Effect of acid on the early strength of aluminum sulfate series alkali-free accelerator

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Abstract. This article introduces the effect of acid on the setting time, early strength and stability of aluminum sulfate alkali-free accelerator. The inorganic acids used are phosphoric acid, hydrofluoric acid and fluorosilicic acid, and the organic acids are oxalic acid and ethylenediaminetetraacetic acid. As a result, it was found that increasing the amount of acid can increase the stability of the accelerator. The product of the anion in acid and calcium ion in cement is easy to form. The product damages the network structure of the cement paste, and the early strength is low.

1. Introduction

In recent years, China's tunnels, underground facilities and other infrastructure have been vigorously promoted. When constructing a tunnel, in order to ensure that no collapse occurs, strong support must be provided. Sprayed concrete can achieve good molding effect without the support of formwork. The time required for concrete hardening is relatively short, which can greatly shorten the construction period, and has a good effect on the reinforcement of the tunnel surrounding rock. The so-called sprayed concrete is actually mixed with additives, cement, etc. with the help of air pressure, and then sprayed to the working surface. In this way, the mixture can quickly harden and solidify, thereby enhancing the supporting force and strength.

In the study of sprayed concrete, the accelerator is often in a key position. The usage and market share of liquid accelerators have developed rapidly. Among them, the proportion of liquid alkali-free quick setting agent is increasing. At present, there are still some problems with the alkali-free liquid accelerator on the market. For example, the price is high, the stable storage period is short, the early strength development is slow, and the cement adaptability range is small. Alkali-free liquid accelerator has greater difficulty in product development [1].

In the aluminum sulfate alkali-free accelerator system, to suppress the hydrolysis of aluminum ions into aluminum hydroxide precipitation, the pH of the solution needs to be controlled below 4.0. When the pH of the system is greater than 4, precipitation inevitably separates out. Under normal storage conditions after production, it is prone to crystallization and delamination, that is, the problem of short storage period [2]. To solve this problem, the researchers will add acid to the liquid alkali-free accelerator system. By adjusting the pH value of the system, the effect of inhibiting the hydrolysis of aluminum ions is achieved. Commonly used acids are divided into inorganic acid and organic acid. Inorganic acids include phosphoric acid, hydrofluoric acid, and fluorosilicic acid [3-8], and organic acids include oxalic acid, lactic acid, methacrylic acid, glycolic acid, and ethylenediaminetetraacetic acid (EDTA) [9-11].
The experiment found that after using acid to solve the problem of short storage period of aluminum sulfate alkali-free quick setting agent, the problem of early strength (1d strength) not meeting the standard will occur. In this paper, three inorganic acids, phosphoric acid, hydrofluoric acid and fluorosilicic acid are selected. Most of the organic acids used are organic carboxylic acids. In this paper, oxalic acid and EDTA are selected. This article explores the effect of acid dosage on the early strength of aluminum sulfate alkali-free accelerator.

2. Materials and methods

2.1. Raw materials

PO42.5 cement is produced by Shandong Shanshui Cement Group Co. Ltd. Standard sand is Xiamen ISO standard sand. Aluminum sulfate, magnesium fluorosilicate, triethanolamine, phosphoric acid, hydrofluoric acid, fluorosilicic acid, oxalic acid and EDTA are industrial grade. Water was deionized water.

2.2. Preparation of alkali-free accelerator

40% water and 5% magnesium fluorosilicate were added to the three-necked flask, after heating to 60°C, 50% aluminum sulfate was added in portions. After 2 hours of reaction, 5% triethanolamine and the acid studied in this article were added in sequence. Stir until the solution is homogeneous. After cooling to room temperature, an alkali-free quick-setting agent is obtained, which is marked as NC-S. The amount of acid added is a percentage of the total.

2.3. Performance test methods

The performance of alkali-free accelerator is tested according to GB / T 35159—2017 "Accelerator for Shotcrete". GB/T 35159-2017 stipulates: water/cement ratio is 0.35. Initial setting time ≤ 5 min, final setting time ≤ 12 min; 1 d compressive strength ≥ 7.0 MPa, 28 d compressive strength ratio ≥ 90%, 90 d The retention rate of compressive strength is ≥ 100%; the stability at 28 days is ≤ 5 ml. In this experiment, the amount of accelerator is 7% of the cement mass. After the synthesis of the sample is completed, it is placed in a transparent sample bottle, sealed and stored in an environment of (20 ± 2)° C, and the changes in the clarity and stratification of the sample are regularly observed, and the stable period is recorded. When the thickness of the supernatant reaches 5 ml after the liquid is layered, it is defined as the unstable state, and the sample is from the end of the synthesis to the unstable state as the stable period (in days).

