Study on the preparation of suspension stabilizer for liquid accelerator

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Abstract. A suspension stabilizer (P-XF) was prepared by copolymerization of acrylamide (AM), acrylic acid (AA), ammonium persulfate (APS), thioglycolic acid (TGA) and potassium hydrogen tartrate (KHT). The suspension stabilizer (P-XF), aluminum sulfate (Al$_2$(SO$_4$)$_3$), p-toluenesulfonic acid (PTSA) and triethanolamine (TEA) were used to prepare a liquid accelerator (P-SN$_2$). The test results show that compared with the liquid accelerator (P-SN1) without P-XF, P-SN$_2$ not only can effectively shorten the setting time, but also has high stability, with a stable period of more than one year.

1. Introduction
Accelerator is an additive that can make concrete or cement mortar set and harden rapidly. Its main function is to accelerate the setting and hardening speed of shotcrete, reduce rebound loss, prevent shotcrete from falling off due to gravity, increase the thickness of one shot and shorten the interval time between shot layers[1]. China began to study powder accelerator around 1990s[2]. 8604 type accelerator successfully developed by Architectural Research Institute of Ministry of metallurgy in 1989, AC type accelerator developed by Changsha mine Research Institute in 1990, MJ-2000 accelerator developed by Coal General Institute in 1995, and the raw materials for this kind of accelerator are bauxite, lime, gypsum, etc. The 28d strength ratio of concrete mixed with these accelerators is increased to about 90%, but the dosage and production cost of these powder accelerators are high, so the application of them is not ideal. With the development and application of wet jet technology, the research direction of accelerator also turns to liquid accelerator.

The research of liquid accelerator began in the late 1980s, mainly in the United States, Japan, Germany, Switzerland and other countries[3-6]. At the end of the 20th century, the research on liquid accelerators began in China. At present, there are some problems in the market, such as short product storage period and long setting time[7]. The short storage period is mainly reflected in the normal construction temperature range, and the product appears layered precipitation or crystallization about 1 month after production. The long setting time means that the product needs to increase the content of accelerator in the use process, thus increasing the construction cost, and at the same time, it will have different degrees of impact on the durability of concrete. Therefore, it is of great significance to develop a liquid accelerator with good stability, short setting time, low dosage, good adaptability to cement and no adverse effect on durability. A suspension stabilizer (P-XF) was prepared by copolymerization of acrylamide (AM), acrylic acid (AA), ammonium persulfate (APS), thioglycolic acid (TGA) and potassium hydrogen tartrate (KHT). When the suspension stabilizer (P-XF) is used in the synthesis of accelerator, it can solve the adverse effects of liquid accelerator, especially in the aspects of stability and coagulation.
2. Experimental

2.1. Materials

2.1.1. The main synthetic experimental raw materials. Acrylamide (AM), industrial grade; acrylic acid (AA), industrial grade; ammonium persulfate (APS), industrial grade; thioglycolic acid (TGA), industrial grade; potassium hydrogen tartrate (KHT), industrial grade; aluminum sulfate (Al$_2$(SO$_4$)$_3$), industrial grade; p-toluenesulfonic acid (PTSA), industrial grade; triethanolamine (TEA), industrial grade;

2.1.2. Main performance test raw materials for experiment. Cement: Min Fu P.O 42.5 Cement; Sand: standard sand (GB/T17671-1999), products of Xiamen ISO standard sand co. Ltd; P-SN$_1$: Liquid accelerator, Self made without P-XF, other synthesis conditions are the same as P-SN$_2$.

2.2. Synthesis of suspension stabilizer P-XF

Metered water and AM were added to the reactor, heating up to 70°C, APS, AA, and TGA were added to the reactor respectively. The dropping was controlled within 3 h. Add KHT after dripping, and then P-DMG was obtained.

2.3. Synthesis of liquid accelerator P-SN$_2$

Metered water, P-XF, Al$_2$(SO$_4$)$_3$, PTSA and TEA were added to the reactor. After the system temperature reached 40°C, and reaction 1 h, and then P-SN$_2$ was obtained.

2.4. Performance test method

2.4.1. Setting time of cement pastes. The tests of the setting time of the cement pastes are conducted in accordance with GB/T35159-2017 "Flash setting admixrutes for Shotcrete ".

2.4.2. Determination of mortar strength. The tests of the mortar strength are conducted in accordance with GB/T35159-2017 "Flash setting admixrutes for Shotcrete ".

2.4.3. Gel chromatography test. Waters 1515 was used. The column was connected in series by UltrahydragelTM 250 and UltrahydragelTM 500. The mobile phase was 0.1 mol/L sodium nitrate aqueous solution at a flow rate of 0.8 mL/min. The standard calibration curve was sodium polyacrylate and the running time was 60 min.

