

Mechanism and preparation of liquid alkali-free liquid setting accelerator for shotcrete

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Abstract. A new alkali-free liquid accelerator for shotcrete was prepared through normal temperature drop process by using the nano activated alumina and the modified alcohol amine as the main raw materials. The effect of alkali-free liquid accelerator on the cement setting time and the mechanical properties of mortar, the effect of the penetration strength on the shotcrete rebound were investigated. And the accelerating mechanism of the as-prepared alkali-free liquid accelerator was also analyzed via XRD and SEM characterization methods. The experimental results indicated that the hydration of C_3A was accelerated by the polyamine complexation of accelerator, resulting in forming a large number of acicular ettringite and reducing the amount of $Ca(OH)_2$ crystal, which would not affect the later hydration of cement. When the content of alkali-free liquid accelerator was 6%, the initial setting time and final setting time were less than 3min and 8min respectively, and 1d and 28d compressive strength ratios reached 207.6% and 114.2% respectively; beside that, the shotcrete rebound was very low because of the high penetration strength within 30min.

Keywords: alkali-free liquid accelerator, penetration of strength, rebound, Mechanism

1. Introduction

Accelerator is a kind of indispensable admixture in the shotcrete construction. The main purpose of adding accelerator is promoting rapidly condense of the fresh concrete, increase the thickness of the primary spray layer, shorten the time interval between the two spraying, enhance the early strength of shotcrete, which can provide timely support resistance [1]. Thus it is possible that the shotcrete used on the wall and the top by introducing the accelerator. At present, most of powder and liquid accelerator are alkaline [2], which was mainly composed of sodium silicate, sodium aluminate and sodium carbonate and so on. Although they can meet the required standards of shotcrete, yet problems are not to be solved. For example, an accelerator with pH greater than 12 causes strong corrosiveness, seriously deducting the later intensity and the durability of concrete and cohesive property of shotcrete, consequently resulting in the increase of shotcrete rebound and serious dust pollution.

The property of accelerator has an impact on congeal time, resilience, adaptability, early and late strength development and durability of shotcrete. In order to bring out the potentials of accelerator in shotcrete, a large number of researches have been performed. The United States and European researchers [3-4] developed the alkali-free liquid accelerator by using the aluminum sulphate [5] and alcohol amine, which significantly improved the cohesion of concrete mixture and decreased its late compression strength loss, while the performance characteristics of the alkali-free accelerator and



alkali accelerator were analyzed and compared [6]. Recently, most of accelerators are aluminum-sulfate, simultaneously introducing sulfur trioxide to exceed sulfur trioxide in cement. And owing to the existence of the sulfate and chloride ions, the durability of concrete will be reduced.

In the present work, the alkali-free liquid accelerator (AFL) was investigated. The alkali-free liquid accelerator was prepared by using the nanometer alumina and modified alkanolamine through complexometric titration process under room temperature. The effect of alkali-free liquid accelerator on the cement setting time and the compression strength of mortar, and the effect of the penetration strength on the shotcrete rebound of concrete have been investigated. Meanwhile the accelerating mechanism of the as-prepared alkali-free liquid accelerator and the morphology of hydration products of cement have also been analyzed via XRD and SEM characterization methods. It is believed that this work will provide theoretical instruction for the application of non-alkali liquid accelerator in shotcrete.

2. Experimental process

2.1. Materials

Nanometer activated-alumina (industrial grade, CHALCO Shandong Co., LTD), magnesium nitrate (analytical grade, Sinopharm Group Co., Ltd), modified polyhydroxy alcohol amine (self-made), phosphoric acid (analytical grade, Sinopharm Group Co., Ltd), PO 42.5 grade portland cement (Onoda Cement Co., Ltd. and its physical and mechanical properties, ISO standard sand are listed; whereas it is under the circumstance of the medium sand with the fineness modulus of 2.7 that the crushed stone with the continuous grading of 5-10mm were selected as raw materials.

Table 1. Physical and mechanical properties of P·O 42.5 cement.

