Effect of curing method on compressive strength of rapid hardening sulphoaluminate cement mortar at -10 °C

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Abstract. Rapid hardening sulphoaluminate cement has been widely studied and applied under low temperature, normal temperature and high temperature conditions, but the research under negative temperature conditions has just started. Through three curing methods: constant negative temperature curing, negative temperature changing positive temperature curing, and pre-curing, the influence of different curing methods on the compressive strength of rapid hardening sulphoaluminate cement mortar at -10 °C is discussed. The results show that pre-curing measures can significantly improve the early compressive strength of rapid hardening sulphoaluminate cement mortar. The longer the pre-curing time, the greater the compressive strength. Under the condition of -10 °C, the rapid hardening sulphoaluminate cement can still be continuously hydrated, and the hydration products remain unchanged.

1. Introduction

In the 1980s, China independently developed sulfoaluminate cement. Compared with portland cement and aluminate cement, this cement has its own performance characteristics and belongs to a different chemical system, so it is called the third series of cement. Sulphoaluminate cement is a kind of cement with good gelling properties obtained after matching anhydrous calcium sulphoaluminate minerals and dicalcium silicate minerals. Researchers have found that it has the characteristics of fast hardening, high strength and suitable for winter construction. In the Harbin-Dalian high-speed railway construction project, the sulphoaluminate cement achieved the design strength requirement of over 20 MPa in 2 hours in the field environment below -25 °C under normal construction conditions. Rapid hardening sulfoaluminate cement is one of the most important varieties of sulphoaluminate cement. It has a faster setting speed and higher strength. It can be widely used under low temperature, normal temperature and high temperature conditions. In recent years, the demand for construction of military facilities in high-cold and high-altitude areas and the demand for development and construction in polar regions have promoted the research and application of rapid hardening sulfoaluminate cement under negative temperature conditions. Based on this, this paper studies the effects of three curing methods, constant negative temperature curing, negative temperature varying positive temperature curing, and pre-curing on the compressive strength of fast hardening sulfoaluminate cement mortar under the condition of -10 °C. Combined with the SEM experiment, the micro morphology of the rapid hardening sulfoaluminate cement mortar under the condition of -10 °C was discussed, and its
application in the extreme cold area was prospected. At the same time, the research direction under the condition of negative temperature was proposed.

2. Experiment materials and methods

2.1. Experiment material
Cement: "Yunhe Brand" rapid hardening sulphoaluminate cement (R-SAC) produced by Shandong Zibo Yunhe Color Cement Co., Ltd., with a strength grade of 42.5. Sand: Choose Bahe sand with a bulk density of 1460 kg/m³, a bulk density of 2635 kg/m³, and a mud content of 1.0%. Water-reducing agent: Select ZY-700 polycarboxylic acid high-performance water-reducing agent produced by Hunan Zhongyan Building Material Technology Co., Ltd., light yellow transparent liquid. Early strength agent: select lithium carbonate, analytically pure, white powder. Water: Use clean tap water.

2.2. Experiment methods
The test mainly includes mixing and forming of mortar, curing of mortar, compressive strength test and SEM test. The specific test procedures are as follows.

(1) Mixing and forming of mortar
It is mainly divided into three steps: material preparation, mixing and forming. (A) Material preparation. Weigh an appropriate amount of cement and sand, seal them with plastic bags, and place the cement, sand and early strength agent together in a negative temperature test system (as shown in Figure 1), and pre-cool for 24 hours to reduce the temperature to -10 ℃. Before the test, mix the water reducing agent and water evenly, then place it in a negative temperature test system to cool down, and control the temperature at 1 ℃. (B) Stirring. Implemented in accordance with "Cement Mortar Strength Inspection Method (ISO Method)". (C) Forming. Spread the release agent evenly on the cleaned inner surface of the test mold, place a small piece of paper on the round hole inside the test mold to prevent slurry leakage, and then put the mortar mixture into the test mold layer by layer, insert it and vibrate. The mixing and forming of the mortar are carried out indoors. In order to reduce the influence of room temperature on the performance of the mortar, the time is controlled within 5 minutes. The mixing ratio of mortar is shown in Table 1.

