Research Article

The Performance and Mechanism Analysis of Cement Pastes Added to Aluminum Sulfate-Based Low-Alkali Setting Accelerator

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We proposed a type of *low-alkali liquid state setting accelerator*, named HLSA; it was environmentally friendly product. To investigate the temperature adaptation and cement flexibilities of HLSA, the setting time and strength development properties of cement with HLSA were discussed in this paper. The effects of HLSA on hydration process, hydration products, and microstructure were studied by means of X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscope (SEM), and mercury intrusion porosimetry (MIP). The results show that four typical 42.5-grade ordinary Portland cement types with 6–8% HLSA could satisfy the first-grade requirements according to JC477-2005 even at a lower temperature (e.g., 10°C). Further, the percentage ratio of 28 d compressive strength of cement with 6–8% HLSA was over 90%; the XRD diffraction peak of AFt integrated area of cement with 7% HLSA was 3818 at 5 min of hydration; SEM observation revealed that AFt crystals were filled in the pore of cement at 28 d of hydration; the temperature adaptation and cement flexibilities of HLSA were excellent; the cement with HLSA coagulating in a short time attributed to promoting the formation of abundant AFt and the hydration of C₃S.

1. Introduction

Shotcrete is a kind of concrete which is conveyed under pressure through a pneumatic hose or pipe and projected into place at high velocity, with simultaneous compaction, condensation, and hardening [1, 2]. The shotcrete can acquire high early age strength and coagulate in a short time [3]; it is often used for hydraulic engineering, slope engineering, emergency rescue, and repairing engineering [4, 5]. The setting accelerator is an essential component of shotcrete. The development of setting accelerator was dated back to the nineteen-thirties; the setting accelerators were mainly powder accelerators at the early stage of development. The powder accelerators easily lead to problems of dust pollution, dispersing unevenly and high energy consumption in construction process. Meanwhile, it is harmful to construction crews' health at some degrees in dry spray of construction process. With the developing of wet sprayed technology of shotcrete, liquid setting accelerators emerged in nineteen-eighties [6].

The liquid setting accelerators can avoid the problems of dust pollution and uneven dispersing caused by powder accelerators in dry spray process. The main chemical components of traditional setting accelerators are classified as (1) sodium silicates-based, such as water glass and modified sodium silicate; (2) aluminate-based, such as sodium aluminate, potassium aluminate, and aluminum sulfate; (3) carbonate and hydroxide-based, such as sodium carbonate and sodium hydroxide [7]. The common problems that existed was that the alkali content of the liquid and powder setting accelerators were very high at the early research stage of setting accelerators. The high alkali setting accelerators could easily lead to the following problems: (1) increasing the risk of alkali-aggregate reaction in concrete; (2) being harmful to the builders' health with extremely high pH level; (3) a severe reduction of the shotcrete long-term mechanical properties [8]. According to EN 934-5 [9], the low-alkali setting accelerators are defined as setting accelerators whose alkali metal content (sodium and potassium), expressed as

TABLE 1: Chemical composition of cement (w/%).

Cement	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	R ₂ O	Loss
H	23.49	58.24	6.00	2.81	2.35	2.39	0.76	3.06
Y	21.02	62.38	4.80	3.68	1.03	2.02	0.60	3.78

TABLE 2: Main chemical composition of HLSA (w/%).

Sample	Al ₂ O ₃	SO ₃	Na ₂ O	F ⁻	Loss
HLSA	8.43	19.82	5.04	3.21	60.15

equivalent of Na₂O% + 0.658K₂O%, is not above 8% by mass. The low-alkali setting accelerators have some significant advantages. Therefore, the preparation of low-alkali setting accelerators has been the main trend and hot topic in this field [10].

The setting accelerators consist of many types and the acceleration mechanism is not conclusive; the present theories of acceleration mechanism are as follows: (1) the formation of abundant AFt in a short time of the setting accelerators based on aluminate. A large amount of SO₄²⁻ from setting accelerator can react with aluminate hydration products of cement to form AFt and high reactive secondary gypsum. The AFt crystals are connecting reticular structure in cement pastes; the formation of cement hydration products especially calcium aluminate hydrate needs to combine free water leading to cement condensation in a short time [11] and (2) the formation of abundant hydrated calcium aluminate of the setting accelerators based on carbonate and sodium silicates. Due to the obvious decrease of gypsum concentration, the retard effect of gypsum is weakened and even vanished, which promotes the hydration of C₃A to form cubic crystal C₃AH₆ in a short time. Then massive heat is released at the same time and the cement paste is setting rapidly [12].

