfoaluminate (CSA) cements are widely being promoted as alternative low CO₂ binders. CSA cements can also be expansive and designed to be shrinkage-compensating. The main phase of CSA cement is ye'elimite, which hydrates in the presence of calcium sulfate to form ettringite as the main hydration product. The availability of calcium sulfate can be used to control the hydration kinetics of ye'elimite, which affects the expansion characteristics of CSA cement. Sulfates in the form of gypsum or anhydrite are usually blended with CSA cement in the manufacturing stage. The presence of sulfates in the external environment also affects the expansion characteristics of CSA cement. This study aims to understand the effect of different exposure conditions on the expansion characteristics of CSA-based blended cement. The expansion of the specimens exposed to calcium sulfate solution was found to increase with the amount of calcium sulfate. The addition of CSA cement to Portland cement was found to have a significant influence on the early age expansion characteristics of the system, without affecting the mechanical properties such as compressive strength and dynamic modulus.

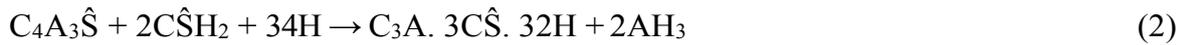
Keywords: Calcium sulfoaluminate cement, Expansion, Supersaturation

1. INTRODUCTION

Concrete, the most used human-made material in the world, is a significant contributor to global CO₂ emissions. Portland cement manufacturing process accounts for around 8% of the global CO₂ emissions (1). Hence, reducing the carbon footprint of Portland cement has been an active area of research. To that end, calcium sulfoaluminate (CSA) cement is being promoted as an alternative low CO₂ binder (2). The overall reduction in the CO₂ emissions in the manufacturing of CSA cement can be up to 25–35% compared to OPC, depending on the phase composition of the CSA cement (4).

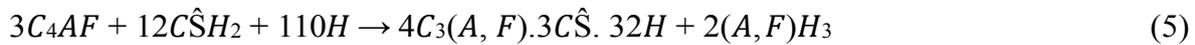
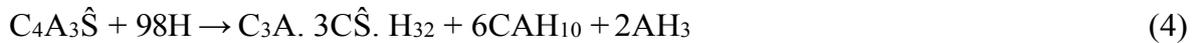
Ye'elimite (C₄A₃Ŝ), the main phase of CSA cement, was initially developed by Alexander Klein (5) as an expansive cement. Other mineralogical phases present in CSA cement are calcium sulfate (CŜ), belite (C₂S), calcium aluminoferrite (C₄AF), and mayenite (C₁₂A₇). Hydration of CSA cement mainly results in the formation of calcium sulfoaluminate phases (ettringite or monosulfate) depending on the availability of sulfates. The main hydration

reactions involved in the CSA cement systems are listed below in Eqs. 1–3 (6–8):



The theoretical water demand for the hydration of pure ye'elinite phase is 0.64 as per Eq. 2 when compared against 0.42 for OPC. As evident from the above-mentioned reactions, the hydration of CSA cement requires higher water content than that of OPC. The $C\hat{S}/C_4A_3\hat{S}$ ratio (by weight) of 1.11 is required for the formation of ettringite according to Eq. 2. When there is a deficit of sulfates, ye'elinite hydrates to form monosulfate and amorphous aluminum hydroxide (Eq. 1). In presence of gypsum, the formation of ettringite (Eq. 2 or Eq. 3) is more favored and faster than the formation of monosulfate as per Eq. 1 (8).

Though ettringite is the main hydration product, metastable phases such as CAH_{10} can also form according to Eq. 4. Belite and calcium aluminoferrite present in the system react to form iron bearing ettringite and strätlingite (Eq. 5 and Eq. 6).



The formation of restrained shrinkage cracks in concrete can be overcome by making the system shrinkage compensating with the creation of expansive stress in the system during the early age of hydration and strength development. The development of expansive stresses can be studied indirectly by monitoring the unrestrained expansion. This expansion can be controlled by understanding the physico-chemical factors influencing it. The expansion characteristics of CSA cement can be attributed to various factors such as the amounts of $C_4A_3\hat{S}$, $C\hat{S}$, water and free lime; the presence of alkali hydroxides; the fineness; and the pore structure features (9). The time of formation of ettringite has a crucial role in governing the final expansion. As the availability of sulfates has a strong influence on the hydration kinetics of ye'elinite, it is important to understand the influence of calcium sulfate on expansion characteristics. The level of expansion increases with the dosage of calcium sulfate until the required stoichiometric amount is reached. With the increasing dosage of calcium sulfate, degree of supersaturation of sulfate is also increased, leading to higher levels of expansion (9,11).