| Water-cement ratio | Lime to sand ratio | Content of early strength agent (%) | Content of water reducing agent (%) | Cement /g | Sand/g | Water/g | Early strength agent /g | Water reducing agent /g |
|--------------------|--------------------|-----------------------------------|-----------------------------------|-----------|-------|--------|------------------------|------------------------|
| 0.22               | 1:1.1              | 0.3                               | 1.0                               | 1000      | 1100  | 220    | 3                      | 10                     |

The negative temperature test system, produced by Jiangsu Bainian Refrigeration Equipment Co., Ltd., is a confined space with a plane size of 3 m × 4 m, a height of 2.4 m, and a minimum temperature of -30 ℃. The system is mainly composed of an air cooler, a temperature control system, an air-cooled condenser and an insulation board.
(2) Curing of mortar

The curing of the mortar is divided into four types: curing under negative temperature conditions, curing under standard conditions, negative temperature changing to positive temperature curing, and pre-curing, and the negative temperatures are all -10°C. (A) Curing under negative temperature conditions. Cover the formed mortar with plastic wrap and place it in a negative temperature test system for curing. Demould after 1 h, the demoulded mortar specimens are wrapped with plastic wrap to prevent water loss. Then, it was cured to 3 h, 1 d, 3 d, 7 d, and 28 d to test its mechanical properties.

(B) Negative temperature change to positive temperature maintenance. Cover the formed mortar with plastic wrap and place it in a negative temperature test system for curing. Demould after 1 h, the demoulded mortar specimens are wrapped with plastic wrap. After curing to 1 d, 3 d and 7 d, they are transferred to a standard curing box for curing. After curing to 28 d, the mechanical properties are tested. (C) Pre-curing. Place the formed mortar in a standard curing box for pre-curing. The pre-curing time is 30 min, 60 min, 90 min, 120 min, and 150 min. Then it was wrapped in plastic wrap and transferred to a negative temperature test system for curing, and cured to 3 h, 1 d, 3 d, 7 d, and 28 d ages to test its mechanical properties.

(3) Compressive strength test

The mortar specimens cured to the corresponding age were taken out and immediately subjected to the compressive strength test. The compressive strength test was carried out indoors using a fully automatic mortar flexural and compressive test integrated machine, as shown in Figure 2. When carrying out the compressive strength test, the loading rate is 2400±200 N/s, and the average value of a set of six compressive strength measured values is used as the test result.
(4) SEM test

The field emission scanning electron microscope was used to analyze the microscopic morphology of the sample. The mortar sample after the compressive strength test was broken into pieces, and some were selected as the sample. The sample was placed in absolute ethanol to terminate the hydration. Then, it was placed in an electric heating constant temperature blast drying oven for 24 hours, and the temperature of the drying oven was set to 60 °C. Finally, a fresh section of the sample was sprayed with gold and observed under a scanning electron microscope.

3. Experiment results and analysis

3.1. The mechanical properties of mortar under the condition of constant negative temperature curing

The compressive strength of the mortar under the constant negative temperature curing condition is shown in Figure 3. It can be seen from the figure that under the curing condition of -10 °C, the fast hardening sulfoaluminate cement can continue to hydrate. With the increase of the curing time, the compressive strength of the mortar gradually increases, and the compressive strength of the mortar increases rapidly in the early stage and slower in the later stage. At the age of 3 h, the compressive strength of the mortar was 22.1 MPa. At the age of 1 d, the compressive strength of the mortar increased by 28.95% compared with that at the age of 3 h. The rapid hardening sulphoaluminate cement has a faster hydration rate and is further promoted by the action of the early strength agent lithium carbonate. Although the curing temperature is -10 °C, the cement hydration exotherms, the internal temperature of the cement paste can still maintain the cement hydration and strength development, and the strength of the mortar has exceeded the frost critical strength before the internal temperature drops to 0 °C. Then the negative temperature curing only delays rather than prevents the strength development of the mortar.
3.2. The mechanical properties of mortar under the condition of negative temperature change and positive temperature curing

