ISSN: 2472-3703 DOI: 10.6911/WSRJ.202602_12(2).0006

Research on the Correlation between Microstructure and Macroscopic Properties of Magnesium Oxysulfide Foamed Lightweight Blocks Based on Proportion Optimization

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Abstract

To address the high carbon emissions and resource consumption of traditional Portland cement, this study prepared lightweight and high-strength magnesium oxysulfide foamed blocks based on magnesium oxysulfide cement by optimizing the raw material ratio, adding composite modifiers and compounding mineral admixtures. The effects of oxygen-sulfur ratio, water-sulfur ratio, citric acid-potassium aluminum sulfate composite modifier, silica-fly ash double admixture system and glass fiber reinforcement on the mechanical properties, water resistance and volume stability of the material were systematically investigated. The intrinsic correlation between macroscopic properties and microscopic structures (hydration product morphology, pore distribution, fiber-matrix interface) was revealed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the optimal raw material ratio was MgO: $MgSO_4$:H_2O = 8:1:20, and the compound modifier (citric acid 1.2wt% + potassium aluminium sulfate 2.0wt%) significantly increased the softening coefficient from 0.41 to 0.91; The double addition of silica fume and fly ash (total dosage 30%, mass ratio 1:2) simultaneously increased compressive strength (66.2 MPa) and flexural strength (13.35 MPa), and significantly improved volume stability (28-day drying shrinkage strain reduced to 2304 μm/m). The lightweight block (with a bulk density of 800 kg/m^3) prepared by physical foaming process has a compressive strength of 12.2 MPa and a 28-day volume shrinkage rate of only 1.11%; An addition of 0.6wt% of glass fibre can further enhance early strength and crack resistance. Microscopic analysis indicates that the increased generation of 5·1·7 phase (5 mg $(OH)_2$·$MgSO_4$·$7H_2O$) after modification, optimized crystal morphology, and densification of structure are the keys to the macroscopic performance improvement. The wall mechanics test confirmed that the compressive, shear and flexural strengths of the masonry met the requirements of the code. This study provides theoretical and experimental evidence for the industrial production and application of magnesium oxysulfide foamed lightweight blocks.

Keywords

Magnesium oxysulfide cement; Mix optimization; Foamed lightweight blocks; Microstructure; Macroscopic properties; Modifiers; Mineral admixtures.

1. INTRODUCTION

The green transition of the construction industry is crucial as it is a key area of global energy consumption and carbon emissions. The production process of traditional Portland cement accounts for about 8% of the global total CO_2 emissions and has drawbacks such as high density and high energy consumption [1]. Therefore, the development of new low-carbon cementitious materials has become an urgent matter. Magnesium oxysulfide cement, which is mainly composed of light-burned magnesium oxide and magnesium sulfate solutions, has a calcination

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temperature (700-900 ° C) much lower than that of Portland cement (~1450 ° C), and has significant advantages such as low carbon, fast hardening, light weight and fire resistance [2, 3]. Most importantly, it overcomes the fundamental flaws of magnesium oxychloride cement, such as moisture absorption and halogenation, as well as corrosion of reinforcing bars, showing good engineering application prospects [4].

However, magnesium oxychloride cement still faces challenges such as insufficient early strength development and poor volume stability in practical promotion [5, 6]. Scientific raw material ratio design, efficient chemical modification and reasonable mineral admixture compounding are the main ways to optimize its performance. In addition, the introduction of physical foaming technology to prepare lightweight blocks can further achieve the lightweighting and energy conservation of buildings. Current research has focused on the impact of a single factor on performance, lacking a systematic correlation analysis from "mix design → microstructure evolution → macroscopic performance output". Based on this, this paper systematically studies the effects of raw material ratios, composite modifiers, mineral admixtures and foaming processes on the performance of magnesium oxysulfide cement and its foamed lightweight blocks, and deeply analyzes their microscopic mechanisms of action, aiming to provide a comprehensive theoretical basis and technical support for the industrial application of this material.

2. TEST MATERIALS AND METHODS

2.1. Raw Materials

Cementitious materials: light-burned magnesium oxide powder (86.73% MgO content, 65% activity) [7, 8]; Magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, 97% purity).

Modifier: citric acid (CA, analytical grade); Potassium aluminium sulfate (Alum, analytical grade).

Mineral admixtures: Grade I fly ash (FA); Silica fume (SF, SiO_2 content ≥95%).

