Scientific paper

Accelerated Early Age Hydration of Cement Pastes Blended with Sulphoaluminate Expansive Agent

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Received 16 March 2021, accepted 27 May 2021 doi:10.3151/jact.19.655

Abstract

Addition of sulphoaluminate expansive agent could be one useful method to reduce the shrinkage crack destruction of shotcrete. While the setting and hardening behavior and early age mechanical strength of cement pastes containing liquid setting accelerators may be influenced by the introduction of sulphoaluminate expansive agent (SEA). Therefore, in this work, the early age hydration behavior of different accelerated cement pastes with SEA was investigated via setting times measurement, early age mechanical strength test, isothermal calorimeter, mineralogical composition, thermal gravimetric analysis (TGA) and scanning electron microscope with EDS detection. Results showed that the ability of liquid setting accelerators on shortening the setting times of cement pastes could be enhanced by the addition of SEA, especially for alkali-free type accelerator due to the prompted formation of massive rod-like ettringite phase. In addition, the further hydration extent of C3S phase in accelerated cement pastes was advanced by more dissipative portlandite phase to form such massive rod-like ettringite, thus improving the initial mechanical strength.

1. Introduction

Wet-mix sprayed concrete, also called “wet-mix shotcrete” for short, is a kind of special spraying of fresh concrete or mortars with high velocity using air or pump pressure-producing equipment. In recent decades, wet-mix shotcrete is widely applied in mining and tunnel or other underground constructions, structural repairs, soil stabilization and installation of shell structures (Brandtner et al. 2018; Belie et al. 2005) owing to its accurate water-binder ratio control, less rebound concrete loss, less dust pollution for workers health (Choi et al. 2016; Won et al. 2013). However, in most cases, high cement content and water-binder ratio of wet-mix shotcrete are adopted to obtain better pumpability and shootability (sprayability), thus leading to high volumetric shrinkage effect of shotcrete. Shrinkage crack destruction of shotcrete is one of the critical factors responsible for leaning and sintering durability issues of shotcrete (Armengaud et al. 2018; Galan et al. 2019).

Aiming at relieving or compensating such volumetric shrinkage effects, many strategies and addition of admixtures are developed and introduced into self-compacting concrete and steel fiber reinforced shotcrete (Huang et al. 2011), such as shrinkage reducing admixture (SRA), internal curing agent (ICA) and expansive agent (EA) (Monosi et al. 2011; Ning et al. 2019). Among them, expansive agent is generally used and recommended to compensate the drying shrinkage of cementitious materials. According to the chemical reaction time and reaction products type, expansive agent is classified basically into sulfoaluminate-type, CaO-type (Tittarelli et al. 2017) and MgO-type (Cao et al. 2018). Compared to MgO-type, expansive agent based on sulfoaluminate (SEA) is more widely used and its volumetric shrinkage compensation effects are achieved with the generation of ettringite phase, especially formed in early age hydration stages (Han et al. 2016).

Liquid setting accelerators are used necessarily to obtain fast setting times and high early strength within minutes or hours, thus leading to good adhesion of the sprayed concrete onto surrounding rock or repaired construction surface (Malmgren et al. 2004; Belie et al. 2005). It is well known that setting accelerators are comprised of many chemical ions like sodium, aluminum, sulfate or organic compounds like alcohol amine, which also influence the early age hydration of cement pastes.
In literature, the $\text{AlO}_2^-$ ions in alkaline type or $\text{Al}^{3+}$ ions in alkali-free type accelerator are always associated with the $\text{Al}[(\text{OH})_4]$ groups, which could react with $\text{C}_3\text{A}$ and gypsum phase to produce massive ettringite in initial hydration stages, thus shortening the setting properties of cement pastes (Paglia et al. 2001; Maltese et al. 2007). According to Salvador’s views (Salvador et al. 2017), active dissolution sites and hydration extent of $\text{C}_3\text{S}$ phase are blocked and reduced with the formation of monosulfoaluminate ($\text{AFm}$) phase, which are affected significantly by the changed $\text{C}_3\text{A}/\text{SO}_3$ ratio in hydration environment with the addition of setting accelerators. Such $\text{C}_3\text{A}/\text{SO}_3$ ratio is ought to be maintained in the 0.67 to 0.90 range (Salvador et al. 2016a, 2016b).

Although some studies have been published about the application of SEA component into shotcrete materials (Huang et al. 2011; Ning et al. 2019), it is still essential to evaluate the accelerated early age hydration of cement pastes with SEA introduction, especially for the formation of ettringite phase, which is necessary for mechanical strength development of wet-mix shotcrete and the volume-compensating effect of SEA in shotcrete.

The main objective of this paper is to evaluate the effect of SEA on the early age hydration of cement pastes containing different liquid setting accelerators. For experimental design, the replacement of SEA into cement is kept constant, as a conventional ratio of 8% falling in the conventional dosage range 6 to 10% and the accelerated cement pastes or mortars are prepared with two types of liquid setting accelerators, alkaline type composed with sodium aluminate and alkali-free type based on aluminum sulfate. In order to characterize this early age hydration behavior, isothermal calorimetry, hydrated ion dissolution analysis, mineralogical composition, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM-EDS) are conducted.

### 2. Methods and materials

#### 2.1 Raw materials

Type 1 Portland cement (CEM 42.5) and expansive agent based on sulfoaluminate (SEA) were used in this study. Mineralogical and chemical compositions of Portland cement and expansive agent were determined by XRD Rietveld analysis and XRF method, respectively, given in Table 1. Physical properties of Portland cement and expansive agent were shown in Table 2.

