Effects of superplasticizers and retarders on the fluidity and strength of sulphoaluminate cement

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HIGHLIGHTS

- The workability of SAC admixed with different types of superplasticizer and retarder was studied.
- The effects of different combinations of superplasticizer and retarder on the fluidity were quite different.
- CA and SG had little negative effects on the fluidity of paste admixed with PC.

ARTICLE INFO

ABSTRACT

The effects of three superplasticizers, β-naphthalenelfonic acid-based superplasticizer (BNS), aminosulfonic acid-based superplasticizer (AS) and polycarboxylate acid-based superplasticizer (PC), and two retarders, citric acid (CA) and sodium gluconate (SG), on the fluidity, flow loss and compressive strength of sulphoaluminate cement were studied. The competition adsorption effects between the retarder CA and the superplasticizers of BNS and AS were intensively and lead to low initial fluidity. Besides, there is not any competition effect between SG and superplasticizer of BNS and AS, and the combinations of the two retarders and superplasticizer of PC had better influence on the fluidity and flow loss. Furthermore, superfluous retarders would lead to decrease of compressive strength due to the inactivity of cement particle.
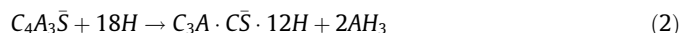
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1. Introduction

Sulphoaluminate cement (SAC) is a high early strength and fast setting cement. It is often used in many applications such as bridges, concrete pipes, precast concrete, waterproof layers, fiber reinforced cement products, shotcrete and low temperature construction [1–6]. The SAC is produced by burning mixtures of limestone, bauxite and gypsum at 1250–1350 °C, about 200 °C lower than that used for Portland cement clinker, which has the advantage of low calcinations temperature and low CO_2 emission [1,7]. Besides, the industrial by-products or waste materials such as fly ash, blast furnace slag, phosphogypsum, baghouse dust or scrubber sludge are always used in producing SAC, which also has the ability of consuming industrial wastes [8–11]. Therefore, SAC is gaining more popularity than Portland cement because of its low price and environment friendliness [1–4,12–14].

SAC is comprised by $4CaO \cdot 3Al_2O_3 \cdot SO_3$ ($C_4A_3\bar{S}$), Ca_2SiO_4, C_2 (A, F) (ferrite), and gypsum [15–17]. The main crystalline hydration products ettringite and monosulfate are formed together with amorphous aluminium hydroxide (Eqs. (1) and (2)) [18].

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \rightarrow C_3A \cdot 3C\bar{S} \cdot 32H + 2AH_3 \qquad (1)$$

$$C_4A_3\bar{S} + 18H \rightarrow C_3A \cdot C\bar{S} \cdot 12H + 2AH_3 \qquad (2)$$

Because of the fast formation of AFt, the cement possesses the feature of fast setting and slight expansion. However, the fast setting may not benefit to the engineering application for there is not enough time to casting before the cement set [19,13,20,21]. The fluidity can be enhanced by using superplasticizer and the setting time can be prolonged by the retarder, both of which helps to maintain the good fluidity and workability. For Portland cement, these chemical admixtures were intensively studied and the results showed that interactions between superplasticizers and retarders had significant effects on the fluidity and fluidity loss of Portland cement paste [22–26].

Ceelepardi et al. reported that both the fluidity of cement paste and the adsorption amount of superplasticizer on the cement particle increased with the increase of the superplasticizer [22]. Lummer and Plank found that the addition of lignosulfonate

retarder can not only delay the hydration process and reduce the setting time of cement, but also increase the fluidity of cement paste. Furthermore, they found that the presence of superplasticizer could lead to the longer setting time, indicating synergistic effect between superplasticizer and retarder [23]. However, other studies showed that the combination of β-naphthalenelfonic acid-based superplasticizer (BNS) and sodium gluconate retarder (SG) result in the increase of fluidity and decrease of fluidity loss of paste [24,25]. Competitive adsorption was found between polycarboxylate-based superplasticizers and retarders such as citrate on the mineral binder surface of ordinary Portland cement and calcium aluminate cement, resulting in lower mortar fluidity [26]. Hence, the combination of different types of superplasticizers and retarders always lead to different effects for Portland cement due to the complex interaction. In this context, research is needed to understand the complex interaction between different types of superplasticizers and retarders, and their effects on the performance of cement especially SAC furtherly.

In view of this, the fluidity and strength of SAC blended with frequently-used superplasticizers and retarders were studied. Three common superplasticizers and two retarders were used. To make further study on these groups, zeta potential, adsorption, and X-ray Diffraction (XRD) were used.

