Preparation, Performance Optimization, and Environmental Benefits of Precisely Carbonated Reactive Magnesia Cement

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Abstract

This study addresses the technical challenges of high carbon emissions in traditional Portland cement and the tendency of Magnesia Oxychloride Cement (MOC) to undergo "backfiring" (oxidative cracking). A novel preparation method for reactive magnesia cement is proposed, based on precise control of CO_2 concentration ($10^{-3.4}$–$10^{-0.7}$ atm), which promotes the stable formation of hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$). This significantly enhances material strength (compressive strength up to 120 MPa) and weather resistance. Combining PHREEQC thermodynamic simulations and X-ray diffraction analysis, the regulatory mechanisms of additives ($FeSO_4 \cdot 7H_2O/KH_2PO_4$) on MOC phase composition were elucidated. The results show that this cement achieves a net carbon sequestration of 0.12 tons per ton over its lifecycle, reducing emissions by 82% compared to traditional cement. Additionally, the calcination temperature of raw materials is lowered by 73% (700–1000°C vs. 1450°C). Reactive magnesia cement is cost-effective, eco-friendly, and holds significant development potential.

Keywords

Reactive Magnesia Cement; Precise Carbonation; Backfiring Suppression; Carbon-Negative Material; Phase Composition Regulation.

1. Introduction

1.1. Research Background

The global construction industry contributes approximately 8% of CO_2 emissions, with cement production being the dominant contributor. The calcination process of traditional Portland cement requires high temperature (1450 °C) and is accompanied by the decomposition of CaCO3 (0.8-1 ton of CO_2 emissions per ton of cement). Although magnesium oxide cement (MOC) has the potential for carbon negativity, its high temperature tendency to "backfire" (oxidation brittleness) restricts its application. Magnesium oxide cement has the characteristics of low cost, ability to absorb carbon dioxide from the air, and the ability to achieve the recycling of magnesium oxide during the production process. 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. 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 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.

1.2. Research Status

Existing studies have improved the water resistance of MOC by adding $FeSO_4$ (3wt%) or KH_2PO_4 (1wt%), but the carbonization kinetics control is insufficient. Literature 6-8 points out that the stable generation of Hydrogegnesite can suppress backfire, but precise control of CO_2 partial pressure is required.

1.3. Research Innovation Points:

--Propose a CO_2 concentration gradient carbonization method to achieve directional control of MOC phase composition;

--Develop a thermodynamic algorithm based on PHREEQC to predict the optimal carbonization conditions;

--Verify the effect of active MgO ratio (4% -7%) on the frost resistance/water resistance of concrete.

2. Product Introduction

Activated magnesium oxide cement is a series of hydrated magnesium carbonate products generated by the reaction of lightly burned magnesium oxide, carbon dioxide, and water added to traditional cement. The magnesium oxide in activated magnesium oxide concrete made from it will carbonize to form different compounds at different concentrations of carbon dioxide, thereby enabling the concrete to achieve various properties. This product, "Precision Carbonized Activated Magnesium Oxide Cement," is an adjustment of magnesium oxide cement based on traditional magnesium oxide cement, and precise carbonization is applied to solve the problem of "backfire" and other defects of traditional magnesium oxide cement, and to produce "personalized" high-performance cement according to specific conditions.

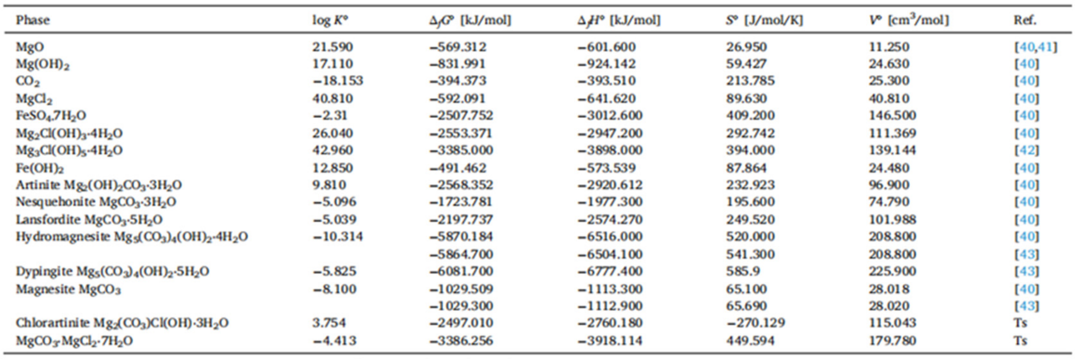
Light burned magnesium oxide has a large specific surface area, high activity, strong adsorption capacity, and fast hydration. It can react quickly with moisture and carbon dioxide in the air to produce stronger MgCO3 • MgCl • 7H2O, thereby improving the overall strength of concrete. However, the high activity of lightly burned magnesium oxide makes traditional magnesium oxide cement prone to backfire in high temperature and high pressure environments, that is, oxidation reactions occur in an oxygen environment, producing impurities, leading to a decrease in its performance and causing concrete to become brittle and fracture. Therefore, safety issues are prone to occur during use.