Apparent density/(g/cm ³)	Water requirement of normal consistency/%	Flexural strength/MPa		Compressive strength/MPa		Setting time/min		Soundness
		3d	28d	3d	28d	Initial	Final	
3.12	26.8	5.6	8.8	26.8	51.3	220	330	Qualified

2.2. Preparation of Alkali - free Liquid Quick - setting Agents

Firstly, alcohol amines were modified by using of dodecyl quaternary ammonium salts. The domiphen was added into the absolute ethyl alcohol to form a solution with the concentration of 20%, and then the solution was heated to reach 60 °C while stirring, after that, N, N, N', N'-methylethylenediamine was dropped into the solution and this process continue for 2 hours, and then modified polyhydroxy alcohol amine solution was prepared.

After adding water and a certain mass of modified polyhydroxy alcohol amine solution in the reaction kettle, the phosphoric acid and magnesium nitrate were introduced in order, while stirring at normal temperature. And then the aqueous solution of nanometer active alumina with the concentration of 5% was dropped into the reaction kettle. After reaction for 3.5 hours, the AFL alkali-free liquid accelerator with the color of transparent light yellow was prepared, and the homogeneity index was shown in table 2.

Table 2. The homogeneity index of AFL liquid alkali-free accelerator.

Apparence	Alkali content/%	Chlorine ion content/%	Density/(g·cm ⁻³)	pH	Solid content/%
Light yellow	0.010	0.001	1.41	3.0	40

2.3. Characterization

2.3.1. Test method of setting time and compressive strength. Tests of the paste setting time and the mortar strength were performed according to JC477-2005 "shotcrete accelerator". The size of mortar specimen was 40 mm×40 mm×160 mm.

2.3.2. Test method of penetration strength of concrete. It is confirmed that the sand rate is 45%, and concrete slump is 120 mm according to JGJ 55-2011 "ordinary concrete mix design rules" and the actual construction experience. The final mix proportion was shown in table 3. The P·O 42.5 conch cement, the M12 polycarboxylate high performance water reducing agent (PCE) (Jiangsu iron Aolait Co., Ltd.), the commercially available BASF167 alkali-free liquid accelerator and SL alkaline liquid accelerator were used as comparative samples. The concrete specimens with size of 150mm × 150mm × 150mm were prepared to test the penetration strength. The penetrating strength was measured at 10min, 20min, 30min, 60min and 180min using a concrete penetration resistance meter.

Table 3. Mix proportion of concrete.

Accelerator type	Accelerator content /%	Mix (kg/m ³)					
		Concrete	Sand	Stone	Water	PCE	Accelerator
KB	0	450	805	873	202	1.35	0
SL	4	450	849	849	202	1.35	18
AFL	6	450	849	849	202	1.35	27
BASF167	6	450	849	849	202	1.35	27

2.3.3. Microstructure analysis. The hardening paste with different ages (10min, 1d and 28d) was prepared. And the carbonized surface layers were removed, then the samples with the size of 3-5mm was obtained from the inner of hardening paste, after that the samples were washed with absolute ethanol and placed in acetone to prevent hydration. After immersed in acetone for 24 hours, the samples were dried in an oven at a temperature of 45 ° C. After cooling, 3-5 small pieces of each sample were selected for SEM analysis. The other samples were crushed and screened by 200 mesh sieve, and then the phase composition of each sample was characterized by XRD.

3. Experimental results and discussion

3.1. The setting time of AFL

The effect of additional amount of AFL accelerator on the c setting time of cement paste has been investigated by using Onoda cement, as shown in table 4.

Table 4. Setting time of cement paste mixed with accelerator.