The compressive strength of the mortar under the condition of negative temperature change and positive temperature curing is shown in Figure 4, where -28 d means that the mortar is cured at constant negative temperature for 28 d, -1 d+28 d, -3 d+28 d, -7 d+28 d respectively means that the mortar is cured at negative temperature for 1 d, 3 d, 28 d and then standard curing, curing to 28 d of age. It can be seen from the figure that the compressive strength of the mortar is the smallest at -28 d. For the three sets of specimens of -1 d+28 d, -3 d+28 d, -7 d+28 d, the longer the negative temperature curing time, the smaller the compressive strength of the mortar. Compared with -28 d, the compressive strength of the specimen at -1 d+28 d increased by 10.31%, and the compressive strength of the specimen at -3 d+28 d increased by 5.28%, the compressive strength of -7 d+28 d specimens increased by 0.96%. It can be seen that under negative temperature conditions, the hydration of rapid hardening sulphoaluminate cement is concentrated in the early stage, and the later stage is transferred to standard curing, and the effect of improving the 28 d compressive strength of the mortar is not good.

3.3. Mechanical properties of mortar under pre-curing conditions

The compressive strength of the mortar under the pre-curing condition is shown in Figure 5. It can be seen from the figure that for the specimens of various ages, the longer the pre-curing time, the greater the compressive strength of the mortar. For the specimens aged 3 h, after pre-curing for 30 min, 90 min, and 150 min, the compressive strength of the mortar increased by 14.48%, 28.51%, and 34.84%, respectively. For the 28 d specimens, after pre-curing for 30 min, 90 min, and 150 min, the compressive strength of the mortar increased by 3.60%, 6.24%, and 9.59%, respectively. It can be seen that pre-curing measures are beneficial to improve the early mechanical properties of fast-hardening sulphoaluminate cement mortar under negative temperature conditions, but the effect of improving the later mechanical properties of the mortar is not good. Fast-hardening sulphoaluminate cement has a fast early hydration rate, and its strength is mainly developed in the early stage, so pre-curing under negative temperature conditions has a significant improvement effect on its early strength.
3.4. Microscopic morphology of mortar

Under the condition of -10 °C, the micro morphology of rapid hardening sulfoaluminate cement mortar at 3 h, 1 d and 28 d are shown in Figure 6. The mineral components of rapid hardening sulfoaluminate cement are mainly anhydrous calcium sulfoaluminate (C₄A₃S) and dicalcium silicate (C₂S). The early strength mainly comes from the formation of ettringite (AFt) by the hydration of C₄A₃S, the later strength is mainly derived from C₂S hydration to produce hydrated calcium silicate gel (CSH gel). The hydration reaction equation is shown in equations (1) and (2). It can be seen from the figure that under negative temperature conditions, the main hydration products of fast hardening sulfoaluminate cement have not changed, and obvious ettringite can be seen, but the amount and main form of ettringite have changed. With the growth of age, the number of ettringite produced gradually increases, and the shape of ettringite also develops into a short column shape from needles and flakes. It can be seen that under negative temperature conditions, rapid hardening sulfoaluminate cement can still be continuously hydrated, and the hydration products remain unchanged.

