



Hydration stage identification and phase transformation of calcium sulfoaluminate cement at early age



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HIGHLIGHTS

- Hydration of CSA paste is characterized.
- Hydration stages are determined.
- Phases transformation is found.

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ABSTRACT

This paper studies hydration stages and phase transformation mechanism of fresh calcium sulfoaluminate (CSA) cement. Features of different hydration stages of CSA cement paste are identified by non-contact impedance measurement (NCIM), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), heat evolution test, ion chromatograph and inductively coupled plasma. Ettringite (Aft) and monosulfate (AFm) are found as metastable phases and have poor crystallization degree at the early-age hydration. The unique transformation between Aft and AFm is observed. The influence of different w/c ratios is further studied by NCIM, setting time and compressive strength test.

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1. Introduction

Cement-based materials are the most used artificial materials in the world, and more than 2.5 tons of cement-based materials are consumed per person yearly [1,2]. This is mainly attributed to many favorable features of cement-based materials: low price, reliable mechanical properties and high versatility [1]. Calcium sulfoaluminate (CSA) cement is one kind of promising high-performance materials as it exhibits a high resistance to free-thaw, rapid strength gain and excellent durability in a range of aggressive environment [3], and thus widely used in bridges, concrete pipes, waterproof layers and other concrete elements [3]. Besides, CSA cement-based materials reveal low pH value, low porosity and

the ability of ettringite (Aft) and monosulfate (AFm) phases to bind heavy metals, and hence, CSA cement and their blends are of interest in the field of hazardous waste encapsulation [3,4]. In particular, CSA cement is considered as green cement as well due to its low energy requirement for production. Its production may have up to 35% lower carbon dioxide footprint than ordinary Portland cement [3,5,6]. The main minerals of CSA cement are tetracalcium trialuminate sulfate or ye'elimite ($C_4A_3\bar{S}$) and belite (C_2S) (abbreviated symbols used in this paper are illustrated as: C=CaO, S=SiO₂, A=Al₂O₃, H=H₂O, F=Fe₂O₃ and \bar{S} =SO₃). Besides, C₄AF, C₃A, C₁₂A₇ and C₆AF₂ are other phases in the raw cement clinker. Previous study shows that Aft and AFm are the key crystal products during the hydration of CSA cement [3,7]. The hydration of CSA cement is primarily associated with chemical reactivity and amount of calcium sulfate in the clinker [8]. Hydration reactions of CSA cement are extremely fast and usually occur between 2 and 24 h when the

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molar ratio calcium sulfate/ye'elimite is about 1.5 in the fresh mixture [3,9]. It is claimed that typical values of heat of hydration of CSA cement approach to 400 J/g after 3 days by heat evolution test [9].

On the other hand, there are only few of in-situ, non-destructive and reliable techniques to characterize transformation features among hydrated phases, change of amount of different phases (either unhydrated clinker or hydrated products) and possible self-desiccation mechanism of CSA cement-based materials at the early age until now [3,9,10]. Traditionally speaking, the calorimetric method may provide an in-situ and simple way to understand cement hydration. The mechanism and stages of hydration are interpreted and identified by heat liberation [11]. However, some drawbacks of this method were pointed out, such as inappropriate test conditions and over-simple theoretical assumption [11]. Therefore, the in-situ hydration process of CSA cement is not well-understood until now [1].

In this work, hydration evolution of the cement paste with w/c 0.7 is investigated using non-contact impedance measurement (NCIM), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FTIR), thermogravimetric analysis test (TGA), heat evolution test, ion chromatograph and inductively coupled plasma. Moreover, the relations among microstructural development, electrical impedance and mechanical property of CSA cement pastes with different water to cement ratios are analyzed.

2. Materials and analytical methods

2.1. Raw materials

In this study, CSA cement provided by Tangshan Polar bear Special Cement CO., Ltd., is used to prepare cement pastes. The chemical composition of CSA cement measured by XRF is shown in Table 1. The content of gypsum by mass is about 16%. Specific surface area of CSA cement is 350 m²/kg by nitrogen adsorption test. Water used in the present study is de-ionized and de-aired.

2.2. Analytical methods

2.2.1. Impedance measurement

The non-contact impedance measurement (NCIM) was a newly promoted non-destructive method to study the hydration, pore structure, chloride ion migration and permeability of cement paste [12–17]. Its working principle can be found in Ref. [13]; metallic test electrodes are replaced by transformer and leakage current meter, compared with traditional electrical impedance system [12,17]. In this work, four cement pastes with different w/c ratios 0.4, 0.5, 0.6 and 0.7 by mass were prepared by mixing CSA cement and water in a planetary-type mixer at 45 rpm for 2 min first and then at 90 rpm for 2 min. The modulus of impedance of cement paste with volume of 1.7 liters was measured and recorded for 1 day. All of cement pastes were cured in an environmental chamber with temperature 20 ± 1 °C and relative humidity 100%. The applied frequency of NCIM was 1 kHz. The temperature development of cement pastes was also recorded by NCIM.