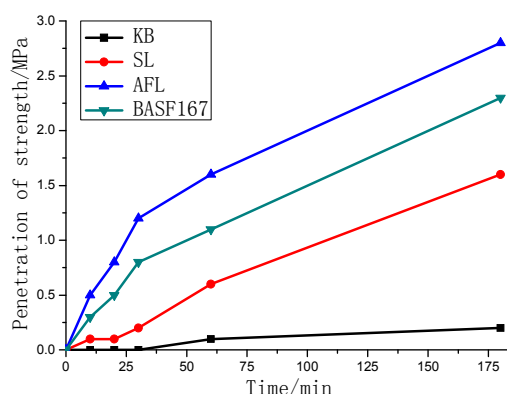
Accelerator type	KB	SL	AFL	BASF167
Accelerator content /%	0	4	6	6
Initial setting time/min:s	235	4:40	2:25	3:30
Final setting time/min:s	405	9:35	8:00	9:20

3.2. Compressive strength of mortar prepared with AFL

Table 5. Compressive strength of concrete mixed with different accelerator.

Accelerator type	Accelerator content /%	Compressive strength					
		1d /MPa	Ratio/%	7d /MPa	Ratio/%	28d/MPa	Ratio/%
KB	0	10.5	100.0	32.5	100	40.8	100
SL	4	16.3	155.2	29.5	90.8	35.2	86.3
AFL	6	21.8	207.6	36.5	112.3	46.6	114.2
BASF167	6	18.9	180	34.6	106.5	44.1	108.1

3.3. Penetration strength of concrete

**Figure 3.** Penetration strength of concrete mixed with different accelerator.

It can be seen from figure 3 that in 30 minutes, the concrete using SL alkali liquid accelerator showed the lowest penetration strength, and the slow strength development. While the concrete using AFL alkali-free liquid accelerator showed the highest penetration strength. The complexation of activated alumina and polyhydroxy alcohol amine in AFL accelerator make the concrete has the property of promoting coagulation.

3.4. shotcrete rebound rate

According to the on-site shotcrete construction situation, the vault of upper step and the sidewall of middle step construction site were selected to calculate the corresponding rebound ratios by using the design amount, the super-cut amount and the actual amount. The effect of different accelerator on the rebound ratios of shotcrete were shown in table 6.

Table 6. Influence of quick setting admixture on rebound resilience of shotcrete.

Construction site	Accelerator type	design amount /m ³	super-cut amount/m ³	actual amount/m ³	rebound amount/m ³	Rebound ratio/%
the vault of upper step	SL	19.3	5.3	33.5	10.5	31.3
	AFL	18.5	5.1	26.2	3.5	13.4
	BASF167	18.9	5.1	28.6	4.8	16.8
Sidewall of middle step	SL	10.8	3.5	16.8	3.2	19.0
	AFL	9.5	2.6	12.5	0.8	6.4
	BASF167	9.3	2.8	13.7	1.5	10.9

It can be seen from table 6 that the vault and side wall with AFL alkali-free liquid accelerator showed a small rebound ratio, were 13.4% and 6.4% respectively. And the vault and side wall with BASF167 alkali-free liquid accelerator showed a larger rebound ratio, were 16.8% and 10.9% respectively. The rebound ratio of vault and side wall with SL alkali liquid accelerator showed a largest rebound ratio, were 31.3% and 19.0% respectively, which is related to the narrower additional

amount of alkali liquid accelerator. Application of AFL alkali-free liquid accelerator showed the best results, which can increase the bond strength and early strength, decrease the coagulation time and the rebound amount.

