Research on Performance and Preparation of High Strength Liquid Alkali-free Setting Accelerator

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Abstract. A high strength liquid alkali-free setting accelerator in sprayed concrete was prepared by ultrasonic heating technology, to inorganic and organic compounds as the main raw material. The cement setting time, mortar and concrete mechanics performance and durability are studied, and its coagulation mechanism is studied by pore structure analysis. The test results show that the SA content was 5%, it initial setting time is less than 4 min, final setting time is less than 8 min, 1 d compressive strength ratio is more than 193.3%, and 28d compressive strength ratio can be increased by 118.5%.

Introduction

With the rapid development of high-speed rail, highway, urban subway in China, tunnel construction is an inevitable engineering stage, which needs timely support and reinforcement of surrounding rocks to avoid collapse accidents in the tunnel. Sprayed concrete is a new technology widely used in tunnel support, waterproofing and leakage-stopping in the city, prevention of landslides and other projects. It can spray the mixture of cement, aggregate and accelerator mixing in certain ratio into the work sites with the help of a power system. Due to the effects of accelerator, the mixture can set and harden fast and reduce rebound to play a role in support and reinforcement. It is obvious that the accelerator is an essential admixture for the sprayed concrete to meet the construction requirements of special engineering. But the quality of the accelerator has significant effects on setting time, resilience [1], adaptability [2], initial and final strength development and durability of the sprayed concrete. Snyder et al [3] prepared liquid alkali setting accelerator by sodium aluminate, alcohol amine and water. The accelerator had high-volume admixtures and poor cohesion. The 28d compressive strength ratio of the concrete was only 70%~80%. In order to improve the compressive strength of the sprayed concrete and reduce the rebound, the researchers in the United States and European countries developed the liquid alkali-free setting accelerator which significantly improved the cohesion of concrete mixtures and played a role in making up for the loss of the final compressive strength. Zhang Shuxiong et al [5] optimized the liquid alkali-free setting accelerator and improved the initial compressive strength. The 28d compressive strength retention rate reached 109.9%. Sulphates are usually used in current setting accelerators to accelerate setting, but the introduction of sulfur trioxide leads to the excessive content of sulfur trioxide in cement. It remains a problem that the presence of sulfate ions and chloride ions has effects on the concrete durability.

This experimental research mainly focuses on the liquid alkali-free setting accelerator with great development potential and further studies the effects of no sulphates and no chloride
ions. In this research, a high strength liquid alkali-free setting accelerator (HSA) was prepared by ultrasonic heating technology using inorganic and organic compounds as main raw materials. It studied the influence of HSA on cement setting time and compressive strength. In addition, the coagulation mechanism and morphologies of cement hydration products were also analyzed by pore structure and SEM. It has meaningful progress for practical applications of the liquid alkali-free setting accelerator in high performance sprayed concrete.

**Experimental Section**

**Raw Materials**

Aluminum hydroxide (industrial grade, HWF-10, Aluminium Corporation of China); ethylenediamine tetraacetic acid (CP, Sinopharm Chemical Reagent Co., Ltd.); modified polyhydroxy alcohol amine (homemade); organic sepiolite (1250 mesh); cement: P·O 42.5 grade portland cement (Nanjing Hailuo Cement Plant), see Table 1; ISO standard sand; medium sand with fineness modulus M=2.7 and 5~10 mm continuous grading macadam were used in the concrete test.

**Table 1. The physical and mechanical properties of P·O 42.5 cement.**

| Apparent density/(g/cm³) | Water requirement of normal consistency/% | Flexural strength/MPa | Compressive strength/MPa | Setting time/min | Soundness |
|--------------------------|------------------------------------------|-----------------------|--------------------------|------------------|-----------|
| 3.12                     | 27.0                                     | 5.9                   | 9.5                      | 27.0             | 49.2      |
|                          |                                          | 3d                    | 28d                      | 3d               | 28d       |
|                          |                                          | Initial               | Final                    | Soundness        |           |

**Preparation of High Strength Liquid Alkali-free Setting Accelerator**

A certain amount of ethylenediamine tetraacetic acid (EDTA) was dissolved in water and heated to 60~70°C under ultrasonic. Then aluminum hydroxide was added and reacted with EDTA until the solution was clear. And then appropriate amount of modified polyhydroxy alcohol amine and organic sepiolite were added and reacted for 3 h in the ultrasound hot-water bath, to obtain the clear light yellow liquid alkali-free setting accelerator HAS. The uniformity of HSA liquid alkali-free setting accelerator is shown in the following Table 2.