Foaming and reinforcing materials: Surfactants for physical foaming; 6mm alkali-resistant glass fiber.

Others: Regular tap water; Polycarboxylate water reducers.

2.2. Mix Proportion Design and Preparation Process

(1) Basic mix optimization: Design a series of mixes with an oxygen-sulfur ratio ($n(MgO)/n(MgSO_4)$, as M) of 5-10 and a water-sulfur ratio ($n(H_2O)/n(MgSO_4)$, as H) of 18-22.

(2) Modification and compounding: On the optimal basis ratio, citric acid (0-3wt%) and potassium aluminum sulfate (0-3wt%) are added alone or in combination. Study the effects of single and double admixtures of fly ash and silica fume (total admixtures 0-60%, mass ratios 1:1, 1:2, 2:1).

(3) Preparation of foamed lightweight blocks [9]: Physical foaming method was used to add prefabricated foam to the optimized magnesium oxysulfide cement-based slurry, stir and inject into molds, and control the preparation of blocks with bulk densities of 400, 600, 800 kg/m^3. Study the reinforcing effect of glass fiber (0, 0.6, 1.2, 1.8wt%). Specimens were demolded after 24 hours of curing at room temperature and were standardly cured until the specified age. As shown in Figure 1.

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Figure 1. Specimen Preparation process Specimen sample diagram

2.3. Testing and Characterization Methods

Mechanical properties: The 3d, 7d, 28d compressive and flexural strengths of 40mm×40mm×160mm specimens were tested in accordance with the standard using a constant stress testing machine.

Water resistance: Evaluated by softening coefficient K, K = compressive strength after saturation/compressive strength in the dry state.

Volume stability: Measure the 28-day drying shrinkage strain and volume shrinkage rate of 40mm×40mm×160mm specimens.

Microscopic characterization:

X-ray diffraction: Analysis of the phase composition of hydration products.

Scanning electron microscopy: Observing the morphology, pore structure and fiber-matrix interface of hydration products. Observation of the cross-section of the sample after gold spraying.

3. RESULTS AND DISCUSSIONS

3.1. Raw material ratio optimization and its microstructure basis

The effects of different oxygen-sulfur ratios (M) and water-sulfur ratios (H) on the 28-day compressive strength of magnesium oxysulfide cement are shown in Figure 2. Strength increases first and then decreases with the increase of M value, reaching a peak at M=8. When M=8 is fixed, the ratio of H=20 ensures good workability and stable strength development in the later stage. Therefore, the optimal molar ratio is determined to be MgO: $MgSO_4$:H_2O = 8:1:20. At this point, the 28-day compressive strength reaches a relatively high level, laying the groundwork for subsequent modification.

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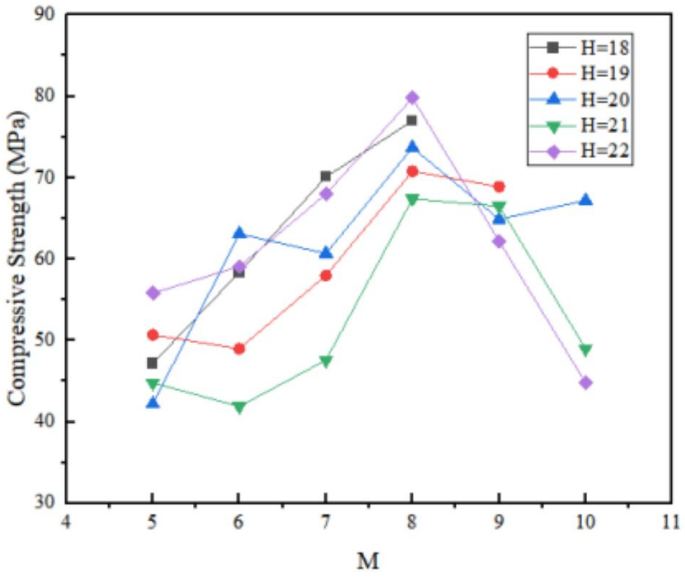


Figure 2. Effects of oxygen-sulfur ratio and water-sulfur ratio on the 28-day compressive strength of magnesium oxysulfide cement

Microscopic analysis reveals the nature of the proportioning effect. [Figure 3] XRD patterns show that when M=8, H=20, the characteristic diffraction peaks of the 5·1·7 phase in the hydration product are most prominent. SEM observations ([Figure 4]) further confirm that at this ratio, the 5·1·7 phase crystals are fully developed, presenting interlaced long needle-rod-like or filamentous structures that interweave with each other to form a solid three-dimensional network, which is an important guarantee of macroscopic high intensity. When M is too low, the 5·1·7 phase is insufficiently generated; When M is too high, there is an unreacted MgO aggregation, both of which are unfavorable for intensity development.