3.5. XRD analysis

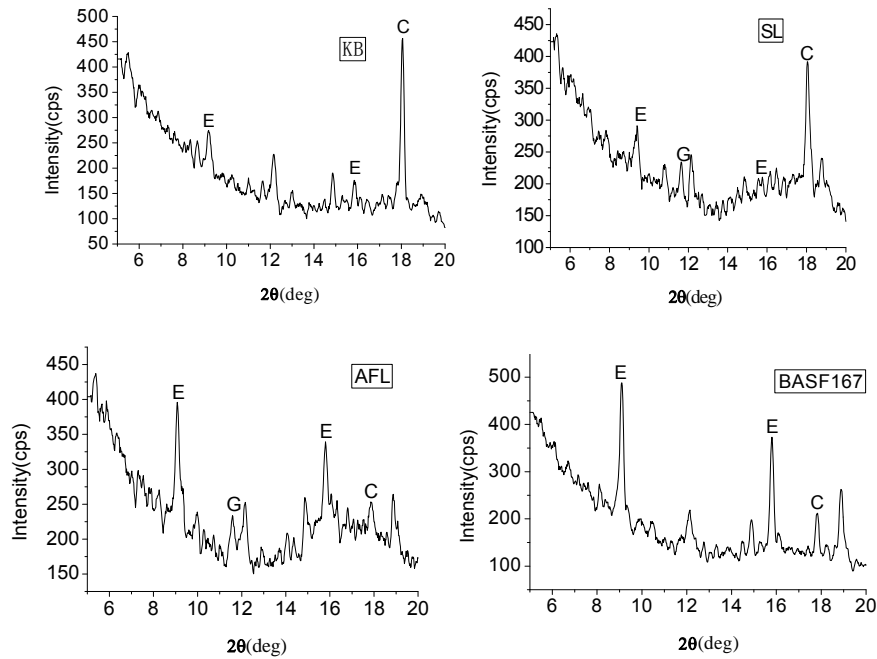


Figure 4. XRD patterns of the hardened paste mixed with different accelerators at the final setting stage. E: ettringite; G: gypsum; C: Ca(OH)_2 .

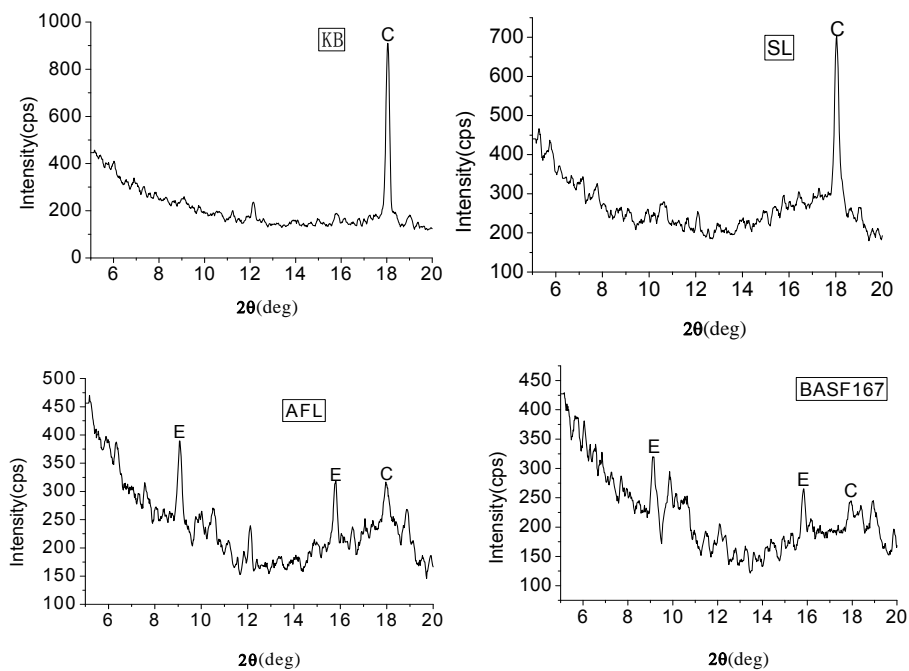


Figure 5. XRD patterns of the hardened paste mixed with different accelerators after 1 day. E: ettringite; G: gypsum; C: Ca(OH)_2 .

Figure 4 and figure 5 showed the XRD patterns of the hardened paste mixed with different accelerators at the final setting and after 1 day. At the initial stage of hydration, a large amount of Ca(OH)_2 and a small amount of ettringite formed in the hardened paste mixed with the SL alkaline liquid accelerators and the blank paste. Meanwhile, a certain amount of ettringite crystal and a small amount of Ca(OH)_2 formed in the hardened paste mixed with AFL and SA167.