**Table 2. Uniformity of HSA liquid alkali-free accelerator.**

| Appearance | Alkali content/% | Chlorine ion content/% | Density/(g·cm⁻³) | pH | Solid content/% |
|------------|------------------|------------------------|------------------|----|-----------------|
| Light yellow | 0.012            | 0.001                  | 1.38             | 3.5 | 50              |

**Experimental Section**

**Test Methods of Setting Time and Compressive Strength.** The tests of setting time of cement paste and mortar strength were conducted according to JC477-2005 Setting Accelerator for Sprayed Concrete. The sample size was 40mm×40mm×160mm.

**Test Method of Concrete Compressive Strength.** According to JGJ 55-2011 Specification for Mix Proportion Design of Ordinary Concrete and actual construction experience, the sand ratio is 45%, and the concrete slump is 120 mm. The final mix proportion of concrete is shown in Table 3. P·O 42.5 Hailuo cement and M12
polycarboxylate superplasticizer (PCE) of Jiangsu China Railway ARIT new materials Co., Ltd. were used. BASF160 liquid alkali-free setting accelerator and commercial liquid alkali-free setting accelerator SA were used as comparative samples.

Table 3. Mix proportion of concrete.

| Accelerator type | Accelerator content /% | Mix (kg/m³) |
|------------------|------------------------|-------------|
|                  |                        | Concrete    | Sand | Stone | Water | PCE | Accelerator |
| SA               | 4                      | 460         | 850  | 1038  | 194   | 1.65| 18.4        |
| HSA              | 5                      | 460         | 850  | 1038  | 194   | 1.65| 23          |
| BASF160          | 8                      | 460         | 850  | 1038  | 194   | 1.65| 36.8        |
| KB               | 0                      | 460         | 850  | 1038  | 194   | 1.65| 0           |

The test was conducted in accordance with GB/T 50081-2002 Standard for Test Method of Mechanical Properties on Ordinary Concrete. After curing for 1d, 7d and 28d, the samples were taken out to conduct the compressive strength test.

**Test Method of Concrete Durability.** The durability test of concrete mixed with setting accelerator was conducted according to GB/T50082-2009 Standard for Test Methods of Long-term Performance and Durability of Ordinary Concrete.

**Pore Structure Analysis.** The blank sample and cement paste mixed with various accelerators were prepared using the water cement ratio for testing cement paste setting time. Then the samples were added into 40mm×40mm×160mm test molds to conduct vibration moulding. After removing molds, the standard curing of samples was carried out to the required curing age. And then the samples were taken out and knocked to particles with the size of soybean. The cement paste particles in the middle part were soaked with anhydrous alcohol until the test started, and drying in a vacuum oven. The pore structure of cement hydration products with different curing ages were analyzed by Quantachrome's mercury porosimeter. The maximum test pressure was 414 MP. The measurement range of pore size was 0.003μm~360μm.

**Analysis of Cement Hydration Products.** The sample was plated with gold on the surface, and JEOL SEM was used to observe the surface morphology of samples. Cement hydration products were analyzed by NORAN VANTAGE DSI energy spectrometer.

**Results and discussion**

**Setting Time of HSA**

The setting time of cement paste mixed with various amounts of HSA was studied by Hailuo cement. The test results were shown in Table 4.

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

| Accelerator content /% | 0     | 4     | 5     | 6     | 7     |
|------------------------|-------|-------|-------|-------|-------|
| Initial setting time/min:s | 238"  | 5′10" | 3′35" | 2′10" | 1′30" |
| Final setting time/min:s   | 402"  | 11′35"| 8′20" | 5′10" | 4′20" |
| Compressive strength 1d/MPa | 7.5   | 20.12 | 20.73 | 21.21 | 21.89 |
| Compressive strength 28d/% | 100   | 110.5 | 115.5 | 117.3 | 115.2 |
Compressive Strength of Concrete Mixed with HSA

Table 5. Compressive strength of concrete mixed with accelerator.

| Accelerator type | Compressive strength |
|------------------|----------------------|
|                  | 1d /MPa | Ratio/%  | 7d /MPa | Ratio/%  | 28d/MPa | Ratio/% |
| SA               | 19.3    | 183.8    | 30.1    | 92.6    | 34.5    | 85.8    |
| HSA              | 20.3    | 193.3    | 37.5    | 115.4   | 47.6    | 118.5   |
| BASF160          | 18.5    | 176.2    | 34.9    | 107.5   | 42.33   | 105.3   |
| KB               | 10.5    | 100.0    | 32.5    | 100     | 40.2    | 100     |