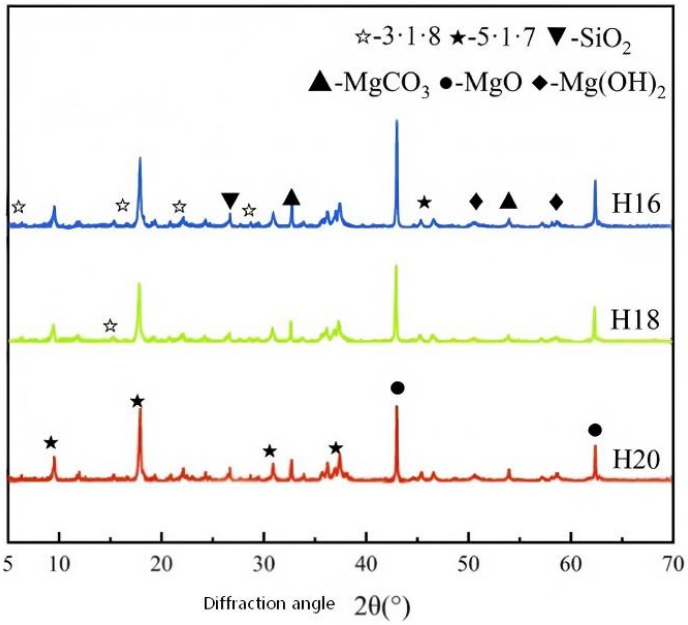


Figure 3. XRD patterns of magnesium oxysulfide cement at different water-sulfur ratios (M=8)

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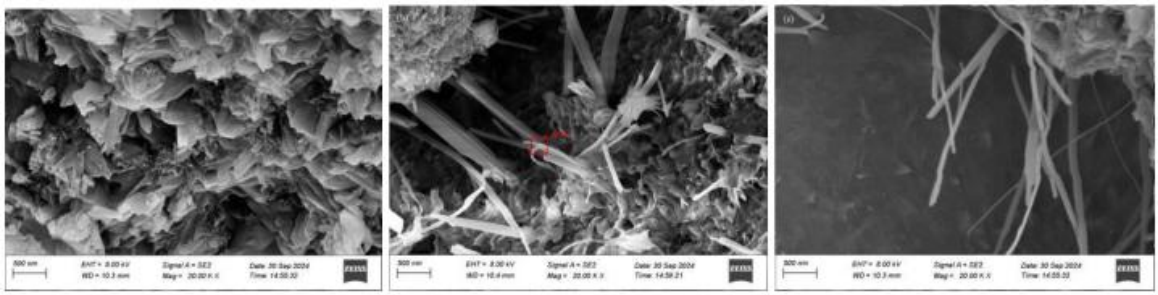


Figure 4. SEM morphology of magnesium oxysulfide cement under different oxygen-sulfur ratios (H=20). (a) M=6; (b) M=8; (c) M=10

3.2. Synergistic Enhancement Mechanism of Composite Modifiers

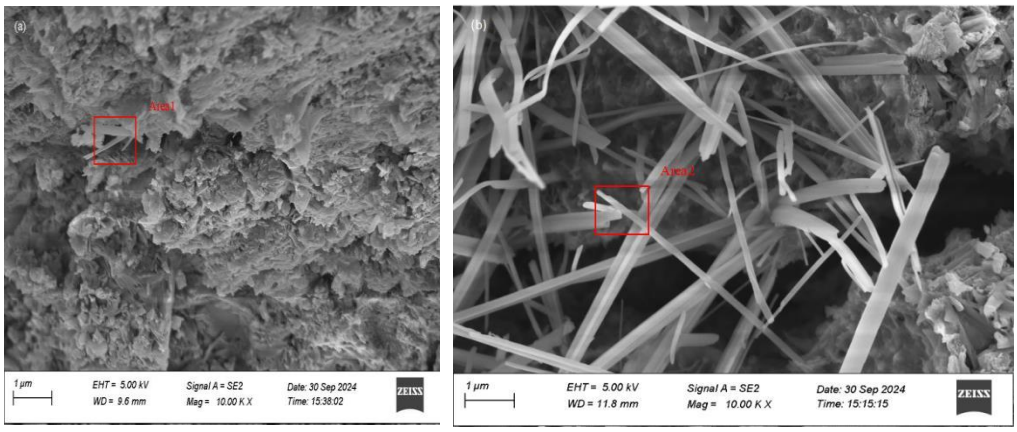
A leap in performance is achieved by introducing composite modifiers on the basis of the optimal ratio. As shown in [Table 1], when citric acid and potassium aluminum sulfate were added at 1.2wt% and 2.0wt% respectively, the 28-day compressive strength increased to 89.4 MPa, and the softening coefficient increased significantly from the unmodified 0.41 to 0.91. This indicates that the composite modification, while enhancing the strength, greatly improves the inherent weakness of magnesium oxysulfide cement - poor water resistance.

