ISSN: 2710-0588

Optimization Research on the Solidification Residual Mud Technology of Magnesium Oxychloride Cement and Its Application in Green Buildings

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Abstract

With the acceleration of urbanization, the treatment of solid waste such as construction waste and river silt has become increasingly prominent. Traditional landfill or stacking methods not only occupy land resources, but may also cause environmental pollution. Magnesium oxychloride cement (MOC), as a low-carbon and environmentally friendly cementitious material, has become an innovative direction for the resource utilization and disposal of residual mud due to its fast hardening, high strength, and strong solid waste compatibility. However, MOC has problems such as frosting, halogen reflux, poor water resistance, and heavy metal leaching during the solidification of residual mud. This study optimized the performance of MOC by adding an appropriate amount of metakaolin and crystal waste residue, significantly improving its frost resistance, water resistance, and heavy metal fixation ability. The experimental results indicate that the comprehensive performance of MOC is optimal when the content of kaolin is 10%. In addition, the production energy consumption and CO_2 emissions of MOC are much lower than those of traditional Portland cement, which has significant environmental and economic benefits. This study provides theoretical and technical support for the application of MOC in the fields of green building and ecological restoration.

Keywords

Magnesium oxychloride cement; Residual mud solidification; Metakaolin; Low carbon and environmental protection; Green Building.

1. Introduction

With the acceleration of urbanization, the production of solid waste such as construction waste and river silt has surged. Traditional landfill or stacking methods not only occupy land resources, but also may cause heavy metal pollution and dust problems. Magnesium Oxychloride Cement (MOC), as a low-carbon and environmentally friendly cementitious material, has become an innovative direction for the resource utilization and disposal of residual mud due to its fast hardening, high strength, and strong solid waste compatibility.

This work focuses on the technology of solidifying residual mud with magnesium oxychloride cement, aiming to achieve the dual goals of efficient utilization of solid waste and green and low-carbon development. The residual mud of MOC solidification exhibits frost and halogen reflux phenomena, and poor water resistance, resulting in a decrease in the strength of the specimen. Under specific conditions, heavy metals in the residual mud can dissolve and cause secondary pollution, leading to safety hazards. Therefore, it is proposed to add an appropriate amount of metakaolin and crystal waste residue to improve the compactness of the internal structure of the specimen, effectively suppressing the infiltration of water and the dissolution of magnesium and chloride ions, thereby improving the frost resistance and water resistance of magnesium oxychloride cement. At the same time, the alkaline environment generated by metakaolin inhibits the release of heavy metals, effectively solving the pain points of residual

ISSN: 2710-0588

raw materials and heavy metal leaching in the solidified slurry of magnesium oxychloride cement. At the same time, the cost is relatively low. The raw material cost per ton of magnesium oxychloride cement is about 60-80% of that of ordinary Portland cement. The calcination energy consumption is low, and the calcination temperature of magnesium oxide is only 800 °C, while that of Portland cement is 1450 °C. The production process emits less CO_2, which is in line with low-carbon policies and can adsorb carbon dioxide from the air. Compared with traditional cement, magnesium oxychloride cement is not only "cost-effective" but also low-carbon and environmentally friendly, with great development prospects. In addition, the use of magnesium oxychloride cement to solidify residual mud with metakaolin and crystal waste as admixtures is currently limited due to its late start. Our team used magnesium oxychloride cement instead of Portland cement and found that the addition ratio of metakaolin has an impact on the performance and environmental protection of magnesium oxychloride cement in solidifying residual mud. Through reasonable proportioning and process optimization, modified magnesium oxychloride cement with metakaolin can efficiently solidify residual mud, achieving "waste treatment with waste", which combines environmental benefits and engineering economy, and is particularly suitable for green building and ecological restoration fields.

2. Development Background and Significance

In recent years, with the strong support of relevant policies in China, the traditional construction industry has entered the path of transformation one after another. Environmentally friendly has become a common pursuit among people, and with the continuous expansion of the total construction area and green building area nationwide, it is urgent to find a more environmentally friendly and green high-performance building material.

At present, many studies at home and abroad have shown that magnesium oxychloride cement with excellent performance is expected to replace traditional cement with high pollution in the future. However, there are still problems that need to be improved in the current magnesium oxychloride cement!