Although, conventionally, expansion is attributed to the formation of ettringite, there is no direct correlation between the expansion and the amount of ettringite formed. Saturation index of ettringite in CSA cement systems has been found to have improved correlation with expansion (12). Using crystallization pressure theory, expansion of CSA cement system could be correlated to the level of supersaturation present in the system (11,13). In a recent study (8), the authors reported that the crystallization pressure due to ettringite and other phases such as AH_3 , strätlingite, CAH_{10} and monosulfate might also contribute to expansive stresses in the system.

Expansion of CSA cement is significantly influenced by the environment in which ettringite is formed; that is the pore structure at the time of ettringite formation and the level of supersaturation of sulfate in the system. All other factors mentioned before also directly or indirectly affect either the pore structure or the level of supersaturation which in turn affects the expansion characteristics.

In this work, early-age properties (i.e. expansion, strength and modulus) of OPC-CSA blends

were examined under different environmental conditions. OPC-CSA blends were prepared by blending 10% CSA cement with 90% OPC, and were exposed to saturated lime solution, unsaturated gypsum solution, supersaturated gypsum solution, relative humidity (RH) of 95% and 65% after initial curing period of 7 days.

2. MATERIALS AND METHODS

A commercially available CSA cement and OPC were used for this study. The phase compositions of both cements are given in Table 1. The expansion studies were performed on cement paste specimens prepared at a constant water-to-cement ratio (by weight) of 0.4. Distilled water was used for casting and preparing exposure solutions. Five different exposure conditions were used in the study — drying at 65% relative humidity (65% RH), moist room with 95% relative humidity (95% RH), saturated lime solution (Lime), undersaturated gypsum solution (USCŜ), and supersaturated gypsum solution (SCŜ). Reagent grade calcium hydroxide was used in the concentration of 2g/l to prepare saturated lime solution. Furthermore, gypsum in the concentrations of 1g/l and 5g/l was used to prepare USCŜ and SCŜ solutions, respectively. All the specimens were cast at a controlled temperature and RH of 25°C and 65%, respectively. The specimens were demolded after 24 hours of casting and cured in saturated lime solution (at 25°C) for 7 days before exposing them to various exposure conditions.

Table 1: Mineralogical phase composition of OPC and CSA cement

CSA Cement						
Ye'elimitite	Anhydrite	Lime	Dolomite	Belite	Mayenite	
14.1%	43.3%	21.2%	5.5%	10.4%	3.8%	
Portland Cement						
Alite	Belite	Aluminate	Ferrite	Gypsum	Calcite	Portlandite
48.8%	28.1%	6.5%	8.5%	1.9%	3.9%	1.3%

Phase identification and mineralogical examination was performed using X-ray diffraction (XRD), which was carried out in an X'pert Pro PANalytical equipment. The XRD patterns were collected for 2-theta (2θ) range of 5° – 60° for with a step size of 0.02°. Each scan was completed in about 9 minutes. The X'Pert HighScore plus software was used to identify the phase composition and phase quantification using Rietveld refinement. The parameters used for refinement were specimen displacement, scale factor, cell factor, and, if required, the preferred orientation and the profile shape (w value). The background was fitted using a polynomial function with the coefficients 1, 2, 3 and 1/x. The final goodness of fit (GoF) value attained was less than 2.75. Hydration stoppage for the samples was done by solvent exchange with isopropyl alcohol (IPA) followed by vacuum filtration. The samples were crushed and immersed in IPA for an initial period of 30 minutes and washed with IPA under vacuum for about 10 minutes. Diethyl ether was then sprayed on the sample to replace the IPA. The sample was dried and stored in a low-vacuum desiccator for at least 3 days before testing. About 2g of sample was crushed and sieved through a 37-micron sieve (400 number) for characterization.

