



Effects of ordinary Portland cement on the early properties and hydration of calcium sulfoaluminate cement



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HIGHLIGHTS

- CSA-OPC blends perform the properties of rapid setting and high early strength.
- Ettringite content of CSA is increased by the addition of OPC at early age.
- Ettringite morphology of CSA-OPC is related to the rise of pH caused by OPC.
- Evolution of ettringite from CSA to CSA-OPC is caused by the presence of lime.

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ABSTRACT

Ordinary Portland cement (OPC) was used to enhance the early performances of calcium sulfoaluminate cement (CSA), and the hydration process of CSA-OPC composite was researched by XRD, TG, and SEM. Results showed that the rapid setting and high early strength of CSA can be achieved by the addition of 10–20 wt% OPC. The addition of OPC can evidently increase the ettringite content of CSA at early age, and change the morphology of ettringite significantly related to its high pH value. The difference of ettringite from CSA to CSA-OPC composite was mainly contributed to the presence of lime.

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1. Introduction

Calcium sulfoaluminate cement (CSA) has been used and standardized in China for about 40 years [1,2], which obtained increasing attention because of lower energy used and CO₂ emitted during production than ordinary Portland cement (OPC). CSA was produced by the burning mixtures of natural limestone (source of calcium), gypsum (source of sulfur), and bauxite (source of aluminum) at around 1350 °C in rotary kiln [3,4]. The main hydraulic phase of CSA was ye'elimite (C₄A₃S̄), and the secondary phases included belite (C₂S), calcium sulfate, and gehlenite (C₂AS), etc. The hydration of ye'elimite was used to gain early age strength, and the hydration of belite could improve long term strength. CSA exhibited the properties of rapid setting, high early

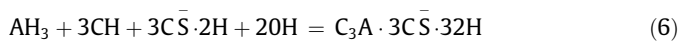
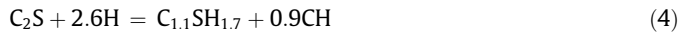
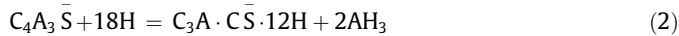
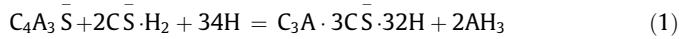
strength, good dimensional stability, low alkalinity, and great durability [5–7]. Hence, it was used in precast concrete applications, cold environment constructions, and repair engineering, etc.

As the main hydraulic phase of CSA, hydration of ye'elimite generally involved calcium sulfate (anhydrite or gypsum, C \bar{S} or C \bar{S} ·H₂) to form ettringite (C₃A·3C \bar{S} ·32H) and gibbsite (AH₃) according to Reaction (1) [8,9]. In the absence of calcium sulfate, ye'elimite can form monosulfate (C₃A·C \bar{S} ·12H) and gibbsite directly as Reaction (2). Thus, ye'elimite to calcium sulfate ratio determined ettringite to monosulfate ratio in the final hydration products [10,11]. Belite can hydrate to form strätlingite (C₂ASH₈) at the aluminum rich environment according to Reaction (3). If gibbsite was depleted, Reaction (4) could take place to form calcium silicate hydrate gel (C-S-H) and portlandite (CH) [12,13]. Lastly the few portlandite produced by Reaction (4) was then consumed by strätlingite, formed katoite (C₃ASH₄) as Reaction (5). If calcium sulfate was excess [14], hydration among gibbsite, portlandite, and gypsum

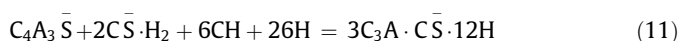
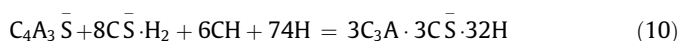
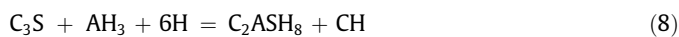
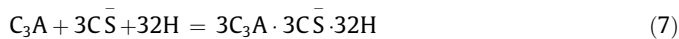
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could form ettringite as Reaction (6). The hardening of CSA was resulted from the formation of initial ettringite skeletons, and the subsequent filling by mixtures of ettringite, monosulfate, gibbsite, and calcium silicate hydrate gel [15,16].