3. Results and discussion

3.1. The effect of phosphoric acid on the performance of alkali-free accelerator.

The amount of phosphoric acid was changed to study the changes in product setting time, early strength and stability. The results are shown in Table 1. It can be seen from Table 1 that as the amount of phosphoric acid increases, the initial setting time and final setting time of the alkali-free quick-setting agent both decrease first and then increase. The shortest time is reached at 4% dosage. The sample gradually became clear from turbidity. When the amount of phosphoric acid is more than 4%, the sample has become transparent, and the stability period is also extended. This is because phosphoric acid is a medium strong acid. Increasing the amount of phosphoric acid increases the concentration of hydrogen ions in the system, which can effectively inhibit the hydrolysis process of aluminum ions.
Table 1. The effect of phosphoric acid on the performance of alkali-free accelerator.

| Dosage /% | Setting time / (min:s) | 1d Compressive strength /MPa | Product properties | pH  | Stability period /d |
|-----------|------------------------|-----------------------------|--------------------|-----|---------------------|
|           | initial | final |                        |                   |     |                     |
| 0         | 5:40    | 11:50 | 8.9                    | yellow-green, turbid, sticky | 5.5 | 3                   |
| 1         | 5:20    | 10:40 | 7.9                    | yellow-green, turbid, sticky | 4.3 | 10                  |
| 2         | 4:40    | 8:30  | 7.2                    | yellow-green, cloudy, sticky | 4.0 | 18                  |
| 3         | 4:20    | 7:40  | 6.8                    | yellow-green, turbid, thick | 3.9 | 23                  |
| 4         | 3:30    | 6:50  | 5.7                    | yellow-green, transparent, sticky | 3.5 | 30                  |
| 5         | 4:10    | 8:20  | 4.5                    | yellow-green, transparent, sticky | 3.3 | 30                  |

However, as the amount of phosphoric acid increases, the early strength decreases. The retardation effect of phosphoric acid itself on cement is not great. But phosphoric acid will form phosphate when added to the alkali-free accelerator system. This phosphate can ionize the charged ions in the aqueous solution, causing displacement and condensation. During the setting and hardening process of cement, phosphate produces an insoluble film. The film layer will affect the precipitation and nucleation of Ca (OH)₂, C-S-H and the formation process of C-A-S-H, and then delay the setting and hardening of cement to produce retardation [12].

3.2. The effect of hydrofluoric acid on the performance of alkali-free accelerator.

Change the content of hydrofluoric acid to study the changes of product setting time, early strength and stability. The results are shown in Table 2.

It can be seen from Table 2 that as the amount of hydrofluoric acid increases, the initial setting time and final setting time of the alkali-free quick-setting agent continue to decrease. The prepared samples are light green, transparent, low viscosity and easy to flow. The period of stability has also been extended. When the content of hydrofluoric acid is 2%, the stable period reaches 60 days. This is because $F^-$ will complex with $Al^{3+}$, which greatly increases the solubility of $Al^{3+}$ and increases its stability.

As the amount of hydrofluoric acid increased, the early strength decreased slightly. This is because $F^-$ will form $CaF_2$ or $F^-$ with $Ca^{2+}$, which will depolymerize the C-S-H gel and damage the network structure of the cement paste, and the early strength is low [4,5].

Table 2. The effect of hydrofluoric acid on the performance of alkali-free accelerator.

| Dosage /% | Setting time / (min:s) | 1d Compressive strength /MPa | Product properties | pH  | Stability period /d |
|-----------|------------------------|-----------------------------|--------------------|-----|---------------------|
|           | initial | final |                        |                   |     |                     |
| 0         | 5:40    | 11:50 | 8.9                    | yellow-green, turbid, sticky | 5.5 | 3                   |
| 0.5       | 4:40    | 7:50  | 7.3                    | light green, transparent and easy to flow | 4.2 | 15                  |
| 1         | 3:50    | 7:30  | 7.2                    | light green, transparent and easy to flow | 3.6 | 30                  |
| 1.5       | 3:00    | 5:00  | 6.5                    | light green, transparent and easy to flow | 3.0 | 40                  |
| 2         | 2:30    | 4:50  | 6.3                    | light green, transparent and easy to flow | 2.6 | 60                  |
Table 3. Effect of fluorosilicic acid on the performance of alkali-free accelerator.

| Dosage /% | Setting time / (min:s) | 1d Compressive strength /MPa | Product properties | pH  | Stability period /d |
|-----------|------------------------|-------------------------------|--------------------|-----|---------------------|
|           | initial                | final                         |                    |     |                     |
| 0         | 5:40 11:50             | 8.9                           | yellow-green, turbid, sticky | 5.5 | 3                   |
| 1         | 4:20 7:50              | 7.0                           | Light green, transparent, sticky | 5.0 | 10                  |
| 2         | 4:50 7:30              | 7.3                           | Light green, transparent, sticky | 4.6 | 15                  |
| 3         | 5:00 8:00              | 7.8                           | Yellow-green, turbid, sticky | 4.5 | 20                  |
| 4         | 5:30 8:50              | 4.3                           | Yellow-green, turbid, sticky | 4.2 | 16                  |

3.3. The effect of fluorosilicic acid on the performance of alkali-free accelerator.

Change the content of fluorosilicic acid to study the changes of product setting time, early strength and stability. The results are shown in Table 3.