For the study on dimensional stability, 25 × 25 × 285 mm prismatic paste specimens were cast for binder systems: OPC, OPC with 5% replacement of CSA, and OPC with 10% replacement of CSA.

The mechanical properties of cement paste specimens were determined at different ages of 1, 3, 7 and 28 days. The compressive strength test was done on 50 × 50 × 50 mm cube size specimens, and the dynamic modulus was calculated using the resonant frequency test on the 25 × 25 × 285 mm size prismatic specimen. The Poisson's ratio of the binder matrix was assumed as 0.17.

3. RESULTS AND DISCUSSION

This section reports the results on the hydration progress and strength development of OPC and OPC-CSA blends.

3.1 Hydration of CSA cement

X-ray diffraction was performed to monitor the hydration of OPC-CSA blend. Fig.1 shows the XRD diffractograms of CSA cement and hydration of OPC-CSA blend at early ages.

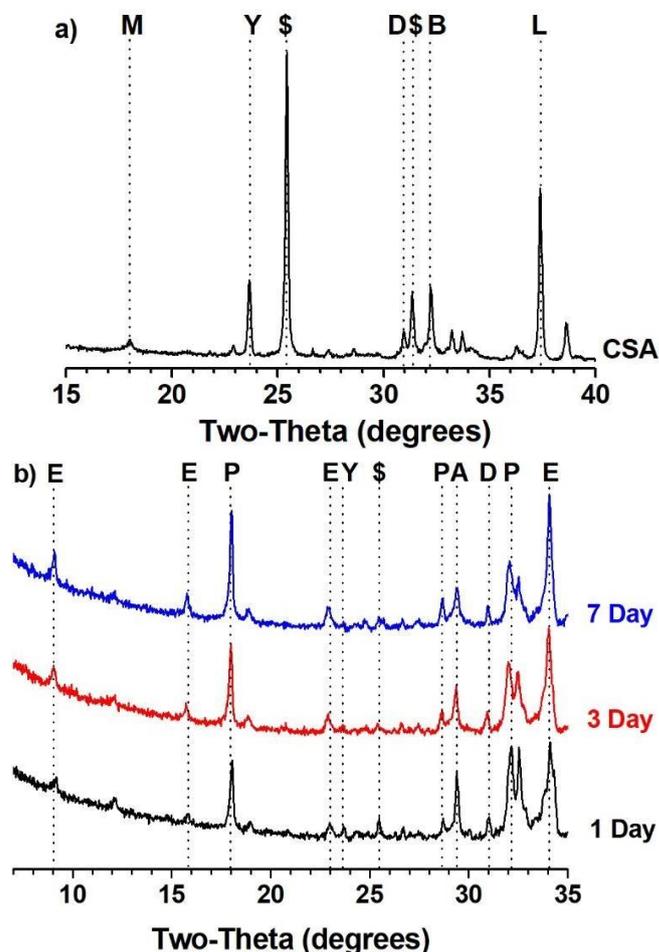


Figure 1: XRD patterns of a) unhydrated CSA cement and b) hydrated OPC-CSA binders after 1, 3 and 7 days
(Note - Y: Ye'elinite, M: Mayenite S: Anhydrite, A: Alite, B: Belite
D: Dolomite, L: Lime, P: Portlandite, E: Ettringite)

It is evident that the ye'elinite phase in CSA cement is completely consumed in 7 days. As the CSA cement hydrates rapidly, the formation of ettringite takes place at early ages. This also influences early-age expansion characteristics of CSA-OPC blended cements.

3.2 Expansion characteristics of OPC-CSA blends

Initially, expansion characteristics of OPC and OPC-CSA blends were measured in saturated lime water, as shown in Fig.2. The control specimen cast with OPC was found to have expanded to 240 microstrains. With the addition of CSA cement, the expansion was increased to 820 and 4250 microstrains after 28 days for 5% and 10% replacement of CSA, respectively (Fig.2). It is clear that addition of CSA cement corresponds to an increase in the amount of ye'elinite present. With higher levels of ye'elinite present, there is a higher amount of ettringite formed at early ages, which causes expansion. The expansion of OPC-CSA blends

increased with the amount of CSA cement in the system (8,13). It was also observed that most of the expansion occurred within the 7 days, beyond which the curve plateaued. The rate of expansion was also found to increase with the increase in dosage of CSA cement. As the consumption of ye’elinite is completed at within 7 days (Fig.1), the expansion due to the hydration of CSA cement also takes place during this period.