Composite of OPC and CSA can potentially be used to combine their advantages and to obtain especial properties such as fast setting and hardening [17]. In OPC-CSA blends, different reactions for the formation of ettringite have been observed. If the calcium sulfate to ye'elimite ratio was high, tricalcium aluminate from OPC could hydrate to form ettringite as Reaction (7). However, the hydration of tricalcium aluminate was retarded when its surface was covered by ettringite [18]. Alite from OPC can be consumed via Reaction (8) and (9), producing strätlingite or calcium silicate hydrate gel in association with portlandite. When the portlandite was present, Reaction (1) can be transformed to Reaction (10) and (11) [19–22]. The addition of CSA would modify the properties of OPC. For low CSA content (20 wt%), the hardening speed of OPC was still slow. CSA hydrated during the first several days and the hydration of ye'elimite formed ettringite. The replacement of CSA to OPC can increase the amount of ettringite, and change the pore structure [23]. For high CSA content (60 wt%), the setting of OPC was shortened due to the quick hydration of ye'elimite. However, the hydration of OPC mainly occurred after several days [24].



The rapid setting and high early strength is very important, in fast repair engineering, which can be maintained with the use of pure CSA. However, CSA demonstrated the property of low alkalinity (pH value lower than 10.5 generally), which is harmful to the stability of ettringite. Because the boundary for the disappearance of ettringite was pH = 10.7 [25]. The addition of OPC to CSA can increase the alkalinity of matrix due to its mineral composition [26]. The improvement of alkalinity in matrix had great effect on the formation, morphology, and stability of ettringite [27–30]. On the other hand, the hydration processes of ye'elimite could be changed as Reaction (10) and (11) if the calcium hydroxide was present [31]. Calcium hydroxide can be obtained by free lime and the hydration of OPC. For CSA-OPC composite, the setting of CSA can be guaranteed by the quick hydration of lots of ye'elimite. The hydration of OPC mainly occurred after several days, which is positive to the development of CSA later strength [32].

In present study, OPC was used to enhance performances of CSA in early age. Specifically, the setting time and compressive strength of CSA-OPC composite were researched, and then the hydration

products and ettringite morphology were measured by XRD, TG-DSC, and SEM. To explain the effects of OPC on the performances of CSA, CSA-CaO composite was prepared, meanwhile of which properties and hydration products were compared with CSA and CSA-OPC composite.

2. Materials and methods

2.1. Materials

Cements used in present study were low alkalinity calcium sulfoaluminate cement (CSA) and ordinary Portland cement (OPC). The chemical compositions of CSA and OPC were listed in Table 1, and their physical properties were shown Tables 2 and 3 respectively. The specific surface of CSA and OPC was 400 and 350 m²/kg. The lime (CaO) was used in the study with the purity more than 98%. Silica sand with average particle size of 0.1 mm was used. Water reducer was used to maintain the fluidity.

2.2. Mix proportions

The CSA-OPC mortars or CSA-CaO mortars were prepared as mixtures of CSA, OPC or CaO, water reducer, sand, and water in diverse proportions, and the details were listed in Table 4. The content of OPC was 10–50 wt% taking place of CSA. The content of CaO was 2–9 wt% taking place of CSA. The water to binder ratio was 0.27, and the binder to sand ratio was 1. The content of water reducer was 0.8 wt% of binder.

After dry-mixing of the binder for 1 min, water, water reducer and sand were added to the mixture and then further 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 ± 2 °C) before test.

2.3. Test methods

2.3.1. Setting time

The setting time of composite was 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

Prismatic mortars of 40 × 40 × 160 mm³ were made for compressive strength test. The specimens were tested at the age of 2 h, 1 day, 7 days, and 28 days. Three specimens were tested for each mix proportion with Universal testing machine, and the displacement speed was set up to (2400 ± 200) N/s.

2.3.3. Free expansion strain

Pastes were cast in moulds of 10 × 10 × 40 mm³ 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. 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 ± 1 μm [19]. 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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