However, the effects of different setting accelerators addition on cement were also different; meanwhile, the variation of hydration products mass percentage of cement containing setting accelerators was rarely studied. As a result, the aluminum sulfate-based low-alkali liquid state setting accelerator named HLSA has been prepared in laboratory. HLSA was environmentally friendly product; it could avoid damaging the crews' health and decrease the energy consumption in construction process. The properties of setting time and strength development of cement in addition to HLSA were investigated. The effects of HLSA on hydration process, hydration products, and microstructure were investigated by means of X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscope (SEM), and mercury intrusion porosimetry (MIP).

2. Experimental

2.1. Raw Materials. The cement used was two typical 42.5-grade ordinary Portland cement types, which were manufactured by Yadong (Y) Cement Company Ltd. (Wuhan, Hubei) and Huaxin (H) Cement Company Ltd. (Wuhan, Hubei),

respectively. The Portland cement blended with less than 20% mineral admixtures. The physical and chemical properties of Portland cement all satisfied China National Standard GB 175-2007; the chemical composition of cement was shown in Table 1.

The HLSA prepared in lab were synthesized by industrial-grade aluminum sulfate (Al₂(SO₄)₃·18H₂O), chemically pure sodium fluoride (NaF), chemically pure triethanolamine ((HOCH₂CH₂)₃N), chemically pure polyacrylamide (-[CH₂CH]_nCONH₂-), and chemically pure phosphoric acid (H₃PO₄). The industrial-grade aluminum sulfate was obtained from the Zibo Guangzheng Aluminum Salt Chemical Industry Co., Ltd. (Zibo, Shandong). The chemically pure sodium fluoride, triethanolamine, polyacrylamide, and phosphoric acid were obtained from Sinopharm.

HLSA was light green homogeneous liquid in appearance with density of 1.61 g/cm³ and solid content of 40.5%. The alkali content expressed as equivalent of Na₂O% + 0.658 × K₂O% was 5.0%, which belongs to low-alkali setting accelerator. The main chemical composition of HLSA was shown in Table 2.

2.2. Experimental Methods

2.2.1. Cement Setting Time. The setting time of cement with HLSA was measured according to Chinese Building Materials Standards JC 477-2005 with water to cement ratio (W/C) 0.40; the dosage of setting accelerator was 6%, 7%, and 8% (by mass of cement) respectively. The cement pastes were cured under the condition of temperature 20 ± 2°C and RH not less than 90%. The effect of HLSA on cement setting time at 10°C and 20°C was investigated, respectively, it used Yangdong P-O 42.5 Portland cement and Huaxin P-O 42.5 Portland cement, and the composition mix was shown in Table 3.

2.2.2. Strength Development of Cement Mortar. The measurement of cement mortar strength development was according to Chinese Building Materials Standards JC 477-2005. With standard sand: cement: water ratio of 3:2:1, the addition of setting accelerator was 6%, 7%, and 8% (by mass of cement), respectively. Cement mortar specimens were 40 mm × 40 mm × 160 mm prisms. The specimens were prepared and cured in molds for 24 h under the condition of temperature 20 ± 2°C and RH over 90%; then they were demoulded and tested for 1d compressive strength immediately; the

TABLE 3: Mix proportions of cement paste.