Table 1. shows the influence of the composite modifier (1.2wt% citric acid + different dosages of potassium aluminium sulfate) on compressive strength and softening coefficient

Dosage of Citric Acid	Potassium Aluminum Sulfate Doping Level	28d strength, MPa	residual strength, MPa	softening coefficient
0	0	36.95	15.3	0.41
0.8wt%	0	51.4	29.3	0.57
1.2wt%	0	81.5	58.1	0.71
1.6wt%	0	74.1	48.5	0.65
2.0wt%	0	71.25	46.9	0.66
2.4wt%	0	69.3	45.5	0.66
1.2wt%	0.4wt%	73.5	51.7	0.70
1.2wt%	0.8wt%	64	48.9	0.76
1.2wt%	1.2wt%	68.2	60	0.88
1.2wt%	1.6wt%	82.6	74.7	0.90
1.2wt%	2.0wt%	89.4	81.3	0.91
1.2wt%	2.4wt%	65.8	64.1	0.97

Microscopic mechanism analysis shows that citric acid, as a retarder, lowers the pH of the system, delays the initial hydration of MgO, and gives the 5·1·7 phase more time for ordered crystallization, resulting in a coarser and denser crystal morphology (compare [Figure 5] a and b). The introduction of potassium aluminium sulfate may partially replace Mg^{2+} with Al^{3+} to form a dense layered double hydroxide phase with OH^- and SO_4^{2-}, effectively filling the pores and blocking the water transport path, which is key to the improvement of water resistance.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202602_12(2).0006



(a) without modifiers (b) with 1.2wt% citric acid added

Figure 5. SEM morphology of magnesium oxysulfide cement

3.3. Composite Effects of Mineral Admixtures and Regulation of Volume Stability

Double blending of silica fume and fly ash can effectively optimize the comprehensive performance of magnesium oxysulfide cement. Tests showed that the best results were achieved when the total dosage was 30% and the mass ratio of silica fume to fly ash was 1:2, with a 28-day compressive strength of 66.2 MPa and a flexural strength of 13.35 MPa, which was significantly higher than that of the non-dosage group. More importantly, the introduction of mineral admixtures greatly improved volume stability, as shown in [Figure 6], with the increase of admixtures, the 28-day drying shrinkage strain continued to decrease, dropping to 2304 μm/m at 60% admixtures.

