Promoting of aragonite and its effect on enzyme-mediated calcite precipitation (EMCP) technique

Keywords: EMCP, aragonite, magnesium, soil improvement

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Introduction

The applicability of calcite precipitation method as a potential soil improvement technique has been confirmed. It can significantly improve the shear strength of the soil (Neupane et al., 2013; Putra et al., 2016), mitigate the liquefaction potential of soil (Ivanov and Chu, 2008), and control the soil permeability (Yasuhara et al., 2012). In this work, magnesium sulfate was added as the substitute material in the enzyme-mediated calcite precipitation technique (EMCP), and its effects on the amount and the mineralogical substance of the precipitated materials were evaluated. The evolution of mechanical properties as the effect of the substitution of magnesium sulfate was also investigated. Magnesium sulfate was added to the grouting solution to promote the formation of aragonite in addition to calcite.

Methods

Magnesium sulfate was newly added to the injecting solution. The concentrations of magnesium sulfate of 0.04 and 0.10 mol/L were substituted to obtain the total concentration of $CaCl_2$-$MgSO_4$ of 1.0 mol/L. A precipitation test for the solution composed the reagent of urea and $CaCl_2$ only (without magnesium) was also conducted. Urease with a concentration of 2.0 g/L was utilized to dissociate the 1.0 mol/L of urea into ammonium and carbonate ions. The effects of magnesium sulfate on the amount and the mineralogical substance of the precipitated materials were evaluated through the precipitation tests and XRD analyses, respectively.

Unconfined compressive strength (UCS) tests were also carried out to evaluate the improvement in mechanical properties of the treated sand. PVC cylinders (5 cm in diameter and 10 cm in height) were used to prepare the sand samples. The injected volume was controlled by the number of pore volumes (PV), one PV being ~75 mL. The sand samples were treated by 1-3 PV with a 3-day curing time. The acid leaching method with a percentage error of 1.8% was used to evaluate the amount of precipitated calcite between the sand samples (Putra et al., 2016). By comparing all of the cases with those obtained from the literatures, the effectivity of magnesium sulfate in the EMCP technique was evaluated. The experimental conditions are listed in **Table 1**.

Table 1: Experiments conditions

Case	Conc. Of $CaCl_2$ [mol\L]	Conc. of $MgSO_4$ [mol\L]
C0	1.00	0.00
C1	0.96	0.04
C2	0.90	0.10

Results

The effect of substitution of magnesium sulfate on the precipitated content is depicted in **Figure 1**. As is apparent, the precipitated mass increased as the concentration of $MgSO_4$ was added. A precipitation ratio of more than 100% of the theoretical mass was obtained when 0.10 mol/L of $MgSO_4$ was substituted. The results indicated that the minerals other than calcite were formed during the precipitation process. Therefore, a mineralogical analysis was needed to determine the substance of the precipitated materials.

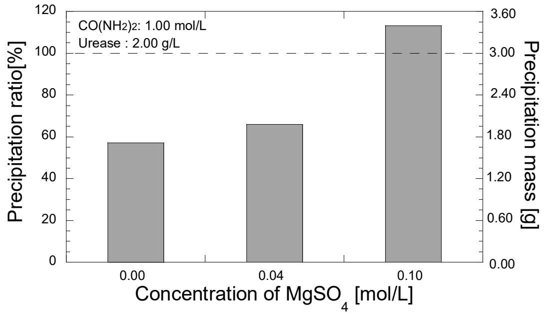

Figure 1: Precipitated mass in various concentrations of $MgSO_4$-$CaCl_2$

XRD analyses were conducted to evaluate the effect of magnesium on the mineralogical morphology. **Figure 2** shows the impact of magnesium on the crystalline material. In C0, without magnesium, the main material was calcite and a low peak of aragonite was also found. In C1, when 0.04 mol/L of magnesium sulfate was added to the grouting solution, the peak of calcite significantly decreased and, in contrast, the peak of aragonite increased. A peak of gypsum was also found in addition to that of calcite and aragonite. As the concentration of magnesium sulfate was increased, the peak of gypsum increased.

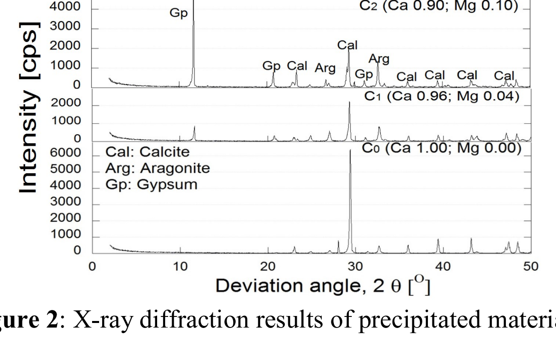

Figure 2: X-ray diffraction results of precipitated materials

The XRD results confirmed that there were three types of minerals in the precipitated materials, namely, calcite,

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aragonite, and gypsum. The substitution of low concentrations (i.e., 0.04 mol/L) and high concentration of magnesium sulfate (i.e., 0.10 mol/L) promoted the formation of aragonite and gypsum in the precipitation process, respectively.

