



Influence of sodium aluminate on cement hydration and concrete properties



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HIGHLIGHTS

- Influence of sodium aluminate (SA) on cement and concrete properties were studied.
- SA can promote setting behavior and hydration heat release rate at first peak.
- SA will change AFt to AFm, AFm contributes to chloride penetration resistance.
- SA promotes AFm forming rate, but depresses calcium silicate hydration process.
- SA enhances early age strength, but impairs later age strength of concrete.

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ABSTRACT

The influences of sodium aluminate (SA) on cement hydration were studied. Heat evolution of cement pastes with and without SA was monitored by a differential scanning calorimeter (DSC). Hydration products were identified using scanning electron microscope (SEM), X-ray diffraction (XRD), thermal analysis (TG–DSC), and mass spectrum (MS). Pore structures of cement pastes were analyzed using nitrogen absorption method. Concrete strength and chloride penetration resistance were also evaluated. The mechanisms by which SA contributes to cement hydration and microstructure development were explored. The results indicate that addition of SA resulted in changed calcium sulfoaluminate morphology, form acicular AFt to tabular AFm. Adding of SA increased the volume of small capillary pores (5–30 nm) and reduced the volume of larger pores (>30 nm). Cement setting time reduced significantly as SA addition reached up to 4%. 1.5% SA addition can enhance concrete strength at early age but reduce it at later age. Addition of SA also improved chloride penetration resistance of concrete.

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1. Introduction

Many concrete applications, such as high speed construction, rapid repair, frost prevention, tunneling, shoring, gas and oil well cementing, require concrete to have rapid setting and strength development abilities. In addition to different curing methods, accelerators are often used to facilitate concrete setting and strength gain speed. Among various accelerators, sodium aluminate (NaAlO₂, to be abbreviated as SA in this paper) is an effective one [1].

Research has revealed that SA can alter the hydration kinetics and microstructure development of cement paste, thus resulting

in changes in macro-properties of the concrete, such as setting behavior, strength development and transport properties [2,3]. Anderson discovered that SA accelerated hydration of alite and belite in white cement and resulted in calcium–silicate–hydrate phases with longer average chain lengths of SiO₄/AlO₄ tetrahedra; and SA reduced the quantity of ettringite and resulted in larger quantities of monosulfate and calcium aluminate hydrate phase [2]. Recently, Li studied the influence of tablet and powdered SA on cement hydration products, setting time, workability and strength, found that SA significantly shortened cement setting time due to the rapidly formed hydration product calcium aluminate hydrate (C–A–H) [3]. In spite of some research have been done, the in-depth study of SA modified cement system is still limited, and the mechanism of SA–cement interaction has not been fully understood.

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In this paper, the heat evolution, hydration products type and morphology, pore structure of SA modified cement paste were investigated. The influence of SA on concrete strength and chloride penetration resistance were also studied.

2. Materials and mix proportions

Type I Portland cement was used, its chemical composition and fineness are given in Table 1. Deionized water with resistivity no less than 10.0 MΩ cm was used as the mixing water. River sand with fineness modulus of 3.1 and limestone with sizes ranging from 5 mm to 10 mm were employed as fine and coarse aggregates respectively. Polycarboxylate-based water reducing admixture (WRA) was used. SA was a reagent of chemical purity. The dosages (weight percent of cement) of SA investigated were 2%, 4%, 6%, and 8%.

Water-to-cement ratio (W/B) of 0.4 (by weight) was used for all pastes and concrete samples. Concrete samples were used for compressive strength and chloride penetration tests. The mix proportion of concrete is given in Table 2. To ensure certain workability of fresh concrete, only 1.5% (by weight of cement) of SA was employed. The slumps of fresh concrete mixtures without and with sodium aluminate were 180 mm and 80 mm, respectively.

2.1. Test methods

2%, 4%, 6% and 8% SA were used for setting time and heat evolution test; 4% SA were used for hydration product morphology and type, thermal analysis, mass spectrum and pore structure test. Concrete samples with 1.5% of SA were tested for compressive strength and chloride penetration resistance.

Setting time of cement pastes with different dosages of SA was measured according to ASTM C191-08 (Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle).

Heat evolution of cement pastes was monitored by a differential scanning calorimeter (DSC), under constant temperature of 25 °C.