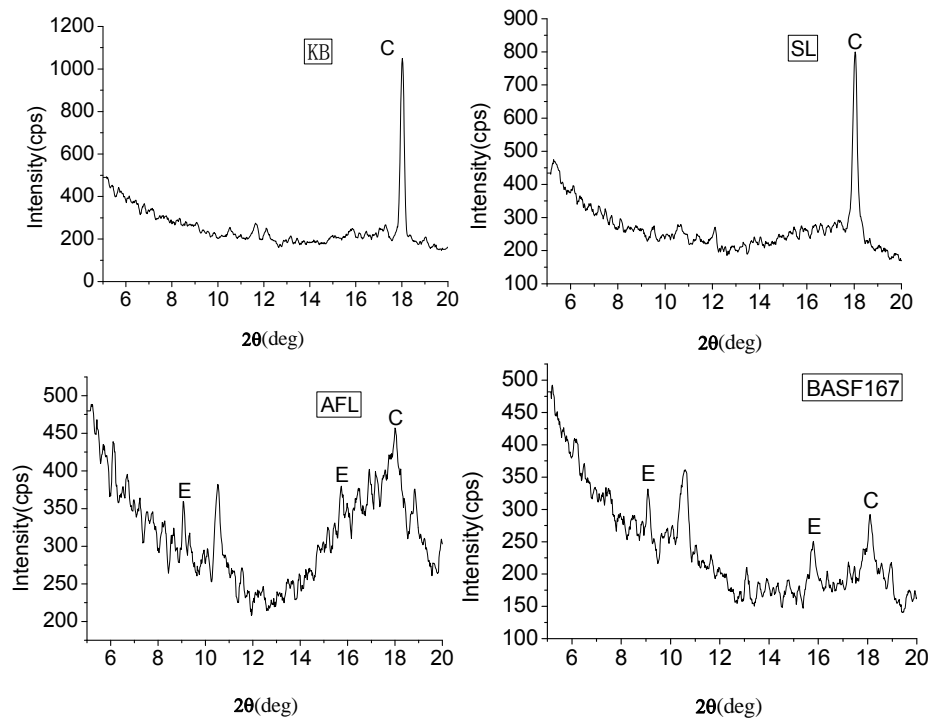


Figure 6. XRD pattern of the hardened paste mixed with different accelerators after 28 days.

E: ettringite; G: gypsum; C: Ca(OH)_2

Figure 6 showed the XRD patterns of hardened paste mixed with different accelerators after 28 days. It can be seen from the figure that a large amount of Ca(OH)_2 formed in the hardened paste mixed with the alkaline liquid accelerators and the blank paste, while a certain amount of ettringite and a small amount of Ca(OH)_2 formed in the hardened paste mixed with AFL and SA167.

Table 7. XRD characteristics of the peak intensity table.

	d value	Blank			SL			AFL			SA167		
		final setting	1d	28d	final setting	1d	28d	final setting	1d	28d	final setting	1d	28d
Ettringite	9.68	65	16	22	52	30	35	119	123	49	242	88	47
Ca(OH)_2	4.91	272	546	635	155	376	480	35	55	28	83	35	40
C_3A	2.6	206	123	0	66	0	0	180	32	0	183	62	0
C_3S	1.75	296	104	17	330	155	115	315	145	18	328	150	28

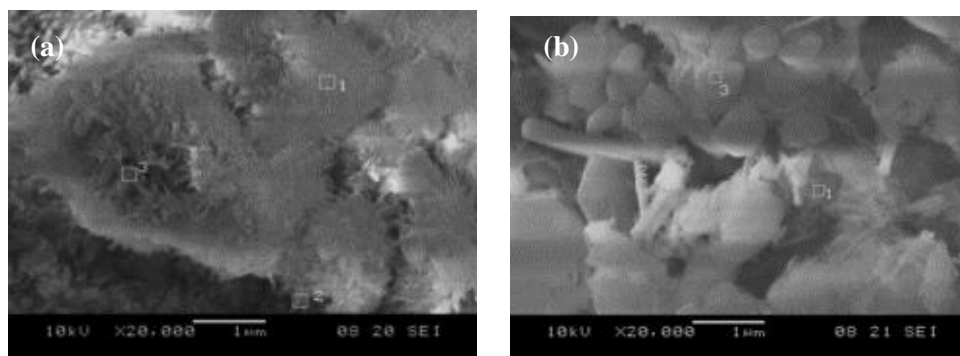
The characteristic peak intensities of hardened cement paste mixed with different accelerator at the final setting, 1 day and 28 days were shown in table 7. It revealed the crystal products and the reaction between different mineral phases at the various stages of hydration. The early behavior of cement hydration is mainly determined by C_3A reaction and the development of condensation and early

