A Review of Carbonated Reactive MgO-stabilized Soil

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Abstract. The application of new reactive magnesium oxide (MgO) binder in ground improvement has become a research hotspot. This paper summarized the latest research about the mechanical property potential of carbonated reactive MgO-stabilized Soil, described the electrical characteristics and permeability characteristics of solidified soil research results, analyzed the durability and corrosion resistance of solidified soil research, introduced the exploration of new curing agent engineering application measures. In view of the existing studies, further research about the relationship between the indicators of carbonation and unconfined compressive strength (UCS) were suggested, comprehensively study the corrosion resistance of the solidified soil, systematically study the reaction mechanism of fly ash with reactive MgO, and improve the field test of reactive MgO-carbonized mixing piles have been suggested.

1 Introduction

Cement (or lime) mixed with weak soil is applied widely in ground improvement. However, there exist such defects as serious pollutant and greenhouse gas emission in the production process, high energy consumption, slow curing and poor durability. John Harrison [1] created a new kind of reactive magnesia (MgO) cement which could strengthen soil by absorbing carbon dioxide (CO_2). Vandeperre et al [2] proved that cement and reactive magnesia hydrate independently. The hydration product of the latter can achieve better curing effect after sufficient carbonation. Yi [3] clarified that the maximum UCS of MgO-solidified silt can reach 5 MPa after 3h carbonation, which of MgO-solidified silty clay can reach 2.6 MPa after 24h carbonation. Liu [4] investigated the microscopic mechanism of MgO-carbonated soil and clarified that hydration products include prismatic nesquehonite ($MgCO_3 \cdot 3H_2O$) and flaky hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) / dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) fill the soil pores to enhance the strength. Yi [3] discovered the application of carbonized mixing piles can reduce almost 90% of curing time, 65% of energy consumption and 77% of CO_2 emission than cement mixing piles.

Recently, new founds have been obtained in the investigation of reactive MgO binder. This paper will review and summarize the research progresses in the following aspects: Physical and mechanical characteristics with influencing factors; Stability and corrosion resistance; Micro-mechanism; Engineering application tests.

2 Research progress on physical and mechanical characteristics

2.1 Mechanics indicators

Previous tests have proved that the UCS of carbonated reactive MgO-stabilized Soil is higher than that of cement-solidified soil. However, the UCS showed different variation patterns for different MgO activities, dosage, water content and other factors. Different consolidation results appeared between silt and silty clay. Meanwhile, the new study also focuses on E_{50}, the secant modulus when the stress is 50% of the peak, which is an important indicator of brittleness or plasticity, and reflects the resistance to elastic-plastic deformation, as Table 1. shows.

Furthermore, it can be concluded that:

(1) For silt, failure strain and deformation modulus E50 are not significantly different from that of cement - solidified soil, which meet the soil deformation requirements. However, reactive MgO binder takes into action much more rapidly than cement.

(2) Previously, the effects of activity, dosage and initial water content on curing effect, especially unconfined compressive strength, were studied separately. At present, studies on the activity index C_A and the ratio of dew-water cement w0/c have revealed the relationship between these four indicators.

Liu proposed a fitting formula about qu related with C_A and w_0/c:

$$q_u = (0.224C_A \text{-} 12.8) \times (w_o/c)^{-0.0326C_A \text{-} 0.0256}, R^2 = 0.97 \quad (1)$$

Cai [8] clarified another formula:

$$q_u = (21.8C_A - 12.5) \times (w_0/c)^{-3.6C_A + 0.25}, R^2 = 0.95 \qquad (2)$$

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Table 1. Summary of the latest mechanical experiments