When activated magnesium oxide cement undergoes carbonization at CO2 concentrations ranging from 10-3.4 to 10-0.7, its stable product is hydromagnesite, which can significantly increase the strength and stability of activated magnesium oxide cement, effectively solving the problem of traditional magnesium oxide cement being prone to "backfire".

Controlling the proportion of magnesium oxide in cement can have an impact on the performance of concrete. Composite cement made from active magnesium oxide can be customized according to different usage environments such as freeze-thaw and drying. When the proportion of active magnesium oxide is 4%, the water resistance and frost resistance are optimal, and the softening coefficient and quality loss are significantly reduced compared to traditional concrete. Activated magnesium oxide cement is an "energy-saving cement". Its main raw material, light burned magnesium oxide, is obtained by calcining natural magnesite ore at 700-1000 °C, which is much lower than the 1450 °C required for traditional Portland cement. Activated magnesium oxide cement is a "low-carbon cement". The hydration reaction of traditional Portland cement is accompanied by the decomposition of CaCO3, releasing a large amount of CO2, which is also produced during hardening. The carbon dioxide generated during the hydration of activated magnesium oxide cement is absorbed by itself and almost never discharged into the atmosphere. When it hardens, it absorbs a large amount of CO2, truly achieving a green manufacturing mode. Activated magnesium oxide cement is a cost-effective cement

3. Experimental Design

Table 1. Compilation of thermodynamic data reported in the literature and used in this study under standard conditions



Phase	log $K°$	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [kJ/mol]	$S°$ [J/mol/K]	$V°$ [cm^3/mol]	Ref.
MgO	21.590	−569.312	−601.600	26.950	11.250	[40,41]
$Mg(OH)_2$	17.110	−831.991	−924.142	59.427	24.630	[40]
CO_2	−18.153	−394.373	−393.510	213.785	25.300	[40]
$MgCl_2$	40.810	−592.091	−641.620	89.630	40.810	[40]
$FeSO_4.7H_2O$	−2.31	−2507.752	−3012.600	409.200	146.500	[40]
$Mg_2Cl(OH)_3·4H_2O$	26.040	−2553.371	−2947.200	292.742	111.369	[40]
$Mg_3Cl(OH)_5·4H_2O$	42.960	−3385.000	−3898.000	394.000	139.144	[42]
$Fe(OH)_2$	12.850	−491.462	−573.539	87.864	24.480	[40]
Artinite $Mg_2(OH)_2CO_3·3H_2O$	9.810	−2568.352	−2920.612	232.923	96.900	[40]
Nesquehonite $MgCO_3·3H_2O$	−5.096	−1723.781	−1977.300	195.600	74.790	[40]
Lansfordite $MgCO_3·5H_2O$	−5.039	−2197.737	−2574.270	249.520	101.988	[40]
Hydromagnesite $Mg_5(CO_3)_4(OH)_2·4H_2O$	−10.314	−5870.184	−6516.000	520.000	208.800	[40]
		−5864.700	−6504.100	541.300	208.800	[43]
Dypingite $Mg_5(CO_3)_4(OH)_2·5H_2O$	−5.825	−6081.700	−6777.400	585.9	225.900	[43]
Magnesite $MgCO_3$	−8.100	−1029.509	−1113.300	65.100	28.018	[40]
		−1029.300	−1112.900	65.690	28.020	[43]
Chlorartinite $Mg_2(CO_3)Cl(OH)·3H_2O$	3.754	−2497.010	−2760.180	−270.129	115.043	Ts
$MgCO_3·MgCl_2·7H_2O$	−4.413	−3386.256	−3918.114	449.594	179.780	Ts