2. Experimental

2.1. Materials

A low alkali sulphoaluminate cement was used and its chemical composition is shown in Table 1. Three types of common superplasticizers used in this study were powder β-naphthalenelfonic acid-based superplasticizer (BNS), liquid aminosulfonic acid-based superplasticizer (AS) with the solid content of 35 wt%, liquid polycarboxylate acid-based superplasticizer (PC) with the solid content of 20 wt%. Two types of retarders used were citric acid (CA) and sodium gluconate (SG) with the purity of 99.5% and 98%.

2.2. Mix proportions

Two types of SAC paste were prepared. They were samples admixed with three types of superplasticizer and different combinations of superplasticizer and retarder. Firstly, five level dosages were selected for each superplasticizer, they were 1.00 wt%, 1.20 wt%, 1.40 wt%, 1.80 wt% and 2.00 wt% for BNS, 1.50 wt%, 1.75 wt%, 2.00 wt%, 2.25 wt% and 2.50 wt% for AS and 0.75 wt%, 1.00 wt%, 1.25 wt%, 1.50 wt% and 1.75 wt% for PC. According to the results of the fluidity, 1.20 wt% BNS, 1.75 wt% AS and 1.25 wt% PC was selected to combine with different dosages of CA and SG. They were 0.03 wt%, 0.06 wt%, 0.09 wt%, 0.12 wt% and 0.15 wt% for CA and SG.

2.3. Methods

2.3.1. Fluidity of the cement paste

The fluidity of cement paste was tested in accordance with the Chinese Standard GB/T 8077-2012 "Methods for testing uniformity of concrete admixture". SAC pastes were prepared by mixing 300 g cement, 87 g water (w/c = 0.29) and a predetermined amount of the admixtures at 20 ± 2 °C. The prepared paste was casted into a conical mold (with the height of 60 mm, top diameter of 36 mm, and bottom diameter of 60 mm). Then the conical mold was lifted up to let the paste flow freely for 30 s on the glass plate. The fluidity was determined by measuring the diameters of the cement paste at two vertical directions and the average value was registered as the fluidity of paste. In order to determine the fluidity loss, the fluidity of the cement pastes was measured repeatedly at 5, 15, 30, and 45 min after mixing.

2.3.2. Setting time

The setting time of SAC pastes was determined according to the Chinese Standard GB/T 1346-2011 "Test methods for water requirement of normal consistency, setting time and soundness of the Portland cement" (corresponding to the ISO 9597: 2008, "Cement – Test methods – Determination of setting time and soundness, NEQ"). Cement paste was prepared with 500 g SAC, 145 g water (water to cement ratio of 0.29) and a predetermined amount of chemical admixtures. A Vicat apparatus was used to measure the setting time.

2.3.3. Adsorption property

CSA paste samples were prepared by 300 g cement, 300 g water (w/c = 1), and predetermined amount of chemical admixtures. At the time of 5 and 15 min, the paste was centrifuged at the rotate speed of 5000 r/min for 5 min. The supernatant liquid was collected and then it was diluted to the designated concentration which conforming to the detectable concentration of ultraviolet spectrophotometer (Nicolet Evolution 300).

The amount of adsorbed superplasticizer was calculated according to Eq. (3), based on the concentration difference before and after superplasticizer adsorption.

$$\text{Adsorption conc.} \ (C) = \text{Initial conc.} \ (C_I) - \text{Residual conc.} \ (C_R)$$

(3)

2.3.4. Zeta potential

Zeta potential analyzer (Zeta Probe, America) was used to examine the zeta potential of cement paste with addition of different types of superplasticizers and retarders. SAC cement paste was prepared by 300 g cement, 150 g water (w/c = 1:2) and predetermined amount of chemical admixtures. In order to achieve the zeta potential change at the plastic state of the cement paste, the zeta potential was measured once every 60 s, and this measurement was last 30 min after adding water.

2.3.5. Compressive strength

The compressive strength was tested according to ISO 679: 2009 "Cement – Test methods – Determination of strength". A batch of three mortar specimens (40 mm × 40 mm × 160 mm) was prepared. Samples were prepared using 800 g SAC cement, 280 g water (w/c = 0.35), 1200 silica sand (s:c = 3:2), and a predetermined amount of chemical admixtures. They were casted at 20 ± 2 °C, and then cured in a Standard curing chamber at the temperature of 20 ± 1 °C and the relative humidity of 95% HR. After casting 24 h, samples were demoded and cured in Standard curing chamber until 1, 7 and 28 days.

Table 1
Chemical composition of SAC.

Components	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	SO$_3$	Na$_2$O	K$_2$O	Loss
Contents (wt%)	41.22	8.56	34.05	3.01	2.41	9.87	0.21	0.05	0.62