Types	W/C	Cement type	Temperature/°C	Dosage/%
Y10-S6	0.4	Yangfang P·O 42.5	10	6
Y10-S7	0.4			7
Y10-S8	0.4			8
Y20-S6	0.4		20	6
Y20-S7	0.4			7
Y20-S8	0.4			8
H10-S6	0.4	Huaxin P·O 42.5	10	6
H10-S7	0.4			7
H10-S8	0.4			8
H20-S6	0.4		20	6
H20-S7	0.4			7
H20-S8	0.4			8

percentage of mortar in addition to HLSA compressive strength growth at 1 d was characterized by the following:

$$C_1 (\%) = 100 \times \frac{C_{(a1)} - C_{(b1)}}{C_{(b1)}} (\%), \quad (1)$$

where $C_1(\%)$ was growth rate of compressive strength at 1 d, $C_{(a1)}$ were compressive strength of specimens containing HLSA at 1 d, and $C_{(b1)}$ were compressive strength of blank specimens at 1 d.

The rest of specimens were cured under the condition of air temperature $20 \pm 2^\circ\text{C}$ and RH not less than 90%. The retention percentage of compressive strength at 28 d was characterized by the following:

$$C_{28} (\%) = 100 \times \frac{C_{(H28)}}{C_{(B28)}} (\%), \quad (2)$$

where $C_{28}(\%)$ was retention percentage of compressive strength at 28 d, $C_{(H28)}$ were compressive strength of specimens containing HLSA at 28 d, and $C_{(B28)}$ were compressive strength of blank specimens at 28 d.

2.2.3. Microstructure of Hardened Cement Pastes. Cement pastes were prepared for X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscope (SEM), and mercury intrusion porosimetry (MIP) analyses on water to cement ratio 0.40 in addition to 7% HLSA. The hydration of hardened cement pastes was stopped after predetermined curing age by breaking test block into small pieces in absolute ethyl alcohol. The small samples were ground into powders with particle size less than $80\mu\text{m}$ by agate grinding for XRD and TGA analyses. The small samples with particle size range from 5 mm to 8 mm were selected for SEM analyses. Fresh paste was cast into capsules (3 mm diameter, 45 mm height) cured under water and stored at 20°C . At required time of hydration, a slice (2 mm thick) of hardened paste was cut for MIP analyses.

XRD was employed to identify the cement hydration phase. The XRD data were collected by Bruker D8 advance diffractometer with a 3 KW Cu $K\alpha$ radiation and the X-ray

tube was operated at 40 kV and 40 mA. The scanning speed of XRD was $10^\circ/\text{min}$. The software MDI Jade 6.5 was used to study the special diffraction peak of ettringite and CH for quantitative phase analyses [13]. TG analysis was used to test the weight loss and decomposition temperature of phase. All samples were tested within the range of 25°C to 800°C using a differential thermal analyzer (STA449C from Netzsch, Germany) under air atmosphere with a scanning rate of $15^\circ\text{C}/\text{min}$. The field emission electron microscopy (Ultra Plus-43-13 from Zeiss, Germany) was used to observe morphology and microstructure of cement pastes. MIP measurement was carried out on micromeritics instrument corporation AutoPore IV 9500 mercury scanning porosimeter, with maximum pressure 228 MPa, and its measurable pore size ranges from 3 nm to 1000 μm .

In order to investigate the amount of cement hydration products in addition to HLSA. Method of semiquantitative analysis was used to study the diffraction peak characteristics of hydration products AFt and $\text{Ca}(\text{OH})_2$ (CH) by software Jade 6. DTG curves clearly showed the relationship between temperature and weight loss in case the weight loss was close. The decomposition peak of CH occurred between 420 and 460°C in DTG curves; the amount of CH could be calculated by the following formula:

$$\text{CH} (\%) = \text{WL}_{\text{CH}} (\%) \frac{\text{MW}_{\text{CH}}}{\text{MW}_{\text{H}_2\text{O}}}, \quad (3)$$

where $\text{WL}_{\text{CH}}(\%)$ corresponds to the weight loss of CH in percent and MW_{CH} and $\text{MW}_{\text{H}_2\text{O}}$ were the molecular weights of portlandite and water, respectively [14].

3. Results and Discussion

3.1. Temperature Adaptation. Temperature was an important external factor affecting chemical reaction rate. The temperature of concrete raw materials was changeable when the regions, seasons, and daily temperature changed, so it should pay attention to the problems caused by the changeable temperature in construction process [15]. In order to investigate the effect of HLSA on cement setting time at

FIGURE 1: Effect of setting time of cement in addition to HLSA at 10°C and 20°C.