Multiple experiments were designed to investigate the effects of different additives and carbon dioxide concentrations on the combination of MOC phases. Objective: To explore the external mechanism of FeSO4 · 7H2O and KH2PO4. Samples with mixing ratios of H=18.5, M=1.5, 2, 3, 3.5, 5, and 7 were prepared separately. There are studies indicating that 3wt% FeSO4 · 7H2O or 1wt% KH2PO4 magnesium oxide powder by mass can effectively improve the water resistance of MOC, therefore the amount of ferrous sulfate used. The magnesium oxide masses of 7H2O and monopotassium phosphate used in this study were 3wt% and 1wt%, respectively. It is worth mentioning that when M is greater than 7, the steel mold method is difficult to extract the pore solution of hardened MOC paste, so the maximum value of M is selected as 7. All samples were sealed and cured below 25 °C for 28 days. After curing for 28 days, collect the supernatant from the grout and seal it in a cup. In addition, the pore solution of the hardening paste was extracted from the samples cured for 28 days using the steel mold method. All collected solutions are immediately filtered through a syringe driven filter. For each sample, dilute a portion of the filtered solution 50 times with nitric acid (6.5%) to prevent solid-phase precipitation. Analyze the concentrations of Mg and Cl using ion chromatography. The remaining filtered solution was used to measure pH. In order to study the phase combination of MOC under carbonization, a molar ratio of M=10 and H=18.5 was used to approximate the mixing ratio used in practical engineering. The mixture was manually stirred for about 3 minutes, placed in a sealed cup, and then cured in a water bath at 25 °C. In order to simulate the expected event sequence during the carbonization process to a certain extent, this article allows MOC paste hydration for 28 days, followed by natural and accelerated carbonization. After 28 days of hydration under the above conditions, the MOC sample was immediately crushed and manually ground to a particle size of less than 80 μ m to achieve rapid and uniform carbonation. Divide each proportion of powder into three parts. The first part is used for conducting X-ray diffraction experiments to determine the phase combination of methanol before carbonization. The second part studied the phase combination of MOC under accelerated carbonization in a carbonization chamber with a carbon dioxide concentration of 20%, relative humidity of 70%, and 25 °C. The final part was placed in a room with a temperature of 25 ± 2 °C and a relative humidity of (50 ± 5) % for 180 days to determine the phase combination of MOC under natural carbonization conditions.

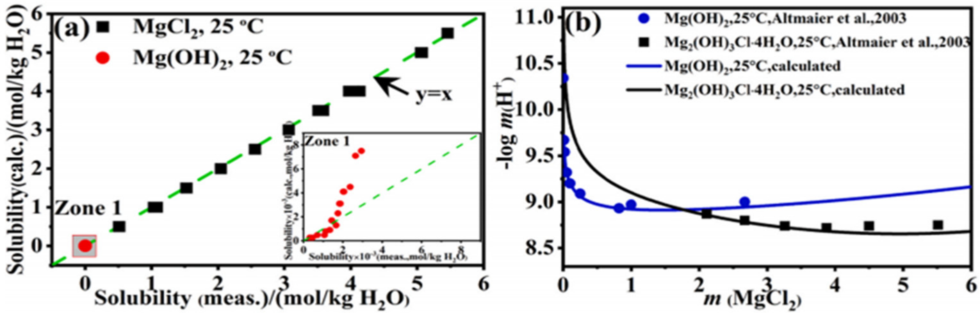


Figure 1. Solubility of Mg $(OH)_2$, $Mg_2Cl(OH)_3·4H_2O$ and $Mg_3Cl(OH)_5·4H_2O$ in the Mg-Cl binary system at different temperatures (P = 0.1 MPa)

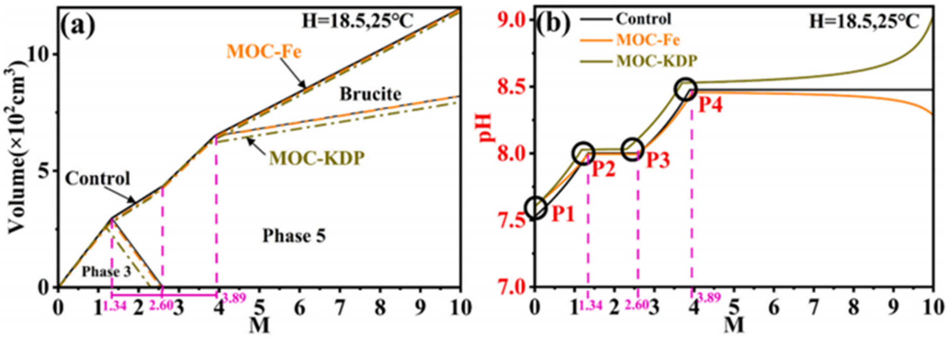


Figure 2. Equilibrium diagram of solutions containing 3 wt% $FeSO_4·7H_2O$ or 1 wt% KH_2PO_4 in the unmodified MgO-$MgCl_2$-H_2O system at 25°C and 0.1 MPa