strength mainly depends on the hydration degree of silicate, especially the hydration degree of C_3S [7]. It can be seen from table 7 that a certain amount of $Ca(OH)_2$ crystals and a very small amount of ettringite formed in the cement paste mixed with SL alkaline liquid accelerator produced in final setting stage, while a certain amount of C_3S and a large number of C_3A was consumed. When the hydration time reached 1 day, the amount of $Ca(OH)_2$ crystals continued to increase, while C_3A was depleted and the amount of C_3S decreased, and the hydration product of C-S-H contributed to the 1 d strength. When the hydration time reached 28 days, there is still a considerable amount of C_3S in the paste mixed with SL alkaline liquid accelerator, which was significantly higher than that of other cement hardening paste, indicating the addition of alkaline accelerator delayed the late hydration of C_3S . This is one of reasons for low compressive strength of 28d.

A certain amount of ettringite and a very small amount of $Ca(OH)_2$ formed in the cement paste mixed with AFL and BASF167 accelerator produced in final setting stage. Compared with the paste mixed with alkaline liquid accelerator, fewer C_3A and comparable C_3S were consumed. When the hydration time reached 1 day, the amount of $Ca(OH)_2$ crystals was still very small, while the amount of C_3A and C_3S was reduced obviously, and the formation of hydrated gel of ettringite and C_3S enhanced the 1d strength of cement hardened paste. When the hydration time reached 28 days, there is still a little amount of C_3S in the paste, while C_3A was depleted and the residual amount of C_3S is very small, which is equivalent to the blank paste without any accelerator. According to the consumption of C_3S and C_3A , the incorporation of alkali-free liquid accelerator has little effect on the late hydration of cement.

The amount of $Ca(OH)_2$ and ettringite in the hardened paste mixed with AFL accelerator is less than that of paste mixed with BASF167D accelerator, but the consumption of C_3S is relatively high. This due to the $Mg(OH)_2$ precipitation was formed in paste mixed with AFL accelerator during the initial stage of hydration, which is more difficult to dissolve than $Ca(OH)_2$, resulting in promoting the hydration of C_3S and reduces the forming amount of $Ca(OH)_2$. The main constituent of SA167 is aluminum salt, and its mechanism of quick setting and early strength mainly promotes the formation of ettringite through aluminum salt. Therefore, AFL has better cement adaptability, which provides the ideal quick-setting early strength, effectively reduces the rebound of shotcrete.

3.6. SEM analysis



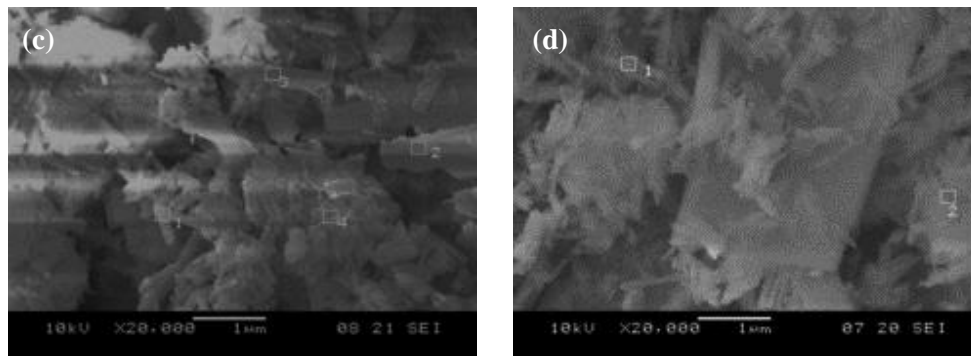


Figure 7. Hydration product morphology of hardened paste mixed with different accelerators at the final setting stage. (a) blank paste; (b) paste mixed with SL; (c) paste mixed with AFL and (d) paste mixed with BASF167.