FIGURE 2: Effect of setting time and strength development of two kinds of cement containing HLSA.

different environment temperature, the tunnel temperature of summer and winter was simulated in lab. The effect of setting time of cement in addition to HLSA at 10°C and 20°C was investigated; the results were shown in Figure 1.

The cement setting time was shortened as the curing temperature was higher at the same dosage. The setting time of cement in addition to 6% HLSA could meet first-grade requirement according to Chinese Building Materials Standards JC 477-2005 at temperature 20°C. The setting time of cement in addition to 6% HLSA could meet acceptable product requirement according to JC 477-2005 at temperature 10°C. It could be supposed that the temperature adaptation of HLSA was excellent, as it could maintain the flash setting effect at lower temperature (e.g., 10°C). The setting time could meet the first-grade requirement by increasing the dosage of setting accelerator at lower temperature.

3.2. Cement Flexibilities. The cement setting time and cement mortar strength development in addition to 6%, 7%, and 8% HLSA were investigated; the results were shown in Figure 2. It was supposed that the adaptation between admixture and cement was good as the concrete or mortars prepared with the admixture could generate desired performance; on the contrary, it could be thought that the adaptation between admixture and cement was not good according to Chinese Standard GB 50119-2013 [16].

The setting time of cement in addition to HLSA at the dosage range from 6% to 8% could meet the first-grade requirement according to Chinese Building Materials Standards JC 477-2005, especially cement Y and cement H which could meet first-grade requirement at the dosage 6%. The higher the dosage was, the shorter the setting time would be. The compressive strength growth of mortars prepared

FIGURE 3: XRD patterns of hydrated cement in addition to 7% HLSA.

with two cement types at 1 d presented an increasing trend as the dosage increased. Compressive strength growths of mortars prepared with two cement types at 1 d were all above 40% at the dosage of 8%; it was noted that compressive strength growth of mortar prepared with cement Y and cement H at 1 d was all above 60%. The 28 d retention percentage of mortar compressive strength was all above 90%, which was much higher than the first-grade requirement of 75% according to JC 477-2005. It is suggested that HLSA could avoid the problems of significant strength loss at late stage caused by high alkali content of traditional setting accelerators. Consequently, the cement flexibilities of HLSA were excellent.

3.3. XRD Analysis. Figure 3 showed XRD patterns of hydrated cement with 7% HLSA (Y20-S7) and blank specimens at the age of 5 min, 5 h, 1 d, and 28 d, respectively. The integrated results of XRD diffraction peak of AFt corresponding to 2θ range of $9.0\text{--}10.0^\circ$ and CH corresponding to 2θ range of $17.0\text{--}19.0^\circ$ were shown in Tables 4 and 5, respectively.

The Y20-S7 specimen presented intensive diffraction peak of AFt while the blank specimens never detected diffraction peak of AFt after 5 min of hydration; it suggested that Y20-S7 specimen had generated AFt at 5 min of hydration. The Y20-S7 specimen diffraction peak integrated area of AFt was 252.0% of the blank specimens at 5 h of hydration. The Y20-S7 specimen diffraction peak integrated area of AFt at 5 h of hydration presented decreasing trend compared to 5 min of hydration. The XRD curve of Y20-S7 specimen detected a weak diffraction peak of AFm at 5 h of hydration; it was possible that the AFt partially converted into AFm due to the concentration of SO_4^{2-} in pore solution of cement decreasing sharply [17]; the chemical reaction occurred:

(see [18, 19]).

The blank specimen diffraction peak integrated area of AFt at 1 d of hydration was approximate to the Y20-S7 specimen at 5 min of hydration. It suggested that the amount of AFt of Y20-S7 specimen generated during 5 min was approximate to the ordinary Portland cement hydration

TABLE 4: The integrated results of XRD diffraction peak of AFt corresponding to 2θ range of $9.0\text{--}10.0^\circ$.

