



# Study on a high strength ternary blend containing calcium sulfoaluminate cement/calcium aluminate cement/ordinary Portland cement



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## HIGHLIGHTS

- Ternary blends perform the properties of rapid setting and high early strength.
- High early strength of blends results from the formation of massive ettringite.
- Strength of ternary blends continues to increase resulted from low porosity.

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## ABSTRACT

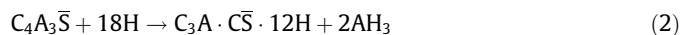
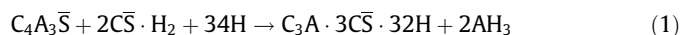
Repair mortars containing calcium sulfoaluminate cement (CSA), calcium aluminate cement (CAC) and ordinary Portland cement (OPC) was prepared. The effects of binder proportion on the mechanical properties of ternary blends were researched. Moreover, the hydration products and microstructure of that were observed by XRD, TG, and SEM. Results showed that the addition of CAC-OPC can accelerate the setting of CSA and enhance its early strength, which is mainly contributed to the rapid formation of massive ettringite. The strength of ternary blends continues to increase with time resulted from the decrease of porosity. Moreover, the microstructure of ettringite in CSA is significantly affected by the presence of CAC and OPC.

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## 1. Introduction

Lots of attention have been drawn to calcium sulfoaluminate cement (CSA) because of its environmental benefits such as lower CO<sub>2</sub> emission and less energy required for production [1,2]. The main hydraulic phase of CSA was ye'elimite (C<sub>4</sub>A<sub>3</sub>S̄), and lower amount belite (C<sub>2</sub>S), anhydrite (C̄S), and gehlenite (C<sub>2</sub>AS) were present [3,4]. The hydration of ye'elimite generally involved anhydrite and then gave rise to ettringite (C<sub>3</sub>A · 3C̄S · 32H) and aluminum hydroxide (AH<sub>3</sub>) via Reaction (1). On the other hand, ye'elimite can hydrate alone via Reaction (2) in consequence of no anhydrite

[5,6]. CSA concretes, mortars or pastes exhibited many interesting properties such as short setting time, high early strength, impermeability, sulfate and chloride corrosion resistance, and low alkalinity [7]. Therefore CSA was mainly used for rapid repairs and precast products [8–10].



Novel materials prepared by various cements with different hydration mechanisms may develop new interesting properties. Further, if new materials could be used as repair mortars, it would be very important to ensure the rapid setting, high early strength, and stable late strength [11–14]. Calcium aluminate cement (CAC) primarily consisted of calcium aluminate such as CA, C<sub>12</sub>A<sub>7</sub>, and CA<sub>2</sub> [15]. The hydration of CA was closely related to temperature.

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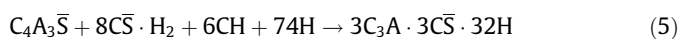
At all temperatures, the stable hydrates of CA were  $C_3AH_6$  and crystalline  $AH_3$  via Reaction (3). The  $CAH_{10}$  was formed between 27 °C and 35 °C, while  $C_2AH_8$  and amorphous  $AH_3$  were found between 35 °C and 65 °C. Those phases would transform or convert to stable phases finally [16]. The mechanical properties of CAC decreased obviously with the hydration temperature increasing, thus its practical application was greatly restricted [17].



When CAC was used to modify the performances of CSA, the CSA-CAC blends may exhibit some special performances. Firstly, CSA as well as CAC expressed the high early strength and good resistance to chemical attack. On the other hand, the hydration of CAC would be changed from Reaction (3) to Reaction (4) due to the presence of calcium sulfate in CSA leading to the rapid formation of ettringite and amorphous  $AH_3$  [18,19]. Both ettringite and amorphous  $AH_3$  played key roles on the mechanical properties of CSA. Hence, the addition of CAC may have great effects on the setting time and strength development of CSA [20].



The stability of ettringite, as the main hydration products of CSA, was closely related to the pH value of matrix. Generally, the boundary for the disappearance of ettringite was  $pH = 10.7$  [21]. However, the pH value in low alkalinity CSA matrix was no more than 10.5, which was negative to the stability of ettringite [22]. The addition of ordinary Portland cement (OPC) can increase the pH value of CSA matrix because of the presence of sulfates [23]. If the content of OPC is high, the calcium hydroxide (CH) would be present in CSA-OPC blends [24]. On the other hand, the ye'elimite hydration rate was changed by the presence of lime via Reaction (5). In CSA-OPC blends containing a low OPC content (no more than 50 wt%), the hydration of CSA focused on the first several days. However, OPC hydration mainly occurred after several days [25]. Hence, the hydration of CSA was affected by the addition of OPC significantly. More importantly, the development of CSA late strength and the stability of ettringite can be guaranteed by the presence of OPC.