The results of the PVC cylinder tests are depicted in **Figure 3**. The mass of the precipitated materials, varying in the range of 4-10% of the soil mass, was obtained by 1-3 PV injections (**Figure 3a**). The precipitated content within the treated sand increased as the number of injections was further increased. When one pore volume (PV) of grouting solution was injected, a lower precipitated content was obtained for C0 than for C1, and C2. In the cases of C0 and C1, the precipitated content increased as the number of injections was increased. However, in the case C2, the increment in precipitated content decreased gradually as the number of injections was increased (**Figure 3a**). A maximum strength of 0.6 MPa was achieved in the presence a 10% precipitated minerals in C1 (**Figure 3b**). The UCS of the treated sand improved 2.5-fold compared to that without magnesium (i.e., C0). In the case of C2, a lower mass of precipitated materials was formed with the same number of injections. The maximum precipitated mass of 8%, which corresponds to the strength of 0.2 MPa was obtained (**Figure 3b**).

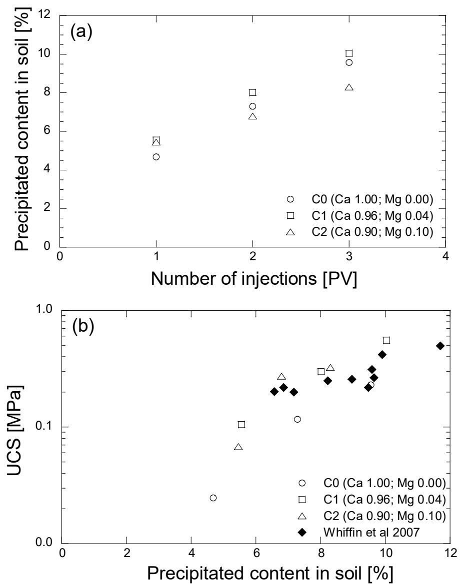

Figure 3: Results of PVC cylinder tests: **(a)** Precipitated content in various number of injections and **(b)** Relation between precipitated content and UCS.

The presence of a high concentration of magnesium sulfate in the grouting solution enhanced the reaction rate. The precipitation process occurred quickly after mixing, and the precipitated materials might have formed before all the solution had been passed through the sand specimens. The precipitated materials were concentrated on the upper side of the sand samples. This may have hampered the permeation of the injecting solution between the soil particles; and hence, the number of injections was limited. In comparison to the previous study, in which the calcite precipitation technique was performed without magnesium sulfate (Whiffin et al., 2007), the maximum strength obtained in this study was roughly 40% higher for the same precipitated content. The combination of calcite-aragonite (i.e., C1) as the precipitated mineral brought about a significant improvement in the strength of the treated sand.

Conclusion

The effects of the substitution of magnesium sulfate on the amount and the mineralogical substance of the precipitated materials have been investigated. The mineralogical analysis revealed that the substitution of magnesium sulfate into the grouting solution composed of urea, $CaCl_2$, and urease was a potential method for promoting the formation of aragonite and gypsum. A low concentration of magnesium sulfate significantly promoted the precipitation of aragonite. Furthermore, a large amount of gypsum was formed when a high concentration of magnesium was substituted.

The UCS test results showed that besides calcite, the presence of aragonite as a precipitated mineral resulted in greater improvement in the strength of the treated sand than the sand treated purely by calcite. In comparison to the previous study, which addressed calcite precipitation only, the obtained strength in this study was higher for the same precipitated content. The results of this study have elucidated that the application of magnesium sulfate to the EMCP technique may be an alternative soil improvement method.

References

Ivanov, V., Chu, J., 2008. Applications of microorganisms to geotechnical engineering for bioclogging and biocementation of soil in situ. Reviews in Environmental Science and Biotechnology 7, 139–153. doi:10.1007/s11157-007-9126-3

Neupane, D., Yasuhara, H., Kinoshita, N., Unno, T., 2013. Applicability of Enzymatic Calcium Carbonate Precipitation as a Soil-Strengthening Technique. Geotechnical and Geoenvironmental Engineering (c) ASCE 139, 2201–2211. doi:10.1061/(ASCE)GT.1943-5606.0000959.

Putra, H., Yasuhara, H., Kinoshita, N., Neupane, D., Lu, C.-W., 2016. Effect of Magnesium as Substitute Material in Enzyme-Mediated Calcite Precipitation for Soil-Improvement Technique. Frontiers in Bioengineering and Biotechnology 4, 37. doi:10.3389/fbioe.2016.00037

Whiffin, V.S., van Paassen, L. a., Harkes, M.P., 2007. Microbial Carbonate Precipitation as a Soil Improvement Technique. Geomicrobiology Journal 24, 417–423. doi:10.1080/01490450701436505

Yasuhara, H., Neupane, D., Hayashi, K., Okamura, M., 2012. Experiments and predictions of physical properties of sand cemented by enzymatically-induced carbonate precipitation. Soil and Foundation 52, 539–549. doi:10.1016/j.sandf.2012.05.011

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