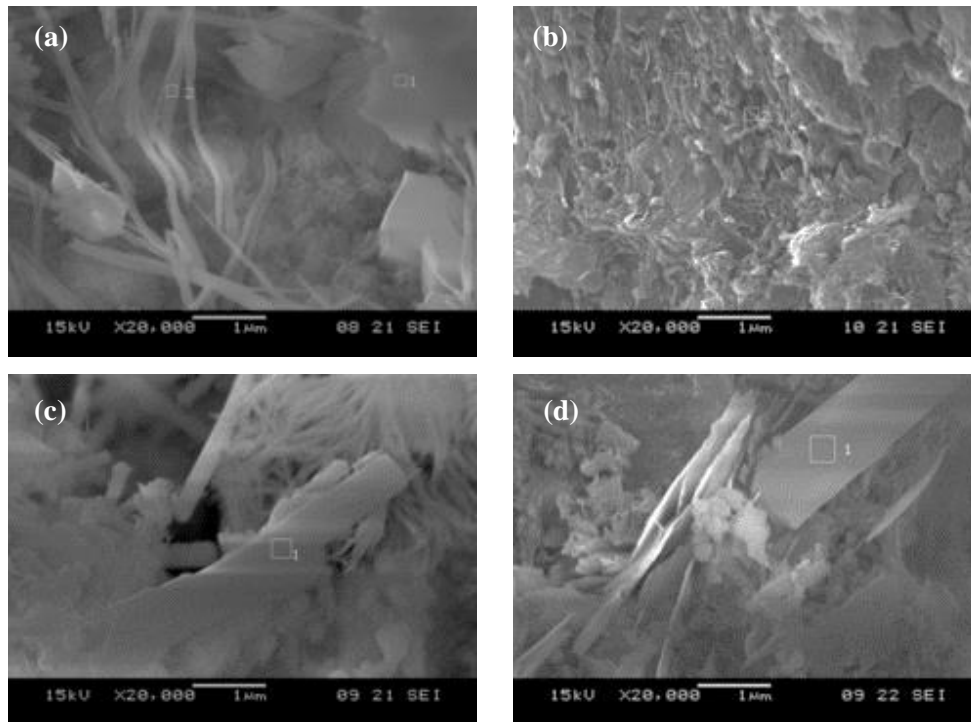
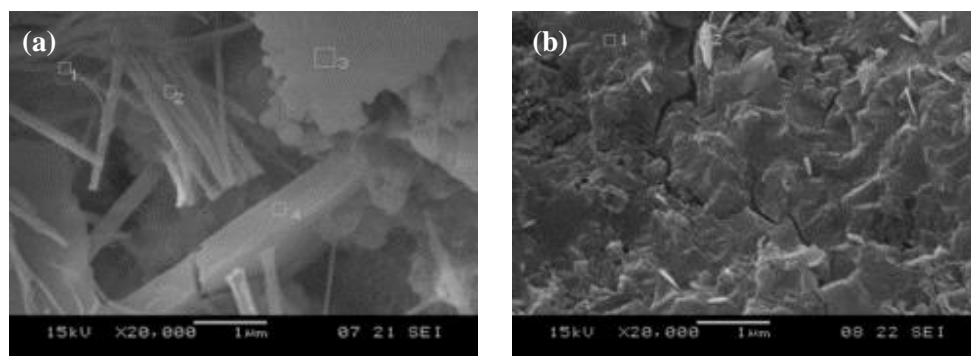


Figure 8. Hydration product morphology of hardened paste mixed with different accelerators after 1 days. (a) blank paste; (b) paste mixed with SL; (c) paste mixed with AFL and (d) paste mixed with BASF167.



