Study on frost resistance of magnesium cement composite sheets

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Abstract: In order to study the frost resistance of magnesium cement composite sheets, the effects of freeze-thaw cycles on the bending properties of glass fiber reinforced basic magnesium sulfate cements blended with mineral admixtures and glass fiber reinforced chlorine were studied by freeze-thaw test method. Magnesium silicate cement is compared. The composition and microstructure of the hydration products of the board before and after freezing and thawing were analyzed by XRD and SEM. The results show that before the 128 freeze-thaw cycles, the flexural strength of the undoped composite sheet is 8.2%, 7.3% and 9.1% higher than the initial strength of the slag, fly ash and silica fume board, respectively. When the number of freeze-thaw cycles reaches 160, the strength retention rate of composite sheets with various ratios has been reduced to less than 75%, and the test pieces fail; the number of freeze-thaw cycles for failure of the magnesium oxychloride cement-based board is about 150 times, The number of basic magnesium sulfate cements is almost the same This indicates that in the freeze-thaw test, the failure of the specimen may be caused only by physical damage, and the number of times depends on the strength of the previous period.

1. Introduction

Glass fiber reinforced basic sulphur oxychloride cement (GRBMC) is a cement-based composite material made of glass fiber as a reinforcing material and a gas-hardened sulphur magnesia cement. It has light weight and good water resistance, does not burn, low cost and simple production process. At present, the main research results of glass fiber reinforced cement board in China are concentrated on magnesium oxychloride cement and low alkali board. Some scholars have conducted mechanical properties and aging tests on glass fiber cement sheets, and their life expectancy has been speculated. For example, Yan Yamei et al. [1] used the SIC (Sleeve In Cement) test method to accelerate the aging test. The results show that the flexural strength of glass fiber reinforced magnesium oxychloride cement material is significantly reduced under hot water conditions; [2] Using the SIC (strip in cement) test method, the bending strength of glass fiber reinforced magnesium oxychloride cement (GRMC) sheet under the condition of 80 °C hot water accelerated aging test was measured. It accelerated the test life and analyzed the hydration product composition and microstructure by XRD, DSC-TG, FT-IR and SEM, and observed the corrosion characteristics of glass fiber in the magnesium oxychloride cement matrix. Liu Qianqian [3] studied the degradation of mechanical properties of GRMC accelerated aging at 50 °C and 80 °C, and the durability of glass fiber reinforced magnesium oxychloride cement. The study found that glass fiber has excellent anti-aging properties to basic magnesium sulfate cement. Zhou Yiyi et al [4] studied the addition of wood chips in sulphaaluminate cement to improve the flexural strength
and compressive strength of cement sheets; Yang Jianming et al [5] found that magnesium phosphate cement mortar matrix and glass fiber have better The bonding force, the combination of the two can greatly improve the flexural strength of the test piece. Xing Sai-nan et al [6] studied the accelerated aging test and durability study of glass fiber reinforced basic magnesium sulphate cement, and obtained the characteristics of long aging life of glass fiber reinforced basic magnesium sulphate cement material. However, most composite panels are used for heat preservation and heat insulation. Therefore, applications in the north or northeast are widely used. According to the research on the freeze-thaw test of ordinary Portland cement concrete, it can be found that its frost resistance is poor, and the large-scale concrete engineering at home and abroad has serious concrete freeze-thaw damage. Due to the terrain and climate in China, the concrete project in the northern region is more susceptible to freezing and thawing, and the northeast region is the most serious [7]. The damage caused by the freeze-thaw cycle seriously affects the safety of the project. According to previous investigations and studies, the main factors causing poor frost resistance of ordinary Portland cement concrete are the structure of concrete internal pores, the degree of water saturation and the length of time of freezing. Glass fiber has excellent stability and good tensile strength and deformation resistance, so it can better inhibit the extension of freeze-thaw crack [8-9]. However, there is no relevant report on the antifreeze performance of glass fiber reinforced basic magnesium sulfate cement in cold regions. Therefore, it is necessary to carry out research on frost resistance. In this paper, the freezing and thawing cycle test method of asbestos cement board in the United States [10] is combined with microscopic experiments to study the variation of mechanical properties of GRMC specimens before and after freezing and thawing cycles.

