Influence of Early Strength Agent on the Strength and Water Resistance of Cement-Desulfurized Building Gypsum Composite Cementitious System

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Abstract. The test takes the cementing system composed of ordinary Portland cement and desulfurized building gypsum as the research object, and the research is carried out based on the mechanism of the early strength agent that can accelerate the cement hydration reaction in the composite cementing system. In the experiment, the influence of the type and dosage of the early strength agent on the strength and water resistance of the composite gelling system was studied to determine the appropriate type and optimal dosage of the early strength agent. The test results show that sodium sulfate has a poor improvement effect on the sample due to the presence of desulfurized building gypsum in the composite cementing system, while calcium chloride and calcium formate can effectively promote the hydration of the cement in the composite cementing system, significantly improving the compressive strength and softening coefficient of the sample. When the calcium chloride content is 2%, the compressive strength of the sample is increased by 57.0% compared with the reference sample, and the softening coefficient is 0.82. When the calcium formate content is 1%, the compressive strength of the sample is increased by 31.1% compared with the reference sample, and the softening coefficient is 0.80.

1. Introduction
Desulfurized gypsum is an industrial by-product produced when lime or limestone wet method is used to remove sulfur dioxide from flue gas, and calcium sulfate dihydrate is the main component. The building gypsum produced by dehydration treatment of desulfurized gypsum has good gelling properties. It is one of the green gelling materials that are currently respected and developed in the world and is widely used in building materials and other related fields[1-2]. Gypsum products produced by using desulfurized building gypsum as raw materials have many advantages such as light-weight sound insulation, fire-proof and thermal insulation, and volume stability. However, it cannot be ignored that the strength and water resistance of gypsum products obviously cannot meet the requirements of certain engineering parts. These two major defects have severely restricted its resource utilization in the building materials industry. To solve this technical problem, it is necessary to optimize and modify the desulfurized building gypsum to improve the strength and water resistance of the hardened body after hydration[3]. For this reason, domestic and foreign experts and scholars
have made corresponding research. Geng Fei et al. mixed the β-type desulfurized gypsum with cement, fly ash, silica fume and additives to prepare a composite cementitious material with a 28d compressive strength of 12.1 MPa and a softening coefficient of 0.81[4]. Guo Huishi et al. used ordinary Portland cement to modify the water resistance of desulfurized building gypsum, and the results showed that when the amount of cement is 18%, the softening coefficient of desulfurized building gypsum is 0.71, and the water resistance is better[5]. Research by Butakova et al. found that adding a certain amount of cement and silica fume into gypsum can improve its water resistance, and the softening coefficient has been increased from 0.33 to 0.50[6].

The above research shows that compounding cement with desulfurized building gypsum is indeed an effective way to improve its strength and water resistance. However, with the increase of cement content, especially in the case of a large amount of cement, the setting and hardening time of the composite cementitious system becomes longer. In actual production, the advantage of using short hardening time of gypsum to improve production efficiency no longer exists. In order to shorten the hardening time of the cement-desulfurized building gypsum composite cementing system, and meet the requirements of mechanized production technology. This experiment is based on the mechanism of early-strength agent that can accelerate the cement hydration reaction in the composite cementing system, and the effect of different types of early-strength agents on the strength and water resistance of the composite cementitious system at different dosages is studied. This has important economic and social benefits.

2. Test

2.1. Raw materials

2.1.1 Desulfurization building gypsum. The desulfurized building gypsum used in the test was provided by Chongqing Muchuan Gypsum Building Materials Co., Ltd., which was light yellow and had gelling properties after being mixed with water. The main chemical components and main physical performance indexes of desulfurized building gypsum are shown in Table 1 and Table 2.

Table 1. Main chemical components of desulfurized building gypsum

| Chemical composition | SO3 | CaO | SiO2 | MgO | Fe2O3 | Al2O3 | Ignition loss | Crystal water |
|----------------------|-----|-----|------|-----|-------|-------|--------------|--------------|
| Content /%           | 41.5 | 32.9 | 1.24 | 1.84 | 0.15  | 0.56  | 15.78        | 18.12        |

Table 2. Main physical performance indexes of desulfurized building gypsum

| Standard water consumption /% | 2h strength /MPa | Compressive strength | 7d strength /MPa | Flexural strength | Compressive strength | Softening factor |
|-------------------------------|------------------|----------------------|------------------|-------------------|----------------------|-----------------|
| 60                            | 3.50             | 6.94                 | 2.85             | 6.35              | 0.47                 |                 |

2.1.2 Cement. The 42.5 ordinary portland cement provided by Chongqing Xiaonanhai Cement Factory was selected for the test, and its main chemical components and physical performance indicators are shown in Table 3 and Table 4.

