Study on the Preparation and Performance of An Early Strength Agent for Liquid Alkali-Free Accelerator

Yu Jiang¹, Lei Deng², Wenhong Chen³ and Jianmei Li⁴

¹KZJ New Materials Group Guizhou Co., Ltd. Longli, Guizhou, China
²KZJ New Materials Group Guizhou Co., Ltd. Longli, Guizhou, China
³KZJ New Materials Group Guizhou Co., Ltd. Longli, Guizhou, China
⁴KZJ New Materials Group Guizhou Co., Ltd. Longli, Guizhou, China

Corresponding author’s e-mail: owen@xmabr-kzj.com

Abstract: An early strength agent applied to liquid alkali-free setting accelerator was synthesized at 60°C-70°C by taking methacrylic acid, silicic acid, calcium hydroxide, and hydroxyethyl ethylenediamine as the raw materials. The experiment showed that after 4% early strength agent was added into the accelerator, the 1d compressive strength and 28d compressive strength of the quick-setting mortar and shotcrete were obviously improved, so the industrialized application of this early strength agent can be realized.

1. Introduction

With the ever-increasing domestic (Chinese) market demand for shotcrete setting accelerators, the advantages of wet spraying technique have become more and more evident. The wet spraying focuses on liquid accelerators, including alkaline liquid accelerator and alkali-free liquid accelerator, where the former is featured by strong smell, intense corrosivity, serious harm to workers, and great later strength reduction in the spraying process. With minor pollution, low corrosivity, and high later strength, etc., the latter has been more and more extensively applied. However, most alkali-free quick-setting mortars in the current market have partially low strengths, or even do not have strength, which impacts the construction schedule, so it is crucial to add certain high-quality early strength agents.

The early strength agents, which are commonly applied to concrete in China, mainly include chloride series, sulfate series, organic matter series, and compound early strength agent series [1-2]. With the addition of chloride ions, the electrode potentials will be formed between the chloride ions and reinforcing steel bars, which can easily give rise to the corrosion of reinforcing steel bars [3]. In the sulfate series, sodium sulfate and potassium sulfate are mostly used, and the adulteration of sodium salt will elevate the alkali content in the concrete. When contained in the concrete, reactive aggregates will facilitate the alkali-aggregate reactions [4]. The liquid alkali-free accelerator is used in shotcrete, where it is required that the alkali content and chloride ion content should not be greater than 1.0% and 0.1%, respectively. However, within the content ranges, the early strength effects of neither sulfuric acid series nor chloride series are unapparent, failing to meet the related requirements. In order to improve the 1d compressive strength of alkali-free quick-setting mortar, a kind of milk white early strength agent was generated through the reaction of raw materials—methacrylic acid, silicic acid, calcium hydroxide, and hydroxyethyl ethylenediamine. With the addition of this early strength
agent, which did not contain K or Na ions, the 1d compressive strength and 28d compressive strength of quick-setting mortar and shotcrete were both enhanced.

2. Experiment

2.1. Experimental raw materials and instruments

The detailed information of the raw materials and main instruments used in the experiment are displayed in Table 1 and Table 2, respectively.

| Table 1 Experimental raw materials |
|------------------------------------|
| **Raw materials** | **Specifications** | **Factory** |
| Synthetic raw materials | | |
| Methacrylic acid | Main content: 99.5% | Ningbo Huajia Chemical Co., Ltd. |
| Silicic acid | Main content: 98% | Shanghai Titan Technology Co., Ltd. |
| Calcium hydroxide | Main content: 95% | Guilin Donghuang Chemical Technology Co., Ltd. |
| Hydroxyethyl ethylenediamine | Main content: 85% | Shanghai Dongtu Chemical Import & Export Co., Ltd. |
| Performance test raw materials | | |
| Cement (P.O 42.5) | Water of standard consistency: 26.2% | Guizhou Red Lion Cement Co., Ltd. |
| Machine-made sand | Fineness modulus: 2.2-3.2 | Guiyang Municipal Construction Co., Ltd. |
| Standard sand | Fineness modulus: 2.8 | Xiamen Aisiou Standard Sand Co., Ltd. |
| Gravel | Particle size: 5-10mm | Guiyang Municipal Construction Co., Ltd. |
| Water | tap water | Made by oneself |
| Alkali-free accelerator | JSN4: Contain 44% solid | A company in Guizhou (Semi-finished products) |
| Water-reducer | Point-400S: Contain 10% solid | KZJ New Materials Group Guizhou Co., Ltd. |

