Experimental study on freeze-thaw resistance of modified magnesium oxychloride cement foam concrete

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Abstract: Magnesium oxychloride cement foam concrete specimens were prepared by applying the inorganic-organic composite modification method to improve the water resistance of magnesium oxychloride cement and using the composite protein foaming agent for the purpose of foaming. Then, freeze-thaw cycle test was performed to examine the frost resistance property of the specimens under the designed mix proportion. The experimental results show that: after 20 freeze-thaw cycles, neither macro-cracks nor hollow spalling are observed on the surface of the specimen, the strength loss rate is only 12%, and the compressive strength remains at a relatively high level of 1.46 MPa. Meanwhile, the microstructure of the specimen before and after the freeze-thaw experiment was analyzed through SEM test, and the failure mechanism during the freeze-thaw process was explained.

1. Introduction
At present, the commonly-used wall insulation materials in construction projects can be roughly divided into two categories, inorganic wall insulation materials and organic wall insulation materials.

Organic thermal insulation materials had once occupied a dominant position in the market of construction thermal insulation materials for their advantages of ultra-lightness and excellent thermal insulation; particularly, expanded polystyrene (EPS) and extruded polystyrene (XPS) used to occupy about 80% of the market share[1]. However, organic thermal insulation materials, represented by polystyrene, have poor chemical stability and flame-retardant properties, and are therefore prone to fire; in addition, such materials would release a large amount of toxic gases, emit dense smoke, and cause serious environmental pollution when burned [2]. From the perspective of construction safety out of long-term considerations, buildings using EPS series thermal insulation materials are subjected to serious hidden risks of fire and environmental pollution.

Compared with organic materials, inorganic wall insulation materials are flame-retardant and anti-aging, featured with advantages of small deformation coefficient, stable performance, and long service life, especially in terms of fire protection [3]. Cement foam concrete has recently become the most widely used wall insulation material because of its stable performance. On the market, the conventional organic insulation materials such as polystyrene and polyurethane have been gradually replaced by inorganic materials such as Portland cement foam concrete. However, traditional Portland cement foam concrete
is generally subjected to a series of defects including low compressive strength, high brittleness, and high water absorption. Thus, the traditional Portland cement foam concrete involves great risks when used as a building insulation material.

Relative to Portland cement materials, magnesium oxychloride cementitious materials have multiple advantages such as excellent mechanical properties, fast setting speed, frost resistance, wear resistance, low alkali, and good processing properties [4-7]. Magnesium oxychloride cement also has some major drawbacks including poor water resistance and significant strength loss after water absorption, making its engineering application greatly restricted [8-10]. Therefore, improvement of water resistance is still the key to the promotion and application of magnesium oxychloride cementitious materials and the related foam concrete.

In this paper, an inorganic-organic composite modification method was adopted to modify the magnesium oxychloride cement by adding phosphoric acid, polymer emulsion (or polymer salts) and fly ash, and the composite protein foaming agent was used for the purpose of foaming to prepare specimens with good water resistance. Then, the freeze-thaw cycle test was carried out to examine the changes in the macroscopic properties and microstructure of the specimen before and after the freeze-thaw process, and to explore the feasibility of modified magnesium oxychloride cement foam concrete to be used as a freeze-resistant building insulation material.

2. Raw materials and test methods

2.1. Raw materials and preparation of test specimens

For the various raw materials used in this experiment, the light-burned magnesia adopted powder-85 manufactured in Yingkou of Liaoning Province; the halogen flakes were sourced from Qinghai Meiyuan Meiye Co., Ltd.; the fly ash was sourced from Jiangsu Yancheng Power Plant. A certain proportion of phosphoric acid, fly ash, silicone acrylic emulsion, calcium stearate and polypropylene fiber were added into the concrete mixture. The composite modification method was applied to mix inorganic with organic additives to improve the water resistance of the magnesium oxychloride cement matrix as well as its related foam concrete.

The composite foaming agent used in this study was composed of: animal protein foaming agent, sodium dodecyl sulfate (SDS), linear alkylbenzene sulfonates (LAS), lauryl alcohol, modified polyethoxylated silicone (MPS), hydroxyethyl cellulose, etc. An air compressor was used to generate a large volume of uniform, fine and stable bubbles to foam the magnesium oxychloride cement in order to prepare magnesium oxychloride cement foam concrete specimens at the size of 300mm×300mm×20mm and 100mm×100mm×100mm. Specifically, 300mm×300mm×20mm specimens were used to conduct the thermal insulation test and 100mm×100mm×100mm specimens were used to conduct the water absorption and frost resistance tests.