Phase identification was conducted using a Discover X-ray diffractometer with Cu-Kα radiation in a 2θ configuration, operating at 40 kV and 35 mA in step-scan mode (step size 0.02°, counting time 0.3 s per step).

For clarity in sample designation:

- MOC-Fe: $FeSO_4·7H_2O$-modified samples
- MOC-KDP: KH_2PO_4-modified samples
- Control: Unmodified MOC samples

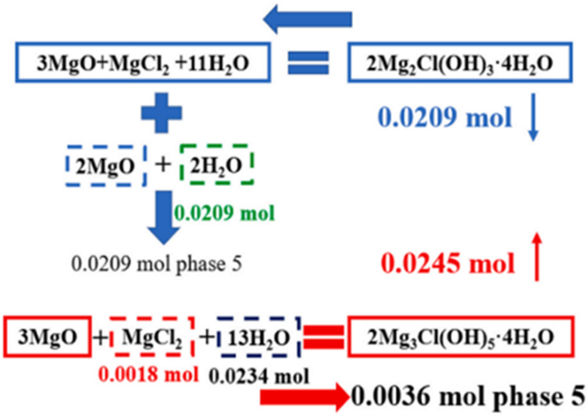


Figure 3. Conversion rates between Phase 3 and Phase 5 within the M range of 1.34-2.60

As shown in the figure, for the unmodified MOC system, when magnesium oxide is gradually added to acidic MgCl2 in the solution, MgO can quickly dissolve and release Mg2+, which then participates in the third stage, indicating an increase in pH from 7.53 (P1) to 8.00 (P2).

Afterwards, there was a plateau from P2 to P3, indicating that in the third stage, the addition of magnesium oxide did not affect the pH of the MOC system, and the simultaneous precipitation in the fifth stage showed a linear correlation between the volumes of stages 3 and 5 within the range of 1.34-2.60 of M (highlighted in red in the figure).

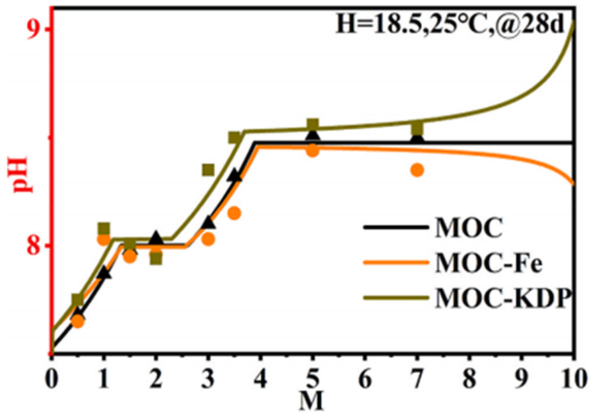


Figure 4. Calculated and measured pH values of samples: unmodified versus modified with 1 wt% KH_2PO_4 or 3 wt% $FeSO_4 \cdot 7H_2O$

Simulation results showed that the content of magnesium oxide in the third stage decreased by about 0.0209 mol, while the content in the fifth stage increased by about 0.0245 mol. Assuming that all 0.0209 mol of the third stage of reduction is converted to 0.0209 mol of the fifth stage, this will consume an additional 0.0209 mol of magnesium oxide and 0.0209 mol of water. Therefore, the remaining 0.0036 mol of the fifth stage (the total increase of 0 mol minus the 0.0209 mol of the fifth stage formed by the third stage conversion) can only be directly reacted with MgCl to form 2 and water. 0.0018mol MgCl2 and 0.0443 moH2O participated in the conversion, and the concentration of MgCl2 solution consumed remained the same as before the gradual addition, resulting in a plateau from P2 to P3. This indicates that when the third stage coexists with the fifth stage, the composition of the solution remains unchanged. The pH value increased from 8.00 to 8.48 due to the continuous precipitation of the fifth phase consuming Mg2+and Cl - in the solution. When the pH reaches 8.48, brown mudstone begins to form. Subsequently, the addition of magnesium oxide led to the continuous precipitation of brown rocks and the fifth stage. Same as coexistence stages 3 and 5, as shown in the figure. 3a, During the precipitation process of dolomite and stage 5, the pH value of the system remains unchanged.