In the traditional cement production process, energy consumption is high and a large amount of carbon dioxide is released. During the construction process, a large amount of construction waste is generated, with residual mud and soil accounting for up to 50% -75%. Construction waste accounts for 40% of the total urban waste, and if it cannot be effectively treated, it will lead to environmental pollution and energy waste. Therefore, the aim of this project is to develop an environmentally friendly residual mud solidification material based on magnesium oxychloride cement. By improving the physical and mechanical properties of the residual mud, resource recycling can be achieved, and production costs and carbon dioxide emissions can be reduced.

Magnesium oxychloride cement, as a gas hardening early strength cementitious material, has been continuously revitalized in the field of building materials since its development by French scientist Sorel in 1867, thanks to its unique ternary system ($MgO-MgCl_2-H_2O$) and environmental characteristics. This material is composed of lightly burned magnesium oxide (active MgO), hexahydrate magnesium chloride ($MgCl_2 \cdot 6H_2O$), and water in a scientific ratio. It undergoes a gas hardening reaction to form a high-strength crystal network structure, which has significant advantages such as high early strength (60-70% of 28 day strength in 24 hours) and strong compressive strength (up to 120MPa).

In terms of raw material resources, China has unique industrial advantages. The raw material for lightly burned magnesium oxide, magnesite, has a global proven reserve of approximately 12.6 billion tons, with China ranking second in the world with a reserve of 3.1 billion tons. Magnesium chloride hexahydrate relies on world-class salt lake resources in the Qaidam Basin.

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The region has proven magnesium salt reserves of 6.003 billion tons (calculated as $MgCl_2$), accounting for 99% of the total national reserves. At the same time, it can also be obtained through the recycling of by-products from potassium fertilizer production, achieving comprehensive resource utilization.

In terms of environmental benefits, this material has revolutionary carbon negative characteristics. During its solidification process, it can undergo carbonization reaction with CO_2 to generate stable basic magnesium carbonate ($3MgCO \propto \cdot Mg(OH)_2 \cdot 3H_2O$). Compared with traditional cement production, it can achieve a net carbon sink of 0.12 tons/ton throughout its entire life cycle. In the application of residual mud solidification, not only can construction waste be converted into artificial stone, but its microporous structure can also sustainably adsorb CO_2 in the environment, forming a dynamic carbon capture system and a dual carbon reduction path of "low-carbon living+active carbon absorption".

In terms of technical and economic aspects, this system also demonstrates competitive advantages, with raw material pretreatment temperatures reduced by 73% compared to traditional cement (400 °C vs 1500 °C), directly reducing the fuel required for high-temperature processes such as coal and natural gas; At the same time, it can also reduce the high temperature resistance requirements of the equipment, rationalize equipment investment, and achieve cost optimization.

3. Product Introduction

In terms of performance, there was a significant frost phenomenon during the solidification process of MOC (magnesium oxychloride cement) residual mud. This phenomenon is mainly due to the absorption of water in the environment by insufficiently reacted $MgCl_2$, forming $MgCl_2$ solution. As the water gradually evaporates, $MgCl_2$ in the solution migrates to the surface of the specimen and accumulates on the surface, ultimately forming a visible frost layer. This process not only affects the appearance of the material, but may also have adverse effects on its long-term durability.

However, by introducing metakaolin, this problem has been effectively alleviated. The addition of metakaolin not only consumes excess free magnesium chloride and excess alkali metal ions in the system, but also significantly inhibits the migration of magnesium and chloride ions inside the specimen. In addition, metakaolin can also block the channels for ion precipitation to a certain extent, effectively improving the frost resistance of magnesium oxychloride cement. This improvement not only enhances the surface quality of the material, but also provides possibilities for its wider application scenarios.

The moderate addition of metakaolin and crystal waste residue improves the compactness of the internal structure of the specimen, effectively suppressing the infiltration of water and the dissolution of magnesium and chloride ions, thereby enhancing the water resistance of magnesium oxychloride cement. We found through quantitative research that adding 10% metakaolin resulted in the best water resistance when changing the mixing ratio of the added raw materials.

The main component of metakaolin is amphoteric oxides, which undergo hydration reactions in magnesium oxychloride cement to produce alkaline substances. Heavy metals are difficult to escape under alkaline conditions, which can reduce the potential heavy metal pollution during production.