2.2. Experiment method and equipment

2.2.1. Experiment method

The freeze-thaw cycle test was carried out in accordance with the provisions specified in GB/T 11969-2008 “Test methods of autoclaved aerated concrete”. First, place the specimen into a drying box at 100°C after surface cleaning, until reaching a constant weight. Measure the mass of the specimen and soak it in water for 72 h. Then, freeze the specimen at -18°C for 6 h in a saturated state and thaw the specimen at 20°C for 5 h to complete a freeze-thaw cycle for the freeze resistance test. After each freeze-thaw cycle, dry the specimen until reaching a constant weight, measure the mass of the specimen, calculate the mass loss rate, detect the compressive strength after freeze-thaw through compressive strength test, and calculate the strength loss rate accordingly. Subsequently, analyze the microstructure of the compressed specimen. The microscopic morphology before and after the freeze-thaw cycle test were examined Scanning Electron Microscopy (SEM) respectively, so as to identify the influencing factors
on the frost resistance of modified magnesium oxychloride cement foam concrete and to explain its freeze-thaw mechanism.

2.2.2. Experiment equipment
The experiment equipment includes 4107R cutting machine, 101A-3B electric heating blast drying box, electronic balance, YAW-300B pressure testing machine, HDK-5 fast freeze-thaw testing machine, DRH-300 thermal conductivity tester, Y500 X-ray diffractometer, and QANTA 200 scanning electron microscope.

3. Experiment results and discussions

3.1. Influence of the number of freeze-thaw cycles on the specimen performance
The freeze-thaw test results of magnesium oxychloride cement foam concrete are shown in Table 1. All the values are the weighted average of 3 specimens, where “-” in the mass loss and mass loss rate indicates an increase rather than a decrease.

Table 1 Freeze-thaw resistance performance of modified magnesium oxychloride cement foam concrete

| No. of freeze-thaw cycles | Drying mass /g | Freezing mass /g | Mass loss /g | Mass loss rate /% | Compressive strength /MPa | Strength loss /MPa | Strength loss rate /% |
|--------------------------|----------------|-----------------|--------------|------------------|--------------------------|------------------|----------------------|
| 0                        | 340.3          | 340.3           | 0            | 0                | 1.61                     | 0                | 0                    |
| 5                        | 338.6          | 368.7           | -30.1        | -8.9             | 1.58                     | 0.08             | 4.8                  |
| 10                       | 334.9          | 357.7           | -22.8        | -6.8             | 1.55                     | 0.11             | 6.6                  |
| 15                       | 341.4          | 356.8           | -15.4        | -4.5             | 1.51                     | 0.15             | 9.0                  |
| 20                       | 337.5          | 342.9           | -5.4         | -1.6             | 1.46                     | 0.20             | 12.0                 |

It can be seen from Table 1 and Figure 1 that the mass loss rates of modified magnesium oxychloride cement foam concrete are generally small, and are all negative values, indicating that the mass of foam concrete is insignificantly affected by the number of freeze-thaw cycles after the freeze-thaw cycle test. The increase rather than decrease of mass may be caused by the silicate gel generated by the further reaction of fly ash with water. However, with the increase in the number of freeze-thaw cycles, the mass loss of foam concrete still shows a gradually increasing trend. After 20 freeze-thaw cycles, neither obvious macro-cracks nor hollow spalling were observed on the surface of the specimen (as shown in Figure 2).
The strength loss rate of the 4 groups of modified magnesium oxychloride cement foam concrete specimens increases gradually with the increase of the number of freeze-thaw cycles, but the loss is much smaller than that of traditional Portland cement concrete. After 20 freeze-thaw cycles, the strength loss rate is only 12%, and the compressive strength remains at a relatively high level of 1.46MPa. In summary, the modified magnesium oxychloride cement foam concrete has excellent freeze-thaw resistance, which is far better than traditional Portland cement foam concrete.

3.2. Microstructure analysis

3.2.1. Analysis of microstructure morphology before the freeze-thaw cycle test

![Figure 3: SEM image of the microstructure of modified magnesium oxychloride cement foam concrete before the freeze-thaw cycle test](image)

Figure 3  SEM image of the microstructure of modified magnesium oxychloride cement foam concrete before the freeze-thaw cycle test

Modified magnesium oxychloride cement foamed concrete will form a large number of blown pores inside the material structure after setting. The pores are evenly and densely distributed before the freeze-thaw cycle, and are mostly closed pores with very few connected pores. The size of the pores is generally ranged 50μm-200μm (Figure 3(a)).The wall of the pores appears to be thick and firm, and the crystal growth is luxuriant (Figure 3(b)).