| Table 2 Main instruments |
|--------------------------|
| **laboratory apparatus** | **Type** | **Main technical parameters** |
| Digital display thermostatic water bath | HH-2 | capacity: 3000ml |
| Electric mixer | JJ-1 | Rotary speed: 3000r/min |
| Peristaltic pump | BT100-01 | Rotary speed: 0.1 ~ 100 rpm |
| Instrument                          | Model   | Specification                  |
|------------------------------------|---------|--------------------------------|
| Cement mixer                       | NJ-160B | Automatic control of program time: 255±3s |
| Single horizontal shaft test mixer | HJW-60  | Quota mixing quantity: 60L      |
| Digital pressure testing machine   | DYE-2000| Maximum load: 2000KN            |
| Motorized bending tester           | DR2-5000| The most strongly value: 5000N |
| Digital display pressure testing machine | YES-300 | Maximum load: 300KN            |
| Cement sand vibrating table        | ZS-15   | Vibrational frequency: 60r/60s |
| Scanning electron microscope      | JSM-6510| Magnification: 5 to 300,000x    |

2.2. Sample synthesis

W (620 kg) was pumped into the reaction kettle, the mixing paddle was started, calcium hydroxide (70 kg) was added, the mixture was heated to 70°C, W (110 kg) was added into the overhead kettle carrying a mixing paddle, which was then started, silicic acid (100 kg) was added, and the mixture was slowly poured into the reaction kettle after being mixed well. After the heat preservation for 2 h, it was cooled to 50°C, methacrylic acid (50 kg) and hydroxyethyl ethylenediamine (50 kg) were slowly added, and thus a milk white liquid early strength agent was prepared, namely ZQ (solid content was 26.5%).

2.3. Performance test method

(1) Setting time of cement paste: The test was conducted in accordance with GB/T 35159-2017 Flash Setting Admixtures for Shotcrete. The mix proportions of cement paste are listed in Table 3.

| Cement | Water | Accelerator |
|--------|-------|-------------|
| 400    | 160   | 24          |

(2) Compressive strength of cement mortar: The compressive strength was tested according to GB/T 35159-2017 Flash Setting Admixtures for Shotcrete. The mix proportions of cement mortar are displayed in Table 4.

| Cement | Sand | Water | Accelerator |
|--------|------|-------|-------------|
| 900    | 1350 | 160   | 54          |

(3) Concrete performance test: The C25 concrete performance test was carried out by reference to GB 8076-2008 Concrete Admixtures and GB/T 35159-2017 Flash Setting Admixtures for Shotcrete. The mix proportions of C25 concrete are seen in Table 5.

| Cement | Machine-made sand | Melon meters of stone | Water | water reducing agent | Accelerator |
|--------|-------------------|-----------------------|-------|----------------------|-------------|
| 480    | 913               | 815                   | 200   | 4.80                 | 28.8        |
(4) Standard requirements for setting accelerator: As required by GB/T 35159-2017 Flash Setting Admixtures for Shotcrete, the adulterate amount of liquid alkali-free accelerator should be within 6%-9%, and the concrete requirements for its technical indexes are presented in Table 6.

| Target | Setting time (min:s) | 1d Compressive strength (MPa) | 28d Ratio of compressive strength (%) |
|--------|----------------------|-------------------------------|---------------------------------------|
| Require | Initial set≤5 | Final set≤12 | ≥7 | ≥90 |

3. Results and Analysis

3.1. Setting time test of cement paste
The early strength agent ZQ was added into the alkali-free accelerator JSN4 by proportions of 2%, 4%, 6% and 8%, respectively to test the influence of ZQ on the setting time of cement paste, and the test results are shown in Figure 1.

![Figure 1 Cement paste time test results](image)

As shown in Figure 1, when 2% ZQ was added into JSN4, the initial setting time was lengthened by 10 s while the final setting time did not experience any obvious change in comparison with the reference; as the adulterate amount of ZQ was increased to 4% of JSN4, the initial setting time and final setting time were lengthened by 1 min and 80 s, respectively, and the setting time of quick-setting cement paste was extended with the continuously increasing adulterate amount of ZQ; when the adulterate amount of ZQ reached 6%, the initial setting time of cement paste was approximate to 5 min, and when the adulterate amount was increased to 8%, the initial setting time of quick-setting cement paste was longer than 5 min, so the national standard requirement was failed.

