ABSTRACT

Heriansyah Putra, Optimization of enzyme-mediated calcite precipitation for soil improvement technique

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The applicability of enzyme-mediated calcite precipitation (EMCP) as a potential soil improvement technique has been studied. This technique employs enzyme of urease to dissociate urea into ammonium and carbonate ions. The produced carbonate ions are precipitated as calcite crystals in the presence of calcium ions. An enzyme-reagent mixed solution (i.e., purified urease and $CaCl_2$-urea), 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.

A series of experiments were conducted. The first series of experiment was conducted to evaluate the efficacy of magnesium chloride as the substituted material in EMCP technique. Magnesium chloride was newly added to the grouting solutions composed of urea, urease, and calcium chloride to control the reaction rate and to enhance the precipitation amount. A precipitation ratio of 90% of the maximum theoretical mass was achieved by adding 0.05 and 0.10 mol/L of magnesium chloride to obtain the total concentrations of $CaCl_2$-$MgCl_2$ of 0.5 mol/L. The addition of magnesium was indeed found to be effective in delaying the reaction rate by more than one hour. Mechanical test results

indicated that precipitated materials within the soil sample brought about a significant improvement in the soil strength. A maximum strength of 0.6 MPa was obtained from the treated samples.

The second series of experiment was performed to examine the applicability of magnesium chloride as the delaying agent to control the precipitation process and improve the homogenous distribution of the precipitated minerals within the soil. Soil specimens were prepared in 1-m PVC cylinders and were treated by the obtained grouting solutions. Thus, the distribution of the precipitated minerals within the soil sample was evaluated. The uniform distribution of the precipitated minerals within a 1-m sand column was obtained when 0.1 mol/L and 0.4 mol/L of magnesium and calcium chloride, respectively, were injected. The mechanical and hydraulic properties tests results showed that the strength increased gradually with the increasing of the mineral mass and the hydraulic conductivity was approximately constant in the presence of a 6% mineral mass. It was revealed that it is possible to control the strength of treated sand by adjusting the amount of precipitated minerals.

The third series of experiment was conducted to evaluate the effectivity of magnesium sulfate as a substituted material in EMCP technique. Magnesium sulfate was added to the grouting solution composed urea, urease, and $CaCl_2$ to increase the precipitated ratio and promote the formation of aragonite and gypsum in addition to calcite. XRD and SEM analyses were carried out to examine the mineralogical morphology of the precipitated minerals and to determine the effect of magnesium on the composition of the precipitated materials. The test-tube experiments results showed a significant improvement

in precipitated amount. A precipitation ratio more than 100% was obtained when magnesium sulfate of 0.1 mol/L was added. The substitutions of low and high concentrations of magnesium sulfate also effectively promoted the formation of aragonite and gypsum, respectively. The grouting solutions, which produced aragonite, calcite, and gypsum brought about a significant improvement in the soil strength. The presence of the precipitated materials, comprising 10% of the soil mass within the treated sand, generated the strength of 0.6 MPa.

The fourth series of experiment was performed to evaluate the applicability of the natural zeolite for the removal of the ammonium ions in the EMCP technique. The natural zeolite of *mordenite* was added to prepared grouting solutions composed of urea and urease and mixed thoroughly using a rotation table for the mixing times of 0.5, 1.0, and 2.0 hrs. Then, the concentrations of evolving ammonium in the solutions were measured. The effects of the presence of zeolite on the amount and the mineralogical substance of the precipitated minerals were also evaluated. Sand samples were treated with the grouting solutions containing zeolite and the improvement in strength was assessed. It was found that utilizing zeolite in grouting solutions can reduce the concentration of ammonium ions. A significant reduction in the concentration of ammonium ions was obtained. The addition of 10 g/L of natural zeolite, combined with the 2-hr mixing time, resulted in removal efficiencies of 75 and 45% in reagent concentrations of 0.5 and 1.0 mol/L, respectively. Mechanical test results showed that the grouting solutions also brought about a significant improvement in the soil strength. A precipitated material, comprising 9% of the sand mass, was produced by three PV injections of the grouting materials, which showed a sufficient

unconfined compressive strength of 300 kPa. This result confirmed that application of the natural zeolite of *mordenite* in EMCP technique could to be a solution for an environmental issue without compromising in the efficacy of EMCP as a soil improvement technique.

This dissertation comprises 4 published papers. The papers included in this dissertation are listed below.

1. Heriansyah Putra, Hideaki Yasuhara, Naoki Kinoshita, Debendra Neupane, Chih-Wei Lu. 2016. Effect of magnesium as substitute material in enzyme-mediated calcite precipitation for soil improvement technique. Frontiers in Bioengineering and Biotechnology. 4 (2016):37. (Chapter 2)
2. Heriansyah Putra, Hideaki Yasuhara, Naoki Kinoshita, Akira Hirata. 2017. Application of magnesium to improve uniform distribution of precipitated minerals in 1-m column specimens. Geomechanics and Engineering. 12:5: 803-813. (Chapter 3)
3. Heriansyah Putra, Hideaki Yasuhara, Naoki Kinoshita, Akira Hirata. 2017. Optimization of enzyme-mediated calcite precipitation as a soil improvement technique: The effect of aragonite and gypsum on the mechanical properties of treated sand. Crystals. 7(2): 59. (Chapter 4)
4. Heriansyah Putra, Hideaki Yasuhara, Naoki Kinoshita. 2017. Applicability of natural zeolite for NH-form removal in enzyme-mediated calcite precipitation technique. Geosciences. 7(3): 61. (Chapter 5)