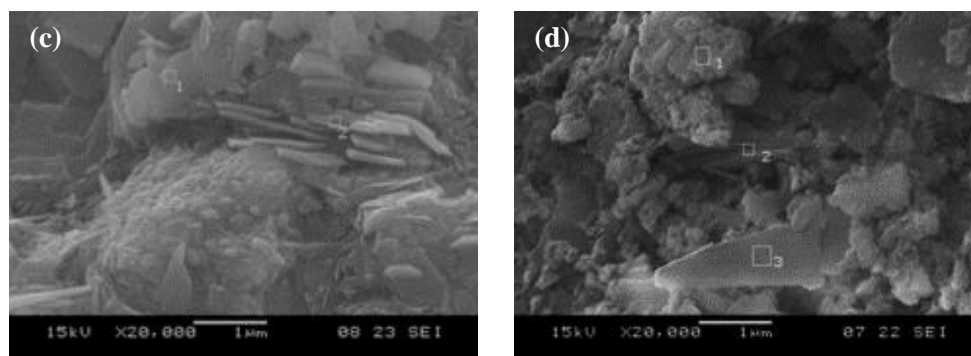


Figure 9. Hydration product morphology of hardened paste mixed with different accelerators after 28 days. (a) blank paste; (b) paste mixed with SL; (c) paste mixed with AFL and (d) paste mixed with BASF167.

It can be seen from figure 7 that there was a significant difference in the microstructures between the pastes mixed with different accelerators at the initial stage of hydration (final setting). The blank paste showed a loose structure. And a large amount of hydration products of C_3A and another amorphous hydration product can be observed in the paste mixed with SL alkaline liquid accelerator, while a large number of acicular ettringite was formed in the paste mixed with AFL and BASF167 alkali-free liquid accelerator.

As indicated in figure 8, when the hydration time reached 1 day, the paste mixed with different accelerators showed a significant difference in the microstructures. A great deal of fiber-like CSH gels was formed in the blank samples. The paste mixed with KD alkaline liquid accelerator showed a loose structure, and some elongated ettringite and hydrated CSH gels were formed in it. And the morphology of the paste mixed with AFL and BASF167 alkali-free liquid accelerator was similar, a large amount of rod-like ettringite with a large size was distributed in them.

As shown in figure 9, when the hydration time reached 28 day, a great deal of CSH gels were formed in all samples those showed denser microstructures. However, the hydration products in the sample mixed with KD alkaline liquid accelerator appeared to be looser than other samples, resulting in a serious loss of 28 d strength. This phenomenon revealed that the addition of alkali-free liquid accelerator HAS is very beneficial to the development of 28 d compressive strength of cement.

4. Conclusions

- (1) A new alkali-free liquid (AFL) accelerator without sulfate ion and chloride ions for shotcrete was prepared. When the content of alkali-free liquid accelerator was 6%, the initial setting time and final setting time were 2min 25s and 8min respectively, and 7d and 28d compressive strength ratios reached 112.3% and 114.2% respectively, which shows good procoagulant performance.
- (2) The penetration strength of concrete prepared by using AFL accelerator is higher than that of concrete prepared by using BASF167 alkali-free liquid accelerator and SL alkali liquid accelerator, which shows a small rebound ratio of the vault and side wall, are 13.4% and 6.4% respectively. It also decreases the coagulation time, increases the bond strength and the early strength.
- (3) XRD analysis show that a large amount of ettringite crystal and a small amount of $Ca(OH)_2$ form in the hardened paste prepared with AFL alkali-free liquid accelerator. According to the consumption of C_3S and C_3A , the incorporation of alkali-free liquid accelerator has little effect on the late hydration of cement.
- (4) SEM analysis indicates that a large amount of CSH gel and needle-like ettringite form in the hardened paste prepared with AFL alkali-free liquid accelerator, showing a denser microstructure. The results reveal that the addition of alkali-free liquid accelerator HAS is very beneficial to the development of 28d compressive strength of cement.

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