The addition of metakaolin can effectively solve the pain points of frost and halogen reflux, poor water resistance, and heavy metal dissolution and release in the solidified material during the solidification of magnesium oxychloride cement residue.

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4. Experimental Design

Multiple experiments were designed to investigate the effects of different mix proportions of magnesium oxychloride cement and metakaolin content on the pain points of frost and halogen return. The main chemical components of metakaolin are shown in Table 1.

Table 1. Main Chemical Components of Metakaolin

Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	Fe_2O_3	P_2O_5	LOI
0.44	0.22	43.11	53.29	0.11	0.42	0.04	0.68	0.52	0.90

Dissolve MgCl2 · 6H20 in pure water and prepare brine with a density of 1.20 g/cm3. Let it stand for 12 hours before use. The experimental mix proportion is shown in Table 2, where A1 is the reference group, and the mass of metakaolin is used to replace some MgO

Table 2. Experimental Mix Proportion

编号	MgO	卤水	偏高岭土
A1	100	100	0
A2	95	100	5
A3	90	100	10
A4	85	100	15
A5	95	100	0
A6	90	100	0
A7	85	100	0
A8	85	100	5
A9	85	100	10
A10	80	100	10

Table 3. Surface Frosting of Magnesium Oxychloride Cement Curing Residual Mud Samples

编号	泛霜情况
A1	吸潮泛霜
A2	轻吸潮泛霜
A3	未泛霜
A4	未泛霜
A5	吸潮泛霜
A6	轻吸潮泛霜
A7	轻吸潮泛霜
A8	轻吸潮泛霜
A9	未泛霜
A10	未泛霜

Surface Frosting Performance: Refer to the Frosting Test Method in JC/T 568-2023 "Magnesium oxychloride Cement Plates" for testing. The specimen size is 40 mmx40 mmx160 mm, and after natural curing for 28 days, it is placed in a constant temperature and humidity chamber with a

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relative humidity of ≥ 90% and a temperature of 30-35 ℃ for 24 hours. Then, the surface of the specimen is taken out and observed for water droplets, moisture regain, and other phenomena.

According to Table 3, compared with Group A1, adding an appropriate amount of metakaolin alone is generally beneficial for improving the surface frost of magnesium oxychloride cement. Among them, A3, A4, A9, and A10 did not frost.

Reason analysis: Moderate amounts of kaolin and crystal waste consumed the residual supercritical free MgCI2 or excess alkali metals inside the specimen, inhibiting the migration of Mg2+and Ci content from the capillary channels inside the specimen. At the same time, it can block the precipitation channels to a certain extent, thereby enhancing the frost resistance of magnesium oxychloride cement.

Water resistance: Place the specimens (size 40mmx40 mmx160 mm) that have been naturally cured for 28 days in clear water and 10% NaS0 solution respectively, soak them in the solution for 28 days, and refer to the softening coefficient method in GB/T30100-2013 "Test Methods for Building Wall Panels" to test the water resistance and sulfate corrosion resistance of the specimens. The calculation formula for softening coefficient I is shown in equation (1).

$$I=R1/R0 \tag{1}$$

In the formula, R1 represents the strength of the specimen after 28 days of natural curing and 28 days of immersion in water; Strength of R0 specimen after 28 days of natural curing.

As shown in Table 4, with the increase of the single dosage of metakaolin, the softening coefficient of the specimen gradually increases. When the dosage of metakaolin is 15%, the flexural and compressive softening coefficients of the A4 specimen are increased by 63.6% and 28.9% respectively compared to the A1 specimen, indicating that adding an appropriate amount of metakaolin can significantly improve the water resistance of magnesium oxychloride cement. This is because the moderate addition of metakaolin and crystal waste residue improves the compactness of the internal structure of the specimen, effectively inhibits water infiltration and the dissolution of Mg+and C1-, and the active components in metakaolin can further promote the stable generation of secondary hydration products in alkaline environments, thereby improving the water resistance of magnesium oxychloride cement.

Table 4. Water resistance test results

编号	抗折软化系数	抗压软化系数
A1	0.33	0.45
A2	0.46	0.54
A3	0.51	0.56
A4	0.54	0.58
A5	0.36	0.57
A6	0.37	0.58
A7	0.36	0.62
A8	0.51	0.62
A9	0.60	0.58
A10	0.63	0.61

5. Innovation Points and Applications

1) Software copyright and algorithm optimization: Based on the simulation experiments of PHREEOC software, the team wrote to understand the algorithm and further optimize it, forming a software copyright with independent intellectual property rights. This not only enhances the technical level of the project, but also lays a solid foundation for future research and application.