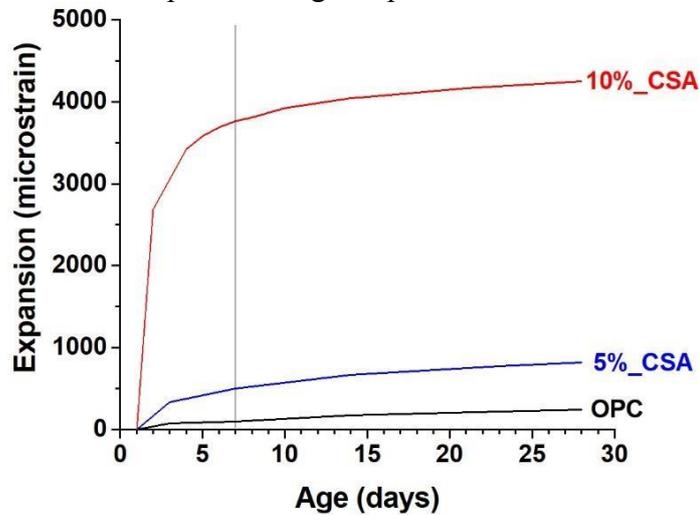


Figure 2: Expansion characteristics of OPC and OPC-CSA blends under lime curing

3.3 Influence of external environment on expansion characteristics

The change in expansion that occurs beyond 7 days can be attributed to the different exposure conditions, as the expansion due to the hydration of ye’elinite is completed within first 7 days. To study the influence of external environments, the specimens cast with 10% CSA cement were exposed to the different exposure conditions after 7 days of curing. The specimens had an expansion of ~3800 microstrains at the time of exposure to different curing environments (Fig.2). The specimens exposed to saturated lime solution and in moist room (~95% RH) had similar levels of expansion (Fig.3). In both cases, there is no loss of moisture from the specimens and leaching of lime is also restricted. This can be considered as the base line to determine the expansion caused due to the presence of external sulfates.

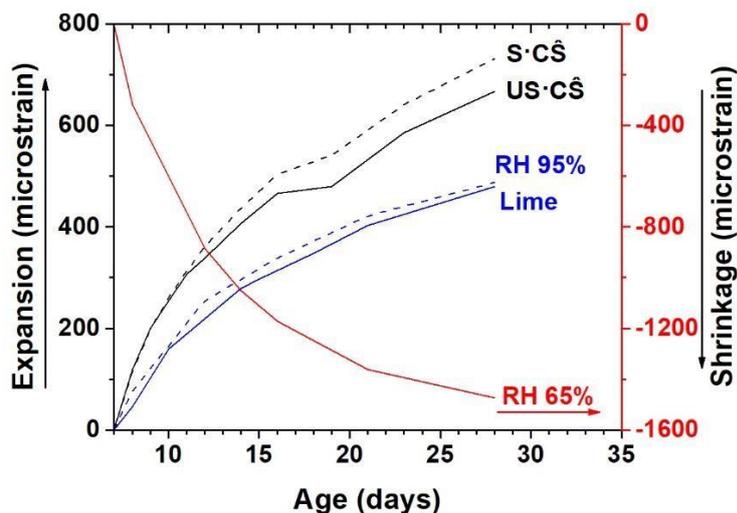


Figure 3: Influence of external environment on expansion and shrinkage Characteristics

When exposed to drying (at 65% RH), ~ 1500 microstrains of shrinkage was recorded at 28

days, which is less than the initial expansion of 3800 microstrains that was attained. This indicates how the CSA based cements can act as a shrinkage compensating agent by inducing additional expansion at early age.

When the specimens were exposed to a sulfate solution, the resultant expansion was found to increase with the increase in the level of sulfates in the solution (14). The increase in sulfate concentration of the solution increased the level of supersaturation with respect to ettringite. This increase led to an increase in the crystallization pressure causing additional expansion. The increase in the level of supersaturation of ettringite has a direct influence on the resultant expansion (10).