It can be seen from Table 3 that with the increase of the amount of fluorosilicic acid, the initial setting time and final setting time of the alkali-free quick-setting agent are continuously increasing. The prepared sample is light green and transparent. After the dosage is increased to 3%, the color changes to yellow-green, and the sample appears small granular crystals. This is because the addition of fluorosilicate can first complex with Al<sup>3+</sup>, forming a large number of network structures in the solution, increasing the solubility of Al<sup>3+</sup>. As the viscosity of the sample increases, the stability period also increases. However, after the amount of fluorosilicic acid is greater than 3%, granular crystals of aluminum fluorosilicate or magnesium fluorosilicate appear in the solution, and the stability of the system decreases.

With the increase of the amount of fluorosilicic acid, the early strength is slightly enhanced. After the amount is increased to 4%, the strength decreases. This is because the fluorosilicate will form calcium fluorosilicate with Ca<sup>2+</sup>, which will depolymerize the C-S-H gel and damage the network structure of the cement paste, and the early strength is low [6].

3.4. The effect of oxalic acid on the performance of alkali-free accelerator.

The amount of oxalic acid was changed to study the changes in product setting time, early strength and stability. The results are shown in Table 4.

It can be seen from Table 4 that with the increase in the amount of oxalic acid, the initial setting time and final setting time of the alkali-free quick setting agent are continuously increasing. The prepared sample is light green and transparent first. After the dosage is increased to 1%, the viscosity of the system drops. This is because oxalate can chelate with Al<sup>3+</sup>, forming a large number of network structures in solution. The solubility of Al<sup>3+</sup> is increased, and the stability period is also extended.

Table 4. The effect of oxalic acid on the performance of alkali-free accelerator.

| Dosage /% | Setting time / (min:s) | 1d Compressive strength /MPa | Product properties | pH  | Stability period /d |
|-----------|------------------------|-------------------------------|--------------------|-----|---------------------|
|           | initial                | final                         |                    |     |                     |
| 0         | 5:40 11:50             | 8.9                           | yellow-green, turbid, sticky | 5.5 | 3                   |
| 1         | 4:25 10:20             | 7.0                           | Light green, transparent, sticky | 4.2 | 14                  |
| 2         | 4:50 11:30             | 6.5                           | Light green, transparent and easy to flow | 3.6 | 20                  |
| 3         | 5:00 12:00             | 4.8                           | Light green, transparent and easy to flow | 3.5 | 21                  |
As the amount of oxalic acid increased, the early strength continued to decline. This is because oxalate will form calcium oxalate with Ca\(^{2+}\), which will depolymerize the C-S-H gel and damage the network structure of the cement paste, and the early strength is low [13].

3.5. The effect of EDTA on the performance of alkali-free accelerator.

Change the dosage of EDTA to study the changes of product setting time, early strength and stability. The results are shown in Table 5.

**Table 5.** Effect of EDTA on the performance of alkali-free accelerator.

| Dosage /% | Setting time / (min:s) | 1d Compressive strength /MPa | Product properties | pH | Stability period /d |
|-----------|------------------------|------------------------------|--------------------|----|---------------------|
| 0         | 5:40/11:50             | 8.9                          | yellow-green, turbid, sticky | 5.5 | 3                   |
| 1         | 3:30/7:30              | 7.5                          | Light yellow, transparent and easy to flow | 5.6 | 20                  |
| 2         | 4:10/8:10              | 7.3                          | Yellow, transparent, easy to flow | 5.4 | 30                  |
| 3         | 4:15/8:30              | 6.7                          | Yellow, transparent, easy to flow | 4.8 | 40                  |
| 4         | 4:30/9:00              | 5.1                          | Yellow, transparent, easy to flow | 4.6 | 40                  |

It can be seen from Table 5 that with the increase in the amount of EDTA, the initial setting time and final setting time of the alkali-free quick-setting agent continue to increase. The prepared sample is light green, transparent and easy to flow. When the dosage is increased to 2%, the color of the system becomes yellow. This is because EDTA is a chelating agent that can chelate with Al\(^{3+}\), forming a large number of network structures in the solution, increasing the solubility of Al\(^{3+}\) and prolonging the stability period.

As the amount of EDTA increased, the early strength continued to decline. This is because EDTA also chelate with Ca\(^{2+}\), which will depolymerize the C-S-H gel and damage the network structure of the cement paste, and the early strength is low [9].

4. Discussion and conclusion

Based on the above experimental results, it can be seen that increasing the amount of acid and reducing the pH of the system is an important way to improve the stability of alkali-free accelerator. Lowering the pH value of the solution can inhibit the hydrolysis of aluminum ions into aluminum hydroxide precipitation and improve the stability of the accelerator.

Adding H\(^+\) to the system will inevitably introduce some anions. These anions will affect the solubility of aluminum ions and at the same time will affect the early strength of cement. For inorganic acids, the anion complexes with aluminum ions, and the aluminum salt formed can increase the solubility of aluminum ions. For organic acids, the anion is generally a carboxylate group, which chelate with aluminum ions, forming a large number of network structures in solution, increasing the solubility of aluminum ions. In terms of strength, the product formed by these anions and calcium ions destroys the network structure of the cement paste, and the early strength is low.

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