Table 3. Chemical composition of ordinary portland cement

| Chemical composition | CaO | SiO2 | Al2O3 | Fe2O3 | MgO | K2O | SO3 | TiO2 |
|----------------------|-----|------|-------|-------|-----|-----|-----|------|
| Content /%           | 62.18 | 20.45 | 4.50  | 2.65  | 1.72 | 0.62 | 2.81 | 0.20 |

Table 4. Main physical performance indexes of ordinary portland cement

| Density /g·cm⁻³ | Setting time /min | Flexural strength /MPa | Compressive strength /MPa |
|-----------------|-------------------|------------------------|---------------------------|
|                 | Initial set | Final set | 3d | 28d | 3d | 28d | 3d | 28d |
| 3.12            | 189        | 305         | 4.7 | 9.1 | 22.7 | 47.8 |
2.1.3 Early Strength Agent. Three types of early-strength agents, calcium chloride, sodium sulfate and calcium formate, were selected for the experiment, all of which were provided by Shanghai Chenqi Chemical Technology Co., Ltd.

2.2. Test method

2.2.1 Method for measuring compressive strength. According to the test design plan, a set of 40mm×40mm×160mm samples were made for each test ratio. The sample is demoulded 2h after it meets with water, and then the compressive strength of the sample 7d is measured according to the relevant regulations of "Determination of Mechanical Properties of Building Gypsum" GB/T 17669.3-1999.

2.2.2 Method for measuring softening coefficient. According to the relevant regulations of "Gypsum Block" JC/T 698-2010, two sets of samples are made for each test ratio, and the maintenance is carried out according to the standard. After curing for 7 days, one group of samples was put into the oven (40±2) °C and dried to constant weight. The other set of samples was soaked in water at (20±3)°C, and then taken out after 24 hours, and the surface was wiped dry with a wet towel. Then, the breaking load of the sample after being saturated with water and the breaking load of drying to constant weight are measured respectively, and the softening coefficient of the sample is obtained by dividing the two.

3. Results and discussion

According to the results of previous experiments, this experiment uses 42.5 ordinary Portland cement to replace 20% desulfurized building gypsum, and the water-to-binder ratio is 0.55 as the benchmark ratio. Experiments were conducted to study the effects of three early-strength agents of calcium chloride, sodium sulfate and calcium formate on the compressive strength and water resistance of the composite gelling system. The mixing amount of early strength agent is calculated as the percentage of cement quality.

3.1 The effect of calcium chloride on the compressive strength and water resistance of composite cementitious system

![Graph 1](image1.png)  ![Graph 2](image2.png)

**Figure 1.** The influence of calcium chloride on the 7d compressive strength of composite cementitious system

**Figure 2.** The influence of calcium chloride on the water resistance of composite cementitious system

Calcium chloride, as a kind of chloride salt inorganic early strength agent, has an outstanding effect in cement cementing materials. Figure 1 shows the effect of calcium chloride early strength agent on the 7d compressive strength of composite cementitious system. It can be seen that with the increase of the calcium chloride content, the compressive strength of the composite gelling system sample takes the calcium chloride content 2% as the turning point, and there is a trend of first increasing and then decreasing, but the results are all higher than the reference sample. This shows that the incorporation
of calcium chloride has a positive effect on improving the mechanical properties of the composite cementitious system, and this effect is mainly based on a series of chemical reactions between calcium chloride and the cement in the composite cementing system. Calcium chloride reacts with C3A in cement clinker to generate chlorate hydrate, which accelerates the consumption of C3A. At the same time, calcium chloride can also react with Ca(OH)$_2$ generated by hydration to form insoluble calcium chlorate. With the help of the decrease in the concentration of Ca(OH)$_2$ in the solution, the C3S reaction can be accelerated to generate more hydration products. So as to achieve the purpose of early strength. But with the increase of the content, calcium chloride will react with the C3A in the cement to produce high-chlorine calcium chloroaluminate. Due to its expansibility, the strength of the sample will be slightly reduced. It can be seen from Figure 1 that when the calcium chloride content is 2%, the compressive strength of the sample reaches its peak value, which is an increase of 57.0% compared with the reference sample, and the early strength effect is significant.

Figure 2 shows the effect of calcium chloride early strength agent on the water resistance of composite cementitious system. It can be seen that with the increase of calcium chloride content, the softening coefficient of the composite gelling system samples has increased. Similar to the effect of calcium chloride on the compressive strength of the sample in Figure 1, when the calcium chloride content is 2%, the water resistance of the sample is the best, and the softening coefficient reaches 0.82, which meets the water resistance requirements of engineering applications. The improvement of the water resistance of composite cementitious system samples mainly depends on the amount of cement hydration products produced. Adding calcium chloride to the composite cementitious system can effectively promote the hydration of the cement, which provides a favorable basic guarantee for improving the water resistance of the composite cementitious system samples.