Content	Phenomenon	Analysis	Sources
Activity of MgO	The UCS of sample MgO-A after 3h of carbonation was significantly higher than cement soil-solidified after 28d and low activity MgO-B	MgO with low activity inhibits cementation and promotes fracture development.	[5]
The compression feature	(1) The compressibility of sludge decreased when the MgO content is higher than 6%. (2) The consolidation yield stress and yield strength increase with MgO content. (3) The compression modulus E_S of the high-content MgO samples had a peak E_{SP}.	The carbonation of the samples with high content produces cementing material, which leads to the increase of E_S due to compaction, while the carbonation of the samples with low content causes structural deficiency, and the increase of E_S is mainly provided by the compaction of soil particles.	[6]
Secant modulus E_{50}	The failure strain ranges between 0.8% and 1.6%, which is close to the cement-sample. q_u and E_{50} ratio in the range of 60-200, close to the cement soil.	No explanation.	[7]
Activity index C_A & quasi-water-cement ratio w_0/c	(1) q_u increased with the increase of C_A and the decrease of w_0/c. (2) The ratio of E_{50} to q_u is about 35-150.	Lower C_A leads to incomplete hydration and limited cementing ability. Increasing C_A or decreasing w_0/c can promote the formation of nesquehonite.	[8]

However, now it is still not possible to establish a quantitative relationship with some other factors that can affect curing, such as soil particle gradation, pore distribution and initial dry density.

2.2 Physical properties

In recent years, the research on solidified soil has been increasingly perfect, and new progress has been made in terms of the electrical characteristics, permeability and other physical properties of solidified soil.

Cai [7] studied the change rule of resistivity and conductivity of reactive MgO-solidified samples. The results show the resistivity increased significantly while the UCS increased linearly with the resistivity. What's more, the conductivity of pore fluid decreased first and then increased with the initial water content, similar to the change law of pH. He predicted that Brucite ($Mg(OH)_2$) and the carbonized product crystals block the current flow. OH- conducts electricity easily, but the carbonized products are difficult to ionize. Water hinders transport and carbonation of CO_2, thus increasing pH and conductivity.

Wang [9] pay attention to the Permeability of reactive MgO-solidified samples and found it is Similar with cement-solidified soil. Hydraulic conductivity K of silty clay increased with the carbonation time, while the K of silt decreased first and then increased. It was predicted that high CO_2 pressure helps produce splitting and expanding soil pores, but helps to increase the rate of carbonation in the other hand. High water content helps MgO to be fully hydrated, but it hinders penetration of CO_2 and forms water film on the surface of $Mg(OH)_2$.

It can be concluded that:

(1) There is a good linear relationship between the unconfined compressive strength and resistivity of MgO-solidified silty clay. At the same time, resistivity can reflect the initial water content and pH of soil. Therefore, it is proved that the resistivity method is theoretically feasible to predict the strength of MgO-solidified soil.

(2) Both MgO-solidified silt and silty clay have good impermeability, which can be tried to be applied to the in-situ isolated restoration of contaminated sites. However, the corrosion resistance and stability of MgO-solidified soil need to be further studied.

3 Research progress on stability and corrosion resistance

Previously, preliminary studies on the stability and corrosion resistance of carbonated reactive MgO-stabilized Soil have been carried out by some scholars. Liska & Al-Tabbaa [10] proved that the strength of reactive MgO cement block was stable at 80℃. Although the resistance to hydrochloric acid is slightly lower than that of cement, the resistance to sulfuric acid is stronger. In recent years, further studies in this field have revealed more stable and anti-corrosion properties of the new binder curing soil, as Table 2. shows.

Through the above research, it can be concluded that:

(1) The freeze-thaw cycling resistance of the reactive MgO-solidified soil is similar to that of the cement-solidified soil, and the drying-wetting cycling resistance of the solidified silt is even better. However, the drying-wetting cycling resistance of the solidified silty clay is relatively poor.