Durability Test Results

**Anti-permeability Performance of Concrete Mixed with Accelerator.** As can be seen from Table 6, compared with concrete without mixing accelerator, the anti-permeability height of concrete mixed with HSA and BASF160 liquid alkali-free setting accelerator reduces 58.3%, 25% respectively. While the anti-permeability height of concrete mixed with SA liquid alkali setting accelerator increases 191.7%. It indicates that HSA liquid alkali-free setting accelerator can significantly improve the anti-permeability performance of concrete.

Table 6. Anti-permeability performance of concrete mixed with accelerator.

| Accelerator type | Seepage pressure /MPa | Seepage height/mm |
|------------------|------------------------|-------------------|
| SA               | 1.3                    | 35                |
| HSA              | 1.3                    | 5                 |
| BASF160          | 1.3                    | 9                 |
| KB               | 1.3                    | 12                |

**Drying Shrinkage.** As can be seen from Fig. 1, the shrinkage ratio of concrete mixed with HSA liquid alkali-free setting accelerator is smaller than concrete mixed with other accelerators, and slightly larger than that without any accelerator. So the durability of concrete mixed with HSA liquid alkali-free setting accelerator is better.

Figure 1. Drying shrinkage curve of concrete.

**Freezing Resistance.** As can be seen from Fig. 2(a), compared with the reference concrete, the mass loss rate of concrete mixed with accelerator is higher, and the freezing resistance is poorer. While the concrete mixed with HSA liquid alkali-free setting accelerator has smaller mass loss rate than that of concrete mixed with BSAF160 liquid alkali-free setting accelerator,
and the freezing resistance of the former is better. The concrete mixed with SA liquid alkali setting accelerator has the highest mass loss rate and worst freezing resistance. As can be seen from Fig. 2(b), after 160 freezing-thawing cycles, the dynamic modulus of the reference concrete, the concrete mixed with HSA liquid alkali-free setting accelerator, the concrete mixed with BSAF160 liquid alkali-free setting accelerator, the concrete mixed with SA liquid alkali setting accelerator are respectively 93.5%, 80.3%, 76.3% and 68.3%. Therefore, the concrete mixed with HSA liquid alkali-free setting accelerator has the minimum loss of dynamic modulus and optimum durability.

![Figure 2. The relationship between concrete mass loss rate and freezing-thawing cycles.](image)

**Pore structure**

![Figure 3. Poresize distribution of the final setting of hardened cement pastes.](image)

![Figure 4. Poresize distribution of hardened cement pastes hydration 1d (a) and 28d (b).](image)
Table 7. The porosity and density table of hardened slurry hydration 28d.

| Parameter                  | SA    | HSA   | BASF160 | KB    |
|----------------------------|-------|-------|---------|-------|
| Total porosity             | 0.189 | 0.210 | 0.196   | 0.230 |
| Apparent density (g/cm³)   | 1.71  | 1.76  | 1.76    | 1.69  |
| density(g/cm³)             | 2.08  | 2.20  | 2.18    | 2.18  |

The pore structure of hardened cement has important effects on the strength and density of cement concrete. Low porosity, small pore size, appropriate gradation and more round holes are essential factors for durable concrete.

As can be seen from Fig. 3 and Fig.4, the pore sizes of all samples become narrow with the hydration. The distribution of pore size centers at 28 d. At the same hydration age, the pore size distribution becomes larger in the following order: SA<BASF160<HSA<no accelerator. From Table 7, it can be seen that the sample mixed with liquid alkali setting accelerator has smallest pore size, most concentrated pore size distribution and smallest porosity, but its hydration products and unhydrated particles has the lowest average density (2.08 g/cm³) for those of other ones are not less than 2.18 g/cm³. This may be due to the lowest hydration degree of C₃S at 28 d and great proportion of C₃A hydration products. The hydration products are relatively loose, which may the reason why the final strength of the concrete mixed with liquid alkali setting accelerator is poor. As can be seen from Fig. 3-2, at the hydration time of 28 d, the total porosity and pores larger than 100 nm of hardened cement pastes mixed with HSA accelerator are slightly reduced than those of cement pastes without accelerators. While the reduction in the total porosity and pores larger than 100 nm can improve the strength of hardened cement. This is the reason why the strength of cement pastes mixed with liquid alkali-free setting accelerator is larger than that of hardened cement without accelerator at 28 d.