3.2. Compressive strength test of cement mortar
Based on the cement setting time test results, 2%, 4% and 6% early strength agent ZQ were respectively added into JSN4 to test the influence of ZQ on the compressive strength of cement mortar under adulterate amount of accelerator of 6%, and the test results are seen in Table 7.

| Experiment number | ZQ Dosage (%) | 1d Compressive strength (MPa) | 28d Ratio of compressive strength (%) |
|-------------------|---------------|-------------------------------|---------------------------------------|
| 1                 | 0             | 5.6                           | 105                                   |
From the compressive strengths of cement mortar in Table 7, compared with the reference, the 1d compressive strength of mortar was enhanced by 1.3 MPa after 2% ZQ was added into the alkali-free accelerator JSN4; as the adulterate amount of ZQ was increased to 4%, the 1d compressive strength of cement mortar reached 8.5 MPa, which satisfied the national standard requirement; when the adulterate amount of ZQ reached 6%, the 1d compressive strength of cement mortar reached 9.8 MPa, it was continuously enhanced with the increase of adulterate amount of ZQ, and the 28d compressive strength was also obviously enhanced.

3.3. SEM graph analysis of cement mortar
The 1d cement mortar test blocks formed in tests 1 and 3 in Table 7 were chosen for the SEM graph analysis.

![Figure 2 JSN4 1d mortar test block SEM](image)

![Figure 3 JSN4(4%ZQ) 1d mortar test blockSEM](image)

It could be seen from the SEM graph that when the early strength agent ZQ was not added into the alkali-free accelerator JSN4, the hydration products in the 1d cement mortar test block in the SEM graph were not totally hydrated, so the strength was partially low. When the adulterate amount of ZQ was increased to 4%, many irregular rodlike structural crystals Aft were formed, indicating that ZQ boosted the cement hydration, and enhanced the 1d compressive strength of cement mortar.

3.4. Shotcrete performance test
In order to ensure that the shotcrete setting time could satisfy the standard requirement, the newly developed early strength agent ZQ (adulterate amount was equivalent to 4% of JSN4) was added into the alkali-free accelerator JSN4 to perform the C25 shotcrete test, and the concrete performance test results are presented in Table 8.

| Experiment number | ZQ Dosage (%) | Setting time (min:s) | 1d Compressive strength (MPa) | 28d Ratio of compressive strength (%) |
|-------------------|---------------|----------------------|--------------------------------|-------------------------------------|
|                   |               | Initial  | Final               |                                    |
| 1                 | 0             | 2:55     | 8:25                | 5.5                                 | 102                                 |
| 2                 | 4             | 3:25     | 8:50                | 8.5                                 | 108                                 |

As seen in Table 8, after 4% ZQ was added into JSN4, the initial setting time and final setting time were lengthened by 30 s and 25 s, respectively, indicating minor influence of ZQ on setting time. However, the 1d compressive strength of concrete was elevated from 5.5 MPa to 8.5 MPa, and the 28d compressive strength was increased from 102% to 108%, manifesting that the ZQ added into the shotcrete setting accelerator had little influence on the setting time, but it could obviously improve the 1d and 28d compressive strengths of concrete.
4. Conclusions

(1) The methacrylic acid, silicic acid, calcium hydroxide, and hydroxyethyl ethylenediamine were used as the raw materials to synthesize the early strength agent for the liquid alkali-free setting accelerator at 60°C-70°C. When the early strength agent ZQ (adulterate amount was equivalent to 4%-6% of the use level of accelerator) was added into the alkali-free accelerator, both setting time and 1d compressive strength of mortar met the requirements specified in GB 35159-2017.

(2) After the early strength agent ZQ was added into the alkali-free accelerator JSN4, the quick-setting components in the accelerator were reduced, and the setting time of quick-setting cement paste was lengthened as the mix proportion of ZQ was increased.

(3) With the increasing adulterate amount of early strength agent ZQ, the promoting effect of cement hydration in the cement mortar was strengthened, and the early strength effect became better.

(4) After 4% early strength agent ZQ was added into the alkali-free accelerator, it exerted little influence on the shotcrete setting time, but both the 1d compressive strength and 28d compressive strength were enhanced.

About the author: Yu Jiang, male, engineer of KZJ New Materials Group (Guizhou) Co., Ltd., mainly engaged in the research and development and application of concrete admixtures

Mailing address: KZJ New Materials Group (Guizhou) Co., Ltd. (551206), Gujiao Town, Longli County, Guizhou Province.

Contact number: 18334237220.

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