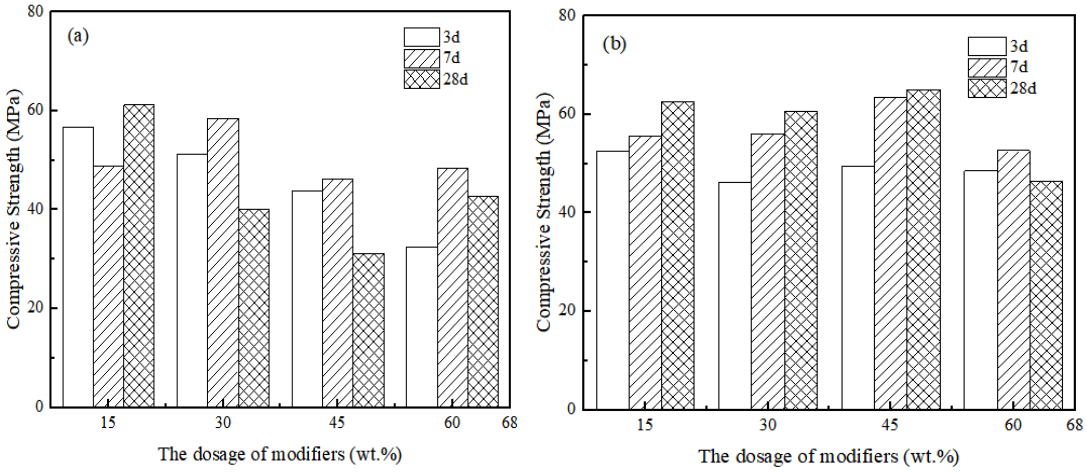


Figure 6. Effect of total mineral admixtures (silica fume: fly ash =1:2) on drying shrinkage of magnesium oxysulfide cement

The role of mineral admixtures is mainly based on physical mechanisms: 1) micro-aggregate filling effect: extremely fine silica fume and spherical fly ash particles effectively fill the micro-pores in the cement matrix, making the structure more compact; 2) Heat of hydration regulation: The admixtures dilute the cementitious system, reduce the rate and peak of heat of hydration release, and decrease the microcracks caused by temperature stress; 3) Moisture migration barrier: The uniform distribution of fine particles extends the internal moisture evaporation path and slows the drying shrinkage. XRD analysis indicated that the admixture did not change the types of hydration products, but the appropriate addition optimized the distribution of 5·1·7 phases in the packed dense matrix.

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3.4. Properties of Foamed Lightweight Blocks and Fiber Reinforcement

Lightweight blocks with controllable bulk density were successfully prepared by physical foaming. As shown in [Figure 7], the compressive strength of the block is positively correlated with its bulk density. When the bulk density is 800 kg/m^3, the compressive strength can reach 12.2 MPa, while the 28-day volume shrinkage remains at a low level (1.11%), achieving a balance between light weight and high strength.

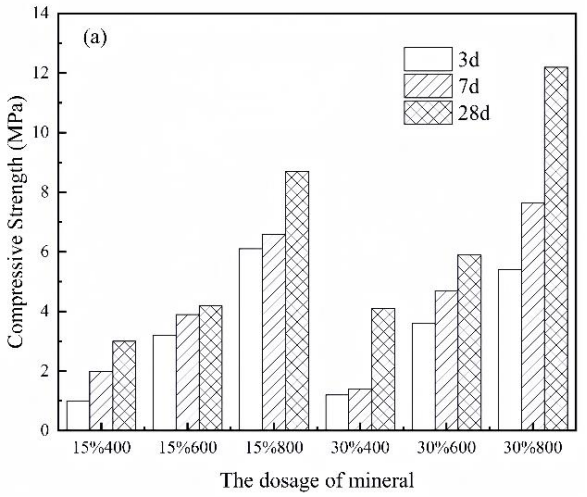


Figure 7. Effect of bulk density on 28-day compressive strength of magnesium oxysulfide foamed lightweight blocks (30% of total mineral admixtures)

However, the large number of pores introduced by foaming leads to increased brittleness of the material. Adding glass fibers is an effective means of toughening. [Figure 8] shows that the best reinforcement effect is achieved when the fiber content is 0.6wt%, with the 28-day compressive and flexural strengths increasing by 130.9% and 67.6%, respectively. SEM observations ([Figure 9]) show that the appropriate number of fibers are evenly dispersed in the matrix, bond well with the cement paste, and can effectively bridge cracks and transfer stress when subjected to force. But excessive fibers (such as 1.8wt%) can cause agglomeration, resulting in interfacial defects and weakening performance instead.