Natural sand with fineness modulus 3.1 and specific surface area 2630 m$^2$/kg was employed for cement mortars. In order to prepare accelerated cement pastes or mortars, two different types of liquid setting accelerators

### Table 1 Mineralogical and chemical compositions of CEM 42.5 and SEA.

| Compound | CEM 42.5 (%) | SEA (%) | Compound | CEM 42.5 (%) | SEA (%) |
|----------|-------------|---------|----------|-------------|---------|
| LOI      | 3.65        | 0.63    | $\text{C}_3\text{S}$ | 52.5        | /       |
| $\text{SiO}_2$ | 21.95       | 1.47    | $\text{C}_3\text{S}$ | 17.5        | /       |
| $\text{Al}_2\text{O}_3$ | 5.70        | 6.28    | $\text{C}_3\text{A}$ | 5.0         | /       |
| CaO      | 59.25       | 68.20   | $\text{C}_3\text{A}_3\text{S}\text{S}^a$ | 0.0         | 28.4    |
| Fe$_2$O$_3$ | 2.72       | 0.88    | $\text{C}_4\text{AF}$ | 8.9         | /       |
| MgO      | 2.18        | 1.44    | $\text{CaSO}_4$ | 0.1         | /       |
| Na$_2$O  | 0.15        | /       | $\text{Ca(OH)}_2$ | 2.3         | 30.7    |
| K$_2$O   | 0.88        | /       | $\text{CaCO}_3$ | 0.1         | /       |
| $\text{SO}_3$ | 3.13       | 21.10   | MgO      | 0.5         | /       |
| $\text{TiO}_2$ | 0.37       | /       | $\text{SiO}_2$ | 0.9         | /       |
| Total sum | 99.98       | 100.0   | $\text{K}_2\text{SO}_4$ | 0.5         | /       |
|          |             |         | $\text{CaSO}_4\cdot2\text{H}_2\text{O}$ | 1.6         | 40.4    |
|          |             |         | $\text{CaSO}_4\cdot1/2\text{H}_2\text{O}$ | 1.0         | /       |
|          |             |         | Amorphous | 8.8         | 0.5     |
|          |             |         | Total sum | 99.7        | 100.0   |

$^a$C$_3$A$_3$S indicates calcium sulfoaluminate.

### Table 2 Physical properties of CEM 42.5 and SEA.

| No. | Density (g·cm$^{-3}$) | Specific surface area (m$^2$/kg) | Setting time (min)$^b$ | Compressive strength (MPa)$^c$ |
|-----|-----------------------|----------------------------------|------------------------|-------------------------------|
|     |                       |                                  | Initial | Final | 3 d  | 7 d  | 28 d |
| Cement | 3.05                 | 350                              | 276     | 283   | 34.2 | 38.9 | 48.0 |
| SEA   | 2.78                 | 410                              | 175     | 213   | 17.5 | 23.4 | 42.1 |
were used. One kind was alkaline solution based on sodium aluminate and the other was alkali-free type composed with aluminum sulfate solution. Basic physical properties of liquid setting accelerators were listed in Table 3, following the Chinese standard GB/T 35159 (GB/T 2017b).

### 2.2 Cement pastes and mortar specimens

The mix proportions of cement pastes and mortars used in the experimental program were shown in Table 4. Expansive agent was added by replacing the cement material partially for a moderate content of 8.0 wt% falling in the conventional dosage range 6 to 10%. The alkaline or alkali-free accelerator was introduced in the dosage of 5.0% and 7.0% by weight of cement, respectively. Water/cement (w/c) ratio in cement pastes or mortars was chosen as 0.40 and the water content of setting accelerators was deducted to assure the constant w/c ratio.

The cement pastes were prepared with the following procedure: Firstly, water and cement or cement blended with SEA were added into the mixing pot and then stirred with a velocity of 140±5 rpm and was kept for 150 s. Secondly, setting accelerators were introduced with special injection devices in 5 to 7 s. Finally, above cement pastes were mixed with stir velocity of 285±10 rpm for 15 to 20 s. Cement mortar specimens were prepared with the same procedure of cement pastes, except that natural sand was added to cement and water. The cement mortars were manufactured with the cubic mould of 40×40×160 mm³. The cement pastes and mortars were cured at room temperature of 20±1°C and in water curing environment.

### 2.3 Test methods

In order to develop the effect of SEA on initial hydration behaviors of different accelerated cement pastes or mortars, different test methods were used. To avoid the interaction of cement pastes with atmospheric CO₂ and moisture, measured samples were immersed into the anhydrous ethanol for 5 days to stop the hydration reaction, then dried under vacuum at 45°C for one week, finally kept in a drier with nitrogen atmosphere and dry silica gel.

#### 2.3.1 Physico-chemical analysis

Isothermal calorimetry was conducted to determine the effect of SEA on the initial hydration kinetics of different accelerated cement pastes. Heat flow curves were measured for 28.0 g cement pastes with the addition of different setting accelerators and SEA during 0 to 48 h of hydration at 20°C, using TAM 08 isothermal calorimeter (TAM AIR from TA Instruments, USA). To determine the exothermic reaction between cement pastes and setting accelerators, setting accelerators were added into the middle part in the measurement vessel with a tiny syringe and hand-mixed for 10 s after this addition.