2. Experiment

2.1 Raw material
(1) Light burned magnesia powder: Magnesium oxide is used to produce calcined magnesite at 750 °C (1382°F) in Dashiqiao, Liaoning Province, China. Its active MgO (α-MgO) is measured according to the standardized hydration method [11], and its chemical composition is shown in Table 1.

| Component | Mass fraction (wt. %) |
|-----------|-----------------------|
| MgO       | 80.20                 |
| CaO       | 1.30                  |
| SiO2      | 6.07                  |
| Fe2O3     | 0.41                  |
| Others    | 11.87                 |

(2) Magnesium Sulfate Solution: A certain amount of industrial grade MgSO4·7H2O (taken from Tianjin Jinnan District Yongxing Chemical Plant) was dissolved in water and prepared.

(3) Magnesium chloride solution: A certain amount of industrial grade MgCl2 (formed by Qinghai Golmud industrial magnesium chloride (magnesium content greater than 45%) dissolved in water.

(4) Mineral ginseng
   1) Slag (SG): the slag is from S95 grade fine slag of Jiangsu Jiangnan Grinding Company.
   2) Silica fume (SF): silica fume is made of encrypted silica fume produced in Ledu, Qinghai.
   3) Fly ash (FA): the fly ash is a Class II fly ash produced by Qinghai Qiaotou Aluminum Power Plant.

(5) Glass fiber: medium alkali glass fiber mesh cloth.

(6) Wood chips: poplar wood chips.

2.2 Test preparation and method
First, the configured magnesium sulfate solution and magnesium chloride solution are mixed with the added water, and then the lightly burned magnesium oxide powder, sodium citrate, wood chip slag and
fly ash are mixed according to 10%, 20%, 30% of the cement amount thereof. The silica fume is mixed with 5%, 10%, 20% of the cement content [12] and mixed in a stirred vessel, and stirred for 90 s. For each ratio, 24 metal molds of 40mmx40mmx160mm are used. Firstly, 50g of the mixed mud is weighed as a protective layer. Three layers of mesh cloth are placed, and the remaining mixed slurry is layered into the mold and smoothed.

The rapid freeze-thaw test is designed with reference to the concrete related standard ASTM C666-97 "Test Methods for Resistance of Concrete to Rapid Freezing and Thawing" (Procedure B) in combination with the material properties. The test piece with the specification of 40mm×40mm×160mm shall be placed in the indoor environment at a temperature of (20±3)°C and relative humidity of (30±5)% for 24 days, and then placed at not less than (5±2) °C. Soak in water for 4 days. Remove the test piece and put it into the freeze-thawed leather bucket. Add water to the top of the flooded test piece to ensure that the bucket does not leak water. Otherwise, the water will melt into the antifreeze solution and destroy the freeze-thaw machine. The freeze-thaw test equipment adopts NJKD-27 computer automatic rapid freeze-thaw tester. According to the AC386 standard, GRMC specimens were visually observed for cracks, delamination or chipping after 25 freeze-thaw cycles. However, the number of freeze-thaw cycles should be adjusted according to the actual situation. The number of each test piece is 3 pieces, and the compressive strength and flexural strength are tested.

3. Test results

3.1 Strength and quality changes of GRMC during freezing and thawing

Figure 1 shows the flexural strength of composite sheets at different freeze-thaw cycles. It can be seen from the figure that before the 128 freeze-thaw cycles, the mineral-incorporated composite material has a smaller reduction in the flexural strength than the undoped composite sheet, and the composite sheet freeze-thaw cycle without mineral admixture. The initial strength is the highest, which is 8.2%, 7.3% and 9.1% higher than the initial strength of the slag, fly ash and silica fume board, respectively. When the number of freeze-thaw cycles reached 128, the flexural strength of the sheet blended with fly ash and silica fume decreased rapidly, decreasing to 37.12% and 38.40% of the initial strength. Therefore, the effect of adding mineral inclusions at this time has been invalid.