When CSA was modified by the combined use of CAC and OPC, except for the interaction between CSA and CAC, CSA and OPC respectively, the CAC and OPC also can interrelate. In OPC-CAC blends, the fast setting and quick strength development can be achieved due to the rapid formation of ettringite [26,27]. However, the strength of OPC-CAC blends decreased significantly with the addition of CAC resulted from the postponed of OPC hydration [26,28]. When the calcium sulfate was present, the hydration of  $C_3S$  was accelerated, thus the late strength was enhanced [29]. In OPC-CAC- $\bar{C}\bar{S}$  blends, massive ettringite formed quickly, which enabled to exhibit excellent performances such as rapid setting and shrinkage compensation [30–33]. Calcium sulfate was one of the important components of CSA, Thus the performances of CSA-CAC-OPC blends may be same as or great than OPC-CAC- $\bar{C}\bar{S}$  blends, and CSA-CAC-OPC blends may be used as repair materials.

In present study, ternary blends containing CSA, CAC, and OPC with various proportions were prepared to be used as repair materials. The effects of total content of CAC and OPC, weight ratio of CAC to OPC on the setting time, compressive strength, and free expansion strain of ternary blends were researched in detail. Moreover, the class, amount, and microstructure of hydration products in ternary blends, especially for ettringite, were researched by XRD, TG, and SEM respectively.

## 2. Materials and methods

### 2.1. Materials

Cements used in present study were low alkalinity calcium sulfoaluminate cement (CSA), calcium aluminate cement (CAC), and ordinary Portland cement (OPC). The chemical compositions (from XRF) and mineral compositions (from XRD) of CSA, CAC, and OPC were listed in Tables 1 and 2 respectively. The physical properties of cements were shown in Table 3. Standard sand with the maximum size no more than 0.25 mm and average size of 0.1 mm was used. The superplasticizer used in this study was power  $\beta$ -naphthalenelfonic acid-based superplasticizer (BNS) with water reduction rate of 25%.

### 2.2. Mix proportions

Mortars were prepared as mixtures of CSA, CAC, OPC, superplasticizer, sand, and water in diverse proportions. The details were listed in Table 4. The water to cement ratio and cement to sand ratio was 0.27 and 1 respectively according to previous research. The content of superplasticizer was 0.8 wt% of binder. In binary blends, the content of CAC accounted for 20–50 wt% of binder. In ternary blends, the content of modified material (CAC and OPC) accounted for 20–50 wt% of binder. Moreover, the weight ratio of CAC to OPC was 3/2, 1/1, and 2/3. The specimen code was related to its composition. For instance, 'C80T32' meant that the content of CSA, CAC, and OPC was 80 wt%, 12 wt%, and 8 wt% in ternary system.

After dry-mixing of cements for 1 min, water, superplasticizer, and sand were added to the mixtures and then mixed for 2 min. Secondly the mixed mortars were casted into the moulds vibrating for 2 min. Finally, mortars were demolded after 1 h and then cured in the water tank at room temperature ( $20 \pm 2$  °C) before compressive strength test.

### 2.3. Test methods

#### 2.3.1. Setting time

The setting time of blends were measured in accordance with the Chinese National Standard GB/T 1346-2011. Pastes were used to setting time test. The mix design between paste and mortar was similar except for sand. Setting time was determined using a Vicat apparatus. The setting situation of specimen was observed for every 30 s.

#### 2.3.2. Compressive strength

Mortars of  $40 \times 40 \times 40$  mm<sup>3</sup> were made for compressive strength test. The specimens were tested at the age of 2 h, 1 day, 7 days, and 28 days. Six specimens were tested for each mix proportion with Universal testing machine, and the displacement speed was set up to ( $2400 \pm 200$ ) N/s.

#### 2.3.3. Free expansion strain

Pastes were cast in moulds of  $10 \times 10 \times 40$  mm<sup>3</sup> with end pieces for the measurement of the length evolution. The specimens were demolded after 2 h, of which length were thought as the initial length. Specimens were then submerged into deionized water before testing [19]. The length of specimens was measured at the age of 1 day, 7 days, 14 days, 21 days, and 28 days. Three prisms were tested for each mix proportion. The length of the specimens was measured with an extensometer having a precision of  $\pm 1$   $\mu$ m. Free expansion strain of specimen was calculated by Eq. (1).

$$\text{Free expansion strain (\%)} = \frac{L_t - L_1}{L_1} * 100\% \quad (1)$$

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