The dehydration of capillary pores (10 ~ 50nm) and gel pores (less than 10 nm) will occur during the drying of concrete. When dehydrating, the liquid level in pores will fall to be meniscus, and the strong capillary pressure will be formed as a result of the surface tension of water. Then the formation of pressure difference between the interior and exterior will cause the shrinkage of concrete. Along with the increase in amounts of dehydration, the capillary pressure will become strong, resulting in increased shrinkage of concrete[6]. At the 28 d, it can be seen from Fig. 4 that the pores less than 50 nm decreases in the following sequence: cement pastes mixed with SA liquid alkali setting accelerator, cement pastes mixed with BASF160 and HSA liquid alkali-free setting accelerator, and pastes of the blank sample without any accelerator. The above results indicate that the hardened cement pastes mixed with liquid alkali setting accelerator contain more gel water and capillary water, and this will lead to a greater shrinkage during the drying process. Thus, it is understandable that the hardened cement pastes mixed with liquid alkali-free setting accelerator have less shrinkage.

**SEM analysis**

At the hydration time of 1 d, the accelerators have great effects on the morphologies of cement paste samples, as shown in the following Fig. 5(a)-5(d). A large number of fibrous CSH gel can be observed from the blank sample. The samples mixed with liquid alkali-free setting accelerator HSA and BASF 160 have very similar morphologies that lots of large ettringite bars are distributed in the samples. The sample mixed with liquid alkali setting
accelerator looks loose, and it has slender ettringite and some CSH hydration gel. The morphologies at 28 d are shown in Fig. 5(e)-5(h). It can be seen that all samples become dense and they have large amounts of CSH gel. Among them, the hydration products of the sample mixed with liquid alkali setting accelerator SA look looser. This phenomenon reveals that liquid alkali-free setting accelerator HSA is beneficial for the compressive strength of 28 d hydration products of cement.

Figure 5.(a) Morphology of hydration products (1 d) of cement pastes mixed with SA.

Figure 5.(b) Morphology of hydration products (1 d) of cement pastes mixed with HSA.

Figure 5.(c) Morphology of hydration products (1 d) of cement pastes mixed with BASF160.

Figure 5.(d) Morphology of cement pastes hydration products (1 d) of the blank sample.

Figure 5.(e) Morphology of hydration products (28 d) of cement pastes mixed with SA.

Figure 5.(f) Morphology of hydration products (28 d) of cement pastes mixed with HAS.
Conclusions

(1) The prepared HSA liquid alkali-free setting accelerator contains no sulfate ions and no chloride ions. With the dosage of 5%, the concrete initial setting time is 3min35s and the final setting time is 8min20s, which shows obvious accelerating effects. The 1 d compressive strength of mortar is 20.73 MPa, and the 28 d compressive strength ratio is up to 115.5%;

(2) The 1 d compressive strength of the concrete mixed with HSA liquid alkali-free setting accelerator reaches 20.3 MPa, increased by 193.3% in comparison with that of the reference concrete; the 7 d compressive strength is 37.5 MPa with the compressive strength ratio increasing by 115.4%; the 28 d compressive strength is 47.6 MPa with the compressive strength ratio increasing by 118.5%; they are all enhanced compressive strength;

(3) The anti-permeability height of concrete mixed with HSA liquid alkali-free setting accelerator decreases 58.3%. After 160 freezing cycles, the concrete mixed with accelerator has high mass loss rate and poor freezing resistance, compared with the reference concrete. But compared with concrete mixed with other accelerators, it has low mass loss rate, dynamic modulus and drying shrinkage, so that it has excellent durability;

(4) The pore structure analysis shows that the total porosity and pores larger than 100 nm of cement pastes mixed with HSA accelerator are slightly reduced after 28 d hydration. Besides, the hydration products and unhydrated particles in hardened cement pastes have high actual average density, so this may improve the final compressive strength.

(5) SEM analysis indicates that large amounts of CSH gel can be observed in the hardened cement paste mixed with liquid alkali-free setting accelerator HSA, and the cement pastes become dense. Consequently, the liquid alkali-free setting accelerator HSA is beneficial for the compressive strength of 28 d hydration products of cement as it significantly improve the compressive strength of cement pastes.

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