2.2.2. Setting time and compressive strength tests

The setting time of cement pastes were tested by Vicat apparatus under the same curing conditions (temperature 20 ± 1 °C and relative humidity 100%) in accordance with ASTM C 191-99. Cement pastes with different w/c ratios were consistent with the ones previously described. The initial setting time was determined when the Vicat needle penetrated 25 mm. The final setting time was the time when the needle made an impression on the surface of the pastes but did not penetrate. Meanwhile, the fresh cement pastes were cast into 4 cm × 4 cm × 4 cm molds for compressive strength tests at 1 day. The tests were undertaken with a loading rate 1 kN/s. Three cubes for each kind of cement paste were tested for the calculation of average value of compressive strength.

Table 1

The chemical composition of CSA measured by XRF (wt%).

MgO	Al ₂ O ₃	SiO ₂	SO ₄	CaO	TiO ₂	Fe ₂ O ₃
2.8072	32.9257	8.1582	11.8391	41.2713	1.4141	1.5845

2.2.3. Pretreatment for XRD, SEM, FTIR, TGA

To make sure that more hydrated products are generated during the hydration and detected easily by various techniques (XRD, SEM, FTIR and TGA), the paste with w/c ratio 0.7 was selected and cast in 300 ml polyethylene bottles, sealed and stored under the condition of temperature 20 ± 1 °C and relative humidity 100%. With respect to XRD, SEM, FTIR and TGA, the hydration of cement paste was stopped after fixed periods of time by successively immersing the crushed pastes into ethyl alcohol for 4 days and drying them in a vacuum chamber with 20% relative humidity at 20 ± 2 °C for 4 days; these hydration periods (A: 15; B: 86; C: 223; D: 400; E: 1020 and F: 1440 min) were selected in the middle or the end of corresponding hydration stages determined by NCIM in the under-mentioned subsection, as shown in Fig. 1.

2.2.4. X-ray diffraction analysis

X-ray diffraction analysis was performed on dried cement pastes mentioned in Section 2.2.3 by PW18300 (Philips) equipped with a graphite monochromator and copper anode. The step size employed in this work was 0.02°, 1 s per step in the 5–65° 2θ range.

2.2.5. Scanning electron microscope

For microstructural investigations, the dried cement pastes were coated with gold and observed by a JEOL 6300 scanning electron microscope (SEM) coupled to energy dispersive spectroscopy (EDS) analyzer.

2.2.6. Fourier transforms infrared spectroscopy

The Fourier transforms infrared spectroscopy (FTIR) was performed at room temperature and conducted in Vertex 70 Hyperion 100 (Bruker) and 16 scans were recorded to register each dried cement pastes. The compressed tablet for FTIR test was prepared by mixing 1 mg of sample with 300 mg of potassium bromide. The scans were performed in the mid-infrared region at frequencies ranged from 4000 cm⁻¹ to 400 cm⁻¹.

2.2.7. Thermogravimetric analysis test

Thermogravimetric analysis test was performed under nitrogen atmosphere on 9 ± 2 mg of ground dried cement pastes using TGA Q5000 at 10 °C/min up to 800 °C.

2.2.8. Pore solution analysis

For the case of pore solution extraction, pore solution in the fresh cement paste was extracted by a vacuum pump in the corresponding hydration periods described in Section 2.2.3 and shown in Fig. 1 (A: 15; B: 86; C: 223 and D: 400 min). Fig. 2 is the illustration of pore solution extraction set-up. The total concentrations of the element in the extracted pore solution were determined by two set-ups, respectively: (1) ion chromatograph equipped with a conductivity detector; and (2) inductively coupled plasma optical emission spectrometer (ICP-OES). pH value of the extracted pore solution was also checked by WTW portable multi-parameter water quality analyzer (Germany, Multi 3420).

2.2.9. Heat evolution

The heat evolution of CSA paste with w/c ratio 0.7 was conducted using isothermal calorimetry. Fig. 3 is the schematic diagram of isothermal calorimetry. The fresh paste was injected into the glass ampoule of calorimetry via the syringe. The de-air water with the same weight as the paste, was also injected into the other glass ampoule as a reference. The heat release of the paste was recorded continuously with hydration time in 1 day.

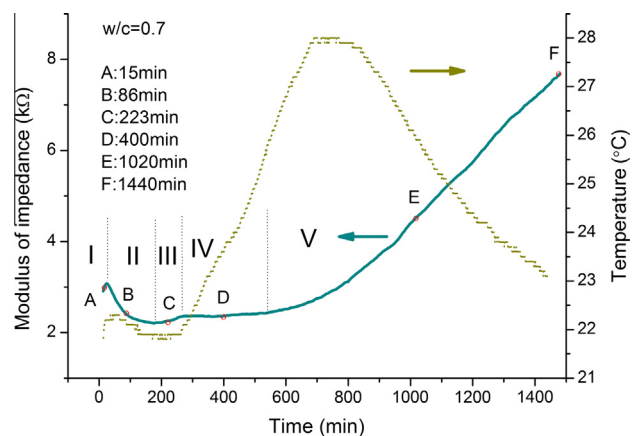


Fig. 1. Hydration stages of the CSA paste with w/c ratio 0.7 and relevant temperature development determined by NCIM.

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