3.4 Mechanical characteristics of OPC-CSA blended cement

Compressive strength and dynamic modulus were used as means to evaluate mechanical properties. Figure 4 shows the evolution of dynamic modulus of OPC and OPC-CSA blends with time. The dynamic modulus of all the three binder systems steadily increased with age (Fig.4). This is also an indicator to confirm that the expansion caused due to CSA cement did not lead to cracking of the matrix. A similar trend was also seen with the compressive strength as shown in Fig.5a. The addition of CSA cement did not affect the mechanical properties negatively, whereas the influence of CSA cement on the expansion is evident (Fig.5b). Stiffness of the matrix also affects the extent of expansion. For example, a matrix having lower stiffness will offer reduced resistance to expansion compared to a matrix having higher stiffness. This could potentially play a significant role when there is significant difference in the stiffness.

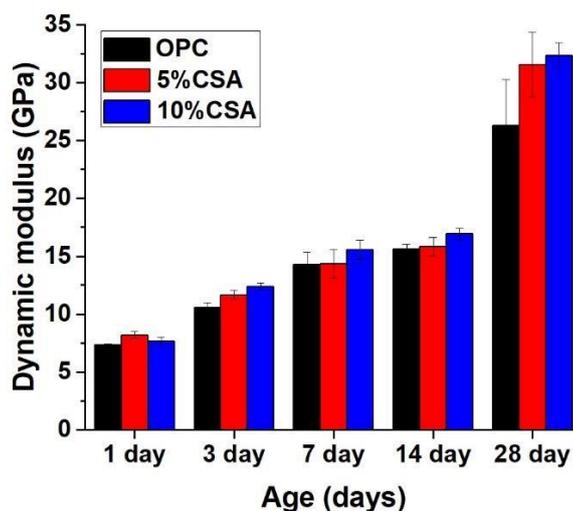


Figure 4: Evolution of dynamic modulus

In this study, the effect of ye'elite and calcium sulfate (from external environment) on the early-age expansion characteristics of OPC-CSA blend was examined. Increase in ye'elite and sulfate concentration also increased the expansion. However, the mechanism and the level of expansion attained through them (increase in ye'elite and sulfate concentration) were different.

The influence of ye'elite addition on expansion is more prominent in OPC-CSA blend with 10% CSA than the OPC-CSA blend with 5% CSA (9). This increase in expansion was attributed to higher ettringite fraction due to increased ye'elite content in OPC-CSA blend. However, increase in sulfate concentration resulted in higher supersaturation with respect to ettringite, and thereby, induced higher crystallization pressure resulting expansion (11). Interestingly, when the mature (no ye'elite present) OPC-CSA paste was exposed to sulfate solution, only ~7% increase in expansion was observed. This indicates the role of curing media

during the formation of ettringite on the extent of expansion. Nonetheless, the change in stiffness of cement matrix will also influence the expansion characteristics. Hence, physico-chemical characterization including pore structure features, pore solution analysis, material stiffness, and phase composition will enable better understanding of expanding cementitious systems based on CSA cement.