The study of the microstructure development of cement pastes consisted of several steps:

- (1) Conducting a completed DSC time history curve for each cement paste.
- (2) Selecting several key time points from the DSC time history curve so that the features of the DSC curve can be well captured by these selected points.
- (3) Performing the same DSC test as step (1) for a series of samples of a given paste; when a selected time point was reached, cement paste sample was taken out of the DSC instrument, and it was cracked into several small pieces.
- (4) Submerging these small pieces into ethanol liquid so as to discontinue the cement hydration process (note: It took less than 2 min from taking the sample out of the DSC chamber to submerging its cracked pieces into the ethanol liquid).
- (5) Studying microstructure of these small pieces of cement paste samples.

The microstructure study included the examinations of hydration product morphology and type, thermogravimetry, differential scanning calorimetry, mass spectrum and pore structure.

Scanning electron microscope (SEM) was used to examine the microstructure and morphology of hydration products. To perform the SEM study, a few pieces of samples were taken out of the ethanol liquid and air dried under a room temperature (23 °C) for 5 min. The air-dried samples were then further oven dried at 60 °C for 6 h. A gold coating was subsequently applied onto the surface of the samples. The samples were then observed under SEM.

Table 1
Chemical composition and fineness of Portland cement.

Oxide (wt%)								Blaine fineness (m ² /kg)
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O _{eq}	f-CaO	
21.58	4.03	3.46	61.49	2.60	2.83	0.51	0.67	346
C ₃ S		C ₂ S		C ₃ A		C ₄ AF		LOI (wt%)
57.34		18.90		6.47		11.25		1.97

Table 2
Concrete mix proportion.

No.	Cement (kg/m ³)	Water (kg/m ³)	W/B	Sand (kg/m ³)	Aggregate (kg/m ³)	WRA (%)	SA (%)
C-SA-0	490	196	0.4	830	880	1.5	0
C-SA-1.5	490	196	0.4	830	880	1.5	1.5

Hydration products of the pastes were identified using the X-ray diffraction (XRD) method. After being taken out of the ethanol liquid, the paste samples were first oven dried at 60 °C for 6 h, then pulverized by an agate mortar and passed an 80 μm sieve. The XRD patterns of the cement paste samples were tested using X-ray diffractometer, with a Cu Kα source and a scanning speed of 2° per minute.

To quantify and identify hydration products, thermogravimetry (TG) – differential scanning calorimetry (DSC) – mass spectrum (MS) hyphenated method was used.

Using TG–DSC instrument, under a controlled temperature program, the mass change of cement paste and the difference of energy inputted into cement paste and a reference material are both measured simultaneously as a function of temperature. Meanwhile, the gas released during TG–DSC process was conducted into MS via capillary tube. The input gas was first ionized and then classified and identified based on the different mass-to-charge ratio of ions, and finally the substances released during the heating progress are identified. During the test, samples were heated from 50 to 1100 °C at a heating rate of 20 °C/min.

Pore structure of the cement pastes was evaluated by Brunauer–Emmett–Teller (BET) absorption method. After paste samples were taken out of ethanol liquid, they were oven dried at 60 °C for 6 h and then vacuum de-aerated for 6 h at 100 °C. Nitrogen gas (N₂) was used as an adsorbate. Pore volume and pore size of a tested sample were calculated based on the amount of N₂ adsorbed.

After casting, concrete specimen were covered with plastic sheet to prevent water loose and demolded 24 h later. Then concrete specimen were stored in environmental room of T = 20 °C and RH ≥ 95% to the specified curing age.

Compressive strength tests were performed using 100 mm cubic concrete samples, according to ASTM C39/C39M-14 (Standard test method for compressive strength of cylindrical concrete specimens.)

Chloride penetration resistance of concrete was evaluated according to ASTM C1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration). During the test, water saturated samples were placed between two testing cells, which were filled with 0.3 M NaOH and 3% (by mass) NaCl solution respectively. The time–current curve was integrated to calculate the total charge (in coulombs) passed through the specimen after 6 h of testing.

3. Results and analysis

3.1. Setting time

The setting times of all cement pastes studied are presented in Fig. 1. The figure indicates that both initial and final setting times of the cement pastes were reduced significantly when SA dosage increased from 0% to 4%. The setting times of cement pastes became stable when the dosage was higher than 4%. This suggests that 4% might be the optimal dosage of SA to be used for acceleration of cement hydration.

3.2. Heat evolution

The influence of SA on the heat evolution of cement paste was measured by DSC. As seen in Fig. 2, the heat evolution curves of cement pastes with SA display 5 typical stages similar to that of the control paste (without SA): (A) pre-induction period, (B) induction period, (C) acceleration period, (D) deceleration period, and (E) steady diffusion period, which are identified at the bottom of heat evolution curve in Fig. 2(a).

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