Hydrated ion dissolution analysis was performed to explore the ion concentrations of calcium and sulfate qualitatively during 0 to 24 h of hydration using a commercial inductively coupled plasma optical emission spectrometer (FMS 26, SPECTRO Analytical Instruments GmbH, Germany). The measured samples were handled with an adaptation of method (Maltese et al. 2007): cement paste specimens at 15 min, 3 h, 6 h, 12 h and 24 h of hydration were ground and dipped in water with water/powder ratio of 5.0, then mixed with a high stirring rate of 500 rpm in a short time of 5 min in order to weaken the secondary hydration effect.

The mineralogical composition of the accelerated cement pastes blended with SEA was determined by X-ray diffraction analysis (Advance D8, Bruker Corp.,

### Table 3 Basic physical properties of liquid setting accelerators.

| Type       | Solids content (%) | pH (20°C) | Na₂O content (%) | Al₂O₃ content (%) | SO₄²⁻ content (%) |
|------------|--------------------|-----------|------------------|-------------------|------------------|
| Alkaline   | 45.6               | 13.5      | 17.8             | 21.5              | -                |
| Alkali-free| 49.1               | 2.7       | -                | 8.6               | 7.5              |

### Table 4 Mix proportion of cement pastes and mortars.

| Type             | Sample ID | Cement | SEA   | w/c ratio | Natural sand | Accelerator (% by weight of cement) |
|------------------|-----------|--------|-------|-----------|--------------|-------------------------------------|
| Cement pastes    | Reference | 100    | 0     | 0.40      | -            | 0                                   |
|                  | Alkaline type | 100    | 0     | 0.40      | -            | 5                                   |
|                  | Alkali-free type | 100    | 0     | 0.40      | -            | 7                                   |
|                  | Alkaline type with SEA | 92     | 8     | 0.40      | -            | 5                                   |
|                  | Alkali-free type with SEA | 92     | 8     | 0.40      | -            | 7                                   |
| Cement mortars   | Reference | 100    | 0     | 0.40      | 150          | 0                                   |
|                  | Alkaline type | 100    | 0     | 0.40      | 150          | 5                                   |
|                  | Alkali-free type | 100    | 0     | 0.40      | 150          | 7                                   |
|                  | Alkaline type with SEA | 92     | 8     | 0.40      | 150          | 5                                   |
|                  | Alkali-free type with SEA | 92     | 8     | 0.40      | 150          | 7                                   |
X-ray patterns were collected in the 5° to 70° 2θ range with a step size of 0.02° 2θ, operating at 40 kV and 40 mA with Cu(Kα) radiation. Then measured patterns were analyzed semi-quantitatively by Rietveld methods (Liu et al. 2021) using the Total Pattern Analysis Solutions software.

Scanning electron microscopy (QUANTA 250, FEI Co., USA) was performed to analyze the microstructure and morphology changes of accelerated cement pastes, with an accelerating voltage of 15 kV and the working distance of 9.5 to 10.0 mm. Characteristic X-rays were collected by the energy dispersive spectrum analysis (EDS) for element composition of hydration products.

Thermal gravimetric analysis (TGA) was conducted to characterize the hydration products like ettringite and portlandite phase in accelerated cement pastes at 24 h of hydration using a Simultaneous Thermal Analyzer (SDT-Q600, TA Instruments, USA), at a heating rate of 10°C/min and the measured temperature range from the room temperature to 1000°C. In literature, the content of ettringite phase could be evaluated approximately from the ratio of the weight loss during 25 to 100°C to a constant 0.35 (Li et al. 2020). The content of portlandite phase could be calculated following Eq. (1) (Tan et al. 2019).

\[ M_{\text{Portlandite}} = \frac{74}{18} M_{\text{H}_2\text{O}} + \frac{74}{44} M_{\text{CO}_2} \]

where \( M_{\text{Portlandite}} \) is the amount of portlandite phase in cement pastes; \( M_{\text{H}_2\text{O}} \) is the weight loss of samples during 400 to 500°C; \( M_{\text{CO}_2} \) is the weight loss of samples during 550 to 800°C

2.3.2 Mechanical and setting times tests

Setting times measurement and early age mechanical strength tests were carried out to evaluate the rapid setting effects and early age hardened properties of different accelerated cement pastes or mortars in the presence of SEA. The setting times of cement pastes were determined using a Vicat apparatus according to the method in the Chinese standard GB/T 35159 (GB/T 2017b). The early age mechanical strength was represented by compressive strengths of cubic mortar specimens.

3. Results and discussion

3.1 Isothermal calorimetry

Heat flow and heat released curves of initial hydration until 72 h are shown in Fig. 1. For the reference with pure Portland cement, its initial hydration stages are generally divided into five stages according to literature, i.e. initial dissolution period (0 to 1.0 h), induction period (1.0 to 10 h) with less C3S hydration reaction, accelerating period (10 to 20 h), deceleration period (20 to 36 h) and stable period (over 36 h) (Skalny et al. 1978; Bullard et al. 2011). However, when different setting accelerators are added with or without SEA, the initial hydration stages of cement pastes are changed obviously, especially for initial dissolution period and induction period.

In the accelerated pastes without SEA, the first exothermic peak in the heat flow reaches 26.03 mW/g for alkaline type and 41.07 mW/g for alkali-free type, over 2 to 3 times intense than that measured for the reference one. Those high exothermic reactions are generated by the hydration reaction between chemical ions of setting accelerators and cement grains, corresponding to the rapid formation of ettringite and AFm phase with significant gypsum content. Besides, it is evidenced that AFm phase are more likely to be formed in cement pastes containing alkaline type, compared to that containing alkali-free type (Salvador et al. 2016a, 2016b).

