

Enzyme-mediated carbonate precipitation (EMCP) for soil improvement: the effect of magnesium substitution

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ABSTRACT

The enzyme-mediated calcite precipitation (EMCP) was evaluated as a soil-improvement technique. In the present work, magnesium chloride was newly added to the injecting solutions to delay the reaction rate and to enhance the amount of carbonate precipitation. Soil specimens were prepared in PVC cylinders and treated with concentration-controlled solutions composed of urea, urease, calcium, and magnesium chloride. The mechanical properties of the treated soil specimens were examined through unconfined compressive strength (UCS) tests. A precipitation ratio of the carbonate up to 90% of the maximum theoretical precipitation was achieved by adding a small amount of magnesium chloride. Adding magnesium chloride as a delaying agent was indeed found to reduce the reaction rate of the precipitation, which may increase the volume of the treated soil if used in real fields because of the slower precipitation rate and the resulting higher injectivity. A mineralogical analysis revealed that magnesium chloride decreases the crystal size of the precipitated materials and that another carbonate of aragonite is newly formed. Mechanical test results indicated that carbonate precipitates within the soils and brings about a significant improvement in strength. A maximum UCS of 0.6 MPa was obtained from the treated samples.

1. INTRODUCTION

Microbially induced calcite precipitation (MICP) may be one of the promising bio-mediated soil-improvement techniques. MICP has been studied extensively for its potential as a novel soil-improvement technique. The increase in compressive strength ranges from 0.2–12 MPa depending upon the amount of precipitated calcite (van Paassen et al. 2010). Enzyme-mediated calcite precipitation (EMCP) (Yasuhara et al. 2011) may be an alternative method for improving soil properties. An enzyme reagent mixed solution (i.e., CaCl₂-urea-urease solution), which produces the precipitated calcite after the chemical reaction, is injected into the soil. The precipitated calcite may provide bridges between the grains of sand, restricting their movement, and hence, improving the stiffness and the strength of the soil (Yasuhara et al. 2011). For instance,

the efficacy of 1-2 g/L of the enzyme with the activity of 2950 U/g was evaluated in our previous works (Neupane et al. 2013). A precipitation ratio of calcite of up to 70% was obtained using a small amount of a urease and reagent solution. The amount of precipitated calcite varied from 1.5 to 6.0% of the sand weight on the inner spherical portion, with a diameter of 30 cm, and the corresponding reduction in porosity ranged from 2 to 7%. The amount of precipitated calcite may be enough to modify the mechanical properties of sandy soil (Neupane et al. 2013). The treated sand displays sufficient strength as a grouting material to counteract soil liquefaction. However, the uniform distribution of calcite within a large domain has not yet been achieved. The precipitation rate may have a remarkable influence on the treatment area (Neupane et al. 2015).

In this work, various amounts of magnesium were used to examine the rate and the magnitude of carbonate precipitation when added to grouting materials (i.e., CaCl_2 -urea-urease solution). Moreover, the effects of the added magnesium exerted on the size and the structure of the precipitated crystals and the formation of other carbonate minerals (e.g., dolomite, magnesite, and aragonite) were also evaluated. The optimal combination of reagents was fixed by test-tube tests and then utilized to improve small-scale specimens. The microstructures of the precipitated carbonates were examined by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) to assess the effects of magnesium on the formation of carbonates. Unconfined compression strength (UCS) tests were also performed to evaluate the improved mechanical properties of the treated specimens by the presence of the magnesium. Finally, by comparing the relation between the UCS and the amount of carbonate precipitated within the treated specimens obtained in this work, with those obtained from the literature, the influence of the added magnesium was explicitly investigated.

2. METHODS

Urea, CaCl_2 , and MgCl_2 , with claimed purity levels greater than 95.0%, were obtained from Kanto Chemicals Co. Inc. Urease (020-83242, Kishida Chemical, Osaka, Japan), purified from jack bean meal and with urease activity of 2950 U/g, was used in the bio-catalytic dissociation of urea. Poorly graded silica sand #6 with e_{max} , e_{min} , CU, and specific gravities of 0.899, 0.549, 1.55, and 2.653, respectively, was used in this work.

Test-tube experiments were conducted to examine the effect of magnesium on the rate of urea hydrolysis in the presence of urease. The measurement of the evolution of pH with time might indirectly define the rates and the magnitude of urea dissociation accelerated by the urease. The amount and the characteristics of the precipitated materials obtained from the test-tube experiments, corresponding to the different ratios of CaCl_2 - MgCl_2 , were also evaluated in this work. XRD and SEM analyses of the precipitated carbonate were conducted to analyze and to examine the mineralogical substances.