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\begin{align*}
3\text{CaO}&\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4 \ (\text{C}_4\text{A}_3\text{S}) + 2\text{CaSO}_4 + 38\text{H}_2\text{O} &\rightarrow 3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O} \ (\text{AFt}) + 4\text{Al(OH)}_3 \\
2\text{CaO}\cdot \text{SiO}_2 \ (\text{C}_2\text{S}) + 2\text{H}_2\text{O} &\rightarrow \text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O} \ (\text{C-S-H gel}) + \text{Ca(OH)}_2
\end{align*}
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Figure 6. Micro morphology of rapid hardening sulfoaluminate cement mortar.
4. Application prospect of rapid hardening sulphoaluminate cement under negative temperature
Rapid hardening sulphoaluminate cement has the unique advantages of fast-setting, fast-setting, early-strength and high-strength under negative temperature conditions. It has broad application prospects in the rapid repair and construction of military facilities in high-cold and high-altitude areas and the strategic development and construction of polar regions. China has built or will build a large number of military facilities in high-cold and high-altitude areas, such as the high-cold areas on the border between China and India, which are all facing severe negative temperature environments. Conventional cement does not solidify and has no strength or solidifies slowly under negative temperature conditions. The current construction mainly adopts physical methods such as heat preservation and heating to ensure cement hydration. In the rush to repair and build military facilities during wartime, the process of directly mixing, pouring, and curing cold materials on site is more time-saving and efficient. Therefore, rapid hardening sulphoaluminate cement has significant military significance and application value in it. The polar regions not only possess a large amount of natural resources, but are also the strategic commanding heights of great powers competing for interests and influence. Strategic development and construction in the polar regions must have a complete infrastructure. Conventional cement is not suitable for such an environment. Rapid hardening sulphoaluminate cement can play a huge role in supporting Chinese polar strategy. During the construction of the Great Wall Station and Zhongshan Station in Antarctica in 1985 and 1989, rapid hardening sulphoaluminate cement was used. In addition, fast-hardening sulphoaluminate cement has a large number of application examples in winter construction and emergency repairs.

5. Research prospect of rapid hardening sulphoaluminate cement under negative temperature
Under negative temperature conditions, the hydration process, microstructure and mineral composition of fast hardening sulphoaluminate cement are affected. The rapid hardening sulphoaluminate cement has made a lot of results in the low temperature, normal temperature and high temperature environment, but the research on its hydration characteristics and mechanical properties under negative temperature conditions has just started. In order to give full play to the negative temperature performance advantages of fast hardening sulphoaluminate cement and provide theoretical support for its application under negative temperature conditions, it is necessary to conduct in-depth research in the following aspects. First, the strength development and microscopic morphology of fast hardening sulphoaluminate cement under negative temperature conditions. The strength development is closely related to the microscopic morphology. The strength of rapid hardening sulphoaluminate cement develops slowly under negative temperature, and its microscopic morphology is obviously different from that at normal temperature, but it has not been studied in depth at present. Secondly, the self-heating material of rapid hardening sulphoaluminate cement under negative temperature conditions. The ambient temperature significantly affects the hydration and hardening of the fast-hardening sulphoaluminate cement, but if self-heating materials or heating materials are added to the fast-hardening sulphoaluminate cement, the internal temperature of the fast-hardening sulphoaluminate cement can be maintained at a relatively high temperature for a long time. A high level will significantly reduce the impact of ambient temperature on its hydration. Finally, the compound admixture of rapid hardening sulphoaluminate cement under negative temperature conditions. The hydration of fast-hardening sulphoaluminate cement changes due to temperature, so composite additives are needed to comprehensively solve the problems of its working performance, mechanical properties, durability, etc., to ensure the large-scale rapid-hardening sulphoaluminate cement under negative temperature conditions application.

6. Conclusion
(1) Taking pre-curing measures can significantly improve the early compressive strength of fast-hardening sulphoaluminate cement mortar. The longer the pre-curing time, the greater the compressive strength.
(2) Under the condition of -10 ℃, the rapid hardening sulfoaluminate cement can still be continuously hydrated, and the hydration products remain unchanged.

(3) Rapid hardening sulfoaluminate cement has broad application prospects in the rapid repair and construction of military facilities in high-cold and high-altitude areas and the strategic development and construction of polar regions.

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