Obviously, the first exothermic peak is increased evidently with SEA introduction compared to those prepared with the addition of single setting accelerators, as indicated by those obtained peak values of 33.42 mW/g (alkaline type) and 54.76 mW/g (alkali-free type), respectively. This phenomenon implies that the rapid formation of ettringite or AFm phase in accelerated pastes are enhanced or affected with SEA introduction. Actually, the experimental samples are prepared with Portland cement blended with SEA component containing cal-
calcium sulphoaluminate, anhydrite and lime (shown in Table 1). Therefore, the formation of ettringite phase is improved easily in the presence of adequate sulfate and calcium ions through hydration reaction Eq. (2) or Eq. (3) (Trauchessec et al. 2015; He et al. 2013; Pourchet et al. 2009), thus leading to higher exothermic peak. Eq. (3) is for the case with adequate gypsum content.

\[ \text{C}_3\text{A} \cdot 3\text{S} + 3\text{CH} + 3\text{H}_2\text{O} \rightarrow 3\text{C}_2\text{AF}_6 \cdot \text{H}_2\text{O} \]  
\[ \text{C}_3\text{A} + 3\text{S} + 3\text{H}_2\text{O} \rightarrow 3\text{C}_2\text{AF}_6 \cdot \text{H}_2\text{O} \]  

Unlike that in the reference one, short induction period (3 to 6 h) and advanced accelerating hydration period are observed in different accelerated pastes. For the alkaline type accelerated pastes, a smaller shoulder could be observed at 4.5 h. The shoulder might be associated with the continuous formation of AFm phase, mainly due to C3A phase reacted with insufficient sulfate ions in hydration environment, as reported in literature (Salvador et al. 2016a, 2016b). However, this smaller shoulder of heat peak disappears nearly with the addition of SEA and indicates the weakened formation of AFm phase.

Similarly, the second exothermic peak of cement pastes belonging to accelerating period is slightly advanced with SEA introduction. Hydration time of 7.3 h or 15.2 h for the second exothermic peak is roughly obtained in cement pastes containing alkaline or alkali-free accelerator with the addition of SEA, respectively. Those advanced accelerating periods may be generated by the promoted hydration reaction of C3S phase due to more dissipative portlandite phase to form massive ettringite phase, happening in initial dissolution period and induction period.

According to the obtained heat released curves, the heat released statuses of cement pastes with hydration times are detected and collected in Table 5. The heat released values of accelerated cement pastes are increased with the addition of SEA during the first 24 h of hydration, implying that the hydration reaction of cement minerals like C3S or C3A phase in initial hydration stages was improved by the addition of SEA (Saout et al. 2013), which may lead to the higher compressive strength obtained in accelerated cement mortars or shotcrete.

### 3.2 Hydrated ion dissolution

In dissolved cement suspensions, the addition of setting accelerators leads to an obvious decreasing trend of calcium or sulfate ion concentrations at 15 min of hydration. This confirms the formation of hydration products like ettringite or AFm phase. After that, lower calcium and sulfate ion concentrations of different accelerated cement pastes compared to the reference one are observed. A slight turn of sulfate ion concentrations evolution at 3 to 6 h of hydration is determined in cement pastes containing alkali-free accelerator. This phenomenon may be associated with the promoted dissolution of gypsum

| Table 5 Heat released of accelerated pastes during hydration time. |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Hydration time       | Reference       | Alkaline type   | Alkali-free type| Alkaline type + SEA | Alkali-free type + SEA |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0 to 1.0 h           | 8.52            | 31.34           | 43.12           | 33.39           | 58.08           |
| 1.0 to 12 h          | 4.64            | 87.2            | 40.63           | 115.61          | 49.25           |
| 12 to 24 h           | 104.85          | 77.22           | 123.46          | 77.15           | 136.6           |
| 24 to 48 h           | 111.09          | 43.14           | 71.79           | 49.06           | 69.78           |
| 48 to 72 h           | 36.99           | 13.96           | 21.94           | 16.01           | 22.28           |
| Total                | 266.09          | 252.86          | 300.94          | 291.22          | 335.99          |

Fig. 2 Dissolution ion concentrations of calcium (a) and sulfate (b) in accelerated cement pastes without or with SEA during the first 24 h of hydration at 20°C.
phase to release more sulfate ions, induced by the retarded hydration effect on cement grains.

The addition of SEA into accelerated cement pastes provides a slight increased trend of sulfate ion concentrations during the first 24 h of hydration, mainly induced by the remaining anhydrite content of SEA (Maltese et al. 2007). However, calcium ion concentrations evolution during 15 min to 24 h of hydration behaves differently when different setting accelerators and SEA are used together. In alkaline type accelerated cement pastes, lower calcium ion concentrations are determined with the addition of SEA compared to that containing single alkaline accelerator. While for alkali-free type accelerated cement pastes, the higher calcium ion concentrations at 3 to 6 h of hydration are observed with the addition of SEA. This implies that the retarded hydration effect on cement grains is enhanced by the addition of SEA, thus promoting the dissolution of gypsum phase to release more calcium ions.