3MgO+MgCl2+11H2O=2Mg2Cl(OH)3·4H2O

5MgO+MgCl2+11H2O=2Mg2Cl(OH)3·4H2O

MgO+H2O=Mg(OH)2

4. Hydrochlorination

The calculated solubility of relevant compounds that may precipitate during the MOC carbonization process is shown in the figure. The results indicate that magnesite is the most stable magnesium carbonate. Nesquerhonite is not as stable as brucite, which is consistent with research that Nesquerhonite has never been more stable than brucite. PCO2 ≤ 1 atm. The solubility of orthoclase at 25 ° C is greater than that of hydrochloric acid and the partial pressure of CO2 in the atmosphere, but as the concentration of CO2 increases, the solubility of hydrochloric acid increases relative to pyroxene. MgCO3. MgCl2. 7H2O is the only known magnesium carbonate containing chloride ions, and is almost the most unstable phase in the figure.

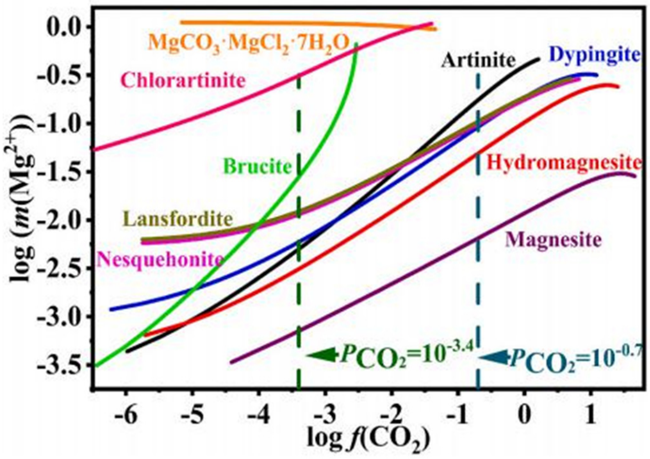


Figure 5. Solubility of various magnesium carbonates and brown copper ores in solutions without foreign ions

Chlorite can form at lower concentrations of carbon dioxide and appears to dissolve more easily than other magnesium carbonates. But some studies have pointed out that chlorite is unstable in water because it was not detected in MOC samples after CO2 attack and waterproof testing. However, he believes that the water solubility of chloroaluminate is lower than that of stages 3 and 5, which to some extent increases the water resistance of MOC. According to research, the formation of chlorite depends on temperature and humidity, and is more favorable when the relative humidity is greater than 60%. Most MOC products exposed to outdoor environments are inevitable. According to research, the formation of chlorite is relatively fast and can be detected in the laboratory in just two weeks. Compared to other magnesium carbonates, the formation of magnesite is expected to be the thermodynamically most stable phase. However, at ambient temperatures, the formation of magnesite is almost impossible and is often suppressed in actual thermodynamic simulations, as it cannot be identified in the carbonization of active magnesium oxide cement [43,50,51] and MOC [16,17,19,21]. This may be due to the strong kinetic control of magnesium carbonate precipitation. Mg2+has high hydration in solution, allowing anhydrous magnesium carbonate to precipitate directly.

5. Research Results

Based on the four SCI papers published by our supervisor, our team has achieved precise control of carbon dioxide concentration during carbonization, effectively solving the pain point of modern magnesium oxide cement prone to "backfire". We conducted simulation experiments using PHREEQC software and developed a new algorithm to analyze the content of relevant products in the experiments. We are conducting research and experiments on three types of cement, including slag activated magnesium oxide cement, to further optimize the data processing algorithm in the experiments and write a soft book.

The precise carbonization technology mastered by our team, in addition to activated magnesium oxide cement, we also hope that this technology can be applied to iterative products such as magnesium oxychloride cement MOS and magnesium oxychloride cement MPC, so that each product can better reduce carbon dioxide emissions, reduce energy consumption, and have high performance

6. Innovation Points and Applications

1) Using PHREEQC software for simulation experiments, a massive amount of data was obtained by real-time monitoring of changes in cement content in each group. A new algorithm

was developed by analyzing the content of relevant products in the experiment, further optimizing and forming software copyright.