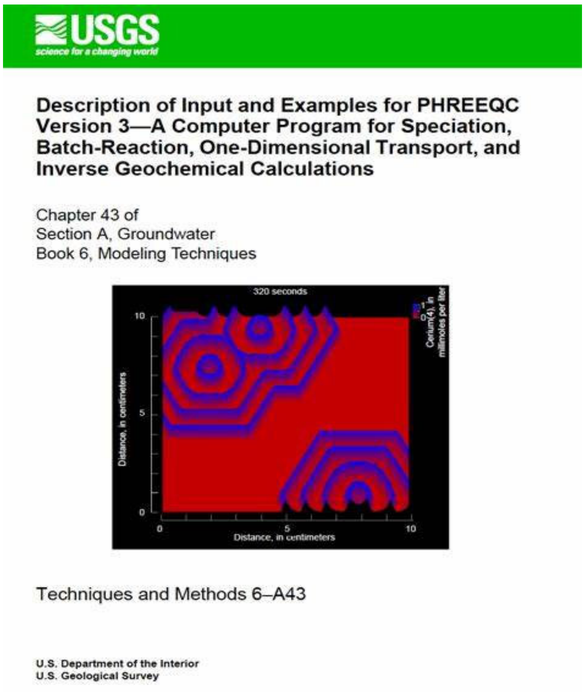

Figure 1. Algorithm Optimization

2) Accurate control of material ratio: Through extensive simulation experiments using PHREEOC software, the team successfully optimized the dosage of magnesium oxychloride cement (MOC) and the initial moisture content of residual mud. Experimental data shows that when the MOC content is 20% and the initial moisture content of the residual mud is 14% or 16%, the strength of the solidified material reaches its extreme value. This precise control not only improves the mechanical properties of materials, but also provides reliable data support for practical engineering applications.

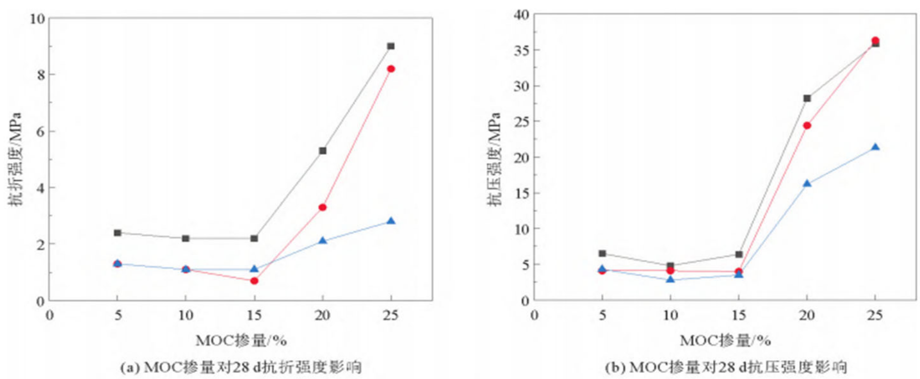

Figure 2. Effect of MOC content on the strength of cured materials

3) Enhanced anti pan oxidation performance: The project effectively suppressed the peak value of supercritical and excessive alkali metals remaining inside the specimen by introducing appropriate amounts of metakaolin and crystal waste residue. This composite material not only blocks the precipitation channel, but also enhances the anti oxidation performance of magnesium oxychloride cement, significantly improving the durability of the material.

4) Improving water resistance: Experimental results show that adding 10% metakaolin results in the best water resistance of magnesium oxychloride cement. The addition of metakaolin and crystal waste residue improved the compactness of the internal structure of the specimen, effectively suppressing the infiltration of water and the dissolution of magnesium and chloride ions, thereby significantly enhancing the water resistance of the material.

Table 5. Water resistance test results

编号	抗折软化系数	抗压软化系数
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A8	0.51	0.62
A9	0.60	0.58
A10	0.63	0.61

5) Inhibition of heavy metal release: The main component of metakaolin is amphoteric oxides, which undergo hydration reactions in magnesium oxychloride cement to produce alkaline substances, making it difficult for heavy metals to overflow under alkaline conditions. This feature not only solves the problem of moisture absorption and halogen return in magnesium oxychloride cement, but also significantly reduces the potential harm of heavy metals to the environment.