Specimens	Hydration age	d -value ($\text{\AA}$)	FWHM ($^\circ$)	Height	Area
Blank	5 min	—	—	—	—
	5 h	9.6494	0.175	124	1312
	1 d	9.6666	0.175	343	3626
	28 d	9.6680	0.132	218	1745
Y20-S7	5 min	9.6888	0.203	311	3818
	5 h	9.6884	0.150	365	3306
	1 d	9.6909	0.108	497	3240
	28 d	9.6798	0.167	300	3035

TABLE 5: The integrated results of XRD diffraction peak of CH corresponding at 2θ range of $17.0\text{--}19.0^\circ$.

Specimens	Hydration age	d -value ($\text{\AA}$)	FWHM ($^\circ$)	Height	Area
Blank	1 d	4.9080	0.154	442	4124
	28 d	4.9033	0.149	914	8269
Y20-S7	1 d	4.9135	0.177	196	2098
	28 d	4.8978	0.189	277	3172

FIGURE 4: DTG curves of hydrated cement.

during 1 d. The Y20-S7 specimen diffraction peak integrated area of CH at 1 d and 28 d was 50.8% and 38.4% of blank specimen, respectively, and the Y20-S7 specimen diffraction peak integrated area of CH was less than the blank specimen from 1 d to 28 d of hydration.

3.4. DTG Analysis. The effect of HLSA on cement hydration products was investigated by the means of differential scanning calorimetry analysis; the results were shown in Figure 4.

The weight loss peaks between 0 and 200°C of DTG curves were complicated. It was generally acknowledged that AFt, C-S-H, and gypsum decomposition occurred in this temperature range. However, the decomposition peaks of C-S-H and AFt were overlapped [20]. Li et al. [21] suggested that the weight loss at $20\text{--}80^\circ\text{C}$ is caused by the decomposition of AFt; according to Chang et al. [22] the transformation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ in temperature ranges from 80 to 140°C . As Odler et al. [19, 23] suggested it was possible to assign the first two peaks at 120 and 145°C to ettringite and

gypsum decomposition. The DTG curve of blank specimen occurred at intensive decomposition peak of AFt at 5 h of hydration; it is suggested that AFt had already been generated at that moment. The decomposition peak corresponding to AFt of Y20-S7 specimen presented increase at first and then decrease from 1 d to 28 d of hydration; it indicated that AFt was transformed to AFm at some degrees; the results were consistent with XRD analysis of Section 3.3. The CH content in hydrated cement pastes was demonstrated in Figure 5. It suggested CH content of Y20-S7 specimen was less than the blank specimen from 1 d to 28 d of hydration again; CH content of Y20-S7 specimen at 1 d and 28 d was 44.0% and 39.9% of the blank specimen, respectively.

3.5. SEM Analysis. Figure 6 showed scanning electron microscope (SEM) photographs of hydrated cement specimens containing 7% HLSA. A large amount of AFt and C-S-H of Y20-S7 specimen was formed at 5 min of hydration; the needle-like AFt connected with each other compactly to

TABLE 6: Parameters and distribution of pore of cement pastes at 1 d and 28 d.

Specimens	Curing age/d	Total pore volume/(mL·g ⁻¹)	Porosity/%	Pore size distribution/(mL·g ⁻¹ /%)			
				3–20 nm	20–50 nm	50–100 nm	>100 nm
Blank	1	0.258	39.5	0.051/19.8	0.051/19.8	0.106/41.1	0.050/19.3
Y20-S7	1	0.235	35.2	0.062/26.4	0.038/16.2	0.095/40.4	0.040/17.0
Blank	28	0.189	29.7	0.034/18.0	0.070/37.0	0.041/21.7	0.044/23.3
Y20-S7	28	0.161	27.1	0.023/14.3	0.073/45.3	0.028/17.4	0.037/23.0

FIGURE 5: CH content in hydrated cement pastes.

form reticular structure. It was observed that some hexagonal shape portlandite crystals and a little of AFt crystals of blank specimen were formed at 5 h of hydration. Some AFt crystals of Y20-S7 specimen were still observed at 5 h of hydration; however, the amount of AFt was decreasing compared to 5 min of hydration; meanwhile the hexagonal shape portlandite crystals were unobserved. The amorphous C-S-H and AFt crystals were distributed in the cement and a few portlandite crystals were formed of Y20-S7 specimen at 1 d of hydration. The apparent morphology of blank specimen was dense and amorphous C-S-H and portlandite crystals grew compactly. However, needle-like AFt and amorphous C-S-H of Y20-S7 specimens grew crisscrossed compactly and AFt crystals were filled in the pore of cement.