3.3 Hydration phase composition

The evolution of hydration phase composition determined by X-ray diffraction Rietveld method is presented in Fig. 3. In order to make a clear presentation of graph results, cement mineral phases like C3S, C3A, gypsum or calcium sulfoaluminate (CAS) and hydration products like ettringite, AFm or portlandite are given respectively. Hydration phases with low degree of crystallization or late hydration activity like C2S, C4AF, quartz and amorphous phase are not included. Figs. 3a to 3c show hydration phase composition obtained in cement pastes for reference one, alkaline and alkali-free accelerator, respectively. Those of different accelerated pastes with the addition of SEA are presented in Figs. 3d and 3e.

In alkaline type accelerated pastes, gypsum phase is consumed sharply with C3A phase and chemical ions of setting accelerators to form AFm and ettringite phase during the initial dissolution period. Simultaneously, Portlandite phase is crystallized by the hydration reaction of C3S phase. After that, a steadily increasing trend of AFm and portlandite phase is observed during the first 12 h of hydration, suggesting that the initial compressive strength of shotcrete could be promoted with the addition of single alkaline accelerator. However, when SEA and alkaline accelerator are introduced together into cement pastes, the formation rate and amount of AFm phase are decelerated but the increasing content of ettringite phase is observed, along with decelerated gypsum consumption. During the hydration time of 12 to 48 h, the hydration reaction of C3S phase and the formation of portlandite phase are advanced by the addition of SEA, thus may leading to better strength development.

In alkali-free type accelerated pastes, C3A phase reacts with gypsum, chemical ions of setting accelerators and portlandite phase to form massive ettringite phase but less AFm phase during the initial dissolution period, thus leading to few portlandite phase existed (Paglia et al. 2001). After that, few consumption of C3S phase and low
formation of portlandite phase are observed at less than hydrated 12 h. Those might be related with the retarded hydration effect on cement grains, thus leading to slow strength development of shotcrete (later shown in Fig. 6). Then portlandite phase begins to be determined gradually at 12 to 24 h of hydration, induced by the hydration reaction of C₃S phase. However, when alkali-free accelerator are used together with SEA, increasing ettringite phase are observed at 15 min of hydration, influenced by the interaction between setting accelerators, SEA component and C₃A phase. Increasing gypsum phase is induced by the remaining anhydrite component of SEA. At 24 h of hydration, much more portlandite phase is observed with the addition of SEA compared to that containing single alkali-free accelerator, related with the advanced hydration extent of C₃S phase during 12 to 48 h of hydration.

### 3.4 Morphology and EDS analysis

Morphology characters of different accelerated cement pastes with the addition of SEA are performed at 15 min, 6 h and 24 h of hydration using SEM method. Corresponding to the SEM images, the element compositions in hydration regions are detected by EDS-point analysis and presented in Table 6. A hydration time of 15 min is chosen to evaluate the accelerating effect induced by the addition of setting accelerators, corresponding to the first exothermic peak in the heat flow curves in Fig. 1 and 24 h of hydration time is usually identified as a significant initial strength development point of shotcrete.

#### 3.4.1 In alkaline type accelerated cement pastes with SEA

In alkaline type accelerated cement pastes at 15 min of hydration, rod-like ettringite phase is formed and some hydration products are deposited on cement grains, as also observed by Salvador and Paglia’s results (Paglia et al. 2001; Salvador et al. 2016a, 2016b). According to the EDS results in Table 6, the deposited hydration product analyzed is composed by AFm phase with Ca/Si, Al/S molar ratios of 5.85 and 3.05, respectively. This phenomenon supports the data obtained in X-ray diffraction results. However, when SEA component is introduced, the deposited hydration product on cement grains turns out to be rod-like ettringite phase rather than AFm phase, as indicated by EDS B (Al/S molar ratio of 0.87). Besides, bar-like gypsum related with the addition of SEA is observed simultaneously, indicating that those alunite hydrate phases like C₃A phase blended with SEA containing anhydrous calcium sulphoaluminate are beneficial for the formation of ettringite phase due to adequate sulfate and calcium ions, corresponding to the data obtained in hydrated ion dissolution results.

As the hydration time reaches 6 h, plate-like portlandite formed in pore structures is observed in cement pastes with the addition of single alkaline accelerator. This confirms the ongoing hydration reaction of C₃S phase, as indicated by the accelerating hydration period in heat flow curves of Fig. 1. While AFm phase or hydrated calcium aluminate (C-A-H) with less solubility continues to be formed and deposited on cement grains surface, thus possibly inhibiting the further hydration reaction of C₃S phase. While such formation of AFm phase is still restrained with the addition of SEA and rod-like ettringite together with layered C-S-H gel are observed in cement pastes containing alkaline type accelerator and SEA, suggesting the promoted hydration reaction of C₃S phase.

With the hydration time continuing to 24 h, hydrated cement grains and hydration products like portlandite and ettringite phase are surrounded with AFm and C-A-H phase in cement pastes with the addition of single alkaline accelerator, thus leading to the strong retarded hydration effect (Salvador et al. 2016a, 2016b) and slow mechanical strength development. However, when SEA is introduced together with alkaline accelerator, net-structure C-S-H gel and plate-like portlandite are observed, indicating that the retarded hydration effect induced by AFm or C-A-H phase is weakened and the hydration reaction of C₃S phase is promoted.