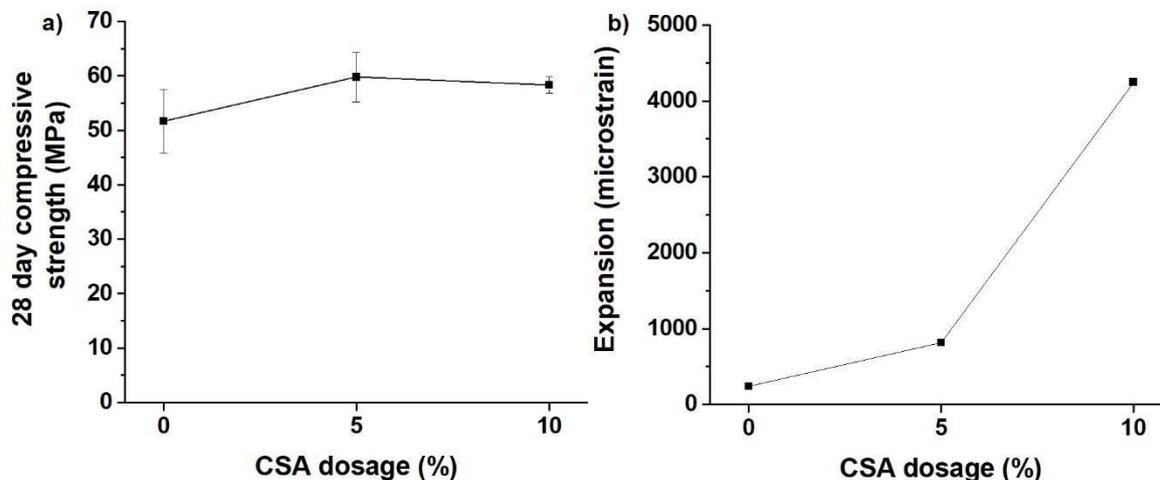


Figure 5: (a) Compressive strength, and (b) expansion of OPC-CSA blends after 28 days

4. CONCLUSION

This study reports the results of the role of different environmental conditions on the expansion characteristics of OPC-CSA blends having 0%, 5%, and 10% CSA cement. The expansion was found to be increasing with the increase in the sulfate concentration of exposure medium. For OPC-CSA blend with 10% CSA cement, the initial expansion during the first 7 days was found to compensate for the drying shrinkage. The addition of CSA cement (up to 10%) with OPC had a strong influence on the expansion characteristics without affecting the strength and dynamic modulus of the system.

Acknowledgements

The first author would like to acknowledge the doctoral scholarship received from the Ministry of Human Resource Development (MHRD), India. All authors would like to acknowledge the financial support of the Department of Civil Engineering at Indian Institute of Technology Madras towards the usage of experimental facilities in this study.

References

1. Andrew RM. Global CO₂ emissions from cement production. *Earth System Science Data*. 2018;10(1):195.
2. Gartner E. Industrially interesting approaches to “low-CO₂” cements. *Cement and Concrete research*. 2004 Sep 1;34(9):1489-98.
3. Glasser FP, Zhang L. High-performance cement matrices based on calcium sulfoaluminate–belite compositions. *Cement and Concrete Research*. 2001 Dec 1;31(12):1881-6.
4. Hanein T, Galvez-Martos JL, Bannerman MN. Carbon footprint of calcium sulfoaluminate clinker production. *Journal of cleaner production*. 2018 Jan 20;172:2278-87.
5. Alexander K, inventor; Chemically Prestressed Concrete Corp, assignee. Expansive and shrinkage-compensated cements. United States patent US 3,251,701. 1966 May 17.
6. Zhang L, Glasser FP. Hydration of calcium sulfoaluminate cement at less than 24 h. *Advances in cement research*. 2002 Oct;14(4):141-55.

7. Zajac M, Skocek J, Bullerjahn F, Lothenbach B, Scrivener K, Haha MB. Early hydration of ye'elinite: Insights from thermodynamic modelling. *Cement and Concrete Research*. 2019 Jun 1;120:152-63.
8. Hargis CW, Lothenbach B, Müller CJ, Winnefeld F. Further insights into calcium sulfoaluminate cement expansion. *Adv Cem Res*. 2018;31(4):160–77.
9. Chen IA, Hargis CW, Juenger MC. Understanding expansion in calcium sulfoaluminate–belite cements. *Cement and Concrete Research*. 2012 Jan 1;42(1):51-60.
10. Winnefeld F, Martin LH, Müller CJ, Lothenbach B. Using gypsum to control hydration kinetics of CSA cements. *Construction and Building Materials*. 2017 Nov 30;155:154-63.
11. Bizzozero J, Gosselin C, Scrivener KL. Expansion mechanisms in calcium aluminate and sulfoaluminate systems with calcium sulfate. *Cement and Concrete Research*. 2014 Feb 1;56:190-202.
12. Chaunsali P, Lim S, Mondal P, Tobias DH, Tobias DH. Factors influencing the early-age volume change of expansive cements relevant for bridge deck concrete. In *Proceedings of the Transportation Research Board 92nd Annual Meeting*, Washington, DC, USA 2013 Jan (pp. 13-17).
13. Bullerjahn F, Skocek J, Haha MB, Scrivener K. Chemical shrinkage of ye'elinite with and without gypsum addition. *Construction and Building Materials*. 2019 Mar 10;200:770-80.
14. Chen IA. *Synthesis of Portland cement and calcium sulfoaluminate-belite cement for sustainable development and performance*. The University of Texas at Austin; 2009.