3. Experimental results and discussion

3.1. Effect of molar ratio of AA to AM on conversion

The effect of the molar ratio of AA to AM on the conversion was investigated under the same conditions, the experimental results are shown in Figure 1. The results showed that with the increase of the molar ratio of AA to AM, the conversion increased first and then decreased. When the molar ratio of AA to AM is 0.8:1, the conversion is the highest, which is 81.5%.
3.2. Orthogonal test and analysis
According to the results of previous tests, the dosage of AA and AM was fixed. APS, TGA and KTH were used as three factors to carry out the uniform test design, and two levels of each factor were selected. Taking the conversion rate of polymerization as the investigation index, the orthogonal experiment was designed and arranged. The dosage of three factors is the percentage of total mass of AA and AM. The optimal material ratio is determined through the test, and the test results and analysis are shown in Table 1.

Table 1. Orthogonal test results and analysis

| Number | APS/% | TGA/% | KTH/% | conversion rate/% |
|--------|-------|-------|-------|------------------|
| 1#     | 1.5   | 0.8   | 0.5   | 76.8             |
| 2#     | 1.5   | 1.6   | 1.0   | 80.5             |
| 3#     | 3.0   | 0.8   | 1.0   | 92.3             |
| 4#     | 3.0   | 1.6   | 0.5   | 81.4             |
| Value K1j | 78.65 | 84.55 |       | 79.1             |
| Value K2j | 86.85 | 80.95 |       | 86.4             |
| Range R | 8.2   | 3.6   |       | 7.3              |

Table 1 shows that APS, TGA and KTH have the following effects on the conversion of polymerization: APS > KTH > TGA. The results of orthogonal test show that the optimal process is APS, TGA and KTH, which are 3.0%, 0.8% and 1.0% of the total mass of AA and AM respectively. The P-XF prepared by this process has the highest conversion.

3.3. Effect of reaction temperature on conversion
On the basis of Orthogonal Optimum Technology, the effect of the reaction temperature on the conversion was investigated under the same conditions, the experimental results are shown in Figure 2. The results showed that with the increase of reaction time, the conversion increased first and then stabilized. When the reaction time is 3.0 h, the conversion rate reaches 93.8%. When the reaction time is extended, the conversion rate shows a stable trend. Therefore, the best reaction time is 3.0 h.
3.4. Effect of reaction time on conversion

The effect of the reaction time on the conversion was investigated under the same conditions, the experimental results are shown in Figure 3. The results showed that the conversion increased first and then stabilized with the increase of reaction time. When the reaction time is 3.0 h, the conversion rate reaches 93.8%. When the reaction time is extended, the conversion rate shows a stable trend. Therefore, the best reaction time is 3.0 h.

3.5. Performance test of liquid accelerator synthesized by P-XF

The preparation conditions of P-XF were as follows: the molar ratio of AA to AM is 0.8:1, the dosage of APS, TGA and kth are 3.0%, 0.8% and 1.0% of the total mass of AA and am respectively. the reaction temperature was 70℃, the reaction time was 3 h. Then P-XF, Al₂(SO₄)₃, PTSA and tea were used as raw materials to prepare liquid accelerator P-SN₂. P-SN₁ was prepared from Al₂(SO₄)₃, PTSA and TEA under the same conditions as P-SN₂.

The setting time, mortar strength and stability of p-sn₁ and p-sn₂ are tested in accordance with GB / T35159-2017 "Flash setting admixrutes for Shotcrete ", the test results are shown in Table 2.
Table 2. Performance test results

| Accelerator | Dosage /% | setting time /min:s | 1 day compressive strength /MPa | Compressive strength ratio /% | Stability/day |
|-------------|-----------|---------------------|---------------------------------|------------------------------|--------------|
|             |           | Initial          | Final                               | 28d                          | 90d          |
| P-SN1       | 8.00      | 4:30             | 11:15                               | 7.8                          | 95           |
| P-SN2       | 7.00      | 4:35             | 10:30                               | 8.9                          | 100          |

The test results show that the initial setting time is the same when P-SN2 is 0.88 times of P-SN1, the final setting time is shorter, the strength is higher in one day, the compressive strength ratio is higher in 28 days and 90 days, and the stability of the product is better. It can be seen that the introduction of p-xf into the accelerator can not only effectively shorten the setting time, but also have obvious advantages in the stability of the product, with the stability up to 15 months.

4. Conclusions

(1) According to the molar ratio of AA to AM of 0.8:1, the dosage of APS, TGA and kth are 3.0%, 0.8% and 1.0% of the total mass of AA and am, The reaction temperature is 70 ℃, and the reaction time is 3.0h. The suspension stabilizer P-XF is prepared.

(2) The suspension stabilizer made in this paper is used in the synthesis of liquid accelerator, which improves the cohesiveness of liquid accelerator, has short setting time, improves the strength of concrete, does not appear stratification or crystallization, and has a stability of up to 15 months.

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