#### 3.4.2 In alkali-free accelerated cement pastes with SEA

In alkali-free type accelerated cement pastes at 15 min of hydration, massive rod-like ettringite phase is crystallized basically in cement pore structure, responsible for the fast setting properties of cement pastes. However, when SEA is introduced together with alkali-free accelerator, the formation regions of ettringite phase are broadened and might be divided into two groups, i.e. in pore structure and on cement grains surface. In this context, rod-like ettringite phase on cement grains sur-

### Table 6 EDS-point analysis in hydration regions of accelerated cement pastes.

| Element | A          | B          | C          | D          | E          |
|---------|------------|------------|------------|------------|------------|
| Ca      | 44.25      | 38.05      | 49.48      | 40.04      | 24.1       |
| Si      | 10.16      | 12.56      | 8.04       | 15.91      | 3.3        |
| Al      | 10.21      | 9.47       | 10.3       | 8.59       | 0.27       |
| O       | 33.31      | 26.98      | 17.03      | 22.98      | 54.2       |
| S       | 2.07       | 12.94      | 15.15      | 12.48      | 18.13      |
| Ca/Si (molar) | 3.05  | 2.12       | 4.31       | 1.76       | Cu/S (molar)=1.06 |
| Al/S (molar)   | 5.85 | 0.87       | 0.81       | 0.82       |            |
face owns longer length compared with that in pore structure due to its low nucleation barrier, as indicated by EDS D (Al/S ratio of 0.81). In the meanwhile, the gypsum columns are observed around rod-like ettringite phase on cement grain surface, as indicated by EDS E (Ca/S ratio of 1.06). This phenomenon confirms that the increased ettringite phase on cement grains surface is likely to be induced by the hydration reaction of anhydrous calcium sulphoaluminate in SEA [shown in Eq. (4)]. The promoted formation of massive rod-like ettringite phase both in pore structure and on cement grains may lead to a better accelerating effect on shortening setting times of cement pastes.

In alkali-free type accelerated cement pastes at 6 h of hydration, rod-like ettringite phase continues to form and prefers to be deposited on cement grains surface, thus may leading to the retarded hydration effect of further C₃S hydration, as indicated by the induction period in Fig. 4 Morphology of cement pastes containing alkaline accelerator without or with SEA at 15 min, 6 h and 24 h of hydration.
heat curves in Fig. 1. While deposited rod-like ettringite phase is increased by the addition of SEA and tends to enfold unhydrated cement grains. This implies that the retarded hydration effect on cement grains during the induction period might be enhanced with the addition of SEA.

With the hydration time continuing to 24 h, layered C-S-H gel and plate-like portlandite are observed in cement pastes with the addition of single alkali-free accelerator. Besides, rod-like ettringite phase is likely to intertwine with C-S-H gel and a net-like hydration structure is provided compared to that with the addition of single alkaline accelerator. However, when SEA is introduced together with alkali-free accelerator, a large amount of plate-like portlandite is observed and a compact hardened hydration structure is composed by rod-like ettringite and net-like C-S-H gel, as indicated by the local magnified region in Fig. 5. This supports the promoted hydration reaction of C₃S phase.

Fig. 5 Morphology of cement pastes containing alkali-free accelerator without or with SEA at 15 min, 6 h and 24 h of hydration.
3.5 Setting and hardened properties of accelerated cement pastes

In order to evaluate the effect of the early hydration behavior on the operating characteristics of shotcrete with the addition of SEA, compressive strengths of cement mortars containing different setting accelerators and SEA at 0 to 48 h of hydration are measured and the setting times of similar cement pastes are performed, as shown in Fig. 6.

Fast setting and hardening effect on cement pastes within few minutes are obtained with the addition of single setting accelerators. However, the accelerating effect on shortening setting times of different setting accelerators is enhanced by the introduction of SEA, especially for alkali-free accelerator type. Those advanced accelerating setting times are connected closely with the prompted formation of massive rod-like ettringite phase, as indicated by the results in X-ray diffraction and SEM images.

For accelerated cement mortars containing single setting accelerators during 0 to 12 h of hydration time, a fast initial compressive strength development is obtained, especially for that with the addition of alkaline accelerator due to its short induction hydration period (shown in Fig. 1). However, when SEA and alkali-free accelerator are used together, lower 6 to 12 h initial compressive strength is measured compared to that with the addition of single alkali-free accelerator. It is perhaps influenced by the much more rod-like ettringite phase deposited on unhydrated cement grains (shown in Fig. 5), thus leading to a strong retarded hydration effect. Significantly, the initial compressive strength during hydration times of 12 to 48 h is increased with the introduction of SEA compared to that with the addition of single setting accelerators. In this context, for cement pastes containing alkaline accelerator and SEA, this confirms that the retarded hydration effect induced by AFm or C-A-H phase on cement grains is weakened by the addition of SEA. However, for that containing alkali-free accelerator and SEA, this supports that the promoted hydration stages of C3S and compact hardened structure are achieved by the addition of SEA.

To evidence that the higher initial compressive strengths of accelerated cement pastes are induced by the addition of SEA, results obtained in TG-DTG analysis of cement pastes at 24 h of hydration are presented in Fig. 7. According to calculated Eq. (1), the content of primary hydration products is calculated.

Main characteristic thermal gravimetric peaks are observed at measured temperature ranges of room temperature to 100°C, 150°C to 180°C, 400 to 500°C and 550 to 800°C, corresponding to physical reaction for water loss of C-S-H gel or ettringite phase, water loss of AFm phase, decomposition of portlandite phase, decomposition of CaCO3 with released carbon dioxide (Liu et al. 2019; Trauchessec et al. 2015), respectively. Compared to cement pastes with the addition of single setting accelerators, the content of ettringite and portlandite phase are increased by the addition of SEA, especially for that with alkali-free accelerator. This phenomenon supports that the formation of ettringite phase at 0 to 6 h of hydration is promoted with the addition of SEA, along with more dissipative portlandite phase. Then the hydration reaction of C3S phase during the accelerating period (10 to 20 h) is enhanced, as indicated by X-ray diffraction analysis and initial compressive strength results in Fig. 6.