3.2.2. Analysis of microstructure morphology after the freeze-thaw cycle test

![Figure 4: SEM image of modified magnesium oxychloride cement foam concrete after 20 freeze-thaw cycles](image)

Figure 4  SEM image of modified magnesium oxychloride cement foam concrete after 20 freeze-thaw cycles

It can be seen from Figure 4 that the modified magnesium oxychloride cement foam concrete has more closed pores and fewer open pores, resulting in a lower water absorption rate (Table 1), which delays the infiltration of water molecules and prolongs the process of freeze-thaw damage. Due to the porosity of foam concrete, the hydration products inside the circular closed pores (i.e., 5·1·8 crystals) grow vigorously and disorderly, and intertwine with each other (as shown in Figure 4(b) and Figure 4(c)).
There is no obvious change in the pore walls compared to the situation before the freeze-thaw cycle test. As can be observed, the walls are still strong and thick, with fewer defects such as holes (Figure 4(d)). Therefore, after 20 freeze-thaw cycles, the modified magnesium oxychloride cement foam concrete does not develop obvious macro-cracks inside its structure (Figure 4(a)) and retains a high degree of compressive strength.

After soaking in water, the $5\cdot1\cdot8$ phase micro-crystals and a small amount of gel phases produced by fly ash in the hydration products of modified magnesium oxychloride cement can not only fill in the tiny old gaps generated during the freeze-thaw process to alleviate the expansion pressure caused by water freezing and the osmotic pressure caused by migration in harmful pores, but also increase the density and strength of the foam concrete matrix to compensate for the strength loss caused by the freeze-thaw cycle. Meanwhile, the addition of polypropylene fiber can improve the continuity of the stress transfer of the magnesium oxychloride cement foam concrete, avoid local stress concentration, and delay or prevent the further development of new cracks, so as to achieve a small strength loss rate and excellent freeze-thaw resistance performance.

4. Conclusions
(1) Modified magnesium oxychloride cement foam concrete has excellent freeze-thaw resistance. After 20 freeze-thaw cycles, the strength loss rate is 12%, and the compressive strength retains at a relatively high level of 1.46MPa, which is far better than traditional Portland cement concrete. Thus, modified magnesium oxychloride cement foam concrete can be used as a good insulation material for frost-resistant buildings.

(2) The circular closed pores existed in the structure of modified magnesium oxychloride cement foam concrete result in a low water absorption rate, which subsequently delays the infiltration of water molecules and prolongs the process of freeze-thaw damage. The further growth of $5\cdot1\cdot8$ phase microcrystals and a small amount of gel phases produced by fly ash can fill the original tiny old gaps and compensate for the strength loss caused by the freeze-thaw cycle.

(3) The addition of polypropylene fiber can enable continuous stress transmission, avoid local stress concentration, and delay or prevent the development of new cracks, so as to achieve a better freeze-thaw resistance for the modified magnesium oxychloride cement foam concrete.

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References
[1] Xiang Zhang et al. Full-Scale Fire Testing of the Traditional Organic Insulation Materials for External Wall of Buildings[J]. Advanced Materials Research, 2013, 2108: 1000-1003.
[2] Xiang Zhang et al. Evaluation of Burning Performance of the Traditional Organic Insulation Materials for External Wall of Buildings[J]. Advanced Materials Research, 2013, 2108 : 995-999.
[3] Dickson T. and Pavía S.. Energy performance, environmental impact and cost of a range of insulation materials[J]. Renewable and Sustainable Energy Reviews, 2021, 140
[4] Zheng Weixin et al. Water-to-Cement Ratio of Magnesium Oxyclylride Cement Foam Concrete with Caustic Dolomite Powder[J]. Sustainability, 2021, 13(5) : 2429-2429.
[5] Timothy A. Aiken et al. Magnesium oxychloride boards: understanding a novel building material[J]. Materials and Structures, 2020, 53(5) : 491-500.
[6] Li Ke et al. Recent progress of magnesium oxychloride cement: Manufacture, curing, structure and performance[J]. Construction and Building Materials, 2020, 255
[7] Kequan Yu et al. Magnesium oxychloride cement-based strain-hardening cementitious composite: Mechanical property and water resistance[J]. Construction and Building Materials, 2020, 261
[8] Misra A K, Mathur R. Magnesium oxychloride cement concrete[J]. Bulletin of materials science, 2007, 30(3): 239-246.

[9] Li ZJ, Chau CK. Influence of molar ratios on properties of magnesium oxychloride cement[J]. Cem Concr Res, 2007, 37(6): 866-870.

[10] Hao Yunhong and Li Yangrui. Study on preparation and properties of modified magnesium oxychloride cement foam concrete[J]. Construction and Building Materials, 2021, 282