(2) The sulfate resistance of reactive MgO-solidified soil is superior to that of ordinary cement-solidified soil. Combined with the excellent impermeability proved in

Table 2. Summary of the latest experiments about stability and corrosion resistance

Content	Method	Phenomenon	Analysis	Sources
Freeze-thaw cycle characteri-stics	(1)1d curing; (2)24h curing in 23℃; (3)23h standard curing; (4)Repeated 10 times.	The water content and mass of cement samples decreased faster than that of MgO samples, the quality of silt samples decreased faster than that of silty clay samples.	The freezing-thaw cycle has no significant effect on the material composition and microstructure.	[11]
Drying-wetting cycle characteri-stics	(1)1d curing; (2)48h curing in 30℃; (3)23h curing in water; (4)Repeat for 28d. (1)1d curing;	(1)The residual strength of the silt samples decreased by only 10%, but that of silty clay samples decreased by 65%; (2)Compared with cement sample, silt sample E_{50} increased by 50%, while silty clay sample E_{50} was less than 50%. (1)Carbonized sample slightly	The pore accumulation increases significantly, resulting in a decrease in strength. The drying-wetting cycle resistance is weaker. SO_4^{2-} reacts with Ca^{2+}	[12]
Sulfate resistance	(2)Immerse in 50g/L Na_2SO_4 solution and $MgSO_4$ solution respectively.	peeled, cement sample cracked and expanded seriously; (2)The strength of carbonized samples basically unchanged, while that of cement samples reduced by 60%.	in cement to form ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$), causing cracks as the volume increases.	[13]
Immersio-n stability	(1)7d and 28d standard curing; (2)Immerse in water.	(1)Carbonized samples kept intact, while the non-solidified sludge began to disintegrate after 0.5h; (2)The immersion stability of samples with MgO only is lower than that containing fly ash.	Fly ash particles fill pores and form certain M-S-H with reactive MgO to play a cementing role.	[14]

[9], the new reactive MgO binder can be applied to the in-situ isolation and remediation of sulphate-contaminated sites.

(3) The addition of fly ash is beneficial to give full play to the cementing and compaction of hydrated carbonation products of reactive MgO binder. However, the reaction mechanism between fly ash and reactive MgO binder is still unclear.

4 Research progress on micro-mechanism

The Micro-mechanism models for silty clay and silty clay were proposed by Cai [15, 16] as the following fig.1. shows. Prismatic nesquehonite was formed within carbonized silt to increase strength significantly. It can be converted into hydromagnesite and dypingite which can be harder but lead to a decrease in strength because of shape and new cracks.

Compared with silt, reactive MgO in silty clay samples tightly encapsulates the soil aggregates and consolidates them to reduce internal pores to gains strength growth as fig.2. shows.

Based on these studies about silt and silty clay, Wang [17] clarified the Micro-mechanism model for reactive MgO-solidified sludge about immersion stability, freeze-thaw cycle characteristics and drying-wetting cycle characteristics as fig.3. shows.

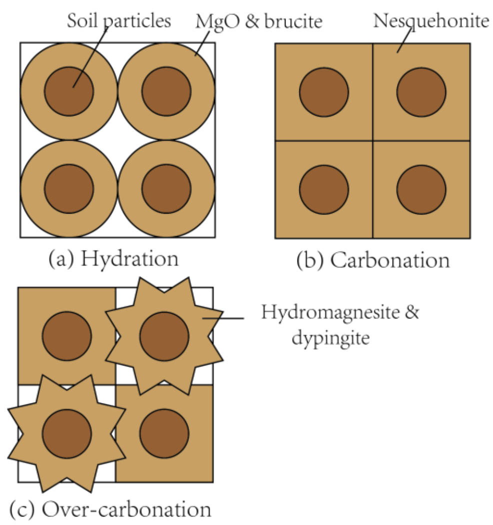

Fig. 1. Micro-mechanism model of carbonated reactive MgO-stabilized silt[15]

When undergoing the immersion tests and the drying-wetting cycle tests, nesquehonite, hydromagnesite and dypingite can convert to each other:

$$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O+Mg_5(CO_3)_4(OH)_2{\cdot}5H_2O+15H_2O \leftrightarrows 8MgCO_3{\cdot}3H_2O+2Mg(OH)_2 \quad (3)$$