4. Conclusions

This study mainly evaluated the early age hydration of different accelerated cement pastes blended with sulphoaluminate expansive agent (SEA) and reasonable hydration interaction mechanisms between Portland cement CEM 42.5, liquid setting accelerators type and SEA component were investigated. Results obtained in physico-chemical experimental tests evidenced the effect of expansive agent on the performance difference of wet-mix sprayed concrete accelerated with different
liquid setting accelerators, like initial strength development, the ability of shortening setting times and early age hydration behavior. The following conclusions may be drawn based on the analysis results using different experimental methods.

1. The ability of liquid setting accelerators on shortening setting times of cement pastes could be enhanced with the introduction of sulphoaluminate expansive agent, especially for alkali-free type accelerator due to the prompted formation of massive rod-like ettringite phase.

2. In alkaline type accelerated cement pastes during the first 12 h of hydration, the original formation of AFm phase deposited on cement grains was restrained by the addition of SEA but the formation of rod-like ettringite was motivated by the anhydrous calcium sulfoaluminate and remained anhydrite of SEA. Then the hydration reaction of C₃S phase during 12 to 48 h of hydration was promoted by consumed portlandite phase to produce more rod-like ettringite, thus leading to higher initial compressive strength.

3. In alkali-free type accelerated cement pastes during the first 12 h of hydration, the content of deposited rod-like ettringite phase was increased obviously by the addition of SEA, which tended to enfold unhydrated cement grains and enhanced the retarded hydration effect on cement grains. Compared to that with the addition of single alkali-free accelerator, a compact hardened hydration structure at 24 h of hydration was composed by rod-like ettringite and net-like C-S-H gel in cement pastes containing alkali-free accelerator and SEA, induced by the promoted hydration reaction of C₃S phase.

Basically, the forms of accelerating hydration product were influenced significantly by the ratio of aluminates to sulfate in hydration environment, which was related to chemical composition of cement, liquid setting accelerators type and other component containing aluminum and sulfate element, like sulphoaluminate expansive agent (SEA). When SEA was introduced into accelerated cement pastes, the formation of rod-like ettringite was motivated by the anhydrous calcium sulfoaluminate of SEA within few minutes and lower ratio of aluminates to sulfate was achieved and maintained, thus reducing the formation of deposited AFm phase on unhydrated cement grains and leading to shorter setting times of accelerated cement pastes. Such promoted massive ettringite phase during the first 12 h of hydration enhanced the consumption of portlandite phase and improved the further hydration extent of C₃S phase, thus leading to higher initial mechanical strength.

Acknowledgements

This work was financially supported by the National Key R&D Program of China (NO. 2020YFC1909900), National Science Fund for Distinguished Young Scholars (51825203) and Technology R&D Planning Project Program of China State Railway Group Co., Ltd. (N2020G046, K2020G035).

References

Armengaud, J., Martin, C., Casaux-Ginestet, G. and Husson, B., (2018). “Durability of dry-mix shotcrete using supplementary cementitious materials.” Construction and Building Materials, 190(1), 1-12.

Belie, N. D., Grosse, C. U., Kurz, J. and Reinhardt, H. W., (2005). “Ultrasound monitoring of the influence of different accelerating admixtures and cement types for shotcrete on setting and hardening behavior.” Cement and Concrete Research, 35(11), 2087-2094.

Brandtner, M., Hofmann, M., Paternesi, A., Sauer, E., Schweiger, H. F. and Walter, H., (2018). “Design strategies for sprayed concrete linings.” Geomechanics and Tunnelling, 11(5), 544-558.

Bullard, J. W., Jennings, H. M., Livingston, R. A., Nonat, A., Scherer, G. W., Schweitzer, J. S., Scrivener, K. L. and Thomas, J. J., (2011). “Mechanisms of cement hydration.” Cement and Concrete Research, 41(12),
Liu, R., Yang, Y., Zhao, X. and Pang, B. B., (2021). “Effects of reactivity of MgO expansive agent on its performance in cement-based materials and an improvement of the evaluating method of MEA reactivity.” Construction and Building Materials, 187, 257-266.

Choi, P., Yeon, J. H. and Yun, K. K., (2016). “Air-void structure, strength and permeability of wet-mix shotcrete before and after shotcreting operation: The influences of silica fume and air-entraining agent.” Cement and Concrete Composites, 70(1), 69-77.

Galan, I., Baldermann, A., Kusterle, W., Dietzel, M. and Mittermayr, F., (2019). “Durability of shotcrete for underground support - Review and update.” Construction and Building Materials, 202(1), 465-493.

GB/T, (2007). “Common Portland cement (PRC Standard GB/T 175).” Beijing: Standardization Administration of the People's Republic of China.

GB/T, (2017a). “Expansive agent for concrete (PRC Standard GB/T 23439).” Beijing: Standardization Administration of the People's Republic of China.

GB/T, (2017b). “Flash setting admixtures for shotcrete (PRC Standard GB/T 35159).” Beijing: Standardization Administration of the People's Republic of China.

Han, J. G., Jia, D. and Yan, P. Y., (2016). “Understanding the shrinkage compensating ability of type K expansive agent in concrete.” Construction and Building Materials, 116, 36-44.