3.6. Pore Structure Analysis. The cumulative pore volume of hardened cement paste was considered a main factor to cement pastes mechanical properties. It was believed that strength development of cement paste increased by the decrease of cumulative pore volume. The differential distribution curve was calculated from the cumulative pore volume curve [24]; according to Wu and Lian [25], the pores of hardened cement pastes were classified as harmless pore (<20 nm), little harmful pore (20–50 nm), and harmful pore (50–200 nm). The pore structures of hardened cement were measured by means of MIP; the results were shown in Table 6. The total porosity of Y20-S7 specimen was less than the blank specimen at 1 d and 28 d of hydration. The pores with pore diameter between 3 and 20 nm of Y20-S7 specimen were 6.6%

more than the blank specimen at 1 d of hydration. It indicated that HLSA could reduce hardened cement paste pore size at early age of hydration. Meanwhile, it was beneficial to improve the cement mechanical properties at early age. The pores with pore diameter less than 50 nm of Y20-S7 specimen were 4.6% more than the blank specimen at 28 d of hydration; it showed that HLSA could refine pore structures at some degrees; it is induced to improve retention percentage of compressive strength at late age.

3.7. Acceleration Mechanism of HLSA. The effect of HLSA on cement hydration products amount was characterized that a large amount of crystallization of AFt was formed at very early age of hydration; the amount of AFt crystals were slightly decreasing at 5 h of hydration; however the content of AFt was still very high at 28 d of hydration. The content of CH crystals was lower than the blank specimen from 1 d to 28 d of hydration.

The main components of HLSA were SO_4^{2-} , Al^{3+} , and F^- . When HLSA and cement contacted, the following reaction would be taking place:

CaF_2 was formed readily because it was more easily crystallized than CH. The balance of electric double layer of C_3S surface was destructed because abundant Ca^{2+} was consumed, which led to the formation of the electric double layer of C_3S difficultly and shortened the induction period of C_3S greatly [26]. The Y20-S7 specimen had generated C-S-H gel at 5 min of hydration; it suggested that C_3S had begun to hydrate at that moment.

Equation (6) showed that the free state of Al^{3+} and SO_4^{2-} readily combined CH in cement to form highly reactive

FIGURE 6: Scanning electron microscope (SEM) photographs of hydrated cement specimens.

secondary gypsum and secondary gypsum easily reacted with the hydration products of C_3A to form AFt. Equation (8) suggested that aluminum sulfate reacted with CH to form AFt in aqueous alkaline medium at normal temperature. The approaches of the formation of AFt were extensive; it led to the formation of a large amount of AFt in a short time. The cement with HLSA coagulating in a short time attributed to a large amount of AFt connected reticular structure and distributed uniformly in cement pastes. Meanwhile, the HLSA shortened induction period of C_3S and promoted the hydration of C_3S greatly.

4. Conclusions

- (1) The temperature adaptation and cement flexibilities of HLSA were excellent. The cement setting time could meet the first-grade requirements according to JC 477-2005 when increasing the dosage of 1% at temperature 10°C compared to temperature 20°C . The setting time of cement with HLSA at the dosage range from 6% to 8% could meet the first-grade requirements according to JC 477-2005; meanwhile the cement retention percentage of compressive strength at 28 d was all above 90%.
- (2) The Y20-S7 specimen XRD diffraction peak of AFt integrated area was 3818; however the blank specimen was 0 at 5 min of hydration. The Y20-S7 specimen diffraction peak of AFt integrated area was 252.0% of the blank specimen at 5 h of hydration. The CH amount of Y20-S7 specimen was less than the blank specimen from 1 d to 28 d of hydration. HLSA could reduce hardened cement paste pores size at early age of hydration and refine the pores structures at some degrees.
- (3) The acceleration mechanism of HLSA attributed to promote the hydration of C_3A and the formation of AFt in a short time. Meanwhile, HLSA could shorten the induction period of C_3S greatly and promote the hydration of C_3S .

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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