Unconfined compressive strength (UCS) tests were carried out to evaluate the improvement in stiffness and strength of the treated sand specimens. PVC cylinders (5 cm in diameter and 10 cm in height) were used to prepare the sand samples. The fixed volume of the solution was injected into each prepared sand specimen. The injected

volume was controlled by the number of pore volumes, one pore volume being ~75 mL. Firstly, 300 g of dry silica sand were poured into the PVC cylinders to obtain a relative density of 50%. Secondly, 75 mL (i.e., one pore volume) of the optimum grout solution, obtained from the test-tube experiments, were poured into the PVC cylinders from the top. The curing time of the PVC cylinder tests was determined by observing the precipitation tests. After the curing time, the treated specimens were removed from the PVC cylinders. The surface of the treated samples was flattened before the UCS tests were conducted. Two tests were performed for each condition to check the reproducibility. The UCS tests were conducted under wet conditions to avoid any unexpected precipitation that may occur when samples are intentionally dried out.

2. RESULTS

The addition of magnesium affected the shape of the precipitated materials. XRD and SEM analyses were conducted to evaluate the effect of magnesium. The XRD results in Fig. 1 show the impact of magnesium on the crystalline material. The main material was calcite. The substitution of magnesium decreased the intensity of the calcite peak and promoted the aragonite peaks. As 10% of magnesium was substituted, the intensity of the primary ($2\theta=29.75$) and the secondary ($2\theta=47.54$) peaks of calcite decreased significantly. Subsequently, the main peak of calcite ($2\theta=29.75$) decreased gradually as the magnesium ratio increased even further. The aragonite peaks are clearly shown when the substitution of more than 20% magnesium was conducted.

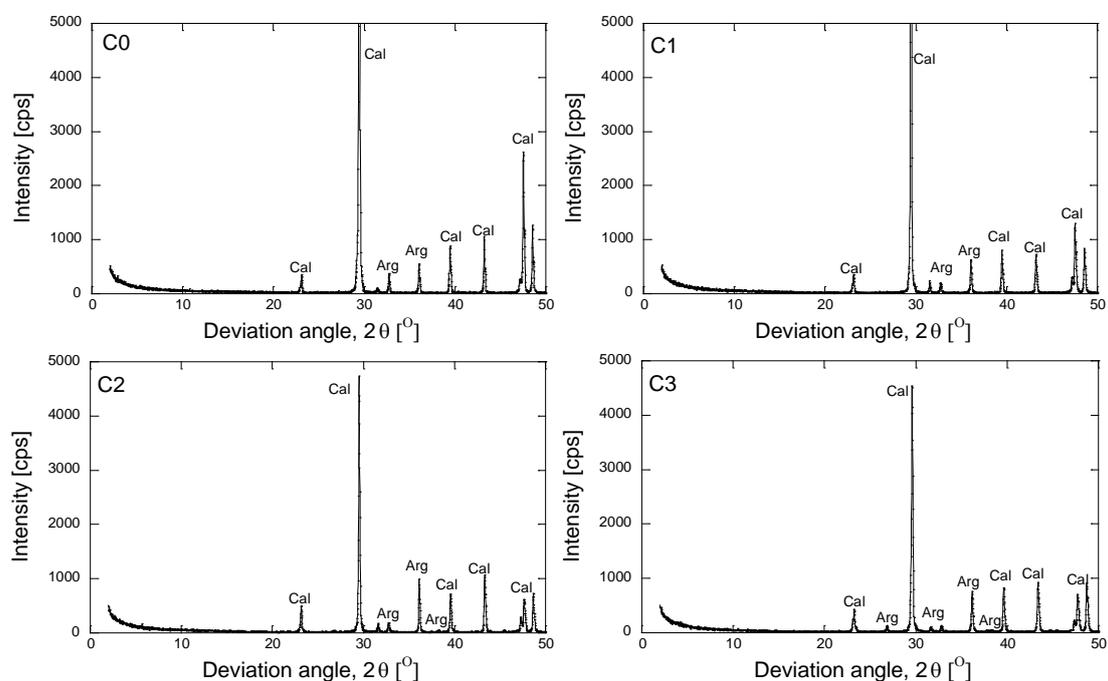


Fig. 1 X-ray diffraction results of precipitated materials

The evolution of the crystal shapes obtained from the SEM analysis is shown in Fig. 2. The C0 is the crystal structure image of calcite without the precipitation of magnesium. In such a case, the carbonation process may cause the formation of rhombohedral calcite. The substitution of magnesium modified the structure of the crystal. The rhombohedral pattern of the calcite could be observed until the additional of 20% magnesium (i.e., C2). The substitutions of magnesium decreased the amount of Ca^{2+} ions. The lower concentration of Ca^{2+} ions promoted the amorphous structure of the precipitated calcite minerals.