He, Z., Yang, H. M. and Liu, M. Y., (2013). “Hydration mechanism of sulfoaluminate cement.” Journal of Wuhan University of Technology, 29(1), 70-74.

Huang, W., Ma, Q. Y. and Cui, P. B., (2011). “Experiment and analysis of flexural strength for shrinkage-compensating steel fiber reinforced shotcrete.” Advanced Materials Research, 163/167, 947-951.

Li, G. X., Zhang, J. B., Niu, M. D. and Song, Z. P., (2020). “The mechanism of alkali-free liquid accelerator on the hydration of cement pastes.” Construction and Building Materials, 233, Article ID 117296.

Liu, R., Yang, Y., Zhao, X. and Pang, B. B., (2021). “Quantitative phase analysis and microstructural characterization of Portland cement blends with diatomite waste using the Rietveld method.” Journal of Materials Science, 56(2), 1242-1254.

Liu, X. H., Ma, B. G., Tan, H. B., Gu, B. and Mei, J., (2019). “Effect of aluminum sulfate on the hydration of Portland cement, tricalcium silicate and tricalcium aluminate.” Construction and Building Materials, 232, Article ID 117179.

Malmgren, L., Nordlund, E. and Rolund, S., (2004). “Adhesion strength and shrinkage of shotcrete.” Tunnelling and Underground Space Technology, 20(1), 33-48.

Maltese, C., Pistolesi, C. and Bravo, A., (2007). “Effects of setting regulators on the efficiency of an inorganic acid based alkali-free accelerator reacting with a Portland cement.” Cement and Concrete Research, 37(4), 528-536.

Maltese, C., Pistolesi, C., Bravo, A., Cella, F., Cerulli, T. and Salvioni, D., (2007). “A case history: Effect of moisture on the setting behaviour of a Portland cement reacting with an alkali-free accelerator.” Cement and Concrete Research, 37, 856-865.

Monosi, S., Troli, R., Favoni, O. and Tittarelli, F., (2011). “Effect of SRA on the expansive behaviour of mortars based on sulphaolunate agent.” Cement and Concrete Composites, 33(1), 485-489.

Ning, F. W., Cai, Y. B., Bai, Y., Chen, B. and Zhang, F., (2019). “Effect of expansive agent and internal curing agent on crack resistance of C50 silica fume wet-mix shotcrete.” Advances in Mechanical Engineering, 11(1), 1-11.

Paglia, C., Wombacher, F. and Bohni, H., (2001). “The influence of alkali-free and alkaline shotcrete accelerators within cement systems, Part I: Characterization of the setting behavior.” Cement and Concrete Research, 31(6), 913-918.

Pourchet, S., Regnaud, J., Perez, J. P. and Nonat, A., (2009). “Early C3A hydration in the presence of different kinds of calcium sulfate.” Cement and Concrete Research, 39, 989-996.

Qiu, Y., Chen, G. X. and Zhu, Y. R., (2018). “Study on properties and mechanism of liquid alkali free set accelerating admixture for sprayed concrete.” In: Superplasticizers and Other Chemical Admixtures in Concrete (ACI Special Publication SP-329). Farmington Hills, Michigan, USA: American Concrete Institute, 117-126.

Salvador, R. P., Cavalaro, S. H. P., Segura, I., Figueiredo, A. D. and Pérez, J., (2016a). “Early age hydration of cement pastes with alkaline and alkali-free accelerators for sprayed concrete.” Construction and Building Materials, 111, 389-398.

Salvador, R. P., Cavalaro, S. H. P., Cincotto, M. A. and Figueiredo, A. D., (2016b). “Parameters controlling early age hydration of cement pastes containing accelerators for sprayed concrete.” Cement and Concrete Research, 89(1), 230-248.

Salvador, R. P., Cavalaro, S. H. P., Monte, R. and Figueiredo, A. D., (2017). “Relation between chemical processes and mechanical properties of sprayed cementitious matrices containing accelerators.” Cement and Concrete Composites, 79(1), 117-132.

Saout, G. L., Lothenbach, B., Hori, A., Higuchi, T. and Winnefeld, F., (2013). “Hydration of Portland cement with additions of calcium sulfoaluminates.” Cement and Concrete Research, 43(1), 81-94.

Skalny, J., Jawed, I. and Taylor, H. F. W., (1978). “Studies on hydration of cement - Recent developments.” World Cement Technology, 9(6), 183-186.

Tan, H. B., Li, M. G., Ren, J., Deng, X., Zhang, X., Nie, K. J., Zhang, J. J. and Yu, Z., (2019). “Effect of aluminum sulfate on the hydration of tricalcium silicate.” Construction and Building Materials, 205,
414-424.
Tittarelli, F., Giosue, C. and Monosi, S., (2017). “Combined use of shrinkage reducing admixture and CaO in cement based materials.” *IOP Conference Series: Materials Science and Engineering*, 245, 2, Article ID 022093.
Trauchessec, R., Mechling, J. M., Lecomte, A., Roux, A. and Rolland, B. L., (2015). “Hydration of ordinary Portland cement and calcium sulfoaluminate cement blends.” *Cement and Concrete Composites*, 56, 106-114.
Won, J. P., Hwang, U. J., Kim, C. K. and Lee, S. J., (2013). “Mechanical performance of shotcrete made with a high-strength cement-based mineral accelerator.” *Construction and Building Materials*, 49, 175-183.