This project has significantly improved the comprehensive performance of magnesium oxychloride cement through precise control of material ratio, enhancement of anti oxidation performance, improvement of water resistance, suppression of heavy metal release, and optimization of algorithms, and has broad application prospects.

6. Application Prospects

Magnesium oxychloride cement residual mud fireproof partition board, as a new environmentally friendly building material, has broad prospects in the field of building fire prevention due to its excellent fire resistance, lightweight and high strength, and environmental characteristics. Especially in high-rise building fire compartments, their excellent fire resistance can effectively block the fire, buy time for rescue, reduce building loads, and enhance structural safety. In the application of fire protection layers in subway tunnels, this material has become the preferred choice for protecting tunnel structures and passenger safety due to its excellent fire resistance and impermeability performance. In addition, its use of construction waste residue as raw materials conforms to the concepts of green building and sustainable

ISSN: 2710-0588

development, and has enormous market potential. In recent years, policy support from national and local governments, as well as the increasing demand for fire safety in the construction industry, have provided strong guarantees and market opportunities for the application of this material.

Although magnesium oxychloride cement (MOC) has advantages such as fast hardening, high strength, and low carbon content, its poor water resistance and easy re halogenation (surface precipitation of magnesium chloride crystals) limit its large-scale application. Metakaolinite (MK) is a highly active aluminosilicate material obtained by high-temperature calcination of kaolin, with high specific surface area and volcanic ash activity. After introducing it into the MOC system, it can optimize various performance aspects. MK-MOC composite material combines high strength ($\geqslant$ 40MPa) and weather resistance, and can replace traditional gypsum board and calcium silicate board for indoor and outdoor decorative panels, fireproof partitions, etc. Previous studies have applied it to imitation stone relief panels, where the surface can be colored with mineral pigments to achieve personalized design; The improved water resistance of MK makes it suitable for coastal slope protection, dock floors and other scenarios that are susceptible to salt spray erosion. Compared with ordinary MOC, its service life can be extended by 3-5 times; The MK-MOC system can simultaneously stabilize heavy metals and organic compounds (such as petroleum hydrocarbons), making it suitable for rapid remediation of chemical contaminated sites. The solidified body can be processed into permeable bricks, roadbed stones, etc., achieving a closed loop of "repair resource utilization". Applied to 3D printing building materials, adaptability MK improves the rheological properties of MOC, reduces interlayer cracks in printing, and is suitable for rapid prototyping of complex components. Compared to traditional 3D printed cement, MK-MOC reduces carbon emissions by over 50%. Special requirements for nuclear waste packaging materials: The aluminum silicon network structure of MK can enhance the chemical bonding ability of MOC to radioactive nuclides (such as Cs^{+}, Sr^{2+}), and has the potential to be used as a barrier material for low-level radioactive waste.

Magnesium oxychloride cement with added metakaolin has broken through the technical bottleneck of traditional MOC through multiple mechanisms of "physical filling chemical bonding environmental synergy", and has shown broad prospects in fields such as construction, environmental protection, and marine engineering. In the future, the combination of industrial solid waste resource utilization (such as synergistic utilization of fly ash and steel slag) and intelligent production processes (such as AI proportioning optimization) is expected to become a new generation of green cementitious materials under the "dual carbon" goal.

At the same time, the promulgation and implementation of documents such as the "Circular Economy Promotion Law of the People's Republic of China" and the "Pilot Work Plan for the Construction of 'Waste Free Cities'" reflect the country's recognition of the solidification of residual sludge. The treatment method of residual mud is gradually shifting towards resource utilization and recycling.

In summary, magnesium oxychloride cement residual mud fireproof partition board has broad application prospects in the field of building fire prevention. It can play an important role in both high-rise building fire compartments and subway tunnel fire protection layers. Meanwhile, with the deepening of green building and sustainable development concepts, as well as strong policy support, the market prospects for this new type of fireproof material will become even broader. Therefore, we have reason to believe that magnesium oxychloride cement residual mud fireproof partition board will become an important force in the future field of building fire prevention.

ISSN: 2710-0588

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