Figure 2 shows the strength retention rate of composite sheets at different freeze-thaw cycles. Figure 2(a) shows the strength retention rate before 60 freeze-thaw cycles. It can be seen that composite sheets with different ratios before 60 cycles of freeze-thaw cycles have a high strength retention rate; Figure 2(b) shows the intensity retention rate for the 60-160 cycle number. It can be seen that when the number of freeze-thaw cycles reaches 160, the strength retention rate of composite sheets of various ratios has been reduced to less than 75%, so the test piece has failed; it is worth noting that the magnesium oxychloride cement-based board reaches about 150, which is almost the same as the freeze-thaw cycle of basic magnesium sulfate cement, even higher than that of mineral-doped plates. This indicates that the sample failure may be due to the freeze-thaw test. The number of times caused by physical damage depends on the strength of the previous period.

Figure 3 is a macroscopic picture of the composite plate in different cycles of freeze-thaw cycles, (a) is a picture after 6 cycles, (b) is a picture after 54 cycles, and (c) is a picture after 103 cycles, which can be clear. It can be seen that there is no obvious erosion and shedding on the surface of the test piece, so there is no obvious drop in strength; (d) is a picture after 128 cycles, it can be seen that the surface of the test piece has been obviously peeled off, and the surface is already It is no longer smooth, so the plate strength drops significantly in 128 freeze-thaw cycles; Figure (e) shows the picture after 160 cycles, it can be seen that the surface of the test piece has been severely eroded and peeled off, and the cement matrix protective layer and mesh The cloth is detached and the strength has reached the failure.
3.2 Changes in phase composition and micromorphology of GRMC during freezing a thawing

Figure 4 is an XRD pattern of composite sheets without mineral admixture at different freeze-thaw cycles. It can be seen from the XRD characteristic diffraction peaks in the figure that the main phase of GRMC is 5Mg(OH)2·MgSO4·7H2O (517 phase), 517 image in natural sample before freezing and thawing and Mg(OH)2 is water of MgO. The product, MgCO3 and SiO2 are mainly derived from the raw material light-burned magnesium oxide powder. It can be seen from the figure that the phase composition of the XRD pattern of the composite sheet before and after freezing and thawing is basically the same, and the diffraction peaks of the individual phases do not change significantly under different freeze-thaw cycles; Figure 6 is the XRD pattern of the composite sheet under 160 freeze-thaw cycles. It can be seen from the figure that after 160 cycles of freeze-thaw cycles, the sample is in the sample. There is no significant change in the intensity peak diffraction peak. Even if any mineral admixture is added, there is no obvious change in the phase. In summary, the freeze-thaw damage of the glass fiber reinforced basic magnesium sulfate cement sample is not chemical damage.
Figure 6 (a), (b), (c) shows the microscopic morphology of GRMC with mineral admixture under 160 freeze-thaw cycles. There are a large number of needle-shaped 517 whiskers in the figure, but no obvious Mg(OH)2 platelet crystals. Combined with the mechanical properties of the sample, freeze-thaw test process diagram, phase composition and micro-morphology, it can be concluded that the freeze-thaw damage of the glass fiber reinforced basic magnesium sulfate cement sample is caused by physical damage, not chemical damage. That is, the phase composition and microscopic morphology of the sample did not change significantly, and the diffraction peaks of the individual phases did not become significantly higher or lower, but as the number of freeze-thaw cycles increased, the intensity decreased below the failure criterion. And it can be seen from the above that the more the number of freeze-thaw cycles, the surface peeling of the sample is severely severe, and the fiber is significantly separated from the matrix, thus demonstrating that the freeze-thaw damage of the glass fiber reinforced basic magnesium sulfate cement sample is caused by physical damage.

4. Conclusion
(1) The strength of the glass fiber reinforced basic magnesium sulfate cement composite board decreased sharply after 128 freeze-thaw cycles, and the later stage tended to be gentle;
(2) Under the condition of freeze-thaw cycle, the strength of glass fiber reinforced basic magnesium sulfate cement sample decreased significantly after 160 cycles; the addition of mineral admixture did not significantly improve the sample;
(3) The antifreeze performance of magnesium oxychloride cement and basic magnesium sulfate cementitious board is almost the same, and the microscopic phase composition does not change; therefore, the freeze-thaw damage of the glass fiber reinforced basic magnesium sulfate cement sample is determined by physics. Destruction causes, not chemical damage.
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