Comprehensive analysis shows that the addition of 2% calcium chloride early-strength agent to the cement-desulfurized building gypsum composite cementing system is beneficial to the improvement of the strength and water resistance of the sample. However, in engineering applications, care should be taken to prevent the corrosion of steel bars caused by chloride ions ionized by calcium chloride. If there are steel bars and other metals in the engineering use parts of the composite cementitious system, it is recommended not to use or use a small resistamount of calcium chloride as an early strength agent to improve strength and water ane.

3.2 The effect of sodium sulfate on the compressive strength and water resistance of composite cementitious system

Sodium sulfate is another widely used inorganic salt early strength agent. After sodium sulfate comes into contact with cement, the alkaline environment created by the generated NaOH promotes the dissolution of C3A and gypsum in the solution, which increases the amount of calcium sulfoaluminate produced. The proportion of the solid phase in the liquid phase has been increased, thereby accelerating the hardening process of cement and improving the early strength[7].
It can be seen from Figure 3 that when sodium sulfate is added to the composite gelling system, the compressive strength of the sample varies from 13.45 to 13.55 MPa. At the same time, Figure 4 shows that with the increase of sodium sulfate content, the softening coefficient of the sample does not change significantly, and even slightly decreases. This shows that the incorporation of sodium sulfate does not play a positive role in improving the compressive strength and water resistance of the composite gelling system. Analyzing the reasons, desulfurized building gypsum occupies a relatively large proportion in the composite gelling system, and it has introduced a large amount of sulfate ions in the slurry. At this time, it is no longer obvious to increase by adding sodium sulfate to introduce sulfate ions. Therefore, it is not recommended to use sodium sulfate as an early strength agent in cement-desulfurized building gypsum composite cementitious systems.

3.3 The effect of calcium formate on the compressive strength and water resistance of composite cementitious system

Calcium formate is different from calcium chloride and sodium sulfate. It is a commonly used organic early-strength agent. Figure 5 shows the effect of calcium formate on the 7d compressive strength of composite cementitious system. It can be seen that when the content of calcium formate is within 1%, the compressive strength of the composite gelling system increases with the increase of the content of calcium formate. When the calcium formate content is 1%, the compressive strength of the sample increases by 31.1% compared with the reference sample. With the further increase of calcium formate content, this effect does not increase, but basically stabilizes. Investigating its mechanism of action, calcium formate solution reduces the PH value of the slurry solution by hydrolyzing and ionizing $H^+$, thereby accelerating the hydration rate of cement clinker C3S. At the same time, adding calcium formate can increase the concentration of Ca$^{2+}$ in the solution, so that the calcium silicate hydrate can be formed faster, the solid matter content increases, and the early strength of the sample is improved.

Figure 6 shows the effect of calcium formate on the water resistance of composite cementitious system. It can be seen that the incorporation of calcium formate has a positive effect on improving the water resistance of the composite cementitious system samples. With the increase of calcium formate content, the softening coefficient of the sample increased significantly, and reached the peak when the calcium formate content was 1%. At this time, the softening coefficient is 0.8, an increase of 19.4% compared with the reference sample, which meets the water resistance requirements of engineering applications.

Through the comprehensive analysis of Figure 5 and Figure 6, calcium formate is beneficial to improve the strength and water resistance of the cement-desulfurized building gypsum composite cementitious system. Under the premise of a given reference ratio, the improvement effect is best
when the calcium formate content is 1%. Especially in engineering parts where the composite cementitious system is used in combination with steel bars and other metals, it is a feasible measure to use calcium formate instead of calcium chloride as an early strength agent.

4. Conclusion
The experiment studied the effects of three early-strength agents of calcium chloride, sodium sulfate, and calcium formate on the strength and water resistance of the cement-desulfurized building gypsum composite cementitious system at different dosages. A composite cementitious system with excellent strength and water resistance was prepared, and the appropriate type and optimal dosage of the early strength agent were determined. The test results show that sodium sulfate has a poor improvement effect on the sample due to the presence of desulfurized building gypsum in the composite cementitious system. Calcium chloride and calcium formate can effectively promote the hydration of cement in the composite cementitious system, and significantly improve the compressive strength and softening coefficient of the sample. When the calcium chloride content is 2%, the compressive strength of the sample is increased by 57.0% compared with the reference sample, and the softening coefficient is 0.82. When the calcium formate content is 1%, the compressive strength of the sample is increased by 31.1% compared with the reference sample, and the softening coefficient is 0.80.

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