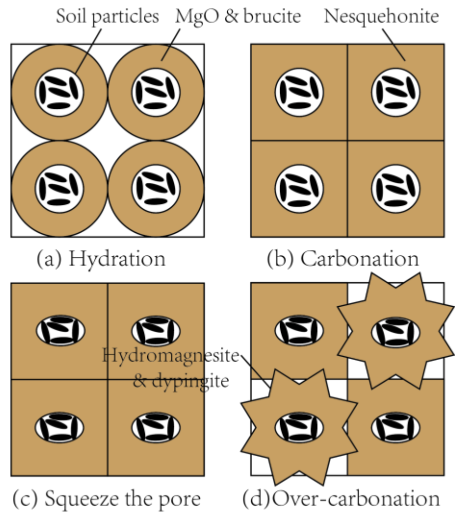

Fig. 2. Micro-mechanism model of carbonated reactive MgO-stabilized silty clay[16]

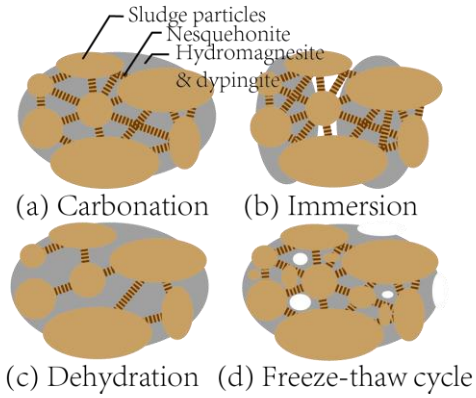

Fig. 3. Durability Micro-mechanism model of carbonated reactive MgO-stabilized sludge[17]

During the freeze-thaw cycle, although the material and microstructure change slightly, a few holes appear on the surface due to the water hiding in samples. Zheng [11] clarified a decrease of UCS because of these holes in silt and silty clay samples. However, Wang believes the dislocation of soil particles induced by freezing-thaw cycle improves the particles structure which leads to higher strength.

5 Exploration of engineering application

To use reactive MgO binder in ground improvement appeared in engineering activities. Liu [18] used the manual excavation method in the laboratory carbonation stirring pile test. The experimental data show that the optimum initial water content is 15%. What's more, the strength of the carbonized piles increases with the increase in CO_2 ventilation pressure. However, in this study, the CO_2 ventilation pressure was limited to 25-200kPa, and it was hard to proved that excessive CO_2 ventilation pressure would have any negative effect on the carbonized piles. In addition, there was no comparison test on soil type, curing time and other variables.

Cai [19] attempted to use CO_2 foam method to reinforce weak foundation soil in view of the difficulty in effectively permeating CO_2 in field application. The 200kPa CO_2 was injected into sodium dodecyl benzene sulfonate (SDBS, $C_{18}H_{29}NaO_3S$) for foaming, and then the foam was mixed with soil, water and reactive MgO for carbonation. After carbonation, the water content and pH of the sample decreased, which proved that CO_2 in the foam could react with $Mg(OH)_2$. However, the UCS did not increase more than 200kPa, so the application effect could not be achieved. This may be due to the low amount of CO_2 in the foam, the high initial water content of the sample caused by foaming agent, and the dispersion of CO_2 in the sample preparation process. Therefore, the CO_2 foam method still needs to be further studied.

6 Conclusion

(1) Compared with cement, reactive MgO binder has advantages of fast curing, high stability and strong corrosion resistance, which has obvious advantages in solidified soil mixing piles and isolating polluted sites. It is better to work together with fly ash, so exploring the effect of more industrial waste slag such as calcium carbide slag should be considered.
(2) At present, the engineering application focus on ventilation while the foam method meets problems. Developing dry ice carbonization method may be a possible choice. Consideration should also be given to the use of industrial CO_2 emissions to reduce costs and protect the environment.
(3) Simulation study on CO_2 migration and reaction in solidified soil was still lacking. The effect of reactive MgO binder on the surrounding ecosystem is unclear. Further experimental studies need to be considered.

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