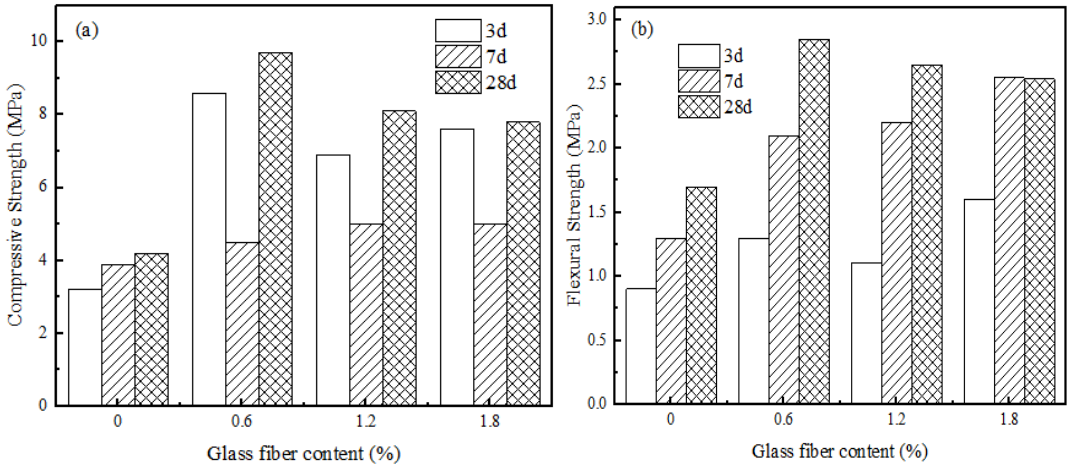


Figure 8. Effects of glass fiber content on mechanical properties of 600 kg/m^3 foamed lightweight blocks

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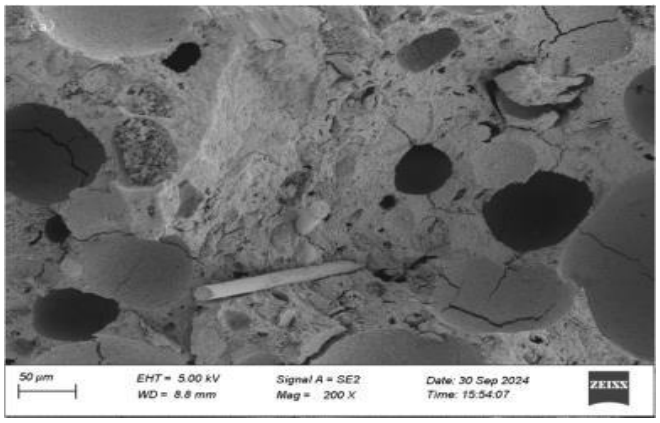


Figure 9. SEM morphology of magnesium oxysulfide foamed lightweight block with 0.6wt% glass fiber added (good bonding between fiber and matrix)

4. VERIFICATION OF MECHANICAL PROPERTIES OF THE WALL AND ITS ENGINEERING APPLICABILITY

Foamed blocks of A5.0 strength grade prepared with an optimized formula were used to build wall specimens with Ma5.0 special mortar for compressive, shear and bending tests. The results show ([Table 2]) that the mechanical property test values of all walls are greater than the calculated values in the Code for Design of Masonry Structures (GB50003-2011) [10], meeting the requirements of the code. The failure mode analysis shows that the compressive failure goes through four stages: elastic, crack initiation, stable development to unstable failure; Shear and flexural failures show brittle characteristics along the mortar joints, indicating that mortar joint bonding performance is a key link in the overall mechanical behavior of the wall. This validates the engineering feasibility of using magnesium oxysulfide foamed lightweight blocks as load-bearing and non-load-bearing components of walls.

Table 2. Comparison of test values of mechanical properties of magnesium oxysulfide foamed lightweight block wall with specified values

Specimen type	strength classes of mortar	Average value of compressive strength test, MPa	Average value of compressive strength calculation, MPa
a	Ma5.0	1.98	1.92
A	Ma5.0	2.66	2.64

5. CONCLUSIONS

(1) The optimal basal molar ratio of magnesium oxysulfide cement was determined to be MgO: $MgSO_4$: H_2O = 8:1:20, at which point the 5·1·7 phase is fully crystallized and the structure is dense.

(2) The combination modification of citric acid (1.2wt%) and potassium aluminium sulfate (2.0wt%) has a synergistic effect, significantly increasing the softening coefficient from 0.41 to 0.91 while enhancing the strength, and microscopically promoting the formation of dense LDH phase.

(3) The double addition of silica fume and fly ash (30% total content, 1:2 mass ratio) significantly improved the volume stability of the material while maintaining high strength (compressive strength 66.2 MPa) through micro-aggregate filling and thermal effect regulation.

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(4) An 800 kg/m^3 magnesium oxysulfide foamed lightweight block with a compressive strength of 12.2 MPa was successfully prepared. The addition of 0.6wt% glass fiber can effectively toughen and enhance early strength.

(5) The optimization of microstructure (5·1·7 phase morphology, pore structure, interfacial bonding) is the fundamental reason for the improvement of macroscopic mechanical properties, water resistance and volume stability. The wall test verified the reliability of its engineering application.

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