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Distribution of mineralized carbonate and its quantification method in enzyme mediated calcite precipitation technique

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Abstract

This study discusses the possible application of enzyme mediated calcite precipitation, EMCP, as a soil-improvement technique. It explains the experimental works on this EMCP technique. The first part of this paper addresses the different methods for quantifying the amount of calcite precipitated within sand. Two methods, namely, the thermal decomposition method and the CO_2 volume evaluation method, are examined. These methods serve to evaluate the calcite distribution within the treated sand. The second part of this paper explains the experimental procedures and the results of drum-can experiments. Homogenous sand specimens, with a diameter of 57 cm and a height of 60 cm, are prepared inside a steel drum-can. A grout solution, comprising urea, urease, and $CaCl_2$, is injected into the centre of the sand specimens. Subsequently, the improved samples within the specimens are collected and their compressive strength is evaluated. The maximum measured unconfined compressive strength is 380 kPa. An attempt is made to relate the improved mechanical properties of EMCP-treated sand to the amount of mineralized carbonate. The obtained calcite-strength relation is found to be in close agreement with the relation obtained in previous literature.

Keywords: Urease; Precipitation; $CaCO_3$; Quantification; Grouting

1. Introduction

In-situ calcite precipitation has been studied for its various possible applications, such as to remove contamination from groundwater systems (Nemati et al., 2005), to repair cracks in concrete (De Belie and De Muynck, 2009), to preserve limestone monuments (Al-Thawadi, 2011), to reduce the swelling potential of clayey soil (Ivanov and Chu, 2008), and to increase the resistance to seismic-induced liquefaction (Burbank et al., 2011). Calcite precipitation is achieved by the microbial-induced calcite precipitation technique, MICP. In this process, urease-producing bacteria are employed to dissociate the dissolved urea. At first, bacteria dissociate urea and produce ammonium that increases the pH of the solution (Eq. (1)).

$$CO(NH_2)_2 + 3H_2O \overset{\text{Urease}}{\rightarrow} 2NH_4^+ + 2OH^- + CO_2 \quad (1)$$

The series of reversible reactions take place in the elevated pH, producing carbonate ions $\left(CO_3^{2-}\right)$ as final product.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad (2)$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad (3)$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \quad (4)$$

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Calcium ions, supplied by a solution of calcium salts, combine with the produced carbonate ions to form mineralized carbonate, i.e., $CaCO_3$ (Eq. (5)).

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3\downarrow \tag{5}$$

Among the many other engineering applications of MICP, it has been extensively adopted as a potential soil-improvement technique because of its appreciable cementing capacity. According to Harkes et al. (2010), precipitated $CaCO_3$ serves as binding material: it binds soil particles and results in the improved mechanical properties of the soil. van Paassen et al. (2010) investigated the feasibility of the calcite precipitation technique as a ground-improvement method via a soil specimen of 100 m^3. Mortensen and DeJong (2011) evaluated the evolution of mechanical properties in specimens subjected to various stress paths using triaxial tests. Cheng et al. (2013) studied calcite cementation at various degrees of saturation. Many of the works on MICP are limited to the laboratory scale. However, the field application of the MICP technique has already been carried out to strengthen gravel for borehole stability during horizontal directional drilling (van der Star et al., 2011).

There are some complexities with the MICP technique. The bacterial incubation requires a special environment. The transport of bacteria (and hence, bacterial activity) may be limited in fine-grained soils (van Paassen et al., 2010). The high concentrations of urea and/or calcium chloride may have an inhibitory effect on the bacterial activity (Nemati et al., 2005). Therefore, enzyme mediated calcite precipitation, EMCP, may be an alternative in-situ calcite precipitation technique (Yasuhara et al., 2012). In this technique, purified urease crystals are employed for the dissociation of urea. Using the enzyme itself is more straightforward than using bacteria, because the cultivation and the fixation of bacteria (i.e., biological treatment) do not need to be considered (Yasuhara et al., 2012). This is because, unlike microbial method, enzyme is mixed and injected along with the reagent solution in enzymatic method, hence the fixation of enzyme is not required. The mineralogical composition of the precipitated material obtained by the enzymatic method is analysed and found to be calcite in our previous work (Neupane et al., 2013).

The efficacy of the EMCP technique on a small scale (50 mm in diameter and 100 mm in height) and on a relatively large scale (57 cm in diameter and 60 cm in height) has already been evaluated in our previous works (Yasuhara et al., 2012, 2014; Neupane et al., 2013).

In order to adopt the EMCP technique as a soil-improvement technique in real fields, the relation between the mechanical properties (i.e., stiffness and strength) of the improved soil and the amount of precipitated calcite must be attained in advance. Furthermore, reliable methods of calcite quantification are required to ascertain that the amount of calcite precipitated is not being misestimated. In our previous works (Yasuhara et al., 2012; Neupane et al., 2013), the amount of precipitated calcite was evaluated by the acid leaching method. In this method, an oven-dried sand sample is reacted several times with hydrochloric acid (i.e., HCl solution) to remove the calcite present in it. The acid-treated sand is then washed with water and allowed to dry in the oven. The difference in the dry mass of the sand before and after removing the precipitated calcite is evaluated. The mass loss during the acid leaching process is considered to be the mass of the calcite. During this process, the sand is washed 3–5 times with acid and water. The soil sample may contain soluble materials, such as the by-products of the calcite precipitation reaction, which may also be flushed away. This may result in the overestimation of the precipitated calcite. In addition, this method requires that the sample be dried two times, resulting in an increase in experiment time. Thus, to quantify the precipitated calcite more accurately and in shorter time, two calcite quantification methods are examined thoroughly in this work.

Another purpose of this study is to conduct drum can experiments and to employ the newly examined calcite quantification method to evaluate the calcite distribution. Although drum-can experiments were conducted in our previous work (Neupane et al., 2013), the mechanical properties of the improved samples were not evaluated. Moreover, the three-time injection of the grout solution was required to achieve adequate cementation on sand because of the low concentration of the adopted solution. The mechanical tests using the same grouting technique (i.e., the EMCP technique) have been maintained as one of the mandatory works. In this work, therefore, a higher concentration of grout solution is adopted to reduce the injection number. Similarly, unconfined compression tests are conducted to evaluate the improved mechanical properties. Subsequently, the relation between the mechanical properties and the amount of calcite precipitated within the soil sample is examined.

2. Calcite quantification methods

Finding a reliable method for quantifying calcite is also an important part of the successful implementation of the calcite precipitation technique as an alternative soil-improvement technique for engineering applications. Studies are being carried out on the quantification of precipitated calcite. Qabany et al. (2011) suggested a method of measuring the S-wave velocity to evaluate the quantity of calcite. Whiffin et al. (2007) utilized the CO_2 gas produced by the reaction of the HCl solution and sand containing calcite to quantify the calcite. One of the objectives of the current research is to find a faster and simpler method of quantifying calcite. This study evaluates two calcite quantification techniques, namely, the thermal decomposition method and the CO_2 volume evaluation method. Both methods utilize the basic principles of chemistry. Afterwards, the methods of calcite precipitation are compared. The amount of calcite on three types of mixtures are quantified using three methods (i.e., the thermal decomposition method, the CO_2 volume evaluation method, and the acid leaching method) separately to suggest the best method of calcite precipitation. The commercial $CaCO_3$ obtained from Kanto