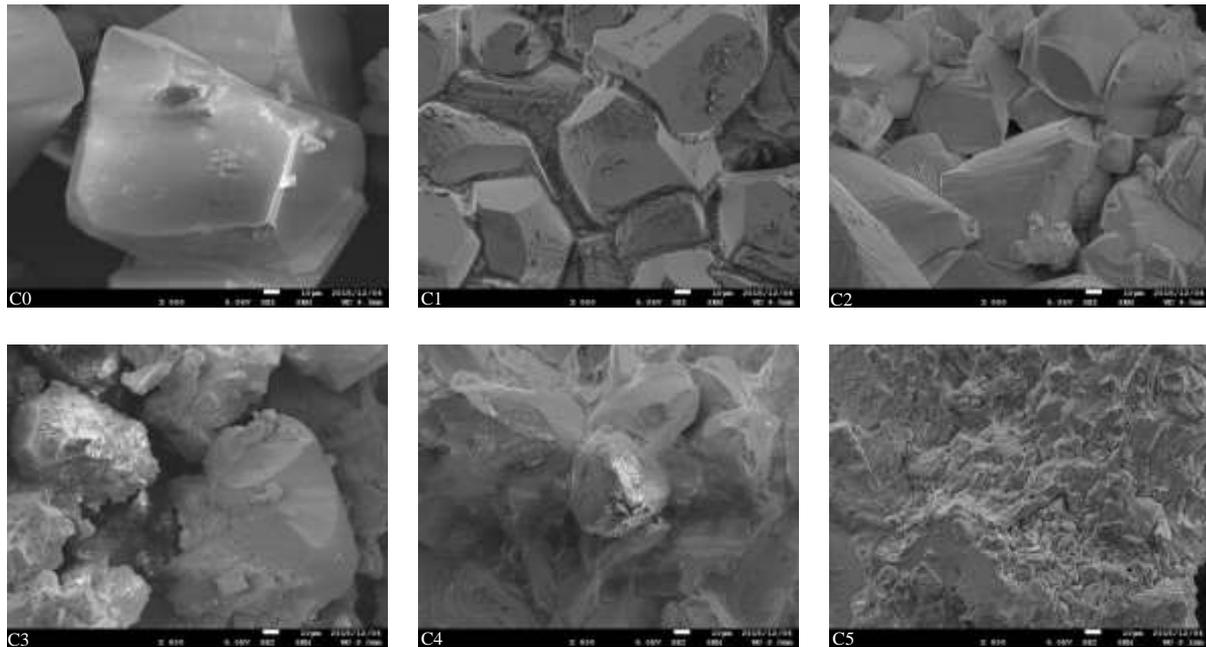


Fig. 2 Evolution of crystal shape as effect of substitution of magnesium

The relation between the content of the precipitated carbonate and UCS is depicted in Fig. 3. The maximum UCS of 0.6 MPa was obtained from the treated sample containing 8% precipitated carbonate. In comparison to the previous study, which addressed calcite precipitation without magnesium (Whiffin et al. 2007), the strength obtained in this study was roughly 40% higher for the same carbonate content. Cheng et al. (2013) obtained the unconfined compressive strength up to 0.8 MPa from the 9% precipitated content. A similar trend to that seen in the previous study was obtained. The existence of aragonite may contribute to the increase in strength of the treated sand. Aragonite is a more compact structure of carbonate groups. The structure and the size of carbonate may influence the strength of the treated sand. The presence of agglomeration crystals in the precipitated materials, as observed in the SEM images, may increase the adhesion of the treated sand. The precipitated carbonate in sandy soil may cause the formation of a coating over the sand grains and bridges between them and bring about the binding of the sand particles. The unconfined compressive strength increased gradually as the precipitated content further increased.

3. CONCLUSIONS

The efficacy of enzyme-mediated calcite precipitation (EMCP) as a soil-improvement technique was evaluated. Purified urease was utilized to bio-catalyze the hydrolysis of urea to precipitate as carbonate. In this work, magnesium was newly added to optimize the rate and the amount of carbonate precipitation. Magnesium increased the precipitation ratio of carbonate up to 90% with the urease concentration of 1.0 g/L, and was able to be used as a delaying agent for the carbonate precipitation. The presence of magnesium changed the shape and the size of the precipitated crystals and may have resulted in the aragonite together with calcite. The presence of Mg^{2+} ions reduced the size of the precipitated crystals. The agglomeration of carbonate was generated by the substitution of a small amount of magnesium. UCS tests on the treated specimens revealed that precipitated carbonate was capable of noticeably modifying the mechanical properties of the soil. Relatively higher strength was obtained in this study - the presence of aragonite, induced by the substituted magnesium, improved the UCS of the treated specimens. The relation between the UCS of the treated sand and the amount of precipitated materials indicated that the strength could be controlled by the mass of the precipitated materials.

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