2) Through extensive experiments on magnesium oxide cement with the same activity by controlling the concentration of carbon dioxide, the optimal concentration of carbon dioxide carbonization was obtained, achieving precise carbonization.

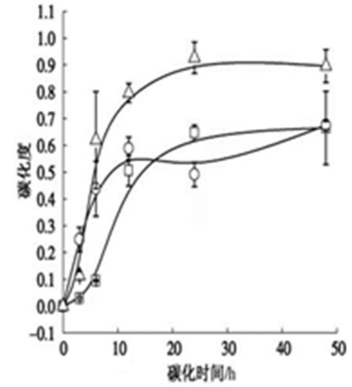


Figure 6. The effect of carbon dioxide concentration on the activity of magnesium oxide cement during carbonization

3) Activated magnesium oxide cement can effectively recycle CO2 resources, reducing carbon emissions by 82% compared to traditional cement

4) The temperature required for producing magnesium oxide cement is much lower than that for producing Portland cement, which not only saves energy consumption but also reduces heat emissions.

5) The water and magnesium carbonate products of the new active magnesium oxide can be regenerated into magnesium oxide after calcination, improving material utilization and reducing production costs.

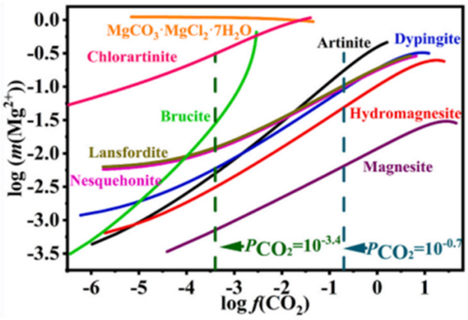


Figure 7. Different compounds formed by carbonization of magnesium oxide at different CO2 concentrations

References

[1] Shen Chen Analysis of Working Mechanism of Magnesium Oxide Carbonized Pipe Pile [D]. Anhui Jianzhu University, 2018.

[2] Xue Bo, Liu Yong, Wang Chen, etc Research progress on carbon capture, storage and utilization technology and coal seam CO2 storage [J]. Chemical World, 2020, 61 (04): 294-297. DOI: 10. 19500/j.cnki. 0367-6358.20190704.

[3] Wang Shaohan Research on the Performance of Activated Magnesium Oxide Carbonized Concrete [D]. Anhui Jianzhu University, 2020. DOI: 10.27784/d.cnki.gahjz.2020.000016.

[4] Dan Jixiong, Chen Wei, Tian Yapo, etc Study on the Effect of Activated Magnesium Oxide on the Carbonization Resistance of Alkali Slag Concrete [J]. Journal of Wuhan University of Technology, 2015, 37 (01): 10-15.

[5] Liu Songyu, Li Chen Study on the Effect of Magnesium Oxide Activity on Carbonization Curing [J]. Journal of Geotechnical Engineering, 2015, 37 (01): 148-155.

[6] Zhang Henian, Chen Kaixiang, Xi Peisheng, etc Research progress on carbonation of magnesium oxide cement blocks [J]. Journal of Anhui Jianzhu University, 2016, 24 (01): 35-39.

[7] Yan Zhigang, Wu Xianpeng A Brief Introduction to the Research Status of Low Temperature Calcination Cement and Magnesium based Cementitious Materials [J]. Guangdong Civil Engineering and Architecture, 2023, 30 (11): 116-119. DOI: 10.19731/j. gdtmyjz. 2023. 11. 031.

[8] Chen Gege The influence and mechanism of solid waste gypsum on the properties of magnesium oxychloride/magnesium oxychloride cement [D]. Central South University, 2022. DOI: 10.27661/d. cnki. gzhnu. 2022.005238.

[9] Yu Haiyan, Hao Zhihan, Hu Lintong Water resistance modification of alkali residue magnesium oxychloride cement [J]. Journal of Tianjin Chengjian University, 2022, 28 (06): 403-407. DOI: 10.19479/j.2095-719x.2206000.

[10] Adanchun, Xiao Xueying, Wenjing, etc Research on the Process of Preparing Active MgO and MOC from Magnesium Hydroxide [J]. Mineral Comprehensive Utilization, 2022, (03): 17- 26+57.